Department of Civil Engineering

Nottingham Transportation Engineering Centre (NTEC)

PERFORMANCE OF WARM MIX ASPHALT COMPACTED AT REDUCED TEMPERATURE

by

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DEDICATED

To My

Father, Mother and Brother…

ABSTRACT

The generic term Warm Mix Asphalt (WMA) refers to a variety of bituminous mixtures, which are produced through specific technologies, at temperatures approximately 15°C to 70°C lower than the typical production temperature range of conventional Hot Mix Asphalt (HMA) (i.e. 135°C to 160°C). The lower production temperatures of WMA offer a sustainable and environmental-friendly alternative to HMA via reducing the fuel consumption and greenhouse gas emission. Application of asphalt involves mixing, hauling, placement and compaction. As a general rule for HMA, if, during delivery and compaction, the mixture's temperature drops below the minimum allowable production temperature at which adequate compaction can be achieved, then significant reductions in the performance of the resultant mixture is expected. In the case of WMA, it is expected that the effects of cool compaction on the properties and performance of the mixture will be less easily described than in HMA. This is due to the complicating presence of additives, which may modify the chemical, rheological and mechanical properties of the bitumen, as well as modifying the surface energy of both bitumen and aggregate, all of which can, consequently, affect the properties and performance of the resultant WMA mixture in a complex way not directly comparable to HMA mixtures. The overall goal of this research has been to investigate the effects and implications of temperature decline on the mechanical performance of WMA mixtures, produced in two different ways, included a 'wax/organic additive' technology (using a Fischer-Tropsch paraffin wax) and a 'chemical additive' technology (using a cationic surfactant liquid), along with determining the fundamental reasons for such effects. For this purpose, a devised comprehensive matrix of laboratory tests was performed on the produced wax-modified and chemical-additive-modified binders in order to provide the mechanical and rheological characterisation of the binders as well as their surface energy properties. The associated wax-WMA and chemical-additive-WMA, also different reference HMA mixtures were fabricated via mixing at recommended and adequate temperatures (according to the standard or the additive supplier's advice) and compacting at a declining series of temperatures using two different compaction methods (i.e. gyratory compaction and roller compaction). A devised comprehensive set of laboratory tests was then carried out to fully characterise the manufactured WMA mixtures and their counterpart reference HMA mixtures via studying and understanding the influence of reduced production temperatures on their mechanical performance characteristics, including volumetric properties, stiffness modulus, fatigue resistance, rutting potential and viscoelastic behaviour representatives (complex stiffness modulus). The binder-aggregate dry bond strength of the various binder and aggregate combinations used in the asphalt mixtures was evaluated using the surface energy calculations combining the surface energy properties of the different binders and aggregates (pure and modified). Moreover, a mechanical assessment test was performed on different coating samples of the various binder and aggregate combinations to evaluate the binder-aggregate adhesive or binder cohesive tensile strength in different mixtures. The results show that compaction

at lower temperatures does not have a considerable effect on the performance of asphalt mixtures, whether they contain additives or not, unless it occurs below 100°C (i.e. 80 and 85°C), in which case, in spite of some limited negative influences on asphalt performance, overall behaviour still remains in acceptable ranges. Moreover, it seems that overall, additives increase the sensitivity of asphalt mixtures' properties to production temperatures variations. It was also found that gyratory compactors compact asphalt mixtures to a certain density regardless of the temperature (and probably material) because they are, in effect, strain-controlled. Thus, the compaction process in a gyratory compactor is widely insensitive to temperature. Therefore gyratory compaction is not a suitable method for investigating the performance of compaction site that imposes a fixed or set vibratory stress.

Keywords: warm mix asphalt, hot mix asphalt, compaction temperature, asphalt compaction, wax additive, chemical additive, gyratory compaction, asphalt performance, surface energy

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AUTHOR'S STATEMENT

The work presented and described in this PhD thesis was conducted at the University of Nottingham, Department of Civil Engineering, Nottingham Transportation Engineering Centre (NTEC), between February 2012 and February 2016. I declare that the work is my own and has not been submitted for a degree of another university.

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1. **Jalali**, **V.**, Grenfell, J.R.A., Dawson, A.R., "Temperature Effects on Warm Mix Asphalt Performance", *The 12th ISAP Conference on Asphalt Pavements (ISAP 2014)*, Paper 841, Raleigh, North Carolina, USA, June 2014.

2. **Jalali**, **V**. Grenfell, J.R.A., Dawson, A.R., "Measuring the Temperature Loss of Asphalt Mixture within a Gyratory Compactor Mould", Paper prepared to be submitted to *ASTM Journal of Testing and Evaluation*.

1. INTRODUCTION

1.1. BACKGROUND

Sustainability-related and environmental-friendly considerations and criteria can contribute to the control and, maybe, even reduction of the serious issue of Global Warming in various industries. The asphalt production industry cannot be exempt from these considerations. Reducing the production temperatures of asphalt can definitely make a considerable reduction in the required fuel consumption and should lower the resulting emissions of CO_2 (carbon dioxide) and other greenhouse gases. Moreover, producing asphalt at lower temperatures reduces paving costs and may be able to extend the paving season, both of which would result in time and money savings. Therefore, the invention and development of Warm Mix Asphalt (WMA) mixtures can be pointed to as a successful achievement.

The generic term Warm Mix Asphalt refers to a variety of bituminous mixtures, which are produced through specific technologies, at temperatures approximately 15°C to 67°C (25°F to 120°F) (NCHRP Report 779; FHWA, 2015) lower than the typical production temperature range of conventional Hot Mix Asphalt (HMA) mixtures (i.e. 135°C to 160°C) (Sargand et al., 2009).

As a general statement, these technologies allow a reduction in the mixing, placement and compaction temperatures of asphalt and this offers a sustainable and environmental-friendly alternative to HMA.

The reduction in fuel consumption for WMA production results also in a lowering demand for non-renewable fuel extraction and a reduced carbon (emissions) footprint in production and transportation. It has been shown that the ranges of possible energy saving in the production process can be between 20% to 70%, dependant on the production technology. The lower energy consumption will also lead to cost reductions. Moreover, as the production temperature is closer to the ambient temperature, maintaining the temperature of the asphalt and avoiding or lowering the temperature loss, can be performed more easily and with less expense. Of course, as a replacement material for conventional HMA, WMA should have similar performance (i.e. strength and durability) characteristics and functional properties.

All-in-all, the main purpose and idea for such an innovation and substitution in asphalt production technologies and pavement materials, has been to produce mixtures with similar mechanical, durability and performance characteristics to HMA, but at lower temperatures to satisfy the sustainability and Global Warming considerations.

1.2. RATIONALE (PROBLEM STATEMENT)

Application of asphalt involves mixing, hauling, placement and compaction. As a general rule, for conventional asphalt mixtures (i.e. Hot Mix Asphalt) if, during delivery and compaction, the mixture's temperature drops below the minimum allowable production temperature at which adequate compaction can be achieved, then significant reductions in the performance of the resultant mixture can be expected.

As soon as a bituminous mixture, whether WMA or HMA, is removed from the heating source of the mixing site, it cools until it is equilibrated to the ambient temperature. Thus, the longer the distance it is carried and the greater the difference between its temperature and the ambient temperature, the larger and more rapid will be its temperature decline. From a practical, on-site, paving point-of-view, such a temperature drop is unavoidable, even if it may be partially controlled (e.g. by transport in insulated trucks).

The compaction of HMA at reduced temperatures (cool compaction) has been the subject of a number of research studies. However, on the matter of the cool compaction of WMA, no research work was found during the literature review phase of the present study. This may have been because the invention of WMA is relatively new.

However, in the case of WMA mixtures, it is expected that the effects of cool compaction on the properties and performance of the asphalt mixture will be less easily described than in HMA due to the complicating presence of additives. The combination of reduced temperature with the WMA additive aims to modify the viscosity, workability, lubricity, compactability and/or adhesion bond strength to deliver HMA-comparable mechanical performance by the WMA at the reduced mixing and compaction temperatures. The lower temperature and additives can result in:

- less ageing in the WMA binder,
- modified chemical, physical, rheological and mechanical properties of the bitumen,

- modified surface energy properties of both bitumen and aggregate, and
- modified binder-aggregate adhesion properties,

all of which can, consequently, affect the physical properties and mechanical performance of the resultant WMA asphalt mixture in a complex way not directly comparable to the behaviour of conventional HMA mixtures.

The overall goal of this research study is to investigate the effects and implications of temperature decline during delivery, placement and compaction phases on the mechanical performance and functional properties of WMA mixtures, produced in two different ways, include a 'wax/organic additive' technology (using a Fischer-Tropsch paraffin wax) and a 'chemical additive' technology (using a liquid cationic chemical surfactant), along with determining the fundamental reasons for such effects.

In particular, it is to investigate the effects of 'reduced compaction temperature' (also reduced mixing temperature) on the performance of these WMA mixtures (also HMA mixture).

In fact, this study investigates and seeks to understand the effects of cool compaction on the volumetric properties, stiffness modulus, rutting/permanent deformation potential, fatigue failure resistance and resistance to moisture damage. This results in a temperature-dependant relationship between the rheological behaviour and surface energy properties of the binders and the mechanical performance characteristics of the mixtures.

Poor performance of asphalt, whether WMA or HMA, will have negative economic consequences, effectively opposing any environmental benefit. Therefore, from both a practical and an economic viewpoint, research to evaluate the effects of temperature decline during the mixing, delivery and placement phases on the mechanical performance of WMA and its potential for distress is needed. Hence this research, which expected to be of both practical benefit and economic value.

1.3. COMMERCIAL CONSIDERATIONS

In this thesis, mentioning the name of the wax additive has been avoided due to commercial considerations, likewise so has mentioning the name of the chemical additive. In this regard, the commercial name of the wax additive in the whole thesis has been replaced by term 'Fischer Tropsch (FT) wax' or similar derivatives or, wherever required, abbreviated or prefixed as

FTWax or FTWx. In the same way, the commercial name of the chemical additive has been replaced by term 'cationic surfactant liquid' or similar derivatives or, wherever required, abbreviated or prefixed as CatSurfLq or CSLq in the whole text.

1.4. AIM

The research aim was to study the effects and implications of compaction temperature decline on the mechanical performance and functional properties of some Warm Mix Asphalt (WMA) mixtures, along with a determination of the fundamental reasons for any observed changes in behaviour.

1.5. OBJECTIVES

1) Compile BSEN-based manufacturing instructions to produce WMA mixture in laboratory using FT wax additive and CatSurfLq chemical additive technologies;

2) Characterisation of the FTWax-modified and the CatSurfLq-modified bituminous binders and their pure base bitumen in order to determine and understand the effect of FT wax additive and CatSurfLq chemical additive on the physico-mechanical, rheological and surface energy characteristics of bitumen;

3) Develop a method to simulate the condition of cool compaction of asphalt (asphalt compaction at reduced temperatures) using asphalt manufacturing equipment in the laboratory;

4) Manufacture FTWax-WMA, CatSurfLq-WMA and conventional HMA mixtures through the devised laboratory method to simulate the conventional and cool temperature compaction of asphalt;

5) Determine the performance (i.e. strength, and durability) characteristics of the produced WMA and HMA mixtures to understand/define the effects of compaction temperature (in particular) and production temperature (in general) on the properties of asphalt mixtures such as stiffness, viscoelastic characteristics (i.e. complex stiffness modulus and phase angle), moisture sensitivity, rutting potential, fatigue resistance and volumetric properties (including permeability), with or without the studied WMA additives;

6) Provide fundamental explanations for the mechanical test results and failure types by evaluating the binder-aggregate bond strength using the surface energy calculations and a mechanical assessment test;

7) Assess the moisture susceptibility of binder-aggregate bond in the mixtures using the surface energy calculations in order to provide fundamental justification for the mechanical moisture sensitivity evaluation test results;

8) Perform visual observations of failed surfaces in order to:

- Provide supporting evidence for the performance test interpretations,
- Investigate the binding/coating quality in the mixtures,
- Study the post-failure structure of the tested specimens, and
- Define the adhesiveness or cohesiveness of the failures in destructive tests;

9) Define a fabrication-temperature-dependant relationship between:

- The rheological behaviour and the surface energy properties of the binder,
- The binder-aggregate adhesion quality and strength, and
- The mechanical performance characteristics of the resultant mixtures;

10) Develop approaches and guidelines to improve the performance of the mixtures (if necessary) or reduce the potential of distresses which may result from the cool compaction of asphalt mixtures

1.6. METHODOLOGY

The present PhD study is generally a laboratory–based research work or a laboratory-scaled experimental and analytical research.

In general definition, the method applied to conduct this research through the objectives and towards the aim of the study, overall, includes:

- Simulating the problem of cool compaction of asphalt at laboratory scale,
- Testing the samples produced through the problem simulation process,
- Analysing the test results/data, and

- Interpreting the outcomes to achieve the aim(s).

However, justifying and interpreting the mixture test results is not possible/credible without considering the rheological and mechanical behaviour of the involved binders, the coating properties and the binder-aggregate adhesion quality, especially in the case of WMA with the likely complications due to the presence of additives and low production temperatures.

Inevitably, the initially planned work programme had to be modified due to:

- Some limitations in the available amount of materials,
- Some difficulties in supplying the additives,
- Some unpredicted/unexpected problems in instrumentation,
- Avoiding tests that proved unnecessary once early results become available,
- Need for a more efficient test matrix, and
- Need for more fundamental laboratory tests.

Therefore, some of the early testing now has lost relevance to the final study and is omitted from the thesis.

All in all, the methodology according to which the present study and laboratory operations have been completed and conducted through the objectives and towards the aim of the study is as follows:

1) LITERATURE REVIEW

A detailed and comprehensive literature review was accomplished and written, studying primarily performed research programs and published literature particularly focused on:

- The studied features of WMA mixtures,
- The influence of wax on bitumen characteristics,
- The function of chemical adhesion promoters and surfactants in bitumen,
- The compaction of asphalt and the cool compaction of asphalt,
- Surface energy characteristics of bitumen (measurement and application) and
- Bitumen-aggregate interaction and adhesion evaluation.

These formed/provided/developed the necessary base knowledge/background for the current research work (test results interpretations and justifications) and also revealed the existing research gaps on the subject to emphasise the necessity for doing the current research.

2) DEVELOP BSEN-BASED MANUFACTURE CONSIDERATIONS

Before starting the main laboratory operations, it was necessary to develop some kind of manufacturing instructions and recommendations for WMA laboratory production, in terms of bitumen preparation temperature, bitumen modification process and mixture fabrication. The mentioned issues were mostly extracted, converted and simulated from the US pioneer codes, standards, research programs and reports. However, they all had to be compatible to and based on BS EN considerations for HMA mixtures. This was firstly because, basically, there has not been any known or reliable experience, recommendations or considerations of manufacturing the mentioned mixture types in BS EN Standards issued at the time the present study started. Secondly, in practice, there have never been any investigations or manufacturing experience on WMA in the background of the Nottingham Transportation Engineering Centre (NTEC) laboratories.

The mentioned lack of experience also made it necessary to organise a series of familiarisation operations for the purpose of making all people involved in the research, including the researcher, the supervisors and the laboratory technicians familiar with the behaviour of this type of mixture (WMA) and improving the quality and reliability of the production and testing process.

3) BINDER SAMPLES PREPARATION

The pure bitumen and the modified binders were produced in the laboratory in order to be used for binder characterisation and mixture manufacture. The modified binders were made in two different ways included adding FTWax as a waxy additive (waxy modifier) and Rediset LQ as a chemical additive (adhesion promoter and surfactant). Each of the mentioned additives has been added at different dosage levels to the virgin bitumen. Using different dosages of the additives have been for the purpose of investigating the effect of additive dosage on bitumen characteristics to have a more clear understanding of the modifier's function.

In this study, three extremely different virgin/pure bitumens, in terms of penetration grade, have been selected for the purpose of binder tests (not manufacture), which included a hard

base binder, a very soft base binder and a mid-range binder (a certain blend of the other two). This combination has been chosen in order to have a wide range of bitumen stiffness in the study to investigate how a virgin/pure binder's stiffness variation can offset or generally influence the additives' effectiveness.

Meanwhile, neat/virgin/pure binders have been used in order to have reference behaviour of the bitumen without additives so that the difference between the types/natures of modification developed by each of the additives could be clearly defined.

4) BINDER CHARACTERISATION TESTING

A devised comprehensive matrix of laboratory tests was performed on the produced neat/pure/virgin and the modified binders (FTWax-modified and CatSurfLq-modified binders) in order to provide the various used binders' physico-mechanical and rheological behaviour characterisation as well as their surface energy properties measurement. The matrix of tests has included:

1) Penetration Grade measurement,
2) Softening Point determination,
3) Fraass Breaking Point determination,
4) Rotational viscometry using a Brookfield viscometer over a high temperature range,
5) Complex Shear Stiffness Modulus and Phase Angle (viscoelastic characteristics) measurement using the Frequency-and-Temperature Sweeps test, and
6) Bitumen Wax Content evaluation

for the purpose of properly understanding of the WMA additives' influences on the used bitumen's Physico-mechanical, rheological properties and the way/process through which the mentioned influences took place, and also

7) Surface energy measurement through the Dynamic Contact Angle (DCA) method using a Wilhelmy Plate apparatus

for the purpose of observing the effects of the WMA additives on the surface energy characteristics and the cohesive strength of the binders, also to evaluate/calculate the binder-aggregate dry bond strength and moisture susceptibility (work of debonding in the presence of water).

As a fact, asphalt mixture's performance and properties are highly affected by its binder characteristics and rheological behaviour. It means that binder characterisation is an essential process which provides fundamental and applicable information to interpret and justify the mixture's response to the performance tests.

5) MANUFACTURE WMA and REFERENCE HMA MIXTURES and SPECIMENS

The process of simulating the situation/state/condition of cool compaction of asphalt (compaction at reduced temperatures) in the laboratory consisted of producing FTWax-WMA, CatSurfLq-WMA and Reference HMA test mixtures and samples, mixed at recommended and adequate mixing temperatures (according to the Standard or the additive supplier's advice) and compacted at a declining series of compaction temperatures.

The test mixtures and samples were fabricated using two different compaction methods (i.e. gyratory compaction and slab roller compaction) to avoid the likely offsetting effect of the compaction methods on the devised cool compaction simulation process. For each method of compaction, the mixtures were produced in various groups of samples, considering the priority, according to their:

1- Type of additive in the mixture (or no additive), and

2- Production temperatures.

In order to narrow the affecting variables in the research to the main studied parameters (i.e. production temperatures and additives), the same:

- Aggregate quarry, type and gradation,
- Bitumen source, pen grade and binder content,
- Compaction setting, and
- Specimen geometric shape and dimensions

were used to produce all groups of the samples of each compaction method.

6) MIXTURES PERFORMANCE CHARACTERISATION TESTING

A devised comprehensive set of laboratory tests was carried out to fully characterise the manufactured WMA mixtures and their counterpart reference HMA mixtures/specimens properties in order to study and understand the influence of reduced production (in general) or

compaction (in particular) temperatures on their performance (i.e. strength and durability) characteristics including volumetric properties, mechanical performance characteristics (stiffness modulus, fatigue resistance, rutting potential), viscoelastic behaviour representatives (complex stiffness modulus and phase angle) and durability properties (moisture sensitivity). This set of mixture tests included:

1) Bulk Density measurement,
2) Air Void Content determination,
3) Indirect Tensile Stiffness Modulus evaluation (ITSM/IT-CY) test,
4) Direct Dynamic Compressive Complex Stiffness Modulus test (DDCCSM), which is a devised modified version of AASHTO TP 62-03 in order to assess the complex stiffness modulus and phase angle of the asphalt mixtures over a range of temperatures and frequencies to have a better and more confident understanding of the mixture properties and the other mechanical performance test results, also a more comprehensive scan of the mixture's performance over a wider range of temperatures,
5) Indirect Tensile Fatigue Test (ITFT),
6) Repeated Load Axial Test (RLAT) for permanent deformation evaluation, and
7) Revised modified Lottman test, which is a devised mode of the modified Lottman test (AASHTO T 283), for assessing the water sensitivity of the mixtures.

7) BINDER-AGGREGATE ADHESION BOND STRENGTH QUANTIFICATION

The binder-aggregate dry bond strength of the various binder and aggregate combinations/systems used in producing the different asphalt mixtures in the study was evaluated using the surface energy calculations for work of adhesion, having/combining the surface energy properties/parameters of the different binders (pure base bitumen, FTWax-modified and CatSurfLq-modified binders) and aggregates (pure and modified aggregates) involved in the study. Moreover, a mechanical assessment test namely PATTI (Pneumatic Adhesion Tensile Testing Instrument) was performed on different coating samples of the various binder and aggregate combinations/systems used in the study to produce the test asphalt mixtures, for the purpose of measuring the tensile strength of the coatings as representative of their binder-aggregate adhesive or binder cohesive tensile strength in their corresponding/counterpart mixtures. The results of both the computational and the mechanical

testing methods for binder-aggregate adhesion quantification provided fundamental explanations for the mechanical test results and failure types.

8) CALCULATE WORK of DEBONDING in the PRESENCE of WATER

The moisture susceptibility of binder-aggregate bond in the manufactured mixtures were evaluated using the surface energy calculations for work of debonding in the presence of water, having/combining the surface energy properties/parameters of water, the different binders (pure base bitumen, FTWax-modified and CatSurfLq-modified binders) and the aggregates involved in the study. This provided a fundamental justification for the results of the revised modified Lottman moisture sensitivity evaluation mechanical test.

9) VISUAL INVESTIGATIONS

Visual investigations were performed occasionally in the form of high definition photography image analysis or, by the naked eye, analytical observations of the failure surface or the deformed shape/structure of the samples failed through the destructive tests in order to:

- Provide supporting evidence for the performance test interpretations,
- Investigate the binding/coating quality in the mixtures,
- Study the post-failure structure of the tested specimens, and
- Define the adhesiveness or cohesiveness of the failures in destructive tests.

10) TEST RESULTS and CONCLUSION

The results of the accomplished

- Binder characterisation tests,
- Binder-aggregate adhesion qualification and quantification evaluations,
- Visual investigation, and
- Mechanical/functional performance tests of the resultant mixtures

were studied. The results were considered as a function of the mixtures' compaction (and mixing) temperatures. Some fabrication-temperature-dependant relationships with these observed responses were defined, extracted and delivered.

Finally, approaches and guidelines were developed for each WMA production technology considering the type of additive, to improve the performance of the mixtures (if necessary) or to reduce/lower the potential of distresses which might result from the cool compaction of the asphalt mixtures.

1.7. SCOPE

Inevitably, there were limitations to the investigations reported in this thesis. These are as follows:

- **Laboratory-Based Asphalt Manufacture:** The performance and behavioural studies in this research have been carried out via laboratory tests performed on asphalt specimens fabricated using laboratory equipment (i.e. mixer and compactor). This means that they may not be fully representative of real field asphalt specimens taken (e.g.) from an actual road pavement.

- **FT Wax Additive and CatSurfLq Chemical Additive Production Technologies of WMA:** The WMA mixtures used in the study were FTWax-WMA and CatSurfLq-WMA mixtures, being representatives of the wax and chemical additives technologies of WMA production respectively. WMA is generally categorised according to the 3 main production technologies (wax, chemical additive and foaming). Therefore, the results of this study, with regards to the characteristics of the FTWax-modified binder(s) and the performance of FTWax-WMA mixture(s), should only be cautiously generalised to other wax-modified binders and wax-WMA mixtures. Similarly, the research results on the CatSurfLq-modified binders and the CatSurfLq-WMA mixtures should only be considered as a qualitative representative for the characteristics of chemical-additive-modified binders and chemical-additive-WMA mixtures. Moreover, the results cannot be generalised separately or in combination as representative of the characteristics of WMA mixtures generated by foaming agents. This is because, in spite of the general similarities between the concept and theory of WMA, there are significant physio-chemical differences between and within WMA mixtures produced in the different ways. These can be expected to cause quantitatively different performance properties.

- **Gyratory and Slab Roller Compaction Methods:** The compaction methods applied in this research have been gyratory and slab roller compaction. Not only can laboratory

compaction methods never be totally simulative of real field compaction, but also they will produce specimens with different properties (i.e. volumetric properties, permeability, durability and to some extent, strength) from the same mixture. This fact has to be considered seriously when generalising the findings of the current study to the same mixtures manufactured by other laboratory compaction methods or to the specimens cored from an actual field pavement. For instance, using a gyratory compactor makes the compaction process independent of temperature in a sense that well-compacted asphalt samples can be fabricated even at low temperatures. This does not happen when a Marshall or a roller compactor is used and certainly is not true on-site.

- **Limestone Aggregate:** All the materials described here were manufactured using limestone aggregate. Two different limestones were used in this study (each for a particular compaction method). Although both were limestone, they had differing physio-chemical (water absorption) and surface energy (acidic/basic) properties. As a result, the asphalt samples manufactured using the two different types of aggregates have differences in properties which are independent of their WMA additive or compaction procedure and temperature. Therefore, the results of this research should not be directly compared or generalised (whether qualitatively or quantitatively), in terms of surface energy (SE) and water absorption (WA) related properties, to other types of limestone with different SE and WA specifications. In addition, the results should not be compared or generalised, in any term, to other types of aggregates than limestone (e.g. granite).

- **Basic Bitumen:** The bitumen used in the current research was slightly basic instead of being acidic as would normally be used with limestone aggregate. Therefore, attention should be paid when applying the findings of the present research to applications likely to be affected by surface energy and binder-aggregate interactions.

- **Other Research Specifications:** There are other properties such as aggregate gradation curve, bitumen pen grade, mixing and compaction temperatures, etc., which should be considered when generalisation or comparison of the results of this research to other studies is desired.

1.8. NOVELTY and CONTRIBUTION to THE RESEARCH COMMUNITY

The most remarkable point of novelty in this research has been to simulate the cool/cold compaction of asphalt in laboratory with significant success. This involved the compaction of asphalt concrete (i.e. HMA and WMA) at significantly reduced temperatures, as low as 80 and 85°C in order to study and determine the full spectrum characterisation of the reduced temperature compacted mixtures' properties (permeability and mechanical performance i.e. durability and strength). In fact, the cool/cold compaction of asphalt was carried out in such a way that the effect of compaction temperature on materials' properties could be observed clearly.

Other novel aspects of this research includes that the HMA mixtures in this study were also mixed at reduced temperatures (as low as WMA mixtures) so the influence of WMA additives could be investigated regardless of the difference in the mixing temperature of WMA and HMA.

The results of this study can be highly beneficial for the environment and sustainability since it has been shown that both HMA and WMA can have reasonably acceptable performance and properties even if they are compacted at as low as 80 or 85°C.

One of the innovative aspects of this study is to measure the surface energy of the WMA additive modified binders and also the additive modified aggregates (aggregates which have been modified by WMA chemical additives). This was done in order to evaluate the mixture properties, provide fundamental support to justify the binder and mixture test results and evaluate the binder-aggregate interactions in the mixtures realistically and precisely. This was also carried out to study and predict the moisture susceptibility of the different types of mixtures. For this purpose, the surface energy of the modified aggregates was measured by devising specific technique to modify the aggregates by WMA additives before testing in the DVS.

Also, in order to evaluate the viscoelastic behaviour of the asphalt mixtures, a modified version of AASHTO TP 62-03 was devised in terms of the test frame settings.

In addition, the moisture sensitivity test in this research has been a specially devised modified method of AASHTO T 283. In contrast with the single destructive nature of the Lottman and

Modified Lottman tests, the newly devised sequence included multi-non-destructive phases which allowed any single test specimen's behaviour and properties to be monitored precisely through the various conditioning phases.

Moreover, the adhesion quality of different binder-aggregate combinations (modified or pure) was evaluated through a mechanical test (PATTI) in order to study the influence of additives and mixing temperature on binder-aggregate interaction in the different WMA and HMA mixtures manufactured.

All devised methods in this study have been helpful in extracting more detailed information about the behaviour of the materials. Therefore, they can be used by other researchers in future asphalt research.

1.9. THESIS STRUCTURE

The present thesis consists of the following 8 chapters:

Chapter 1 introduces the project through presenting the aims, objectives, methodology, scope and novelty of the conducted research. This follows a background and rationale, firstly to emphasise the importance of using Warm Mix Asphalt and secondly to mention importance and necessity of studying the possible changes in the performance and properties of WMA mixtures where they are, due to any practical and possible reason, compacted at reduced temperatures

Chapter 2 presents a comprehensive literature review on Warm Mix Asphalt, the history of the innovation, WMA production technologies, additives, studied and discovered aspects of behaviour and performance and advantages and disadvantages of application. Then, the structure and constitution of bitumen, theories of bitumen-aggregate interaction and adhesion, results of the studies on the behaviour of wax-modified and chemical-additive-modified bitumen and the resulted WMA mixtures are investigated. Also, the compaction of asphalt and the issue of cool compaction of asphalt mixtures are looked at. This chapter provides a proper background for studying the results and discussions of the current research. At the end of this chapter, a conclusion has been provided in order to mention the key gaps related to the topic, which have been found through the literature review and are tried to be covered through the current project.

Chapter 3 introduces the methodology of the project in full details in terms of the materials and tests which have been used in the project, methods of mixture production and compaction and the comprehensive matrix of binder, mixture, binder-aggregate laboratory tests.

Chapter 4 presents the results of the rheological and mechanical tests (DSR, viscometry, etc.) and surface energy measurements (DCA) which were performed on the pure bitumen samples and their modified derivatives by FT wax and CatSurfLq chemical additive in order to fully characterise the binders of FTWax-WMA and CatSurfLq-WMA mixtures.

Chapter 5 includes the results of the DVS test on pure and modified aggregates and the results of surface energy calculations to evaluate the binder-aggregate 'dry bond strength' and 'moisture sensitivity'. Also, the results from the PATTI, as a mechanical test method for characterising the binder-aggregate adhesive tensile strength are presented to provide a better understanding of the quality of binder-aggregate adhesion quality in the manufactured WMA specimens.

Chapter 6 provides the results of the performance tests which were accomplished on the manufactured asphalt samples in the laboratory in order to fully characterise the various WMA and HMA mixtures which were manufactured/compacted at reduced temperatures. The tests included ITSM for stiffness modulus, ITFT for fatigue resistance, RLAT for permanent deformation potential, revised modified Lottman for moisture sensitivity, Direct Dynamic Complex Stiffness Modulus (DDCCSM) for evaluating the viscoelastic behaviour and volumetric measurements. The results were discussed in detail through the chapter and it was tried to link them together. A conclusion was provided at the end of the chapter as the summary of the findings.

Chapter 7 presents an outline of the key findings and conclusions from the conducted research study.

Chapter 8 provides an outline of proposals for future research.

2. LITERATURE REVIEW

This chapter includes an up-to-date comprehensive summary of the studied literature relevant to the present research.

2.1. WARM MIX ASPHALT (WMA) MIXTURES

The generic term Warm Mix Asphalt (WMA) refers to a variety of bituminous mixtures, which are produced through specific technologies, at temperatures approximately 15°C to 67°C (25°F to 120°F) (NCHRP Report 779; FHWA, 2015) lower than the typical production temperature range of conventional Hot Mix Asphalt (HMA) mixtures (i.e. 135°C to 160°C) (Sargand et al., 2009). The production technologies allow a reduction in the mixing, placement and compaction temperatures of asphalt and offer an alternative to Hot Mix Asphalt.

In fact, various WMA technologies use different additives (e.g. wax/organic additives, chemical additives, foaming agents), in some cases combined with particular methods, to improve the workability of mixture, increase mixture's lubricity or reduce the viscosity of binder at reduced mixing, placing and compaction temperatures, while providing reasonable and adequate or even improved coating of aggregates (dried) to deliver comparable performance to conventional HMA at operating temperatures.

In other words, the main purpose and idea for such an innovation and substitution in asphalt production technologies and pavement materials, has been to produce mixtures with similar strength, durability and performance characteristics to HMA but at lower temperatures. However, WMA offers several advantages over conventional HMA. From the viewpoints of sustainability and environmental considerations, reducing asphalt production temperature can make a considerable reduction in fuel consumption and therefore should lower greenhouse gas emissions. Other benefits of replacing HMA by WMA can include (FHWA, 2015):

- Reducing paving costs,
- Extending paving season,
- Improving asphalt compaction,
- Allowing asphalt mixture to be hauled longer distances, and

- Improving working conditions by reducing exposure to fuel emissions, fumes, and odours.

2.2. A SHORT HISTORY of WMA

A glance at the former attempts in asphalt industry for lowering the asphalt production heat, as follows, illustrates that this issue refers to the several past decades as basically, the idea of saving energy and lowering greenhouse gas emissions is not a new concept (Sargand et al., 2009).

In this regard, using foamed bitumen as soil binder can be considered as one of the very first cases, which has been devised by Professor Ladis Csanyi of Iowa State University in 1956. In this process, steam was injected into hot bitumen to reduce the mixing temperature. Later, in 1968, Mobil Oil Australia replaced the hot steam in the process with cold water in order to foam hot bitumen (Sargand et al., 2009).

In the early 1970s, Chevron Corporation developed new methods to prepare paving mixtures stabilised by emulsified bitumen. In 1977, Chevron published their "Bitumuls Mix Manual" (Sargand et al., 2009).

However, WMA in its present form was first developed in Europe in the late 1990s as a measure to reduce greenhouse gas emissions.

In 1994, Maccarone et al. evaluated the performance of Cold Mix Asphalt by using two different materials including foamed bitumen and very high binder content emulsions. They concluded that due to the energy efficiency and lower emissions of Cold Mix Asphalt technologies, they would be accepted worldwide and represented the future of road surfacing (Sargand et al., 2009).

In 1995, MHI (Mitteldeutsche Hartstein-Industrie AG) started testing Aspha-min® Zeolite. The zeolite is in fact a foaming agent which through the foaming action increases the workability of the mixture at lower production temperatures (Sargand et al., 2009).

In the same year, Shell Bitumen filed a patent for a two-component process to produce Warm Mix Asphalt (Button et al., 2007).

In 1996, Koenders et al. of Shell Global Solutions described the WAM (Warm Asphalt Mix) Emulsion as an innovation which was tested in the laboratory and evaluated in large-scale field trials in Norway, in the UK and Netherlands. This work of Shell, later in 2002, resulted in the development of WAM-Foam® (Button et al., 2007).

In 1997, Sasol Wax International AG started selling Sasobit®, a Fischer-Tropsch wax, in Europe as an asphalt mixture compaction promoter. This material became one of the most famous and frequently used technologies in producing Warm Mix Asphalt mixtures (Button et al., 2007). The first pavements by the use of Sasobit® were constructed in Hamburg, Germany in 1997 (Prowell, Hurley & Frank, 2012).

In 1999, Jenkins et al. introduced a new method that included a half-warm foamed bitumen process through which the aggregate was preheated to temperatures above ambient and below 100°C before adding the foamed bitumen. Studying the advantages of the new technology illustrated an acceptable aggregate coating, binder cohesion, tensile strength and compaction (Sargand et al., 2009).

Moreover, the first WAM-Foam® trial in Norway (by Kolo Veidekke) and the earliest Aspha-min® Zeolite trials on public roads in Germany were placed in 1999 (Prowell, Hurley & Frank, 2012).

In 2000, Warm Mix Asphalt was demonstrated by Harrison and Christodulaki at the First International Conference of Asphalt Pavements (FICAP) in Sydney, Australia (Harrison & Christodulaki, cited in Sargand et al. 2009).

In 2002, the National Asphalt Pavement Association (NAPA), from the US, identified new technologies in Europe which held the promise of reducing production and construction temperatures (Prowell, Hurley & Frank, 2012). They led a research tour to Europe to Denmark, Germany and Norway to examine WMA technologies including Aspha-min®, WAM-Foam® and Sasobit®.

In fact, research at the National Centre for Asphalt Technology (NCAT) and elsewhere had previously shown that lowering the plant mix temperature even by 6°C can significantly reduce the production of emissions from asphalt mixtures. In the same year, NAPA did a study tour to introduce WMA technology to the US (Prowell, Hurley & Frank, 2012).

In 2002, Koenders introduced the use of WAM-Foam® technology to produce asphalt mixtures at lower temperatures.

Then, at the Eurobitume congress in 2004, Barthel et al. introduced the use of a synthetic zeolite additive to produce Warm Mix Asphalt (Sargand et al., 2009).

In 2003, WMA was featured at NAPA's Annual Convention. In the same year, research on WMA began at NCAT.

In 2004, MeadWestvaco Company introduced Evotherm™ ET, an additive for producing WMA. Moreover, the first field trials were constructed in Florida and North Carolina of US in this year.

In 2005, numerous field trials were conducted in Florida, Indiana, Maryland, New Hampshire, Ohio and Texas of America and also in Ontario and Quebec of Canada.

Moreover, in 2005, NAPA and the Federal HighWay Administration (FHWA) formed the WMA Technical Working Group (WMA TWG) in order to develop a data collection framework for WMA trials, which had been examined and evaluated by different individual agencies. In fact, they were of the opinion that if WMA was to be used widely in the US or even all over the World, companies should be confident in the performance of WMA pavements and have a generic method of specification (Prowell, Hurley & Frank, 2012).

Meanwhile, in 2005, NCAT published two reports on the use of Sasobit® and Aspha-min® as two WMA additives.

In 2006, the WMA TWG published a testing framework for Warm Mix Asphalt trials, which is still available at www.warmmixasphalt.org (2016). It covered various engineering, environmental and worker health and safety aspects of WMA. As an important aspect of the framework, an HMA control section was included along with any of the WMA trials in order to provide a side-by-side comparison. The WMA TWG assimilated the data and short-term field performance collected from the various early trials. The collected data were used to develop a generic guide specification for WMA, in such a way that agencies do not need to specify a particular technology (Prowell, Hurley & Frank, 2012). Meanwhile, in 2006, another report was published by NCAT about using Evotherm® to produce Warm Mix Asphalt. In

addition, lots of field trials were conducted in America (California, Michigan, New York, South Carolina, Texas, Virginia and Wisconsin).

Moreover, in 2006, FHWA, in conjunction with the American Association of State Highway and Transportation Officials (AASHTO) and the National Cooperative Highway Research Program (NCHRP), began planning and organising an International Technology Scanning Tour on WMA. The purpose of the scan tour was to gather additional information on WMA technologies, which could be useful in execution and especially long-term performance (Prowell, Hurley & Frank, 2012).

In May 2007, the scan team, which consisted of 13 US materials experts, travelled to Europe and visited four European countries including Belgium, France, Germany and Norway, in order to observe the various WMA technologies they were using at the time and also to evaluate the performance of some of the oldest WMA projects in Europe. By this means, the US experts could meet the agencies which first used the WMA technologies, the suppliers and contractors that developed them and the contractors which constructed the WMA pavements. According to the team, although some WMA technologies originated in Europe, the US had made greater steps in evaluating and implementing this new type of asphalt. Moreover, in this year (2007), the first National Cooperative Highway Research Project (NCHRP) 9-43 on WMA began. It was completed in 2011 to develop mix design methods for WMA (NCHRP Report 714).

In addition, in 2007, MeadWestvaco introduced Dispersed Asphalt Technology (DAT) introduction system for Evotherm™, Astec introduced foamed asphalt technology, Advera® zeolite WMA was introduced by PQ Corporation and Rediset™ was introduced by AkzoNobel. In addition, numerous WMA field trials were conducted across the US and Canada.

In 2008, the WMA TWG developed a Warm-Mix Asphalt (WMA) Guide Specification for Highway Construction in AASHTO format. The Texas Department of Transportation (TxDOT) developed a specification, which allowed contractors state-wide to use WMA instead of HMA. In this year, another NCHRP research project, NCHRP 9-47, was initiated to record the engineering properties, emissions, and field performance of WMA (Prowell, Hurley & Frank, 2012).

In November 2008, the first International Conference on WMA, which was held in Nashville, Tennessee was sold-out by over 750 attendees. The attendees showed a keen interest in Warm Mix Asphalt and the presentations were webcast worldwide.

Between 2008 and 2010, there was a considerable increase in the number of WMA technologies marketed in the US, especially the mechanical foaming technologies, which did not use any additive (Prowell, Hurley & Frank, 2012).

In 2010, FHWA made WMA one of its five Every Day Counts (EDC) inventions to speed the deployment of technologies, which could improve highway projects' quality, sustainability, and safety (WMA TWG, 2016). EDC inventions are designed to identify and deploy innovations with the potential of shortening project delivery, raising roadways' safety and protecting the environment.

According to a survey, which was conducted by NAPA in 2009 and 2010, the estimated use of WMA in the United States has increased from 19.2 million tons in 2009 to 47.6 million tons in 2010, representing approximately 13 percent of total asphalt production in 2010. The majority of the WMA has been produced using mechanical foaming devices (Prowell, Hurley & Frank, 2012).

The latest NAPA/FHWA survey of asphalt producers' use of recycled materials and Warm Mix Asphalt found that nearly 25 percent of all asphalt produced during the 2012 construction season has been Warm Mix Asphalt. The survey, conducted by NAPA under contract to FHWA, found the amount of WMA to be about 86.7 million tons in 2012. This is a 26 percent increase since 2011 and a 416 percent increase in the use of Warm Mix since the survey was first conducted in 2009 (WMA TWG, 2016).

In 2013, NAPA and FHWA were honored by the Construction Innovation Forum, earning a NOVA Award for their work promoting the uptake of WMA (WMA TWG, 2016).

Moreover, in 2013, the total WMA tonnage in the US was estimated at about 106.4 million tons, a 23 percent increase from 2012 and a greater than 533 percent increase since 2009. Most WMA in the US was produced using a plant foaming process, which injects a small amount of water into the mix. However, Warm Mix additive technologies accounted for a little more than 13 percent of the whole WMA tons produced.

At the time of writing the current thesis, the 2014 Survey of Asphalt Mix Producers is still in process of requesting for more participates in order to gather more information and extend the associated required data base (WMA TWG, 2016).

2.3. WMA PRODUCTION TECHNOLOGIES and ADDITIVES

In this section, the main Warm Mix Asphalt (WMA) technologies will be described with a brief explanation of the various methods included in each of them.

2.3.1. CLASSIFICATION of WMA TECHNOLOGIES

WMA technologies can be classified mainly in two ways. In the first way, they can be classified according to the production temperature or in other words based on the temperature reduction achieved through the technology. There can also be another classification of WMA products, which is according to the production technology and the process which is applied to reduce the temperature.

2.3.1.1. Classification of WMA According to Production Temperature

There is a wide range of production temperatures within WMA, from products which are 10°C to 20°C below HMA to temperatures slightly above 100°C and for some technologies even below the boiling point of water. As shown in Figure 2.1 a common asphalt classification by the production temperature is suggested as follows (D'Angelo et al., 2008):

- Cold Mix Asphalt (0-30°C)
- Half-Warm Mix Asphalt (65-100°C)
- Warm Mix Asphalt (100-140°C)
- Hot Mix Asphalt (above 140°C)

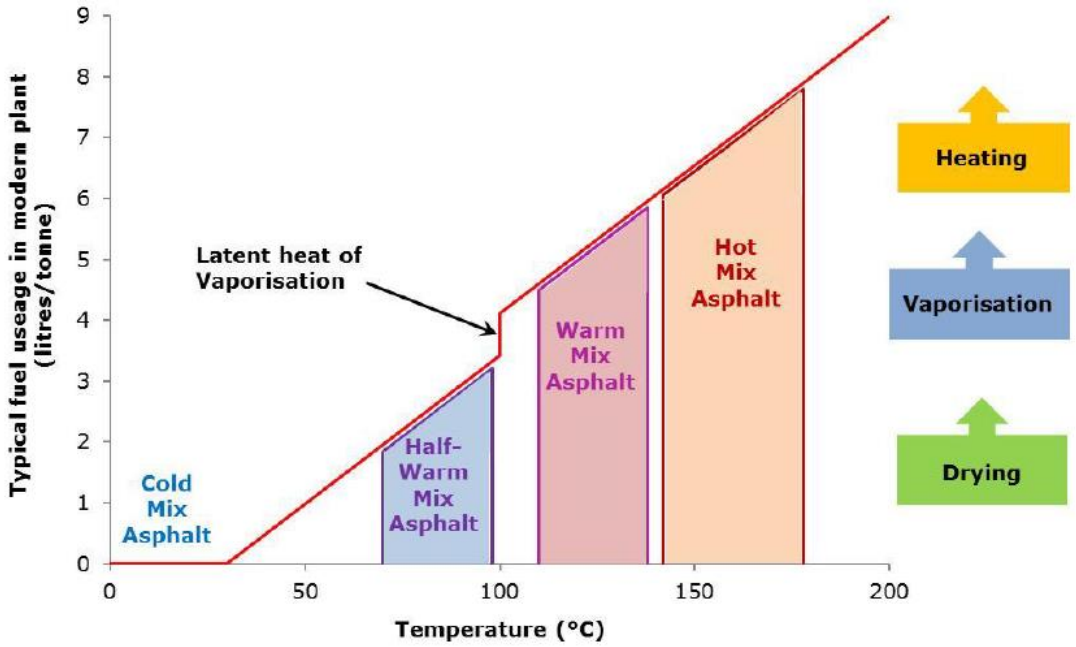


Figure 2.1 : Schematic of classification for Hot, Warm, Half-Warm and Cold mix asphalt mixtures (Nicholla et al., 2015)

2.3.1.2. Classification of WMA According to Production Technology

According to this classification, WMA technologies can be divided into the following categories:

- Organic or Wax Additives Technologies
- Chemical Additives Technologies
- Foaming Technologies (which are divided into water-based and water-containing)

All of the existing products use at least one of the above mentioned technologies. Meanwhile, there may be combinations of them as well. The earliest WMA processes developed in Europe were based on using either waxes or foamed asphalt (D'Angelo et al., 2008).

2.3.2. DESCRIPTION of WMA TECHNOLOGIES

A summary of the products can be found in Table 2.1, Table 2.2 and Table 2.3 containing the mostly reported regions of application for each production technology. Due to finding different recommendations in different reports regarding the production temperature for a single product, the most commonly reported data or the data reported by the production company are listed in the table. A more detailed description of each production technology has been provided

in the following table. Some main factors such as type and dosage of the additives, humidity of the materials, mixture design method, climatic conditions, aggregate type and gradation, bitumen grade etc. could be the reason for getting different results in different reports in terms of recommended additive dosage or production temperature.

Table 2.1 : Summary of WMA production technologies using organic (wax) additives (D'Angelo et al., 2008)

Sasobit		
	Company:	Sasol Wax (South Africa)
	Description:	Fischer-Tropsch wax
	Additive:	Yes, in Germany added on average 2.5% by weight of binder; Lower doses, 1.0-1.5%, used in U.S.
	Production Temperature at Plant (°C):	Varies, 20-30°C drop from HMA. German guideline recommends 130 to 170°C, depending on binder stiffness
	Use Reported in:	Germany, U.S. and 20 other countries worldwide
Asphaltan-A, Romanta-N		
	Company:	Romanta GMbH
	Description:	Montan wax for mastic asphalt
	Additive:	Yes, 1.5-2.0% by weight of binder
	Production Temperature at Plant (°C):	20°C drop from HMA
	Use Reported in:	Germany
Asphaltan-B		
	Company:	Romanta GMbH
	Description:	Refined Montan wax with fatty acid amid for rolled asphalt
	Additive:	Yes, in Germany by 2.0-4.0% by weight of binder
	Production Temperature at Plant (°C):	Varies, 20-30°C drop from HMA; German guideline recommends 130 to 170°C, depending on binder stiffness
	Use Reported in:	Germany
Licomont BS 100 (additive) or Subit (binder)		
	Company:	Clariant
	Description:	Fatty acid amide
	Additive:	Yes, approximately 3% by weight of binder
	Production Temperature at Plant (°C):	Varies, 20-30°C drop from HMA; German guideline recommends 130 to 170°C, depending on binder
	Use Reported in:	Germany
3E LT or Ecoflex		
	Company:	Colas
	Description:	Proprietary
	Additive:	Yes, not specified
	Production Temperature at Plant (°C):	Varies, 30-40°C drop from HMA
	Use Reported in:	France

Table 2.2 : Summary of WMA production technologies using chemical additives (D'Angelo et al., 2008)

Evotherm™ ET		
	Company:	Mead-Westvaco
	Description:	Chemical bitumen emulsion (hot aggregate coated with emulsion)
	Additive:	Delivered in form of bitumen emulsion
	Production Temperature at Plant (°C):	85–115°C
	Use Reported in:	France, Canada, China, South Africa and U.S.
Evotherm™ DAT		
	Company:	Mead-Westvaco
	Description:	Chemical package plus water
	Additive:	3.0% by weight of binder
	Production Temperature at Plant (°C):	85–115°C
	Use Reported in:	U.S., France and worldwide
Evotherm™ 3G		
	Company:	Mead-Westvaco
	Description:	Water-free chemical package
	Additive:	Not specified
	Production Temperature at Plant (°C):	Varies, 33-45°C drop from HMA
	Use Reported in:	U.S.
CECABASE RT		
	Company:	CECA Arkema Group
	Description:	Chemical package
	Additive:	0.2-0.4% by mixture weight
	Production Temperature at Plant (°C):	120°C
	Use Reported in:	U.S. and France
Rediset WMX		
	Company:	AkzoNobel
	Description:	Cationic surfactant and organic additives
	Additive:	1.5-2.0% by bitumen weight
	Production Temperature at Plant (°C):	126°C
	Use Reported in:	U.S. and Norway
Rediset LQ		
	Company:	AkzoNobel
	Description:	Surfactant and anti-stripping additives
	Additive:	0.4-0.6% by the weight of binder
	Production Temperature at Plant (°C):	125°C
	Use Reported in:	U.S. and Norway
REVIX		
	Company:	Mathy-Ergon
	Description:	Surface-active agents, waxes, processing acids, polymers
	Additive:	Not Specified
	Production Temperature at Plant (°C):	Varies, 15-26°C drop from HMA
	Use Reported in:	U.S.

Table 2.3 : Summary of WMA production technologies using foaming technologies (D'Angelo et al., 2008)

Aquablack WMA		
	Company:	MAXAM Equipment
	Description:	Water-based foaming process
	Additive:	Not necessary
	Production Temperature at Plant (°C):	Not specified
	Use Reported in:	U.S.
Aspha-min		
	Company:	Eurovia and MHI
	Description:	Water-containing Zeolite
	Additive:	Yes, approximately 0.3% by total weight of mix
	Production Temperature at Plant (°C):	Varies, 20-30°C drop from HMA; German guideline recommends 130 to 170°C, depending on binder stiffness
	Use Reported in:	France, Germany and U.S.
ECOMAC		
	Company:	Screg
	Description:	Cold mix warmed before laying
	Additive:	Yes (unknown type/quantity)
	Production Temperature at Plant (°C):	Placed at about 45°C
	Use Reported in:	France
LEA (Low Energy Asphalt), also EBE and EBT		
	Company:	LEACO, Fairco and EIFFAGE Travaux Publics
	Description:	Water-based; Hot coarse aggregate mixed with wet sand (foaming from portion of aggregate fraction)
	Additive:	Yes, 0.2 to 0.5% by weight of binder of a coating and adhesion additive
	Production Temperature at Plant (°C):	≤100°C
	Use Reported in:	France, Italy, Spain and U.S.
LEAB®		
	Company:	BAM
	Description:	Water-based; Mixing of aggregates below water boiling point (direct foam with binder additive)
	Additive:	Yes, added at 0.1% by weight of binder to stabilise foam, aid in coating, and promote adhesion
	Production Temperature at Plant (°C):	90°C
	Use Reported in:	Netherlands
LT Asphalt		
	Company:	Nynas
	Description:	Water-based; Binder foaming+hydrophilic filler (foamed asphalt with addition of hygroscopic filler to maintain workability)
	Additive:	0.5 to 1.0% of a hygroscopic filler by mixture weight
	Production Temperature at Plant (°C):	90°C
	Use Reported in:	Netherlands and Italy

WAM-Foam		
	Company:	Kolo-Viedekke, Shell and BP
	Description:	Foaming process using two binder grades (soft binder coating followed by foamed hard binder)
	Additive:	Not necessary; A surfactant may be added to aid in the foaming of certain binders and an anti-stripping agent may be added to the softer binder
	Production Temperature at Plant (°C):	110–120°C
	Use Reported in:	France, Norway, Canada, Italy, Luxembourg, Netherlands, Sweden, Switzerland, UK and U.S.
Warm Mix Asphalt System		
	Company:	Terex Roadbuilding
	Description:	Water-based foaming process
	Additive:	Not necessary
	Production Temperature at Plant (°C):	Max 32°C drop from HMA
	Use Reported in:	U.S.
Advera		
	Company:	PQ Corporation
	Description:	Water-containing using Zeolite
	Additive:	0.25% by mixture weight
	Production Temperature at Plant (°C):	Varies, 20-30°C drop from HMA
	Use Reported in:	U.S.
Ultrafoam GX		
	Company:	Gencor Industries
	Description:	Water-based foaming process
	Additive:	Not necessary
	Production Temperature at Plant (°C):	Not specified
	Use Reported in:	U.S.
Low Emission Asphalt		
	Company:	Mc Connaughay Technologies
	Description:	Combination of chemical and water-based technologies
	Additive:	Yes, 0.4%of bitumen weight
	Production Temperature at Plant (°C):	90°C
	Use Reported in:	U.S.
Double-Barrel Green		
	Company:	Astec
	Description:	Water-based foaming process
	Additive:	Not necessary; An anti-stripping agent may be added similar to normal HMA
	Production Temperature at Plant (°C):	116-135°C
	Use Reported in:	U.S.

2.3.2.2. Organic or Wax Additives

Waxes are a class of chemical compounds that are plastic (malleable) near ambient temperatures. Characteristically, they melt above 45°C to give a low viscosity (very fluid)

liquid. Waxes are insoluble in water but soluble in organic, nonpolar solvents. All waxes are organic compounds, both synthetic and naturally occurring. Waxes can be divided into Petroleum Waxes and Wax Modifiers. Petroleum waxes naturally exist in bitumen and include (Polacco et al., 2012):

- Paraffin waxes: n-Alkanes with linear Carbon backbone chains and low molecular weight (Carbon chain length < C45)
- Microcrystalline waxes: Aliphatic Hydrocarbon compounds with branched chains, chemically referable to Iso-Alkanes and Cycloalkanes characterised by high molecular weight and carbon backbone chain length > C45
- Aromatics and other molecules with polar functional groups which may crystallise on cooling

Wax modifiers are typically identified as (Polacco et al., 2012):

- Synthetic waxes derived from the Fischer–Tropsch process
- Montan waxes and modified Montan waxes
- Functionalised waxes

Figure 2.2 shows the viscosity change of two different waxes over a range of temperatures. The sudden considerable decrease in the viscosity refers to the transition temperature of wax at which it begins to melt and its viscosity decreases. However, as this process occurs suddenly, a plunge occurs in the viscosity-temperature curve.

It should be mentioned that the purity of wax refers to the length of its hydrocarbon molecule chain and the variety of the molecules it consists of. The longer the chains its molecules have, the higher the viscosity it will have. This matter can be seen in Figure 2.2 as the blue curve which belongs to a pure commercial PIC wax, represents a lower viscosity in comparison with the red one which refers to the viscosity of the same wax with some modifiers such as Glycerine.

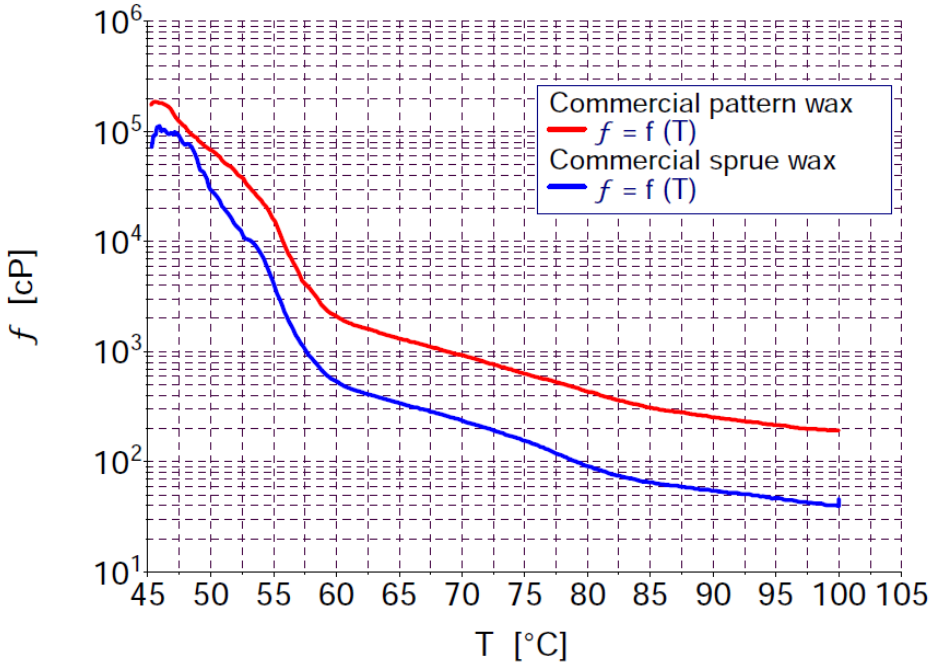


Figure 2.2: The viscosity of wax plummets over its transition temperature range (Fielder et al., 2005)

Due to the above mentioned general behavioural properties of waxes, they are added to bitumen in WMA to decrease the viscosity and improve the lubrication, both of which result in improving the mixtures workability and compactability at lower temperatures. Waxes typically have transition points below normal HMA production temperatures. Above their transition temperature, these materials reduce the viscosity of the bitumen. However, below their melting point, because of crystallisation, they tend to increase the stiffness of the binder and the resistance against deformation. As can be seen in Figure 2.3, adding Sasobit wax to neat bitumen has changed the bitumen's viscosity-temperature curve from a linear form to a nonlinear one. The nonlinearity of the curve refers to the Sasobit's transition temperature range (85-115°C) at which it begins to melt and decrease in viscosity.

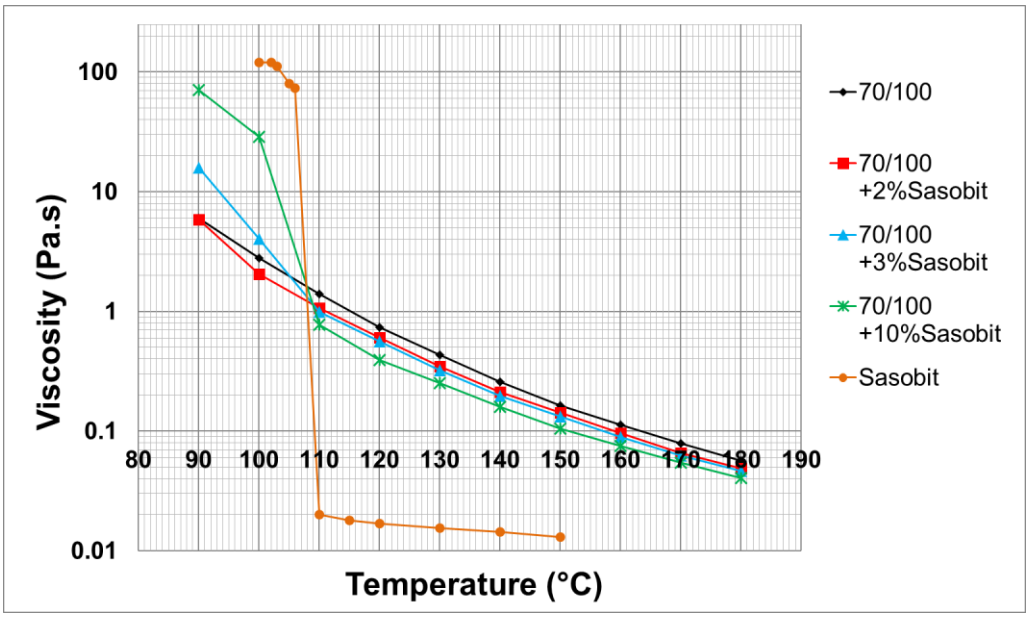


Figure 2.3 : Viscosity change of a pure binder 70/100 pen and Sasobit-modified binders over a range of temperatures including the wax transition range (i.e. 90-115°C) (Jalali, Grenfell and Dawson, 2014)

As an important consideration for selecting a proper type of wax it should be mentioned that the selected wax has to have a melting point higher than the maximum in-service temperatures to avoid increasing rutting distress.

On the matter of the crystallised structure of wax after congealing, referring to Figure 2.4, the Polarised Optical Microscopy (POM) images of three pure waxes (above) and their corresponding blends with the bitumen (below) can be seen. Regarding the pure waxes, the images of P1 and P3 are quite similar, showing the presence of crystals with dimensions considerably smaller than those of wax P2. All the crystals have a similar spherulitic-like structure. However, the situation changes after blending with bitumen. In the B-P1 blend, the presence of wax is hardly detectable. In contrast, waxes P2 and P3 maintain their ability to crystallise in the blend with bitumen and the image shows a bi-phasic pattern where the whiter zone can be intuitively attributed to the wax. B-P2 and B-P3 crystals appear quite similar in shape and dimension and the presence of some spherulites can be seen. For wax P2, the reduced dimension of crystals, when compared with pure wax, denotes a higher interaction with the bitumen. This general microstructural behaviour can be the main reason for such a change in the viscosity of WMA wax-modified bitumen and is predicted to help in interpreting the response of the corresponding WMA mixtures to the performance tests (Polacco et al., 2012).

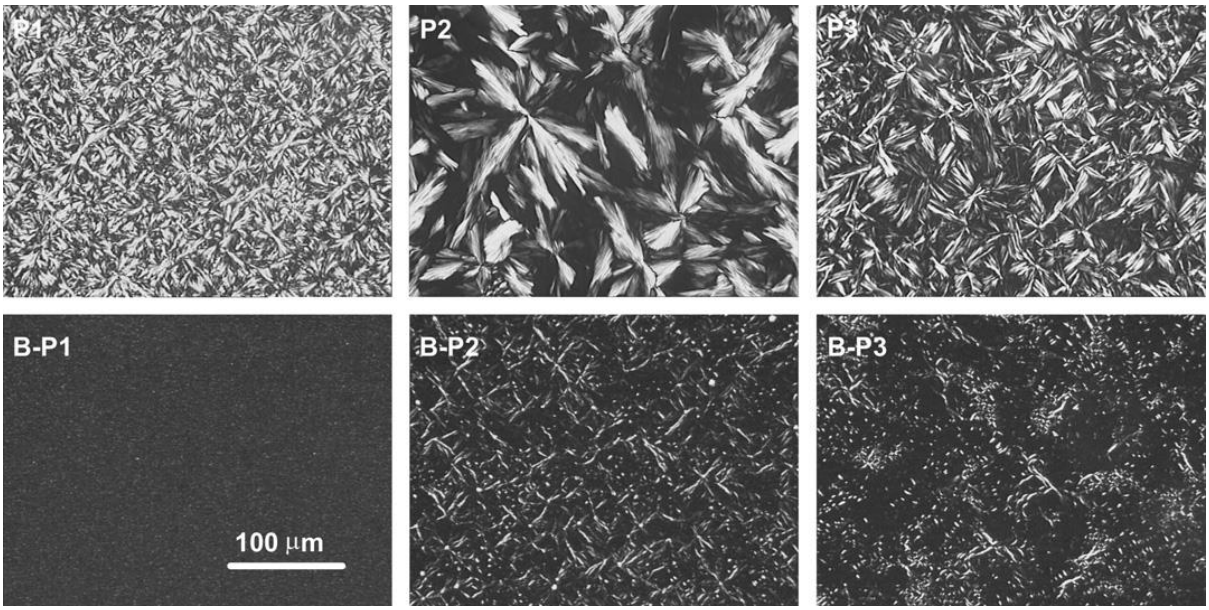


Figure 2.4 : Comparing POM micrographs of 3 pure waxes (P1, P2 & P3) (above) with their blend with bitumen (BP1, BP2, BP3) (below) (Polacco et al., 2012)

- ***Sasobit***

Sasobit is a long-chain aliphatic hydrocarbon wax with a melting point between 85°C and 115°C. It has high viscosity at lower temperatures and low viscosity at higher temperatures. Sasobit can be either in form of a white powder/flakes or pellets (also "ready-to-use" bitumen in Germany). It is a by-product from the synthetic petrol production process called the Fischer-Tropsch process. It results from coal gasification. When Sasobit cools down, the crystallisation begins at 105°C and is completed by 65°C forming into regularly distributed, microscopic, stick-shaped particles. At service temperatures, Sasobit forms a lattice structure in the binder that provides stability for the mixture. Adding 3% Sasobit by the mass of binder, the softening point of bitumen is increased by 20-40°C and the penetration decreases by 10-80mm. This effect is argued as a reason for the reported resistance of Sasobit-modified WMA to rutting distress (D'Angelo et al., 2008; Zaumanis, 2010).

Sasobit is typically added at a dosage of 1.5 per cent by the weight of binder. The pellets can be added to the binder either at the asphalt terminal or in the plant supply tank. It can also be added to the mixture by being blown into the drum.

Sasobit may be pre-blended with the binder, blended in-line (if it is in the form of flakes) in a molten state or added during the mixing process as pellets (Zaumanis, 2010).



Figure 2.5 : Sasobit flakes (left) (Hurley & Prowell, 2005b), Sasobit pellets (right and top)

- ***Asphaltan A, Romanta N***

Theses waxy additives are two types of Montan waxes with solidifying points of about 78°C and 125°C respectively. Montan wax is a hard wax obtained by solvent extraction of certain types of lignite or brown coal. Both Asphaltan A and Romanta N acts in a similar way to FT-waxes on the binder. The stiffness is increased after cooling, like with fatty acid amide. As they could modify the consistency of the bitumen and improve the adhesion between binder and aggregates, they have been previously used as an additive for mastic asphalt such as Gussasphalt in Germany (Zaumanis, 2010).

- ***Asphaltan B***

Resulting from refining of Montan wax blended with a fatty acid amide, this additive acts similarly to Fischer-Tropsch waxes to improve the bitumen flow at low temperatures. This wax has a melting point just below 100°C (Zaumanis, 2010). The producer reports increased

compactibility, resistance to rutting and moisture resistance of the Asphaltan B WMA mixtures.

- ***Licomont BS 100***

This is another fatty acid amide which is used as wax technologi to produce WMA with a melting point between 140°C and 145°C and a solidification range from 135°C to 145°C. An addition of 3% to the binder increases the softening point by 40-45°C (D'Angelo et al., 2008).

2.3.2.3. Chemical Additives

In addition to the mentioned technologies to produce WMA, a number of other processes based on using chemical additives have been developed in the United States and Europe. Basically, the manufacturers and licence owners of such products do not tend to disclose specific information on the chemicals they used in these processes. It seems to be quite difficult or in some cases impossible to study their behaviour based on the specifications or structure of the materials. Chemical technologies usually include a combination of emulsification agents, surfactants, polymers and additives to improve coating, mixture workability, and compactability, as well as adhesion promoters (anti-stripping agents). The additive dosage and the level of temperature reduction are different according to the specific technology which is applied.

- ***Rediset LQ***

Rediset LQ is a chemical Warm Mix Asphalt liquid additive which has recently been developed by AkzoNobel. It is said that it allows the production and compaction of asphalt pavements at temperatures typically 22 to 33°C (40 to 60°F) lower than conventional HMA. The surfactants in Rediset LQ modify the properties of the binder in such a way that readily allows it to bond with the active sites on the aggregate surface. The surfactants also reduce the surface tension of the asphalt binder, which enables efficient coating of asphalt binder on the aggregate surface. This property enables the binder to readily coat the aggregate and eventually increases the workability of the mix and allows the mix to be more compactable at lower temperatures (AkzoNobel, 2012). According to the producer, it will not change the penetration grade of the binder.



Figure 2.6 : Rediset LQ 1102 CE, a liquid adhesion promoter and antistripping chemical WMA additive produced by AkzoNobel

- ***Rediset WMX***

This chemical process was introduced in the United States in 2007. The additive, which was produced by AkzoNobel and marketed as a Warm Mix Asphalt additive with adhesion promoting properties, is a combination of cationic surfactants and organic additive based rheology modifiers. It modifies the bitumen chemically and reinforces active adhesion which results in improving the aggregate coating by the binder. Other components of the additive lower the viscosity of the binder at the production temperature. Rediset WMX is supplied in pellet form and does not contain water. By an addition of 1.5-2.0% by weight of bitumen, it allows 15-30°C production temperature reduction compared to HMA (AkzoNobel, 2011).

- ***Evotherm***

MeadWestvaco developed and introduced this technology in 2004. Evotherm was the first chemical additive process used in the United States. The active ingredients in Evotherm are chemical additives that reportedly improve coating, workability and adhesion at lower temperatures. This method includes three different technologies namely Evotherm ET (Emulsion Technology, often referred as just Evotherm) which has eventually been replaced by Evotherm DAT and Evotherm 3G.

The Evotherm chemical package is delivered in the form of a bitumen emulsion with a binder residue of about 70 per cent. The emulsion should be stored at about 80°C. Evotherm may be utilised with or without polymer modifier (Bonaquist, 2011).

- ***Evotherm ET***

Evotherm ET is a technology, through which a chemical package of emulsification and anti-stripping agent additives are applied to improve aggregate coating, mixture workability and compactability. Evotherm makes up 30 per cent by mass of the binder and decreases the viscosity at lower mixing temperatures, which results in fully coating of the aggregates at the same temperature. Different chemical packages are available for different aggregate types (with different adhesion agents). When the emulsion is mixed with the aggregates, the majority of its water flashes off as vapour. This process reduces the production temperature by 30% (Bonaquist, 2011; Zaumanis, 2010).

- ***Evotherm DAT (Dispersed Asphalt/Additive Technology)***

This material is the same chemical package as Evotherm ET which has been rarefied with a small amount of water and is injected into the asphalt line just before the mixing chamber. It decreases the viscosity of the binder at lower mixing temperatures, which fully coats the aggregates. Similar to Evotherm ET, this process reduces the production temperature by 30% as well (Hurley & Prowell, 2006a). In order to produce WMA with this technology, Evotherm DAT is stored in a tank at 80°C. This tank is linked to the binder line by one or two heated valves to keep the Evotherm warm in the asphalt plant. The chemical package and small amount of water are injected directly into the binder line, just before it comes into the mixing chamber. Evotherm DAT makes up 30% by mass of the binder. As a considerable advantage of this process in comparison with the initial Evotherm ET, it can be mentioned that it reduces shipping cost comparing with the ET type and allows the contractor to switch quickly and easily between HMA and WMA (Sargand et al., 2009).

- ***Evotherm 3G***

The third-generation process of Evotherm, which has recently been introduced by MeadWestvaco is Evotherm 3G. It is a water-free WMA technology developed jointly by Ergon Asphalt and Emulsions Inc. and Mathy Construction Co. This process allows the

additive to be mixed with the binder at a terminal and distributed to asphalt plants through the normal binder distribution process (Bonaquist, 2011).

- ***REVIX***

This chemical additive does not act as a foaming agent or a viscosity reduction additive to lower the mixing and compaction temperatures. It is actually a variety of surfactants, waxes, processing aids, polymers and other materials that are used in this technology and provides about 15-27°C reduction in the production temperature compared with the similar HMA mixture (Prowell, Harley & Frank, 2012).

2.3.2.4. Foaming Technologies

Several foaming technologies are being used to provide enough workability and let adequate coating take place at lower production temperatures. When small amounts of water are added to hot bitumen, the water vaporises and the vapour is encapsulated in the bitumen. This process produces a foaming action in the bitumen which temporarily increases the volume of the bitumen and lowers its viscosity. At this point, an improved coating and workability can be obtained at a lower temperature. Foamed asphalt has been used for over 50 years to produce cold mixes (Zaumanis, 2010). It is recommended that in the foaming processes, enough water has to be added in order to perform a foaming action that does not cause stripping problems. To ensure this, it is advised by some of the producers to use anti-stripping (adhesion, coating) additives to minimise the moisture susceptibility of the asphalt mixtures. Anti-stripping additives can provide chemical adhesion between bitumen and aggregate surfaces and for WMA production processes, liquid anti-stripping additives are recommended to be used (D'Angelo et al., 2008). They should be added to the binder just before mixing with aggregates, typically 0.5% by weight of binder. There are several foaming technologies available that could be sub-categorised into two groups, water-containing and water-based.

2.3.2.4.1. Water-Containing

In this category, based on the properties of the special additives named zeolite, when they are added to the mixture at the same time as the binder, water is released as a fine mist, which foams the bitumen.

- ***Aspha-min, Advera***

Both of these water containing foaming additives are synthetic zeolites. Zeolites are minerals that have approximately 20 weight per cent water trapped by means of crystallisation in their porous structure. In fact, they use finely powdered synthetic zeolite that has been hydro-thermally crystallised. Synthetic zeolite additives are typically added at the rate of 0.25 per cent by weight of the asphalt mixture. As soon as they are heated up to approximately 85°C, the water is released and in the presence of bitumen, foamed asphalt is produced (Bonaquist, 2011). As the main result of this action, the viscosity of the binder at high temperatures is lowered more than usual and this makes it possible to mix and place the asphalt mixture at considerably lower temperatures. These materials are claimed not to change the performance grade of the bitumen (i.e. its response at operating temperature is not affected). A variety of methods can be used to add synthetic zeolites at plant. It is technically vital and critical that the additive is quickly encapsulated in the asphalt binder and not lost in the exhaust air stream of the plant. Zeolites have been used on several projects in the United States. Advera passes 100 % through the 0.075 mm sieve. It can be added in the same manner as Aspha-min, although PQ Corporation, the licence holder of Advera WMA is working on a method to blend it in-line with the binder (Zaumanis, 2010).

2.3.2.4.2. Water-Based

Water-based foaming technologies produce foamed asphalt by injecting water directly into the hot bitumen at the mixing drum using special equipment. The water rapidly evaporates, producing a large volume of foam, which slowly collapses (D'Angelo et al., 2008).

Water is added at a rate of approximately 1 to 2 per cent by the weight of binder. These foaming systems can have benefits as there is no change in the mixing process and no special additives are required.

- ***Double Barrel Green, Ultrafoam GX, Aquablack WMA, Warm Mix Asphalt System***

In all these WMA foaming processes, some type of nozzle is used to inject water into the asphalt binder stream. However, each of them uses equipment developed by the individual company. The nozzles can be controlled by computer to adjust the foaming rate. A small amount of water is added in order to create steam which is encapsulated in the binder resulting in microscopic foam and a large volume increase of the binder (Zaumanis, 2010).

- ***Low Energy Asphalt (LEA)***

This is a process, through which the coarse aggregates and a portion of fine aggregate are heated up to typical HMA temperatures (approximately 150°C). Then they are mixed with the binder, containing some coating and adhesion additives. After the coarse aggregate is coated with the binder, it is mixed with the cold and wet fine aggregate. Adding the wet fine aggregates to the hot mixture of coarse aggregates coated with bitumen results in a foaming action, which aids in the coating of the fine aggregates (Bonaquist, 2011; Zaumanis, 2010) The compatibility of this method with the climatic circumstance of Nordic countries still has to be verified as the reports are mostly from countries with a slightly warmer climate. A key point regarding the energy saving in this process is that steaming water consumes five times as much energy as heating the aggregate from 0°C to 100°C.

- ***Low Emission Asphalt***

This technology is essentially a further development of Low Energy Asphalt, a combination of chemical and water based foaming technology is used. The process is based on consecutive mixing of the binder containing a chemical additive being added to the hot coarse aggregates, followed by adding wet sand, which creates a foaming action (D'Angelo et al., 2008).

- ***WAM-Foam***

WAM-Foam technology is a two-stage process and differs slightly from the other foaming technologies. In the first stage, the aggregate is heated up to about 130°C and then fully-coated with a soft binder, which is typically 20 to 30 per cent of the total binder, through a mixing process. The hard binder at about 180°C is then foamed onto the mixture by adding cold water (2% to 5% by mass of the hard bitumen). Coating the coarse aggregates with the softer binder is to achieve full coating of the coarse aggregates, which may not otherwise occur with the stiffer binder at lower temperatures (D'Angelo et al., 2008). The grades of the two binders are selected to produce a blended binder that satisfies the performance grade requirement for the project location. The WAM Foam process has not been used to date in the United States.

- ***LT-Asphalt***

Another water-based foaming technology to produce WMA is LT-Asphalt thorugh which the binder is foamed by the means of special nozzles just before adding to the mixture chamber

containing the heated aggregates with an approximate temperature of about 90°C. 0.5 to 1.0% by hydrophilic filler should be added to hold and control the captured moisture inside the residual mixture from foaming (D'Angelo et al., 2008).

2.4. POSSIBLE ADVANTAGES and DISADVANTAGES of WMA

As briefly mentioned before, WMA technologies use technological advances that not only reduce the temperature of compaction and production but also promise a number of environmental and health benefits as the direct effect of the reduced production temperatures including lower greenhouse gas emissions, lower fuel consumption, and reduced exposure of workers to asphalt fumes.

2.4.1. ADVANTAGES

Although the degree/level of benefits depends on the technology used for producing WMA and the type of fuel used in the process, the benefits can be generally categorised as follows:

2.4.1.1. Environmental Benefits

Includes reducing the emissions of CO_2 (carbon dioxide) and other greenhouse gases because of the lower temperature used for manufacturing and placing of the production. This will also result in improving the working conditions for the site workers. Reduction of fuel consumption for WMA production results also in reducing the demand of non-renewable fuel extraction and lowering the carbon footprint of fuel production and transportation. In addition, the ranges of possible energy saving in the production process can be as below (Zaumanis, 2010):

- Evotherm – 50% to 70%
- WAM Foam – 30% to 40%
- Aspha-Min – 30%
- Sasobit – 20%

2.4.1.2. Economic Benefits

Can be lowering the energy consumption and decreasing the associated costs. Moreover, as the production temperature is closer to the ambient temperature, maintaining the temperature of asphalt plant and avoiding or lowering the temperature loss, can be performed easier and with

less expense. In fact, energy saving of WMA mainly depends on the amount by which the production temperature is lowered and the type of fuel which is used (Bonaquist, 2011).

2.4.1.3. Production-Related Benefits

Due to the lower environmental pollution and fumes, which is produced through the production of WMA (compared to HMA), it is possible to allow WMA plant sites to be built up in urban areas (Zaumanis. 2010).

2.4.1.4. Compaction and Placement-Related Benefits

WMA mixtures are expected/promised to have nearly the same workability and compactability as HMA at lower placement temperature. That is because the binder viscosity of WMA mixtures will normally be less than that of HMA at the same temperature. As the difference between the ambient temperature and that of mixture is smaller for WMA compared with HMA, the drop in temperature with time is less significant allowing a longer time for paving and compaction. Moreover, a longer paving season and/or paving during the nights can be performed by using WMA mixtures.

From another viewpoint, because of approaching a lower binder viscosity at the same temperature in comparison with HMA, WMA can be compacted at lower temperatures but to achieve the same density as HMA. With a same argument as cold weather paving, longer haul distances are possible because mixtures can be compacted at lower temperature. Then more placement sites can be served without losing the workability (D'Angelo et al., 2008).

D'Angelo et al. (2008) report that WAM-Foam was stored in a silo for 48 hours and still had the normal specifications of being placed and compacted.

According to Zaumanis (2010), a similar report states that LEA was left in trucks at a temperature of 70-90°C for a time of 5 to 6 hours and had no problems with paving or compaction.

Moreover the above advantages, because of the lower initial temperature of the pavement and overall a shorter cooling time, it can be opened to traffic and go into service earlier than HMA. This promises to be beneficial for high maintenance roads or intersections that need to be opened as soon as possible.

2.4.2. DISADVANTAGES

Although each WMA technology has its own flaws, there are some general concerns about the performance and implementation of WMA as pointed out in following:

2.4.2.1. Rutting Potential

As it will be discussed later, some studies have reported permanent deformation for WMA mixtures. The mentioned problem is basically because of the lower degree of ageing in WMA binder, because of lower exposing to high production temperatures, and also because of the greater moisture content in foaming technologies (Bonaquist, 2011).

2.4.2.2. Water/Moisture Sensitivity

Incomplete vaporisation of water during the mixing and laying process, particularly for foaming and some of the chemical WMA technologies which have a water-based process, will let some residual water remain in the mixtures and it may cause problems of premature rutting and stripping of the pavements. To resist this problem, most of the foaming technologies use chemical anti-stripping additives to improve coating and adhesion (You, Goh & Shu, 2011).

2.4.2.3. Low Temperature Behaviour

WMA mixtures produced with wax technology can have slightly different low temperature behaviour than what is expected for HMA. In fact, crystallisation of wax in the modified binder at low temperatures will increase the viscosity and decrease the elasticity of the binder which will result in friability of the bitumen at low temperature (NCHRP Report 779).

2.4.2.4. Insufficient Data for Evaluation

WMA is quite a newly-innovated material, and the history of experiencing WMA in the real fields of construction and service, whether in the U.S or in Europe, is just about one decade or two. Thus it seems to be too early to confidently judge the long-term performance of this material (NCHRP Report 779).

2.4.2.5. Economic Drawbacks

Regarding the economic concerns of producing WMA, it seems that there are still insufficient reasons to prove that the reduced amount of energy consumption will overbalance the increase

of other costs of WMA production (Zaumanis, 2010). In the case of such an unclear result, contractors will probably have less desire to choose this technology just because of its other benefits alone. WMA may have some particular costs such as the investment and the depreciation of plant modification, the costs of additives and the possible costs for licensing the technology.

2.4.2.6. Life Cycle Assessment-Related Drawbacks

There are some concerns that the carbon footprint for producing additives and/or any additional equipment supporting the production of WMA may offset the environmental benefits of WMA (Zaumanis, 2010).

2.5. BITUMEN CONSTITUTION

Bitumen contains organic compounds, which are mostly hydrocarbons. In fact, 80% of bitumen weight consists of carbon. Hydrogen includes about 10% and up to 6% of bitumen weight consists of sulphur. There are also small amounts of oxygen and nitrogen and trace amounts of metals such as iron, nickel and vanadium (Whiteoak & Read, 2003).

In terms of molecular content, bitumen is made of two broad different chemical groups called asphaltenes and malthenes. The maltenes can be further separated into saturates, aromatics and resins.

Asphaltenes are n-heptane insoluble black or brown amorphous solids containing, besides carbon and hydrogen, some nitrogen, sulphur and oxygen. They form 5 to 25% of bitumen (Arce, 2007).

Resins are soluble in n-heptane and, similar to asphaltenes, they are largely composed of hydrogen and carbon and contain a small amount of oxygen, sulphates and nitrogen. Resins have a dark brown colour (Arce, 2007).

Aromatics represent the major proportion of the dispersion medium for the asphaltenes. They constitute 40 to 65% of the total bitumen and are dark brown viscous liquids.

Saturates are non-polar viscous oils, which are straw or white in colour forming 5 to 20% of the bitumen. Their components include both waxy and non-waxy saturates (Arce, 2007).

2.6. BITUMEN STRUCTURE

From the viewpoint of structure, bitumen has been considered as a colloidal system consisting of heavy molecular weight asphaltene micelles, which are dispersed or dissolved in a lower molecular weight oily medium, the maltenes (Arce, 2007).

Bitumen structure can vary by the proportions of its asphaltenes and maltenes (resins, aromatics and saturates). The proportion of resins to asphaltenes specifies and qualifies, to a degree, the solution (SOL) or the gelatinous (GEL) type of the bitumen. Bitumen can be considered as a SOL-type if the asphaltenes are kept separated by the presence of sufficient quantities of resins and aromatics with adequate solvating power. In this type of bitumen, the resulting micelles have a good mobility within the bitumen. However, a GEL-type bitumen is resulted either when there is not sufficient quantities of resins/aromatics or if they do not have sufficient solvent power to separate the asphaltenes (even though there are sufficient quantities of them). In this situation, the asphaltenes can connect to each other and develop an irregular open packed net structure. Figure 2.7 shows the difference between GEL and SOL-type bitumen. In practice, most bitumens are somewhere between these two states (Arce, 2007; Whiteoak & Read, 2003).

Saturates can be viewed as carriers for the polar aromatics (also for resins and asphaltenes).

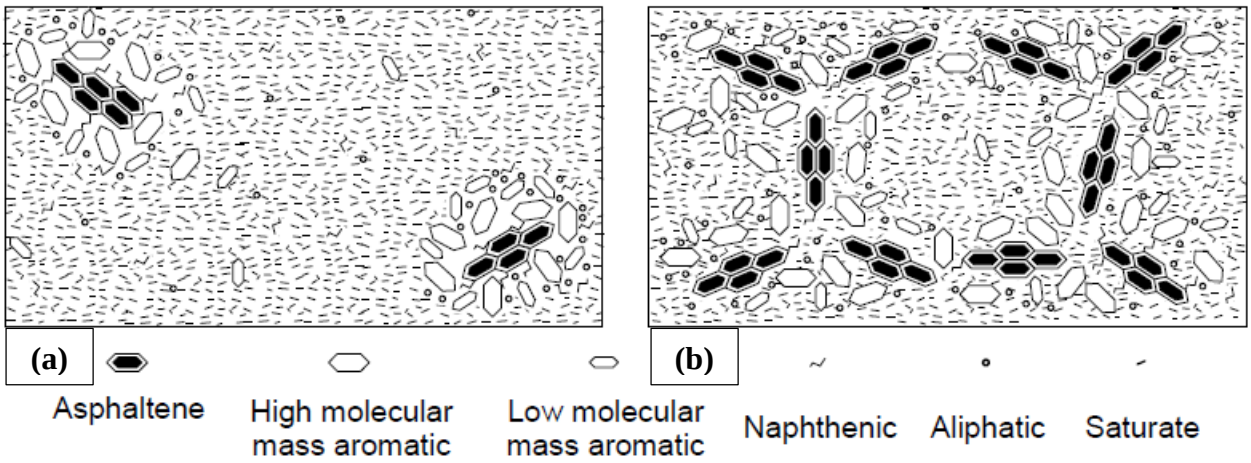


Figure 2.7 : The schematic structure of bitumen: (a) SOL-Type, (b) Gel-Type (Gaskin, 2013)

2.7. BITUMEN VISCOSITY and RHEOLOGY

2.7.1. The RELATIONSHIP of BITUMEN VIISCOSITY with CONSTITUTION and STRUCTURE

Rheology is the study of materials' flow and deformation under applied forces. The rheological characteristics are time-temperature dependent, which means that they vary through any change in temperature and/or loading frequency. Viscosity, as one of the most fundamental representatives of the rheological characteristics, is an internal property of the bulk of a material/liquid which is developed by the material's internal friction and retards its flow and resists its deformation under applied forces. Therefore, when a force is applied to a liquid, the higher the viscosity is, the slower will be its movement, deformation and flow (Whiteoak & Read, 2003).

In the case of bitumen, the rheological properties at a particular temperature are defined by both the constitution (chemical composition) and the structure (physical arrangement) of the molecules in the material. It means that any changes in the constitution and/or structure will modify the rheological characteristics of bitumen.

As described earlier, bitumen can be subdivided into groups of molecules which can have common structures: maltenes (saturates, aromatics and resins) and asphaltenes. The interaction of these components affect the properties of bitumen significantly (Liang, Feng &YU, 2010).

According to previous studies, the asphaltene content strongly influences the rheological properties (e.g. viscosity) of bitumen. It is believed that the aged bitumen shows a reduced thermal susceptibility and becomes less sensitive to temperature due to the increase of asphaltenes content, which displays the lowest temperature susceptibility among the four generic bitumen fractions. In fact, the viscosity as well as temperature susceptibility of bitumen is primarily dominated by the existence of asphaltenes (Liang, Feng &YU, 2010). In other words, the higher the asphaltenes content the harder the bitumen and the higher the viscosity at a constant temperature. This will lead to a lower penetration and higher softening point.

Apart from the content of asphaltenes, the shape of their particles also controls the extent of viscosity change. The asphaltene particles are believed to be formed from stacks of plate-shaped sheets of aromatic/naphthenic ring structures, which are held together by hydrogen bonds. However, the asphaltenes can also form into extended sheets and combine with

aromatics and resins. This produces different shapes for the asphaltene particles, following which the viscosity of bitumen varies.

Asphaltenes also may tend to aggregate and the greater the degree of aggregation the higher the viscosity of bitumen.

The maltenes continuum is influenced by the saturated oils, which have low molecular weight and consequently low viscosity. The saturates have little power and tendency to solve the asphaltenes. Therefore, the bigger the saturates fraction the higher the tendency of the asphaltenes to aggregate and form a gel structure.

Therefore, the higher proportion of saturates, on the one hand, tends to reduce the viscosity of bitumen due to their lower molecular weight, but on the other hand, results in the higher amount of asphaltene micelles aggregation, which increases the viscosity. The relative importance of these two opposing effects depends on the stabilising influence on the asphaltenes by the aromatics (Whiteoak & Read, 2003).

According to the Shell Bitumen handbook, depending on the proportions of asphaltenes and maltenes, the rheology of the binder in question can change. Keeping the asphaltenes content constant it has been demonstrated that (Whiteoak & Read, 2003):

- There is some reduction in shear susceptibility if the aromatics content is increased keeping constant the saturates/resins ratio;
- A softer bitumen is produced if the resins/aromatics ratio is kept constant and the amount of saturates increases;
- Increasing the resins content hardens the bitumen, reducing the penetration index and shear susceptibility but increasing the viscosity.

Among the four bitumen fractions, the polar aromatics (also resins and asphaltenes) are responsible for the viscoelastic properties of the bitumen at ambient temperature (Arce, 2007).

Table 2.4 : The effect of polarity on the viscosity of bitumen fractions (Peterson, cited in Liang, Feng & YU 2010)

Fraction	Molecular weight (g/mol)	Viscosity at 25°C (Pa-s)
Saturates	500	10
Aromatics	500	1000
Resins	500	1000000

2.7.2. TEMPERATURE DEPENDENCY of BITUMEN VISCOSITY

Bitumen viscosity has high sensitivity to temperature variations (Liang, Feng &YU, 2010). Generally, the viscosity of bitumen increases through the reduction of temperature and vice versa. This issue indicates that reducing the temperature develops more resistance inside the material's bulk against the flow or deformation of bitumen under the applied loads. The reverse story happens through increasing the temperature. Considering what was mentioned in the previous section regarding the dependency of bitumen viscosity/rheological characteristics to its structure and composition, also referring to Lu and Isacsson's work indicating the relationship between bitumen's temperature susceptibility and its asphaltenes content, it can be stated that the viscosity as well as temperature susceptibility of bitumen is primarily dominated by the content of asphaltenes. In other words, temperature changes should vary the asphaltene content, shape and aggregation, through which the viscosity of bitumen changes (Liang, Feng &YU, 2010).

However, another interesting phenomenon is outlined in a study performed by Liang et al. indicating that the temperature susceptibility of bitumen is not always accurately dependent on the content of asphaltenes. This means that the bitumen's sensitivity to temperature is not necessarily reduced through the increase of asphaltenes. According to this study, it can be speculated that the other fractions (may be only one or two of them) must also have some influence on the temperature susceptibility of bitumens. In fact, the four generic fractions of bitumen play an inconsistent role in its temperature susceptibility and the degree of correlation of each fraction is somewhat different. Liang et al. conclude that saturates can have a negative effect on bitumen's temperature susceptibility due to their low molecular weight, whereas aromatics can improve the temperature susceptibility because the lightly condensed aromatic rings may provide "protection" from the temperature changes. Resins may have an adverse

impact on the temperature susceptibility of bitumen due to their high flow activation energy. Finally, the thermal susceptibility of bitumen is reduced with the increase of asphaltenes. Liang et al. state that among the four mentioned fractions, resins show the closest correlation with the temperature susceptibility of bitumens, then asphaltenes and aromatics. Finally, the correlation between bitumen's temperature susceptibility and saturates is relatively weak (Liang, Feng &YU, 2010).

At the end, regarding the importance of the viscosity-temperature relationship of bitumen it should be mentioned that it plays an important role in determining many aspects of pavement performance. For example, the bitumen should be viscous enough at high temperatures in order to resist permanent deformation such as rutting, upheaval, etc., whereas the viscosity of bitumen needs to be low enough at low temperatures to avoid fatigue cracking of pavement.

2.8. ADHESION and COHESION in ASPHALT MIXTURES

"Adhesion" between two different substances is defined as the attraction force between the particles (molecules) of the two materials (i.e. adhesive and substrates), which acts to hold them together (Copeland, cited in Jakarini 2012). Regarding the bituminous mixtures, the term "Adhesion" refers to the bond or attraction force developed between the molecules of bitumen (bitumen-filler mastic) and those of aggregate at the bitumen-aggregate (mastic-aggregate) interface. The term "Bond Strength" or "Adhesion Tensile Strength" is defined as the amount of energy, which is required to break the adhesive bond between the bitumen (bitumen-filler mastic) and aggregates (Jakarini, 2012).

By contrast, "Cohesion" is the inter-particle (inter-molecular) force developed within the bitumen or bitumen-filler mastic, which keeps the bitumen (mastic) molecules together and influences its viscosity. Figure 2.8 shows the general microscopic schematics of cohesive and adhesive forces in asphalt mixtures (Jakarini, 2012).

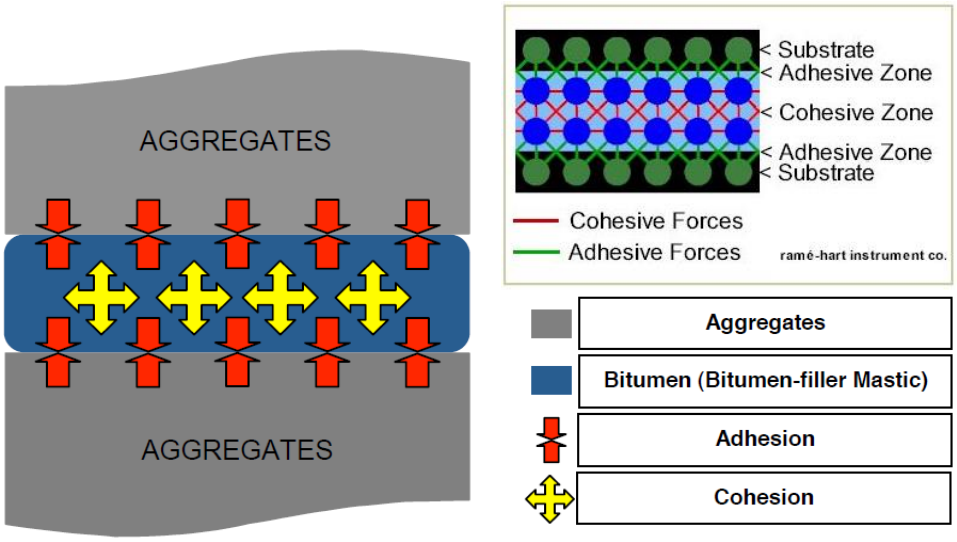


Figure 2.8 : General microscopic schematic of cohesion and adhesion in bituminous mixture (Jakarini, 2012)

2.8.2. The COMMON THEORIES of ADHESION in ASPHALT MIXTURES

A good overview of previous research and current thinking on explaining bitumen-aggregate adhesion was provided by Shute and Terrel (cited in Terrel & Al-Swailmi 1994). They developed and proposed four theories of adhesion as follows, which are often used:

- Mechanical Adhesion/Bonding Theory
- Chemical Reaction Theory
- Molecular Orientation Theory (Electrostatic Theory)
- Surface Energy Theory (Thermodynamics Theory)

They stated that the four proposed theories were affected by various factors including: surface tension/energy of bitumen and aggregate, chemical composition of bitumen and aggregate, bitumen viscosity, surface texture of aggregate, aggregate porosity, aggregate cleanliness, aggregate moisture content and temperature at the time of mixing with binder (Little & Jones, 2003). Regarding bitumen-aggregate adhesion, Hefer (cited in Gronniger, Wistuba & Renken 2010) presented a comprehensive and well-structured compilation of theories and mechanisms of fundamental adhesion, which were quite similar and conformed to the theories of Terrel and Shute (cited in Gronniger, Wistuba & Renken 2010). It should be mentioned that, in fact, no single theory seems to be able to completely explain the adhesion mechanism and a

combination should likely be used. In this respect, probably two or more mechanisms take place simultaneously in any one mixture to cause loss of adhesion (Little & Jones, 2003).

The four theories of bitumen-aggregate adhesion, considering the work and explanations of both Shute and Hefer (cited in Gronniger, Wistuba & Renken 2010) have been compiled and summarised as follows:

2.8.2.1. The Theory of Mechanical Bonding

According to this theory, adhesion is developed by bitumen-aggregate mechanical interlocking at their interface such that bitumen permeates the aggregate surface irregularities and pores and hardens. According to Terrel and Al-Swailmi (1994) mechanical adhesion relies on multiple aggregate properties including: surface texture, porosity or absorption, surface coatings, surface area, and particle size. In general, the more the porosity, the larger the surface area and the higher the roughness of the aggregate surface, the stronger the adhesive bond developed between the bitumen and aggregate. However, according to Tarrar and Wagh (1991), aggregates with relatively smooth surface textures, compared to those with rough surface textures, are easier to be coated by bitumen. This theory indicates that the presence of water or moisture on the aggregates surface may decrease the mechanical interlock since water pre-occupies some of the aggregate surface pores, which decreases the potential permeability of the aggregate for bitumen adsorption. Therefore, the presence of water or moisture in asphalt mixtures increases the susceptibility of them to the stripping phenomenon (Jakarini, 2012).

2.8.2.2. The Theory of Chemical Bonding

In accordance with this theory, which has been recognised as another possible mechanism for adhesion between bitumen and aggregate surfaces, adhesion is developed following the chemical reactions between certain elements (functional groups) of aggregate and binder. Many researchers have mentioned that using basic aggregates in asphalt mixtures may result in achieving better adhesion with bitumen compared to acidic aggregates. However, mixtures produced using all types of aggregates have been reasonably acceptable, as well (Terrel & Al-Swailmi, 1994).

In fact, the Chemical Reaction Theory premises that acidic and basic components of both bitumen and aggregate react to form water-insoluble compounds, which resist stripping (Terrel & Al-Swailmi, 1994). In addition, from the view point of this theory, aggregates, based on their

main properties such as surface chemistry, may be classified as either having hydrophilic or hydrophobic characteristics. The hydrophilic aggregates are the siliceous aggregates (e.g. granite) which tend to strip easier than hydrophobic aggregates (e.g. limestone). Generally, the more acidic the aggregate surface the less the possibility of forming strong bonds with bitumen and therefore the higher the susceptibility of the asphalt mixtures to stripping. In other words, the bitumen-aggregate adhesive bond strength in asphalt mixtures is affected by the pH values of the aggregate surface and the bitumen, as well (Jakarini, 2012).

It has been mentioned that the overall polarity or separation of charges within the organic molecules of bitumen caused the polar bitumen components to be attracted to the polar components of aggregate. It is described that neither bitumen nor aggregate had an overall net charge. However, the components within both of them formed non-uniform charge distributions causing the materials to behave overall as if they had charges in such a way that attracted the opposite charge of the other material. Then the types of reactions which might take place between the polar aggregate surface and bitumen were explained. It was stated that, in the molecular scale, basic nitrogen compounds (pyridines) adhere strongly to the aggregate surface. It is also described that although carboxylic acids in bitumen composition are totally polar and adhere strongly to the dry surface of aggregate, they can be replaced and removed easily by the polar molecules of water in the presence of water. However, according to Robertson (cited in Little & Jones 2003), this varied by the type of acid.

Looking through the view point of Chemical Bonding Theory, the moisture susceptibility of asphalt mixtures to the bitumen viscosity has been related by researchers. As a fact, the viscosity of bitumen (bitumen-filler mastic) can be due to the concentrations and aggregation of its asphaltenes, which constitute the biggest group of polar molecules in bitumen. Asphaltenes can develop stronger adhesion between bitumen (bitumen-filler mastic) and aggregates due to their greater attraction and molecular orientation. Therefore, it is concluded that asphalt mixtures of lower viscosities, which may represent lower concentrations of asphaltenes, are generally susceptible to moisture damage (Jakarini, 2012). Although this conclusion may look systematic, it is a matter of opinion as it does not conform to some logical expectations regarding asphalt mixtures which have been experienced. For instance, if the lower viscosity of bitumen (due to the separation of the asphaltene aggregations) has been achieved via increasing the mixture's temperature, the amount of moisture, which potentially exists in the mixture, should have been reduced, as a logical result of the increased temperature.

This means that the moisture susceptibility of the mixture should have been reduced, which is in contrast with Hicks' (cited in Jakarini 2012) argument stated above. Moreover, looking at the issue through the view point of Surface Energy Theory, the higher the surface energy of bitumen the lower the wetting potential and the lower the coating adequacy, all of which means the higher the moisture susceptibility and stripping potential. This conflict, as a matter of fact, can prove and stress the importance of combining different adhesion theories, which was mentioned previously, for justifying various bitumen-aggregate adhesion-related phenomena.

Hicks (cited in Jakarini 2012) also stated that individual components in bitumen such as sulfoxides, carboxylic acids, phenols and nitrogen bases can also affect moisture susceptibility.

2.8.2.3. The Theory of Electrostatic Bonding

This theory justifies the adhesion phenomenon via relating the issue to the polarity of the materials involved in adhesion and the consequent interactions between them. According to this theory, bitumen's polarity is resulted from the orientation of the electrically charged binder molecules, which meet the ion arrangement developed at the aggregate surface (Gronniger, Wistuba & Renken 2010).

This theory, also known as the "Molecular Orientation" theory of adhesion, expresses that the molecules of bitumen (bituminous binder) when it is in contact with the aggregate surface, tend to orient themselves such that they satisfy the energy demand of the aggregate's surface. This theory is based on presuming the fact that bitumen consists of a combination of non-polar (Lifshitz-van der Waals) and polar (Lewis acid and Lewis base) molecules (Jakarini, 2012).

On the matter of the moisture susceptibility of asphalt mixtures, looking through this theory, Hicks (1991) has stated that "Molecules of water are dipolar. Molecules of bitumen are generally non-polar though some components are polar. Consequently, molecules of water, being more polar, may more readily satisfy the energy demand of the aggregates surface (Jakarini, 2012).

Depending on the surface composition of the aggregate involved in an adhesive system, molecules of water or moisture, compared to those of bitumen, may be able to satisfy the energy demand of the aggregates surface better and more effectively. Thus, the presence of water results in degradation of the adhesive bond between bitumen (bitumen-filler mastic) and

aggregates and as an ongoing phenomenon increases the susceptibility of the asphalt mixtures to stripping (Jakarini, 2012).

In the next sections, this theory will be used combined with the Chemical Bonding theory in more detail in order to fundamentally explain the adhesion process and mechanism between bitumen and aggregate.

2.8.2.4. The Surface Energy Theory of Bonding

The Surface Energy theory of adhesion is sometimes coupled with the Molecular Orientation theory of adhesion. This is because both are derived from the same theory, which relates the bitumen-aggregate adhesion to the arrangement of bitumen molecules at bitumen–aggregate interface (Little & Jones, 2003). The theory presumes that the adhesion between bitumen and aggregate is followed by a surface energy reduction at the aggregate surface as bitumen is adsorbed onto the aggregate surface. The Surface Energy theory of adhesion is also used to explain the relative wettability of aggregate surfaces by bitumen and water. Compared to bitumen, water is a better wetting agent. This is because water has a lower viscosity and lower surface tension than bitumen (Little & Jones, 2003).

Researchers at Texas A & M University and the Western Research Institute in Wyoming conducted research on measuring and calculating bitumen-aggregate adhesive bond strength based on the surface free energy characteristics of bitumen, aggregate and water in thermodynamics (Bhasin, 2006; Cheng et, al, 2002). Through their research work, a number of new terms and parameters related to adhesive bond strength were introduced and devised including adhesive bond energy of aggregate and bitumen in dry conditions and in the presence of water (Jakarini, 2012).

According to this theory of adhesion, for an asphalt mixture, in order to perform as a durable pavement, high bitumen-aggregate adhesive bond strength in the dry situation is desirable. Meantime, the adhesion tensile strength between bitumen (bitumen-filler mastic) and aggregate is generally less than the adhesion tensile strength between water and aggregate. On this matter, regarding the moisture susceptibility of asphalt mixtures from the view point of this theory, Hicks (cited in Jakarini 2012) has stated that: "Water or moisture will tend to displace bitumen (bitumen-filler mastic) at the interfaces of the bitumen (bitumen-filler mastic) and aggregates where there is contact between water or moisture, bitumen (bitumen-filler mastic) and aggregates."

According to Bhasin et al. (cited in Little & Jones 2003), in a bitumen-aggregate adhesion system, the higher the dry adhesion bond strength and the lower the magnitude of reduction in the surface free energy in the presence of water, the lower the debonding and stripping potential and the higher the resistance to moisture damage.

The Surface Energy subject and theory will be explained in more detail in the following sections including all associated concepts and calculations.

Moreover, the moisture susceptibility phenomenon will be explained in more details from the view point of Surface Energy theory along with calculations.

2.8.3. BITUMEN FUNCTIONAL GROUPS

As mentioned in the previous sections, bitumen is a complex of multiple hydrocarbons consisting of a colloidal dispersion of asphaltenes in maltenes, stabilised by resins (Ivann Harnish, 2010).

The hydrocarbons in bitumen may contain atoms such as nitrogen (N), sulphur (S), and oxygen (O) in their molecular structure. In addition, small amounts of metal elements exist, considered as the ‘fingerprints’ of the crude source (Robertson, cited in Hefer & Little 2005).

Although hydrocarbons are generally known as non-polar materials, they contain certain amounts of polar organic compounds which can have acidic or basic nature (Ahmad, 2011).

Petersen (cited in Hefer & Little 2005) has identified polar and strongly associated functional groups in bitumen. The chemical groups in the molecular structure of a material which cause in charge development can be regarded as the functional groups of that material (Johnston, cited in Hefer & Little 2005).

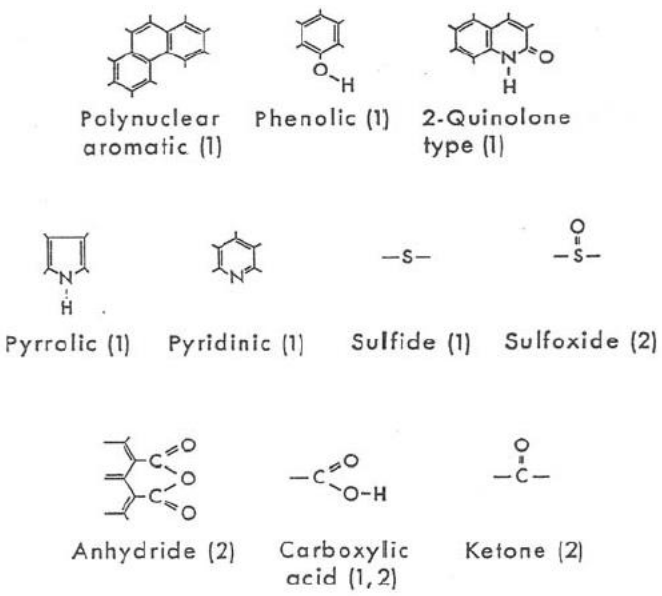


Figure 2.9 : Some of the important functional groups in bitumen; (1): Naturally occurring, (2): Formed during oxidative ageing (Peterson, cited in Hefer & Little 2005)

Despite small amounts in bitumen, they are essentially the acidic compounds of bitumen such as carboxylic acids, anhydrides, and 2-quinolone types, which highly concentrate in the adsorbed fraction (during binder-aggregate interactions). This is along with the fact that bitumen generally shows an excess amount of acidic component compared to the amount of basic component which is developed due to its organic compounds (Morgan & Mulder, cited in Hefer & Little 2005). The acidic value of bitumen normally ranges from 1.5-5 mg KOH/g while the basic value varies from 0-1 mg KOH/g (MS-24, 2007). This is an indication that bitumen is mostly acidic (Ahmad, 2011).

In a more detailed description, asphaltenes are the most polar components with the highest molecular weight in bitumen (Ivann Harnish, 2010).

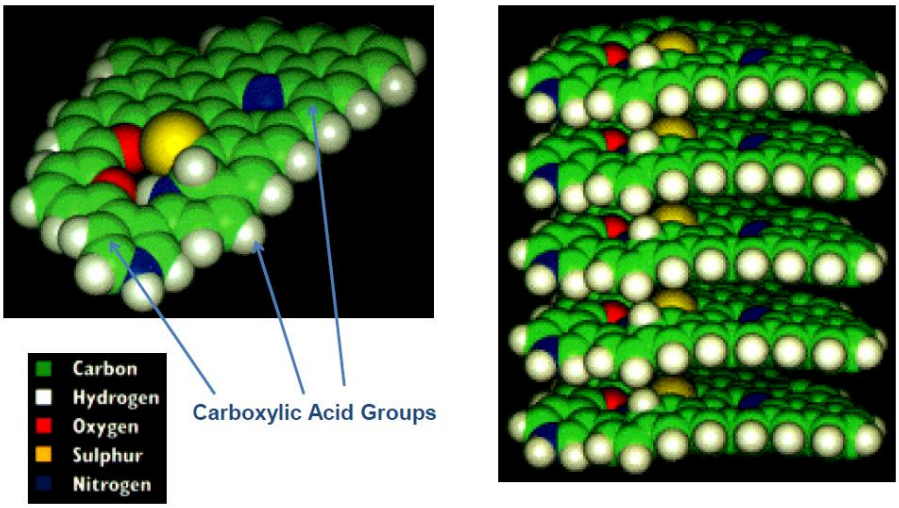


Figure 2.10 : Schematic sheet-like structure of asphaltenes in bitumen (Ivann Harnish, 2010)

As can be seen in Figure 2.10, asphaltenes are arranged in sheet-like structures of condensed aromatic rings with C (carbon) side chains. Carboxylic acids are grouped as asphaltenes (Ivann Harnish, 2010).

When carboxylic acid groups of bitumen at the bitumen-aggregate interface (R-COOH) come into contact with H_2O, a reaction takes place yielding a negative charge on bitumen. This makes it negatively charged at the interface with aggregate through the following reaction:

$$R\text{-}COOH + H_2O \rightarrow [R\text{-}COO^-] + H_3O^+ \qquad \text{Equation 2.1}$$

In Equation 2.1, R-COOH is the acid group at binder-aggregate interface (proton donor in Lewis Acid-Base theory).

The polarity of Asphaltenes let them ‘cluster’ or aggregate together. There are some other atoms such as sulphur (0.3-10)%, nitrogen (0.5-3.3)%, oxygen (0.3-6.6)% and also metals such as Ni (nickel) and Fe (iron) that exist in asphaltene molecules. However, depending on the source of the crude oil, the amount or basically the presence of these atoms may totally vary. These atoms and elements (though only trace amounts of them exist in bitumen) along with aromatic rings contribute to the polarity of asphaltenes. In fact, they significantly control and affect bitumen’s acidic-basic characteristics, polarity and bitumen interaction with aggregate surface (Petersen et al., cited in Little & Jones 2003). Polarity enables the adhesive properties of asphaltenes.

Resins are similar to asphaltenes but with lower molecular weight. Resin molecules have lipophilic (non-polar) and hydrophilic (polar) ends. They surround asphaltene clusters and let them be dispersed in maltenes (Hefer & Little, 2005).

Asphaltenes and Resins are the components of bitumen which provide the adhesive properties of bitumen. Maltenes are non-polar fractions of bitumen which consist mainly of naphthenic (aromatic) and paraffinic waxes and oils (Ivann Harnish, 2010).

2.8.4. AGGREGATE FUNCTIONAL GROUPS and SURFACE CHARGES

In terms of composition, all aggregates are more or less made up of the assemblage of one or more minerals. They have definite chemical composition and an ordered atomic arrangement or lattices, in which each atom is bound to the neighbour atoms through electrostatic bonds (Hefer & Little, 2005).

When aggregates are crushed or cleaved, the atoms at the newly developed surfaces lose some of their neighbouring atoms and the associated electrostatic bonds because the matter of crushing, cleaving cutting and similar actions at the microscopic scale breaks the bonds between the material's particles, which here is meant to be the electrostatic bonds between atoms.

These atoms seek to form new coordination bonds to replace the old broken ones (Thelen, Hefer & Little, 2005). This description, as can be seen in the following sections, is considered as the rationale for the development of surface charge, as well as the concept of Surface Free Energy (Hefer & Little, 2005).

New bonds can be developed via directing some forces inward, which makes the atoms pulled closer together. This phenomenon is such that the atoms are adjusted in a consequent orientation that conforms to that of the existing crystal lattice. Another way to satisfy the broken bonds is to attract other substances such as water or organics to the surface or giving bonding sites for functional groups in bitumen. In this respect, Petersen et al. (cited in Little & Jones 2003) illustrated the importance of the surface site density on aggregates. In fact, the higher the surface area, the more active sites per unit mass of aggregate are available for interaction (Little & Jones, 2003)

Moreover, Jamieson et al. (cited in Hefer & Little 2005) reported that, in general, those chemical sites on aggregate surfaces, which have high affinity for bitumen, include elements such as aluminium, iron, magnesium and calcium, whereas the elements associated with low bonding affinity include sodium and potassium.

The mechanisms of charge development on aggregate surface presented below are as discussed by Mertens and Wright (cited in Hefer & Little 2005) and describe the creation of fundamental forces of adhesion, which, as mentioned previously, also serve as a molecular description for the concept of Surface Free Energy.

The following processes occur typically for oxides such as silica (SiO_2), which is essentially pure mineral quartz and makes up a large portion of aggregates such as quartzite and granite. As soon as a fracture takes place in aggregate, the creation of free charges on the newly created surfaces can be presented in a simplified way as follows:

$$Agg\text{-}O_3\text{-}Si\text{-}O\text{-}Si\text{-}O_3\text{-}Agg \rightarrow [Agg\text{-}O_3\text{-}Si^+] + [Ag\text{-}O_3\text{-}SiO^-] \qquad \text{Equation 2.2}$$

Where ‘Agg’ represents the bulk structure of the aggregate, with atomic lattice forming silicate tetrahedron unit cells in which silicon (Si) is coordinated with four oxygen atoms. As previously mentioned, a hydration process occurs in order to satisfy the unsatisfied surface charges. The chemical adsorption of water takes place following the dissociation of H_2O molecules into H^+ and OH^- during adsorption onto the aggregate’s new surface to make it hydroxylated. By this means, the polar silanol (Si-OH) groups form along the Silicate mineral perimeter surfaces where the Si-O bond is broken (Ivann Harnish, 2010). Further adsorption of water results in layers of hydrogen-bonded water, of which the outer layer is in equilibrium with water vapour in the air and presents nearly the same properties as free water at ambient temperature (Hefer & Little 2005).

$$[Agg\text{-}O_3\text{-}Si^+] + [Ag\text{-}O_3\text{-}SiO^-] + H_2O \rightarrow Agg\text{-}O_3\text{-}Si\text{-}OH + Agg\text{-}O_3\text{-}Si\text{-}OH \qquad \text{Equation 2.3}$$

This bonding reaction between the OH derived from H_2O vapours in air and the silicon atoms of aggregate is ever present, even at typical HMA mixing temperatures. When silanol (Si-OH) comes into contact with H_2O along the bitumen-aggregate interface, a reaction occurs yielding a negative charge on the aggregate (Ivann Harnish, 2010).

This is what happens in the case of aggregates such as granite, which are rich in silicates. The silanol groups at the surface of the aggregate react with water (H_2O) and liberate H^+ as follows:

$$Si\text{-}OH + H_2O \rightarrow Si\text{-}O^- + H_3O^+ \qquad \text{Equation 2.4}$$

Equation 2.4 can be written in the following format, as well:

$$Agg\text{-}O_3\text{-}Si\text{-}OH \rightarrow [Agg\text{-}O_3\text{-}SiO^-] + H^+ \qquad \text{Equation 2.5}$$

As a result, the granite aggregate surface becomes negatively charged. This reaction is the reason why granite and other rocks rich in silicates are termed 'acidic'. In fact, silanol groups make the aggregate surface very hydrophilic (water loving). Such aggregates, if used in bituminous mixtures (asphalt mixtures), may have a higher tendency to adsorb (interact with) water rather than bitumen. This means that either the aggregate cannot be effectively wetted by bitumen (as the aggregate may have initially some interactions with water even at the mixing temperature) or the existing bitumen coating can be debonded (aggregate stripping) and replaced by water since the binder-aggregate adhesion has not been strong enough to resist against the aggregate's affinity to adsorb water. In fact, using hydrophilic aggregates increases the moisture susceptibility of the resulting bituminous mixture. Therefore, the higher the percentage of silica in the volume of aggregate, the higher the moisture susceptibility of the resulting asphalt mixture, which means the higher the stripping potential of the aggregate in the mixture (Ivann Harnish, 2010).

Other functional groups on aggregate surfaces which dissociate to form surface charges include: carboxyl, sulphate and amino groups. Similar to silanol, adsorption of H^+ and OH^- ions can result in the development of charges on the aggregate surfaces with the above-mentioned functional groups, as well. The pH of the water in contact with the mineral surface controls the extent to which these reactions proceed.

Water with a high pH (high concentration of OH^- ions) excites the silanol groups to dissociate more which results in liberating more H^+ ions and therefore causes the surface to become more negatively charged. However, at low pH levels, silica surfaces can be positively charged (Gast; Butt et al., cited in Hefer & Little 2005). Although Equations 3 and 4 imply that the release of protons into water should result in lowering the pH of water, studies indicate a reverse story proving that water pH increases over the time. Scott (cited in Jakarini 2012), Yoon & Tarrer

(cited in Jakarini 2012) refer this phenomenon to the hydrolysis of compounds on aggregate surfaces containing alkaline earth metals such as sodium, potassium, calcium, and magnesium.

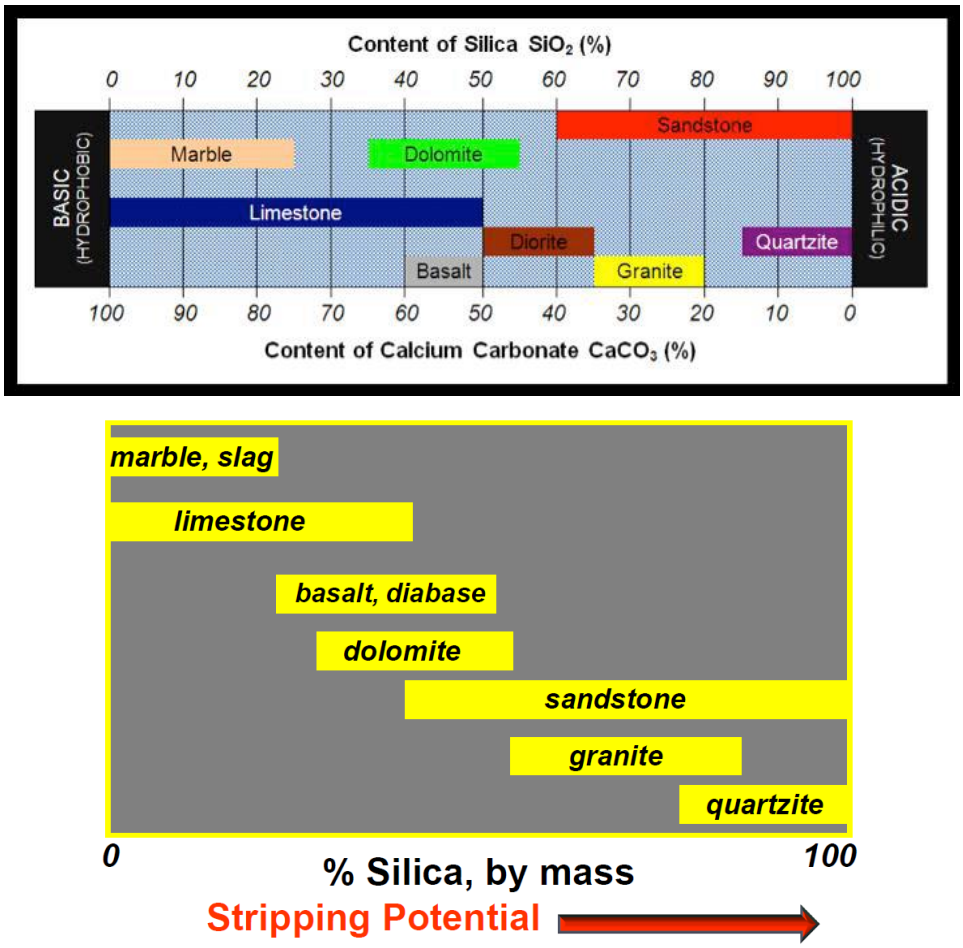


Figure 2.11 : The relation of aggregate's stripping potential and its silica percentage (Ivann Harnish, 2010)

As an example of an aggregate type with totally different behaviour compared to granite in terms of surface charge development and stripping potential, limestone can be looked at since it is one of the most useful aggregate types in the asphalt industry.

Looking at Figure 2.11 illustrates that limestone has a significantly lower stripping potential in comparison to granite. This characteristic refers to its lower silica content as mentioned before.

Moreover, regarding the development of surface charges, limestone shows a totally different tendency in comparison with granite. This difference is due to their different chemical composition and functional groups. In order to explain the issue, it should be considered that limestone is mainly made up of calcium carbonate (the mineral calcite, $CaCO_3$) and is known

to have electropositive surface charges. When limestone aggregate is fractured, the electrostatic bonds between the atoms are broken following a reaction simplified below. Consequently, a countless number of unsatisfied charges of calcium and carbonate ions are formed as follows and left on the newly formed surfaces (Ivann Harnish, 2010):

$$Agg\text{-}Ca\text{-}CO_3\text{-}Ca\text{-}Agg \rightarrow [Agg\text{-}Ca^+] + [Agg\text{-}Ca\text{-}CO_3^-] \qquad \text{Equation 2.6}$$

In Equation 2.6, 'Agg' represents the bulk aggregate structure, with the atomic lattice constituting the $CaCO_3$ rhombohedral unit cells. Water vapour adsorbs instantaneously onto the aggregate to satisfy the broken bonds through a hydration reaction that occurs as follows (Ivann Harnish, 2010):

$$[Agg\text{-}Ca^+] + [Agg\text{-}Ca\text{-}CO_3^-] + H_2O \rightarrow Agg\text{-}CaOH + Agg\text{-}Ca\text{-}CO_3H \qquad \text{Equation 2.7}$$

where the unsatisfied calcium ions adsorb the hydroxyl groups (OH) of water and tend to further react with carbon dioxide dissolved in the surface water ($CO_2 + H_2O \rightarrow H_2CO_3$). As a result, the following additional reaction takes place (Ivann Harnish, 2010):

$$Agg\text{-}CaOH + H_2CO_3 \rightarrow Agg\text{-}Ca\text{-}CO_3H + H_2O \qquad \text{Equation 2.8}$$

Therefore, regardless of the type of charge developed immediately after fracture, the molecular structure of the newly developed post-fracture surfaces of limestone is as shown on the right hand side of Equation 2.8. However, in the presence of water, this structure dissociates to produce a final characteristic electropositive charge on the limestone surface as follows (Hefer & Little (2005):

$$Agg\text{-}Ca\text{-}CO_3H \rightarrow [Agg\text{-}Ca^+] + [HCO_3^-] \qquad \text{Equation 2.9}$$

Equation 2.9 illustrates that limestone has accepted a proton, as a result of which, the aggregate's surface becomes positively charged. This reaction is the reason why limestone and other rocks with similar structures are termed 'basic'.

2.8.5. FUNDAMENTALS of BITUMEN-AGGREGATE ADHESION

Bitumen-aggregate adhesion takes place following the process of developing chemical bonds between the bitumen film and aggregate surface. In other words, adhesion bond is developed

following certain interactions between the bitumen and aggregate surface which mainly take place between their functional groups (Ivann Harnish, 2010).

In this respect, the bitumen-aggregate bond strength between a given bitumen and different types of aggregates may vary. It may also alter by changing the aggregate source even if the aggregate type does not change. Moreover, changing the source of bitumen may change the adhesion bond strength, as well, even if the physico-mechanical properties of the two bitumen types are the same. The reason for the above facts is the dependency of the bitumen-aggregate bond strength to the surface physico-chemical characteristics of both bitumen and aggregate. Different types of aggregates have different chemical characteristics, which influences their affinity to bitumen. Moreover, different bitumen coming from different sources may have various chemical characteristics (i.e. different types or amounts of functional groups), which affect the adhesion quality and strength. Similarly, the surface characteristics of the aggregates vary depending upon the source of the material even if they are made up of similar constituents. This is because the amount and surface density of the functional groups may still be different. Therefore, it is not always possible to achieve a similar strength or quality of adhesion even with the same aggregate and bitumen type.

Aggregates with high silicon oxide content, e.g. quartz and granite (i.e. acidic rocks) are classified as ‘hydrophilic’ (water loving), as described in the previous sections, and are generally more difficult to be coated with bitumen compared to basic rocks such as limestone (Ahmad, 2011).

Following the previous section, the review of bitumen and aggregate functional groups illustrates that carboxylic acids in bitumen play a prominent role in the surface chemistry-associated phenomena of bitumen though these compounds are often found only in trace amounts in bitumen. They usually contribute significantly to the strongly adsorbed fractions (Hefer & Little, 2005).

It has been experimentally proved by a number of researchers (e.g. research by the Western Research Institute in Wyoming, USA under a Federal Highway Administration grant) that carboxylic acids in bitumen can easily be displaced by water (aggregate stripping or binder de-bonding) in a coating on a siliceous aggregate despite that they readily make bonds with siliceous aggregate surfaces. The interaction between a silanol group (as the functional group of siliceous aggregates such as granite) and a carboxylic acid is presented in the reaction shown

below. These interactions between the mineral functional group and the organic functional group can range from completely covalent to completely ionic (Hefer & Little, 2005).

In this respect, it can be said that the bond energy increases as the equilibrium shifts to the right. This makes the bond more ionic. When the surface hydroxyl group act as a strong base and the organic functional group act as a strong acid, the maximum strength of bitumen-aggregate bond is achieved (Ivann Harnish, 2010).

$$\text{Agg-O}_3\text{-Si-OH} + \text{R-COOH} \rightleftharpoons \text{Agg-O}_3\text{-Si-}\overset{\text{H}}{\text{O}}\cdots\text{HOOC-R} \rightleftharpoons \text{Agg-O}_3\text{-Si-OH}_2^{+}\ ^{-}\text{OOC-R}$$

Equation 2.10

Where '⋯' denotes hydrogen bonding. The strength of an acid is determined by the length and type of the R group. Strong acids tend to donate a proton (de-protonise) more readily. It is known that carboxylic acids in bitumen are weak acids. This means that they are not easily dissociated to form ionic species. Therefore, the right side of the reaction is less likely to occur in Equation 2.10. In fact, the middle situation is more likely to take place. Hydrogen bonds, however, are susceptible to displacement or interruption by water according to the following reaction:

$$\text{Agg-O}_3\text{-Si-}\overset{\text{H}}{\text{O}}\cdots\text{HOOC-R} + 2\text{H}_2\text{O} \rightleftharpoons \text{Agg-O}_3\text{-Si-}\overset{\text{H}}{\text{O}}\cdots\text{HOH} + \text{H}_2\text{O} + \text{R-COOH}$$

Equation 2.11

In this hydrolysis reaction, water, acting as either a base or an acid, forms a stronger hydrogen bond with the silanol group than the hydrogen bond between the functional group and the silanol group (Ivann Harnish, 2010). This equation shows the reaction happens in aggregate stripping; a phenomenon, through which water replaces and de-bonds the bitumen coating from the surface of aggregate (e.g. granite).

On the matter of limestone aggregates, calcium carbonate in limestone's structure reacts with carboxylic acids in bitumen, which are weak acids. As can be seen in the associated reaction shown in Equation 2.12, at conventional mixing temperatures of asphalt, an insoluble salt of carboxylic acid, water, and carbon dioxide are formed (Hefer & Little, 2005):

$$\text{CaCO}_3 + 2\text{R-COOH} \rightarrow (\text{R-COO}^{-})_2\text{Ca} + \text{H}_2\text{O} + \text{CO}_2 \qquad \text{Equation 2.12}$$

2.9. SURFACE ENERGY

2.9.1. The CONCEPT of SURFACE ENERGY

The amount of energy, which is required to create a unit surface area of a material in vacuum, is called the Surface Energy of that material. Surface Energy dimensions correspond to that of energy per unit area (i.e. mJ/m2 or erg/cm2). However, in essence, any unit of energy can sit as numerator and any unit of area can sit as denominator in the unit fraction.

Surface Energy (Surface Free Energy) exists as the extra free energy in the molecules of a material's surface layer compared to the molecules inside the bulk of material. In fact, the existence of Surface Free Energy is due to the differences in the intermolecular forces acting on the surface molecules as compared to those acting on the molecules which are in the bulk of the material. In other words, as can be seen in Figure 2.12, the molecules at the surface of a material are attracted inwards by the molecules in the bulk of material and also pulled at a tangent to the surface of the material by the neighbouring surface molecules of the material. However, the molecules inside the material's bulk are pulled equally by their neighbouring molecules in all directions resulting in a net force of zero. This different situation provides more degrees of freedom in the molecules at a material's surface compared to those in the material's bulk. Therefore, the molecules at the material's surface layer are more active or unstable compared to those in the bulk. This means that the molecules at the surface of the material have more energy due to the difference in the intermolecular forces at the surface and in the bulk of material. This energy is referred to as Surface (Free) Energy.

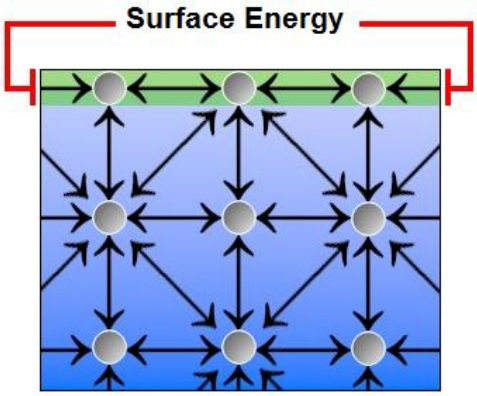


Figure 2.12 : The schematic difference between the inter-particle forces in the bulk and at the surface of a substance (HubPages, 2016)

From another point of view, during a cutting or breaking process, the energy, which in the form of "Work" is spent to break the intermolecular bonds, is given to the molecules of the two created surfaces on both sides of the interface layer. This extra energy in a material's surface layer molecules is called Surface Free Energy and causes them to be more unstable compared to the molecules inside the material's bulk. In fact, breaking or cutting a material can happen only if the molecules energy per unit area at the splitting surface is increased to the material Surface Energy by the breaking process.

Basically, any system tends to minimise its energy level to become more stable. In the case of a system including two objects, the stronger the bond between them, the more the tendency they have had to lower their energy or the lower the energy state they are at and the more energy is required to separate them (Barton, cited in Ahmad 2011).

According to thermodynamics, which is the study of energy changes, bitumen-aggregate adhesive bond strength and bitumen cohesive strength characteristics are directly related to the surface energy properties of bitumen and aggregate. As will be shown in the current section, binder and aggregate adhesive bond parameters, with and without the presence of water, can be studied and calculated for different bitumen, aggregate and filler combinations using the surface energy values of bitumen and aggregate (Cheng et al., cited in Ahmad 2011).

2.9.2. WORK of ADHESION and WORK of COHESION

The energy or work required to create a unit area of de-bonding at the adhesion interface (interfacial area) between two different materials is called their Work of Adhesion, which is actually the energy of the bond between those two materials.

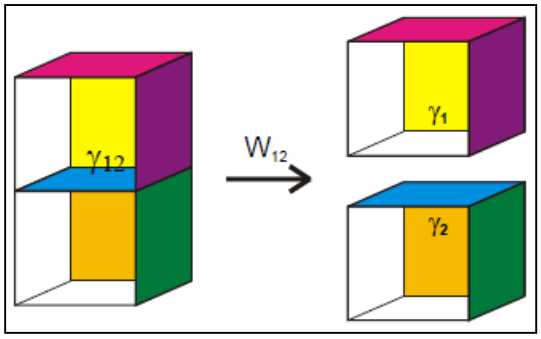


Figure 2.13 : Work of Adhesion (Hansen, cited in Ahmad 2011)

The Work of Adhesion between two incompatible (different) substances is calculated through Dupre's general equation as follows:

$$W^A = W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad \text{Equation 2.13}$$

Where:

$W^A = W_{12}$ = Work of Adhesion between materials 1 and 2

γ_1= The total Surface Energy of material 1

γ_2= The total Surface Energy of material 2

γ_{12}= The interfacial Surface Energy of the two materials (the energy required to increase the interfacial area between the two materials as much as a unit area)

(All parameters are in mJ/m^2 or other compatible units)

In a particular situation that the two involved materials are the same or identical or in the case that a uniform material is being broken, the term 'Work of Adhesion' is replaced by 'Work of Cohesion' and it is the energy needed to split a unit area of the material.

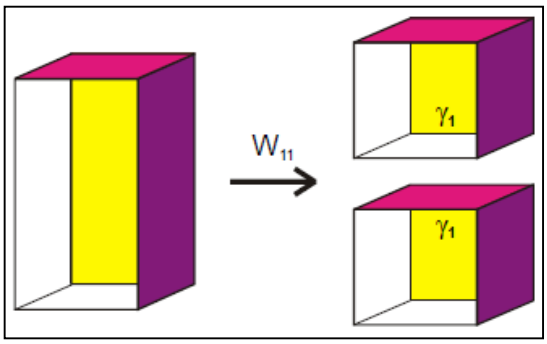


Figure 2.14 : Work of Cohesion (Hansen, cited in Ahmad 2011)

The Work of Cohesion of a single substance is calculated through a simplified form of Dupre's general equation as follows:

$$W^C = \gamma_1 + \gamma_1 - 0 = 2\gamma_1 \qquad \text{Equation 2.14}$$

Where:

$W^C = W_{11}$ = Work of Cohesion of material (material 1)

γ_1= The total Surface Energy of material (material 1)

(All parameters are in mJ/m^2 or other compatible units)

Following the explanations of 'Work of Adhesion' and 'Work of Cohesion', it should be stated that the former concept involves the intermolecular (or generally inter-particle) forces of two different substances while the latter involves that of one single material.

2.9.3. SURFACE TENSION and SURFACE ENERGY of LIQUIDS

The term 'Surface Energy' or 'Surface Free Energy', in the case of liquids, is referred to as 'Surface Tension'. Surface Tension and Surface Energy are interchangeable definitions with the same units. Surface Tension of a liquid is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the imbalance in cohesive forces of the surface layer. In the absence of other forces, including gravity, drops of virtually all liquids would be approximately spherical. In fact, the consequence of the forces applied to a liquid droplet's surface molecules from the other neighbouring molecules inside the bulk of the droplet (inward) and at the surface of the droplet (tangent to the surface) creates a net inward pressure (which develops some internal pressure) and makes the surface contract to the minimal possible area. The spherical shape minimizes the necessary 'wall tension' of the surface layer according to Laplace's law. However, in practice, external forces such as gravity and substrate reaction deform the droplet and, as a result, a Contact Angle is formed (as shown in Figure 2.16), which can be determined through Statics equilibrium equations or the Young's equation (as will be discussed in the next pages).

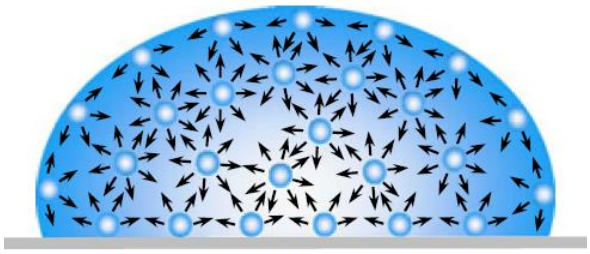


Figure 2.15 : Molecular interactions in the bulk and at the surface of a liquid droplet (Yuan & Lee, 2013)



Figure 2.16 : Formation of contact angle at the liquid-solid-vapour interface

It should be mentioned that in the case of solids, the reduction in surface area is not obvious due to the limited mobility of the solid molecules, but the intermolecular forces still exist.

2.9.4. EVALUATING the SURFACE ENERGY of a MATERIAL

Referring to the explanations regarding the concept of surface (free) energy (surface tension) of a material, it is evident that this concept involves the intermolecular, or in general, the inter-particle forces of material. Therefore, in order to evaluate the surface energy of a substance as a parameter, evaluation and characterisation of its intermolecular forces are essential.

According to the Good, Van Oss and Chaudhury approach, the forces responsible for the surface energy of a material are divided into two different components namely, the non-polar (dispersive) component and the polar component. The dispersive forces are termed as Lifshitz-van der Waals forces and the polar forces are divided into Lewis acid and Lewis base forces (Van Oss et al., cited in Ahmad 2011).

In order to explain the fundamental background of the above approach, it is necessary to mention that a molecule is formed as a result of the formation of chemical bonds between atoms. In polar molecules, the arrangement of atoms is in such a way that one end of the molecule becomes positively charged while the other end becomes negatively charged. This is because of the un-even distribution of electrons in the orbitals or shells. This phenomenon makes them unstable and provides them with a tendency to interact with other polar molecules. However, in nonpolar molecules, the electrons are distributed more symmetrically. As a result, all developed charges cancel each other out. The Lifshitz-van der Waals forces, which are considered to be the non-polar or dispersive forces, are believed to consist of three main components; London dispersion forces, Debye induction forces and Keesom orientation forces

(Kim; Rieke, cited in Ahmad 2011). All these forces represent different types of dipole/induced dipole interactions between neighbouring molecules and electronic shells. These forces between molecules in a material are viewed as residual electrostatic forces (Ahmad, 2011).

Regarding the polar components, the acid-base interactions include electron acceptor-electron donor interactions and hydrogen bonding (Morrison & Boyd, cited in Ahmad 2011). Referring to the Acid-Base theory of Lewis, basically, in a chemical interaction between two substances, regardless of the type of chemical bond being formed, the party which has the potential of giving protons (electron acceptor) is considered as the Acid (Lewis Acid) whereas the party which has the potential of accepting proton (electron donor) is considered as the Base (Lewis Base). Therefore, through a chemical reaction, a Lewis Acid releases a proton (accepts an electron) and will become negatively charged at the end of the reaction, while the Lewis Base accepts a proton (releases an electron) and will be positively charged following the reaction. However, due to the issue that the Lewis Acid is expected to release a proton and the Lewis Base is potentially an electron donor, in the Surface Energy formulations, a γ^+ represents Lewis Acid and a γ^- represents Lewis Base (Ahmad, 2011; Good & Chaudhury, 1991).

Putting everything together, according to the Good, Van Oss and Chaudhury approach, the total surface energy of a material, γ^{Total}, can be calculated by the following equation:

$$\gamma^{Total} = \gamma^{LW} + \gamma^{AB} \qquad \text{Equation 2.15}$$

Where:

γ^{Total} = The total Surface Energy of material

γ^{LW} = Lifshitz-Van der Waals SE component (non-polar/dispersive component)

γ^{AB} = Lewis Acid-Base SE component (polar component)

(All parameters are in mJ/m^2 or other compatible units)

According to acid-base theory (Van Oss et al., cited in Ahmad 2011), the acid-base component can be given as:

$$\gamma^{AB} = 2\left((\gamma^+)(\gamma^-)\right)^{0.5} \qquad \text{Equation 2.16}$$

Where:

γ^{AB} = Lewis Acid-Base Surface Energy component (polar component)

γ^{+} = Lewis Acid component of surface interaction

γ^{-} = Lewis Base component of surface interaction

(All parameters are in mJ/m^2 or other compatible units)

Considering Figure 2.15, Equation 2.15 and Equation 2.16 together, the total Surface Energy of a material can be calculated as follows:

$$\gamma^{Total} = \gamma^{LW} + 2\left((\gamma^{+})(\gamma^{-})\right)^{0.5} \qquad \text{Equation 2.17}$$

2.9.5. EVALUATION of BITUMEN-AGGREGATE DRY BOND STRENGH

The energy or work required to create a unit area of de-bonding at the adhesion interface (interfacial area) between a solid substance (aggregate) and a liquid substance (bitumen) is called the Work of Adhesion between the solid and liquid. It is actually the bond energy of that solid-liquid adhesion.

The Work of Adhesion between a solid and a liquid is actually the energy of that solid-liquid bond that can be obtained through Dupre's general equation for solid-liquid adhesion (Ahmad, 2011):

$$W_{LS}^{A} = \gamma_{LA} + \gamma_{SA} - \gamma_{LS} \qquad \text{Equation 2.18}$$

Where:

W_{LS}^{A} = Liquid-Solid (Bitumen-Aggregate) Work of Adhesion

γ_{LA} = The total Surface Tension of the liquid substance (binder/bitumen)

γ_{SA} = The total Surface Energy of the solid substance (aggregate)

γ_{LS} = The interfacial Surface Energy of the liquid (binder/bitumen) and solid (aggregate)

(All parameters are in mJ/m^2 or other compatible units)

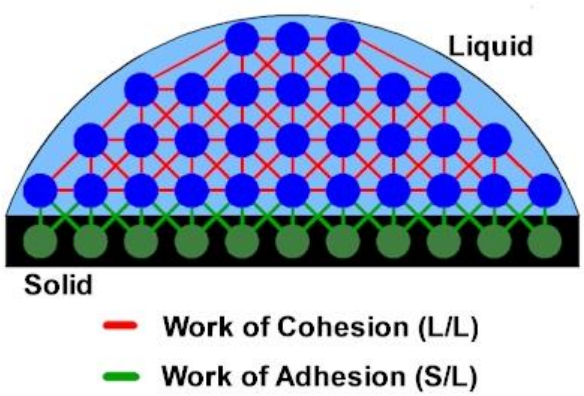


Figure 2.17 : Schematics of Liquid-Solid Work of Adhesion and Liquid Work of Cohesion

Several theories have been presented in the past in order to describe the adhesion forces between two materials. In this regard, the view point of thermodynamics is the most widely used theory to quantify adhesion between two materials (Hefer & Little, 2005). The intermolecular forces at the interface of materials are related to the surface energies of the substances involved in adhesion.

Similar to the theory of Van Oss-Chaudhury-Good, which was described in the previous pages regarding calculating the surface free energy of a substance, the Work of Adhesion (bond strength) between two materials, in our case, liquid (bitumen) and solid (aggregate) can also be considered as a combination of Lifshitz-Van der Waals (non-polar) and Lewis Acid-Base forces in such a way that the total bond strength can be given as follows (Ahmad, 2011):

$$W_{BA}^{A} = W_{BA}^{LW} + W_{BA}^{AB} \qquad \text{Equation 2.19}$$

As mentioned before, according to Dupre's general equation (Equation 2.18), both the non-polar and the polar components of bond strength (Work of Adhesion) in Equation 2.19 can be determined with the following equations (Ahmad, 2011):

$$W_{BA}^{LW} = \gamma_{B}^{LW} + \gamma_{A}^{LW} - \gamma_{BA}^{LW} \qquad \text{Equation 2.20}$$

$$W_{BA}^{AB} = \gamma_{B}^{AB} + \gamma_{A}^{AB} - \gamma_{BA}^{AB} \qquad \text{Equation 2.21}$$

At this point, it should be mentioned that the interfacial surface energy can also be written as a sum of the Lifshitz-Van der Waals and Lewis acid/base contributions.

$$\gamma_{BA} = \gamma_{BA}^{LW} + \gamma_{BA}^{AB} \qquad \text{Equation 2.22}$$

Good, Grifalco and Fowkes demonstrated experimentally that if only dispersion interaction forces (the non-polar Lifshitz-Van der Waals component) take place between two condensed phase materials, e.g. a solid (aggregate) and a liquid (bitumen), the interfacial tension between them (γ_{BA}^{LW}) is calculated through the following equation, which is referred to as Good-Girifalco-Fowkes combining rule (Ahmad, 2011):

$$\gamma_{BA}^{LW} = ((\gamma_B^{LW})^{0.5} - (\gamma_A^{LW})^{0.5})^2 \qquad \text{Equation 2.23}$$

Equation 2.23 has been shown experimentally to be accurate to within 2%.

The polar Acid-Base component of the interfacial surface energy (γ_{BA}^{AB}) is given by the equation below referring to Small's combining rule (Erbil, cited in Ahmad 2011):

$$\gamma_{BA}^{AB} = 2((\gamma_B^{+})^{0.5} - (\gamma_A^{+})^{0.5})((\gamma_B^{-})^{0.5} - (\gamma_A^{-})^{0.5}) \qquad \text{Equation 2.24}$$

Combining Equation 2.19, Equation 2.20, Equation 2.21, Equation 2.23 and Equation 2.24 results in the following Equation, which gives the bond strength of adhesion between a solid (aggregate) and a liquid (bitumen/binder) in the dry situation (Ahmad, 2011):

$$W_{BA}^{A} = 2\left(\left((\gamma_B^{LW})(\gamma_A^{LW})\right)^{0.5} + \left((\gamma_B^{+})(\gamma_A^{-})\right)^{0.5} + \left((\gamma_B^{-})(\gamma_A^{+})\right)^{0.5}\right) \qquad \text{Equation 2.25}$$

The parameters and indices (subscripts and superscripts) used in Equation 2.19 toEquation 2.25 are defined as follows:

$W_{\square}^{\square}$ (parameter) = Work of Adhesion

$\gamma_{\square}^{\square}$ (parameter) = Surface Energy

$\square_{BA}^{\square}$ (subscript) = Bitumen/Binder-Aggregate

$\square_{\square}^{LW}$ (superscript) = Lifshitz-Van der waals

$\square_{\square}^{AB}$ (superscript) = Acid-Base

$\square_{A}^{\square}$ (subscript) = Aggregate

$\square_{B}^{\square}$ (subscript) = Bitumen/Binder

$\square_{\square}^{A}$ (superscript) = Adhesion

(All parameters are in mJ/m^2 or other compatible units)

It should be mentioned that the results of the surface energy calculations are idealistic and may not be totally confirmed by to the results of the associated laboratory field tests on the samples which have been manufactured using the same materials as used in calculations. This issue is due to the presence of the factors which inevitably influence the production process of asphalt (whether in the laboratory or in the asphalt factory) and affect the bitumen-aggregate adhesion bond quality and strength.

The surface energy calculations, present a quantitative parameter for the potential of the compatibility of a certain binder-aggregate combination, independent from any manufacturing-related factors, which may affect the adhesion of the mixture during the practical asphalt production phase.

2.9.6. WETTING and SPREADING

The terms ‘Wetting’, ‘Spreading’ and ‘Contact Angle’ have become meaningful through the concept of adhesion. Wetting the surface of a solid (substrate) by a liquid is a process through which the liquid spreads over the solid surface. Spreading takes place following the wetting mechanism through developing molecular contacts (fundamental forces of adhesion) between the liquid and the substrate surface to the point of complete wetting (Ivann Harnish, 2010).

Wetting is considered as a prerequisite for good adhesion. In fact, strong adhesion and weak cohesion results in a high degree of wetting. Naturally, wetting and spreading depend also on the viscosity of the liquid and roughness and heterogeneity of the solid surface involved. From a thermodynamics point of view, wetting and spreading depend on the competition between the liquid-solid adhesive forces on the one hand and the liquid cohesive forces on the other hand (Hefer & Little, 2005). High energy substrates are held together by bonds, while low energy substrates are held together by forces. Covalent, ionic, and metallic bonds are much stronger than forces such as Van der Waals and hydrogen bonding. High energy substrates are more easily wetted than the low energy ones. In addition, more complete wetting will occur if the substrate has a much higher surface energy than the liquid. As shown in Figure 2.18, the wettability of a material is directly related to its surface energy. Wettability is the degree of wetting and as will be explained in the next pages, is determined in a way by a force balance between adhesive and cohesive forces.

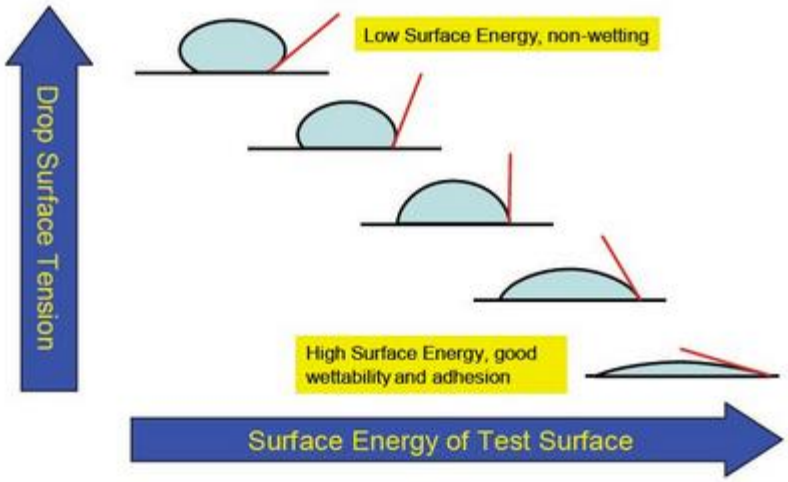


Figure 2.18 : The relationship diagram between wettability, surface tension of liquid and surface energy of substrate

In this regard, the Spreading Coefficient (*S*), as a quantitative representative parameter for spreading, has been defined, which is in fact a measure of the difference between the surface energy of the bare dry solid and the wetted solid coated by a macroscopic film of the liquid (Good & Hawa, 1997). Equation 2.26 can be used to define a spreading coefficient, *S*:

$$S = W_{SL}^{A} - W_{L}^{C} \qquad \text{Equation 2.26}$$

S = Spreading parameter

W_{LS}^{A} = Liquid-Solid Work of Adhesion

W_{L}^{C} = Work of Cohesion of the liquid

(All parameters are in mJ/m^2 or other compatible units)

Thus, the higher and the more positive the value of S, the greater the work of adhesion compared to the cohesive strength of the liquid (Ivann Harnish, 2010).

In addition, considering Equation 2.13 andEquation 2.14, Equation 2.26 can be written in the following form, as well:

$$S = \gamma_S - (\gamma_{SL} + \gamma_L) \qquad \text{Equation 2.27}$$

In which all parameters have been defined previously.

If $S \geq 0$, spreading happens (complete wetting) or, in other words, the Work of Adhesion is higher than the Work of Cohesion. When $S < 0$, the substrate surface prefers to remain dry, which is the situation in referred to as partial wetting. In both cases, the total surface free energy of the system is minimised (Figure 2.20) (Good & Chaudhury, 1991).

It should be emphasised that, in Equation 2.27, if γ_L is greater than γ_S, the liquid will only spread to cover part of the solid and in equilibrium it will assume a finite and measurable 'Contact Angle'. However, when $\gamma_L < \gamma_S$, the liquid spreads and wets the substrate completely, in which case no 'Contact Angle' will be formed between the liquid and solid (Good & Hawa, 1997).

2.9.7. CONTACT ANGLE and the YOUNG'S EQUATION

Any liquid droplet resting on a flat solid surface will stay statically in a balanced state forming an angle with the solid substrate's surface (Ahmad, 2011). The contact angle is basically the angle measured between the static droplet of the liquid with the flat solid surface (equilibrium contact angle) (Good & Chaudhury, 1991). It is actually defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapour interface (geometrically acquired by applying a tangent line from the contact point along the liquid-vapour interface in the droplet profile). The interface where solid, liquid, and vapour co-exist is referred to as the 'three phase contact line' (Yuan & Lee, 2013).

The shape of a liquid drop on a solid surface is usually described through the contact angle between them and provides information on the intermolecular forces of the individual phases involved as well as the interfacial forces between them. In fact, the contact angle between a liquid and a solid surface, represents a state of mechanical equilibrium, and as such is determined by a balance between three interfacial tensions: the liquid-vapour surface tension, γ_{LV}, the solid-vapour surface tension, γ_{SV}, and the solid-liquid interfacial tension, γ_{SL} (Figure 2.19).

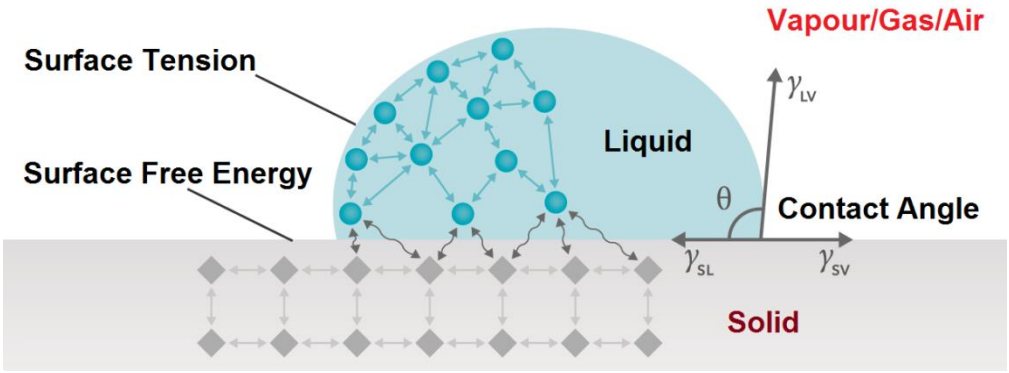


Figure 2.19 : Interfacial surface energy components and molecular interactions at liquid-solid-vapour interface (Biolin Scientific, 2016)

In fact, the contact angle can be used to qualify and provide a measure of wetting and spreading at a macroscopic scale. For instance, the lower the contact angle value, the better the wetting. At the opposite extreme, complete wetting occurs when the liquid fully covers the solid surface and spreading takes place. In that case, the liquid spreads spontaneously over the surface and no contact angle can be defined (Figure 2.20) (Good & Chaudhury, 1991).

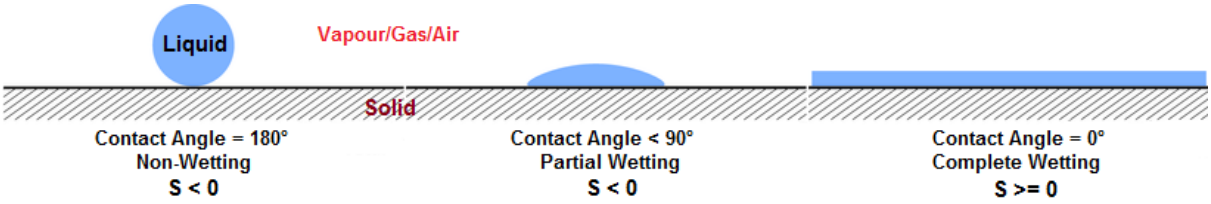


Figure 2.20 : Wetting, spreading and contact angle (Wikipedia, 2016b)

Figure 2.21 shows that a small contact angle is observed when the liquid spreads on the surface, while a large contact angle is observed when the liquid beads on the surface. More specifically, a contact angle less than 90° indicates that wetting of the surface is favourable, and the fluid will spread over a large area on the surface; while contact angles greater than 90° generally mean that wetting of the surface is unfavourable so the fluid will minimise its contact with the surface and form a compact liquid droplet. For example, complete wetting occurs when the contact angle is 0°, as the droplet turns into a flat puddle. For super hydrophobic surfaces, water contact angles are usually greater than 150°, showing almost no contact between the liquid drop and the surface (Yuan & Lee, 2013).

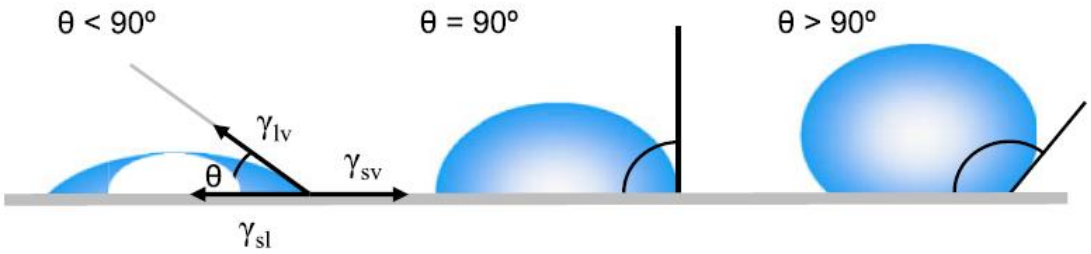


Figure 2.21 : Contact angle and wetting interpretation (Yuan & Lee, 2013)

Overall:

- If $\theta = 0°$, the liquid completely wets the substrate.
- If $0° < \theta < 90°$, high wetting occurs.
- If $90° \leq \theta < 180°$, low wetting occurs.
- If $\theta = 180°$, the liquid does not wet the substrate at all.

2.9.8. CONTACT ANGLE MEASUREMENT and the YOUNG'S EQUATION

The contact Angle (θ) measurement, first stated in qualitative form by Thomas Young in 1805 [8], remains at present the most accurate method for determining the interaction energy between a liquid (L) and a solid (S). Considering, for example, a process in which a liquid drop is brought to the surface of a solid previously in contact with air/vapour (V) (Figure 2.22). Young's paper contained no mathematical equations whatsoever, but its text expresses clearly Young's proposition as the following equation (the Young's Equation), which is actually the balance between the forces on the surface (Ahmad, 2011; Good & Hawa, 1997):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \quad \text{Equation 2.28}$$

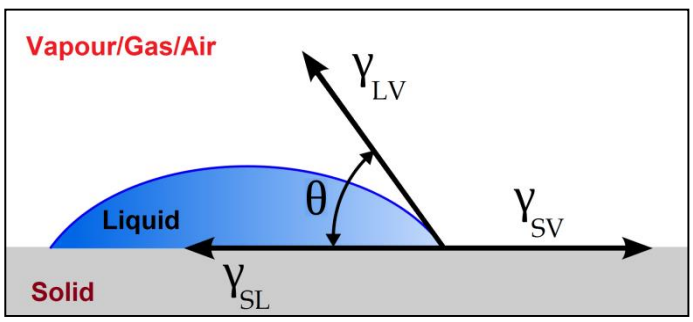


Figure 2.22 : The Young's Equation's Components at the Three Phase Contact Line

The terms γ_{LV}, γ_{SV} and γ_{SL} represent the interfacial surface energies at the liquid-vapour, solid-vapour and solid-liquid interfaces, respectively (Good & Hawa, 1997).

The derivation of the Young's equation assumes that the solid surface is smooth, homogenous and rigid; it should also be chemically and physically inert with respect to the liquid to being employed. Ideally, a unique contact angle is expected for a given system, according to Young's equation (Good & Chaudhury, 1991).

In Equation 2.28, γ_{SV} (the solid-vapour interfacial surface energy) will be identical to the Surface Free Energy of the solid (γ_S) if no vapour (vapour molecule) adsorption takes place onto the surface of the solid (at the solid-vapour interface). On this matter, 'vapour' refers to either the surrounding gas/air or the vapour of the involved liquid. In other words, the term 'no vapour' means neither the surrounding gas/air phase nor the involved liquid's vapour.

If the liquid vapour is not adsorbed onto the solid surface, the status is referred to as 'dry wetting'. As mentioned before, in this situation $\gamma_{SV} = \gamma_S$.

However, in the case that the liquid vapour is adsorbed onto the surface of the solid, 'wet wetting' takes place following which γ_{SV} will no longer be identical to γ_S. In fact, this status is a suspected source of heterogeneity which may occur with even the most homogeneous surfaces because of the deposition of molecules emanating from the contact angle liquid, via the gaseous phase, by re-condensation (Good & Hawa, 1997).

Bangham & Razouk's 1937 study (cited in Ahmad 2011) showed that this condensation of liquid from the contact angle liquid gives rise to complete wetting of the solid surface (Figure 2.19), which seriously reduces the contact angle. In view of this wetting effect, Bangham & Razouk (cited in Ahmad 2011) introduced the terms γ_{LV} and γ_{SV} (for liquid-vapour and solid-vapour surface energy).

Adsorption of vapour molecules onto the solid surface reduces the surface energy of the solid. When the solid surface is in equilibrium with the liquid vapour, the reduction of the surface free energy of the solid (γ_S) due to the vapour adsorption is termed the equilibrium spreading surface pressure, π_e. Therefore, the solid-vapour surface energy (γ_{SV}) can be calculated through the following equation (Good & Hawa, 1997):

$$\gamma_{SV} = \gamma_S - \pi_e \qquad \text{Equation 2.29}$$

Accordingly, Equation 17 (the Young's equation) can be written in a more general form as follows (Good & Hawa, 1997):

$$\gamma_S = \gamma_{LV} \cos\theta + \gamma_{SL} + \pi_e \qquad \text{Equation 2.30}$$

However, for low energy, homogeneous, smooth surfaces, the approximation that the term π_e is not significant is a reasonable one. Wu demonstrated that on a low energy surface π_e is usually negligible if the contact angle is larger than 10°. Yildirim (cited in Ahmad 2011) experimentally determined that the change in the contact angle of water by exposing talc to water vapour was negligible, which indicated that the vapours of high-energy water were not absorbed onto the low-energy talc surface. Fowkes et al. (cited in Ahmad 2011) studied the possibility of spreading pressures arising with high-energy liquids (e.g. water vapour) deposited on low-energy solids, and found that it did not occur. On the other hand, when a vapour of a low-energy liquid (e.g. cyclohexane or heptane) interacted with a higher-energy solid surface, the effect of resulting positive spreading pressure caused an increase in the contact angle of the liquid on that solid surface, which allowed the determination of π_e (Ahmad, 2011).

Van Oss showed that with non-spreading liquids (i.e. $\gamma_L > \gamma_S$ and $\cos\theta < 1$) neither spreading nor pre-wetting takes place on low-energy solid surfaces. Thus, it was concluded that it appeared not to be justified to take the equilibrium spreading pressure into account, under non-spreading conditions and where vapours of low energy substances were absent (Hefer & Little, 2005).

In other work, Van Oss et al. (cited in Ahmad 2011) studied both moderately hydrophobic and very hydrophilic solids, poly(methyl methacrylate) and poly(ethylene oxide), respectively, and showed that in all cases the contamination of the surface by gas molecules emanating from the liquid drop could be safely neglected since the error introduced by the effect of the spreading pressure was in the same order of magnitude of the precision of the contact angle measurements (±1%). In conclusion, Van Oss suggested that the designations γ_{LV} and γ_{SV} instead of the simplistic γ_L and γ_S are superfluous and misleading and thus are best avoided (Good and Chaudhury, 1991).

In the light of above statement, Young's equation can then be written in a simpler form as:

$$\gamma_S = \gamma_L \cos\theta + \gamma_{SL} \qquad \text{Equation 2.31}$$

Where γ_S is the surface free energy of the solid, γ_L is the surface free energy of the testing liquid and γ_{SL} is the surface free energy of the solid-liquid interface. In this form of Young's equation, the spreading pressure, π_e, has been neglected [18].

Although equilibrium spreading for the liquid phase should also be possible, this value has historically been assumed to be equal to zero (Hefer & Little, 2005).

By substituting the Dupre's equation (Equation 2.18) with the above mentioned Young's equation, Work of Adhesion between the two materials (e.g. liquid and solid) can be obtained through the following Young-Dupre's equation (Ahmad, 2011):

$$W_{LS}^{A} = \gamma_L(1 + \cos\theta) \qquad \text{Equation 2.32}$$

The Young-Dupré equation is the starting point for any method that utilises contact angles to obtain surface free energies by relating the contact angle to the Work of Adhesion. This is also the way to tie contact angles back to adhesion (Ivann Harnish, 2010).

Considering the Work of Adhesion between a bituminous binder and an aggregate, combining Equation 2.25 andEquation 2.32 results in the following Equation (Ahmad, 2011):

$$\gamma_B^{Total}(1 + \cos\theta) = 2\left(\left((\gamma_B^{LW})(\gamma_A^{LW})\right)^{0.5} + \left((\gamma_B^{+})(\gamma_A^{-})\right)^{0.5} + \left((\gamma_B^{-})(\gamma_A^{+})\right)^{0.5}\right) \qquad \text{Equation 2.33}$$

Equation 2.33 presents a relationship between the three surface energy components of aggregate, those of binder and the contact angle between them. All parameters in Equation 2.33 have been defined previously.

Moreover, combining Equation 2.28 which defines the Spreading parameter, with the Young's equation results in the following form of Spreading parameter:

$$S = \gamma_{LV}(\cos\theta - 1) \qquad \text{Equation 2.34}$$

Which only has physical solutions for θ when $S < 0$ (partial wetting).

2.10.COHESIVE FAILURE and ADHESIVE FAILURES in ASPHALT

Damage in asphalt mixtures can happen within the mastic (cohesive fracture) or at the mastic-aggregate interface (adhesive fracture or failure) (Little & Jones, 2003).

'Cohesive Failure' refers to the tensile failure within bitumen or bitumen-filler mastic itself due to the low ultimate tensile strength of bitumen or mastic compared to the adhesive bond strength (Jakarini, 2012).

'Adhesive Failure' in asphalt mixture is the detachment of bitumen (mastic) or bituminous binder from the aggregate surface. This type of failure indicates the low magnitude of binder-aggregate (mastic-aggregate) adhesive bond strength in an asphalt mixture. Adhesive bond strength between bitumen or mastic and aggregate in an asphalt mixture is mainly influenced by the physical, chemical and mechanical properties of the mixture's ingredients (Jakarini, 2012). As to bitumen, factors like the binder provenance, the chemical composition, the surface tension, the viscosity, and the ageing resistance play a role. As to aggregate, important factors are the mineralogical and chemical composition, the surface roughness, and the porosity. In addition, adhesion is negatively affected by the presence of water, and thus, the characteristics of the water like surface tension, polarity and pH-value need to be considered too (Bhasin & Little; Majidzadeh & Brovold; Thelen, cited in Gronniger, Wistuba & Renken 2010). Moreover, the dosage and characteristics of the additives or adhesion promoters (if used) to produce the asphalt mixture influences the issue, as well (Jakarini, 2012).

Figure 2.23 shows the general microscopic schematics of the possible types of adhesive/cohesive tensile failures (i.e. adhesive failure, cohesive failure and mixed cohesive and adhesive failure), which may occur in asphalt mixtures developing the majority of pavement distresses. However, failure due to the moisture damage of asphalt is usually neither entirely adhesive nor entirely cohesive. The simplest and easiest method to identify the forms of failure is via visual observation and calculation based on the percentage area of adhesive and cohesive failure (Jakarini, 2012).

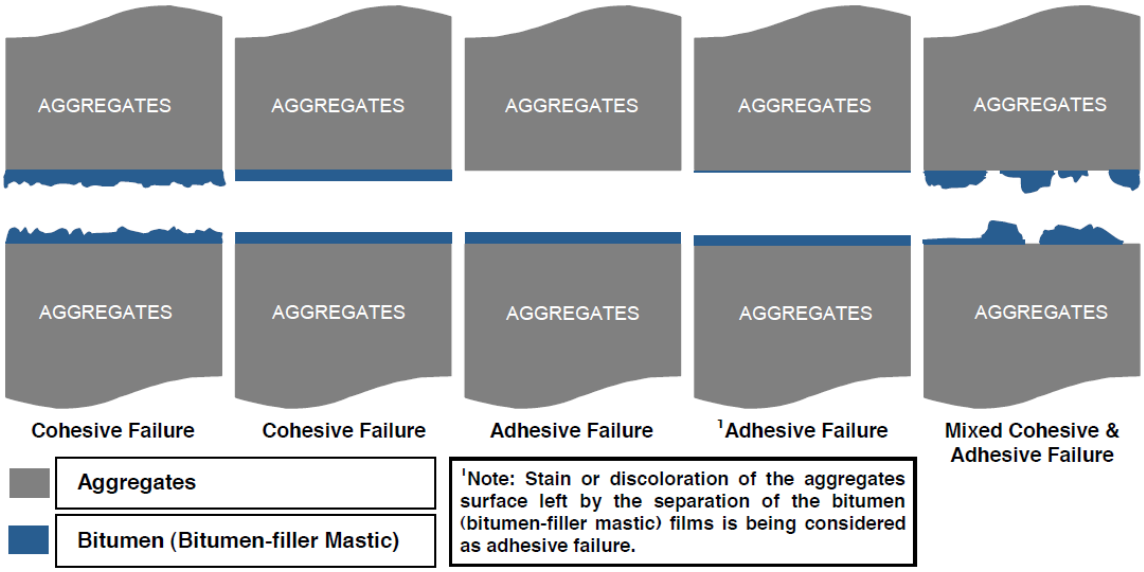


Figure 2.23 : Possible types of tensile failures which may happen in the asphalt mixtures (Jakarini, 2012)

The properties of mastic and its relative thickness around the coarse and fine aggregates in asphalt mixture define whether or not cohesive or adhesive failure takes place. Lytton used micromechanics to determine the bitumen film 'thickness' at which adhesive failure gives way to cohesive failure (Little & Jones, 2003).

Figure 2.24 presents the cohesive and adhesive bond strength assessed by the use of cohesive and adhesive surface energies versus the thickness of bitumen or mastic (Little & Jones, 2003). The theory which has been extracted from Figure 2.24 states that, basically, in asphalt mixtures, the failure of bitumen-aggregate bond in tension will be in the form of (Little & Jones, 2003):

- Adhesion/adhesive failure, if the bitumen film is thin,
- Cohesion/cohesive failure due to damage within the bitumen (or mastic) as opposed to interfacial debonding, if the bitumen (or mastic) film is relatively thick (thicker than the transition point in Figure 2.24).

The thickness, which differentiates these two types of failures (the transition thickness) depends on the rheology of the bitumen (or mastic), the amount of damage the bitumen or mastic can bear prior to failure, the rate of loading, and the test temperature (Little & Jones, 2003).

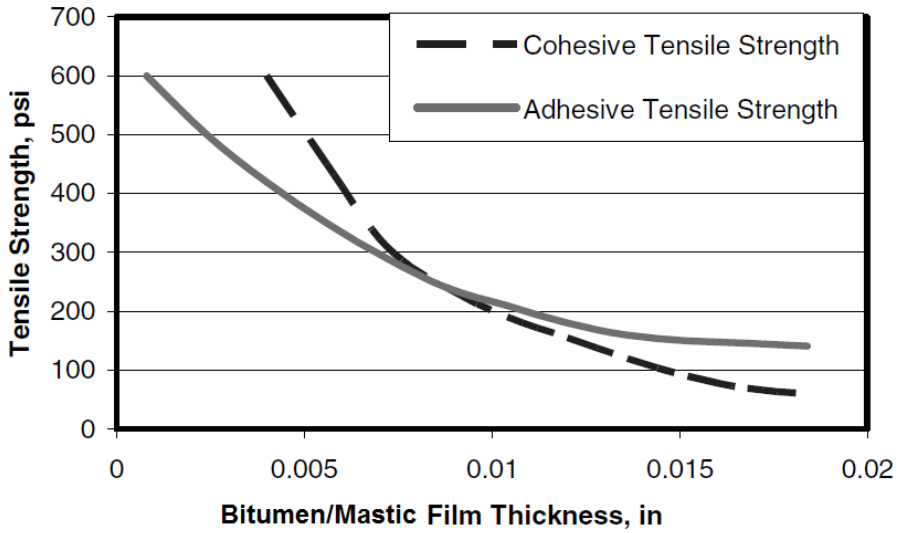


Figure 2.24 : Adhesive versus cohesive bond failure based on bitumen/mastic film thickness (Little & Jones, 2003)

According to Figure 2.24, when bitumen or mastic coatings are thin, the adhesive strength controls the performance of the bitumen-aggregate adhesion system. However, when bitumen or mastic coatings are relatively thick (thicker than the transition point of Figure 2.24) the cohesive strength limits or controls the damage resistance (Jakarini, 2012).

It should be noticed that in Figure 2.24, within relatively close ranges of the transition point bitumen film thickness, a combination of both adhesion and cohesion failures may take place in such a way that the failure surface passes partly through the bitumen and partly the bitumen-aggregate interface. Meanwhile, in very rare cases it may also pass through the aggregate, as well.

In fact, it is necessary to consider both adhesive and cohesive strength properties of the mixtures as mastic coatings range from relatively thin to relatively thick throughout the mixture. Mixture strength then becomes a question of the statistical distribution of conditions where adhesion or cohesion strengths control (Little & Jones, 2003).

2.10.2. The THEORY of (WEAK) BOUNDARY LAYERS

The theory of ‘Weak Boundary Layers’ states that adhesion bonds may fail in either the adhesive or substrate due to the presence of an interphase region with low cohesive strength. Pocius (cited in Jakaini 2012) reports that this theory has been used as a backup or an alternative

justification by the adhesion scientists in any adhesion bonding failure situation which could not be explained through other common rationalisations used before.

Regardless of some dispute in how widespread the weak boundary layers are, the existence of weak boundary layers is a fact and cannot be denied (Brewis, cited in Hefer & Little 2005). However, some researchers (e.g. Ensley et al., cited in Jakarini 2012), as will be explained in the following pages, consider certain types of weak boundary layers as important contributors to good adhesion.

The presence of pollutants with low molecular weight (and therefore low cohesive strength) such as some organics and water on the substrate surface commonly results in developing weak boundary layers. The presence of dust on substrate can prevent effective wetting taking place, as a result of which the intimate contact with the adhesive is not made. According to Tarrar and Wagh's report (1991), dust on aggregate tends to trap air when mixed with bitumen and this issue weakens the bitumen-aggregate bond.

Podoll and Becker (cited in Jakarini 2012) used Surface Analysis by Laser Ionization (SALI) and noticed that some of the failures in bitumen-aggregate pairs had taken place inside the aggregate. It means that the failure surface had formed partly inside the aggregate bulk but close to the bitumen-aggregate interface. This may have happened due to the intrinsic weakness or local deficiencies of the particular aggregate used. It may also be developed by the dissolution of the aggregate surface complexes (Labib, cited in Jakarini 2012) or the mineral itself in the presence of water. However, the occurrence of dissolution depends on the pH of the water which has been introduced to the adhesion system. For instance, the dissolution of carbonates (at the surface layers of basic aggregate such as limestone) occurs at pH levels lower than 6, whereas in the case of silica minerals (which exist in acidic aggregates such as granite), this takes place at pH levels greater than about 8 (Jamieson et al. cited in Jakarini 2012).

Considering the surface energy characteristics, chemical and physio-mechanical properties of both bitumen and aggregate in an adhesion system makes it possible to define the compatibility of the binder and aggregate as well as the quality, strength and water sensitivity of the resulting adhesion bond. However, there are some physical properties (e.g. the porosity of aggregate), which should be considered because they may lead to the formation of weak boundary layers. According to Jeon and Curtis (cited in Jakarini 2012) aggregate surfaces with high porosity can act as molecule sieves, separating big and small molecules of bitumen fractions from each

other. In this regard, phenomenological observations indicate that when bitumen is absorbed by aggregate at the interface, the part of bitumen which is not able to permeate the aggregate and remains outside the interface becomes hard and brittle (Curtis et al., cited in Jakarini 2012). From the theory of weak boundary layers, it is postulated that a brittle interphase will be formed due to the highly associated polar molecules left behind. This is similar to the short-term aging phenomenon during the manufacturing and construction processes of Hot Mix Asphalt through which the volatiles of bitumen evaporate. Curtis et al. (cited in Jakarini 2012) reported that no evidence of selective absorption could be found among various research studies on this phenomenon. Therefore, it can be theorised that brittle and weak boundary layers may be formed when the aggregate acts as a catalyst for oxidative ageing. The catalytic effect of aggregate on the oxidation of bitumen was proved by Harnsberger (cited in Jakarini 2012). More description regarding his approach is seen as unnecessary due to its complicated nature.

Ensley et al. (cited in Jakarini 2012) postulated the formation of a structured interphase of bitumen molecules on aggregate surface in a bitumen-aggregate adhesion system. The energy released during bitumen-aggregate interaction was measured by the use of a sensitive micro-calorimeter. The results of this investigation showed that the energy release due to the development of bitumen-aggregate adhesion bond continued for an extensive while after (extended longer than expected) the initial contact took place between bitumen and aggregate. They proposed that the initial peak of the released energy might be related to the adhesion bond of the initial layer of molecules which were adsorbed onto the aggregate surface. According to Ensley et al., when the bitumen molecules of the initial layer attach to the aggregate sites, they become further polarised and their opposite ends provide bonding sites for other bitumen molecules. The extended energy release is the consequence of the formation of an interphase region around the aggregates due to the propagation of the polarisation mechanism. Ensley and his colleagues postulated that these layers should decrease the water susceptibility and increase the strength of the resulting bond. They also argued that the proposed structured interphases increase stability near the bitumen-aggregate interface (Jakarini, 2012).

Ross et al. (cited in Jakarini 2012) postulated that high mixing temperatures initiate extensive acid-base interactions, which result in changing and most likely aggregating the bitumen groups into larger and probably cross-linked assemblies at the boundary region. On the one hand, if too much cross-linking takes place, the brittleness of this region may form a weak boundary layer. On the other hand, the aggregated region can provide a sealing layer against

water diffusion to the bitumen-aggregate interface, which may inhibit the occurrence of adhesive failure. In this research, bitumen-coated aggregate was cooled and then cut in order to expose the bitumen-aggregate interaction region. For the purpose of identifying the concentrations of certain labelled or 'tagged' compounds in bitumen within the adhesion boundary regions, an auto-radiographic (AR) procedure was used. Ideally, if according to some of the approaches in the Theory of Weak Boundary Layers, migration, separation or filtration of the labelled compounds had taken place, a gradient would have been expected to be visible from radiographs. However, the auto-radiography images did not confirm the existence of any interphase region providing no evidence in this respect (Ross et al., cited in Jakarini 2012).

Curtis (cited in Jakarini 2012) supported the above conclusions stating that sampling of the boundary region within every (24-100)μm showed no variation in the chemical composition in such a way that it could be detectable in the infrared analysis. It was also stated that the extended energy release found in earlier work by Ensley could not be reproduced during the SHRP Research (Jakarini, 2012).

However, later, Nuclear Magnetic Resonance (NMR) spectroscopy did show the changes of rigidity within the boundary region for specific bitumen-aggregate systems (Curtis et al., cited in Jakarini 2012).

2.10.3. WATER SUSCEPTIBILITY, MOISTURE DAMAGE and STRIPPING

The adhesion between bitumen (bitumen-filler mastic) and aggregates asphalt mixtures which has never been in contact with water or moisture in their life time usually does not develop any difficulties (Gronniger, Wistuba & Renken, 2010). However, as mentioned in the previous pages, bitumen-aggregate adhesion is negatively affected by the presence of water in the sense that due to the presence of water, stripping is observed. Stripping is the deterioration of the bitumen-aggregate bond in the presence of water. Stripping contributes to pavement distresses such as ravelling, potholes and rutting due to loss of adhesion. It means that the deterioration of chemical bonding between bitumen and aggregate (poor adhesion) results in loss of fine aggregate (ravelling). The loss of adhesion between surface aggregate and bitumen results in developing potholes. Also, tensile strength reduction due to the loss of adhesion between bitumen and aggregate causes the rutting phenomenon to take place. Therefore, it seems that reducing the stripping phenomenon significantly extends pavement life and the quality of roadway network (Ivann Harnish, 2010).

It is therefore important to study how to predict or quantify the moisture susceptibility of asphalt mixtures and/or recommend any water-damage preventive solutions such as material treatments or modifications (Ahmad, 2011).

The process of stripping is generally explained by four basic theories (Güßfeld; Neumann; Fluss, cited in Gronniger, Wistuba & Renken, 2010), summarised as follows:

- **Displacement Theory:** In this mechanism, in the presence of water, bitumen is detached from the aggregate surface and replaced by water as a result of differential interfacial tensions.
- **Pore pressure theory:** In this process, the pore pressure in the cavities/voids of compacted asphalt mixture arises due to the traffic stresses and/or thermally-induced stresses.
- **Infiltration theory:** When water particles infiltrate the binder film, which has coated the aggregate, they solve the binder-aggregate interaction by separating the bitumen from the aggregate.
- **Rupture of thin film theory:** In this mechanism, traffic stresses and/or thermally-induced stresses or the stresses from high capillary pressures within the compacted asphalt mixture cause the binder film to be ruptured at aggregates' sharp edges. This issue takes place especially in the case of thin binder films or when the film thickness has decreased as a result of binder contraction at low temperatures.

In Section 2.8.2 the moisture susceptibility phenomenon was looked at very briefly and justified from the view point of each of the four theories of adhesion. However, more explanations regarding the Displacement Theory of Stripping have been provided in the following sub-section from the view point of the thermodynamics theory of adhesion.

2.10.4. DISPLACEMENT THEORY from the VIEW POINT of SURFACE ENERGY

Aggregates are materials with high surface energy which have unbalanced surface charges (Bhasin, cited in Ahmad 2011). As mentioned earlier, aggregate and water are both polar materials while bitumen is a non-polar substance. Coating the aggregate surface with a liquid of opposite polarity can satisfy its surface energy demands and result in strong adhesion. If two different liquids (e.g. bitumen and water) are available to be introduced to a certain type of aggregate, the one which better satisfies the surface energy requirement of the aggregate will

make stronger adhesion with the aggregate surface. Water has a greater tendency than bitumen to wet aggregate surface and the stripping of bitumen from the aggregate surface in the presence of water is due to this fact. Basically, water is a polar material in nature and this issue results in better satisfying the surface energy demands of aggregates compared to bitumen, which is a naturally non-polar substance. Therefore, exposing a bitumen-aggregate adhesion system to water or moisture can result in the replacement of the bitumen from the aggregate surface by water (Read and Whiteoak, 2003). Bitumen, being non-polar in nature hardly makes any chemical bond with aggregates, except for having a weak acidic character due to the presence of carboxylic acids. As mentioned before, carboxylic acids in bitumen make it possible to bond well with basic aggregates such as limestone (Ahmad, 2011).

When quantifying the level of moisture damage or susceptibility, it should be mentioned that it depends on the interactions between the surface energy components of aggregate, bitumen and water. Previously, in Section 2.9, the bitumen-aggregate adhesive bond strength and the cohesive bond strength of bitumen without considering the presence of water (dry bond strength) have been calculated using the surface energy concepts and fundamental calculations (Ahmad, 2011).

However, in this section, the bitumen-aggregate bond strength in the presence of water will be calculated.

Theoretically, when there are three substances introduced to each other at the same interface (e.g. water introduced to bitumen-aggregate adhesion interface), the general formula to calculate the associated adhesive bond strength at the interface can be as follows (Ahmad, 2011):

$$W_{BWA}^{A} = \gamma_{BW} + \gamma_{AW} - \gamma_{BA} \qquad \text{Equation 2.35}$$

Equation 2.35 results in Equation 2.36, which can be used to calculate the binder-aggregate adhesive bond strength in the presence of water (bitumen-aggregate wet bond strength), as follows (Cheng et al., cited in Ahmad 2011):

$$W_{BWA}^{A} = \gamma_{BW} + \gamma_{AW} - \gamma_{BA}$$

$$= 2\gamma_W^{LW} + 2\left((\gamma_B^{LW})(\gamma_A^{LW})\right)^{0.5} - 2\left((\gamma_B^{LW})(\gamma_W^{LW})\right)^{0.5} - 2\left((\gamma_A^{LW})(\gamma_W^{LW})\right)^{0.5}$$

$$+4\left((\gamma_W^{+})(\gamma_W^{-})\right)^{0.5} - 2(\gamma_W^{+})^{0.5}((\gamma_B^{-})^{0.5} + (\gamma_A^{-})^{0.5}) - 2(\gamma_W^{-})^{0.5}((\gamma_B^{+})^{0.5} + (\gamma_A^{+})^{0.5})$$

$$+2\left((\gamma_B^{+})(\gamma_A^{-})\right)^{0.5} + 2\left((\gamma_B^{-})(\gamma_A^{+})\right)^{0.5} \qquad \text{Equation 2.36}$$

Comparing the values of W_{BWA}^{A} (binder-aggregate bond strength in the presence of water) with W_{BA}^{A} (binder-aggregate dry bond strength), for a certain type of bitumen and aggregate, as a quantifying measure, illustrates the moisture susceptibility of the 'possible' bond between the materials (Ahmad, 2011).

However, it should be mentioned that the results of surface energy calculations, as well as the bond strength calculations, are idealistic. Therefore, they may not be totally confirmed by the results of the associated laboratory or field tests on the samples which have been manufactured using the same materials as used in calculations. This issue is due to the presence of factors which inevitably influence the production process of asphalt (whether in the laboratory or in the asphalt plant) and affect the bitumen-aggregate adhesive bond quality and strength.

The surface energy calculations present a quantitative parameter for the potential of compatibility or moisture sensitivity of a certain binder-aggregate combination, independent from any manufacturing-related factor, which may affect the adhesion or moisture sensitivity of the mixture during the asphalt production phase.

2.10.5. ANTI-STRIPPING AGENTS/ADDITIVES

An anti-stripping additive is a material in the form of a liquid or solid which is added to bitumen or asphalt mixture during the mixture production to increase the occurrence and strength of bitumen-aggregate adhesion (Ivan Harnish, 2010).

Adding a basic amine anti-stripping agent to bitumen or mixture during the mixture production phase has generally been used as an approach to improve the adhesion between bitumen and 'siliceous' aggregates such as granite (Hefer & Little, 2005). This is because siliceous aggregates have acidic (hydrophilic) tendencies, which prevents them having strong adhesive bond with bitumen, which also usually has acidic tendency due to the presence of carboxylic

acids in its composition. Logaraj (cited in Hefer & Little 2005) states that the two main characteristics of anti-stripping additives are as follows:

- They have a polar amine end group which will chemically bond with siliceous aggregate surfaces.
- They have a hydrocarbon chain with similar properties to that of bitumen so they can interact, be dissolved and become a part of bitumen.

A primary amine (RNH2) and tertiary amine (NR3) have been shown schematically in Figure 2.25. The number of amine groups and the length of the hydrocarbon chains can greatly influence the adhesion of bitumen. An optimum performance is typically achieved with 14 to 18 carbon chain amines with one or two amine groups (Tarrar & Wagh, cited in Hajj & Cortez, 2011). The functional group head is hydrophilic (water-loving) and polar which bonds to the aggregate surface, while the hydrocarbon tail is lipophilic (oil-loving) and non-polar. It stands outward from the aggregate surface, towards the bitumen making a chemical molecular bond with bitumen molecules. By this means, it acts as a mediator to bond bitumen to the aggregate surface.

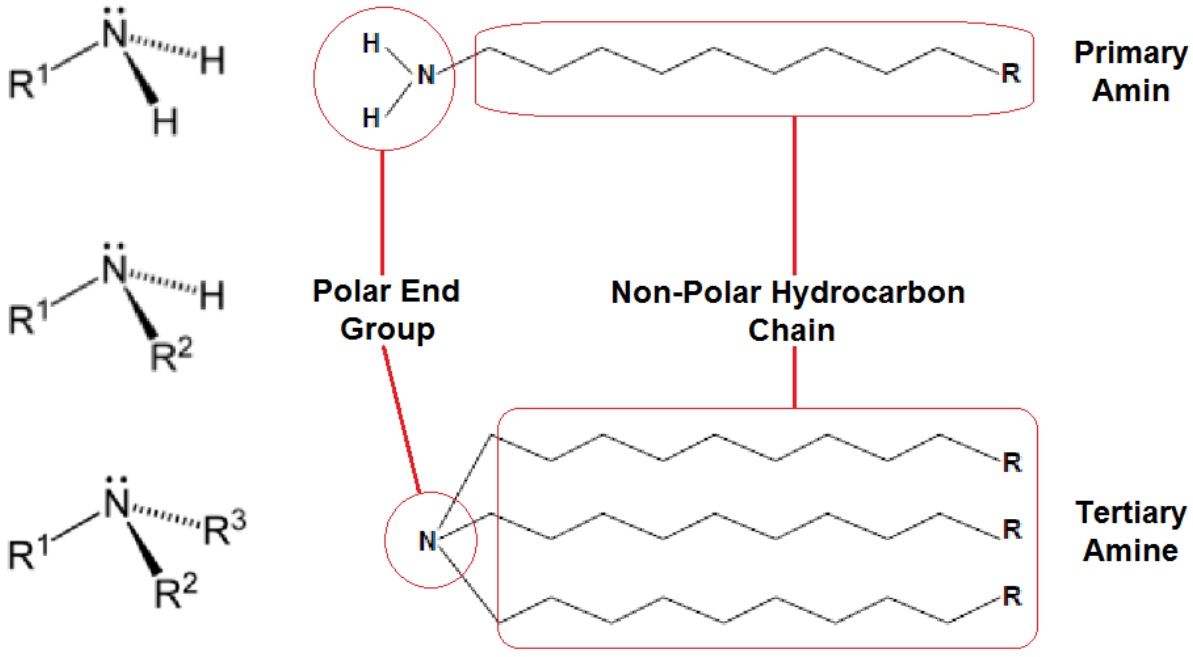


Figure 2.25 : The schematic illustration of various typical amine functional groups used in anti-stripping agents and adhesion promoting additives (Ivann Harnish, 2010)

Amines of anti-strip are surfactants at asphalt-aggregate interface (Ivann Harnish, 2010). One of the classic theories regarding how amine anti-strips reduce stripping, is Bridge theory, which states that lone pair of N electrons of amine functional group chemically bonds (covalent, hydrogen) with positively charged and electron deficient sites (Ca, Fe, Na, K cations) along the surface of aggregate, long hydrocarbon tail miscible in & attached to asphalt (Liu et al., 2011).

Another theory, considers the amine anti-strip a 'wetting agent', which improves bitumen-aggregate adhesion by reducing the surface tension of bitumen (Liu et al., 2011).

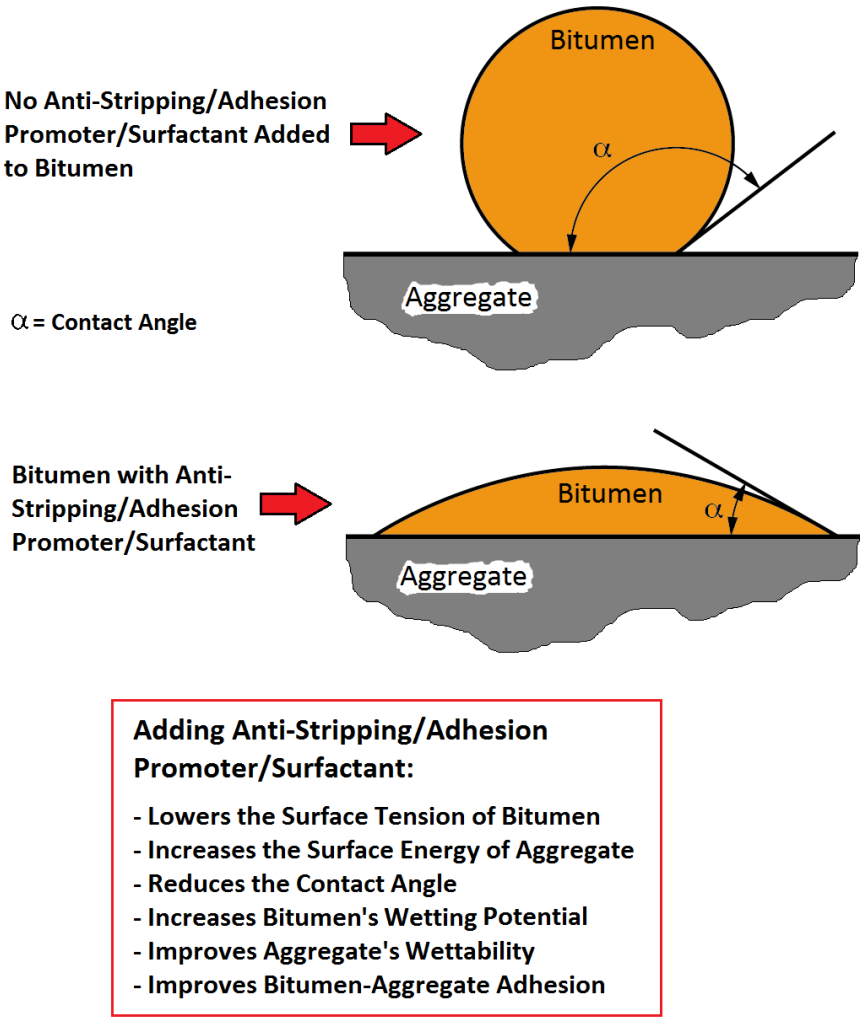


Figure 2.26 : Anti-stripping additive works as a wetting agent

2.11.SPECIAL FEATURES of WAX and CHEMICAL WMA MIXTURES

2.11.1. MIXING and COMPACTION TEMPERATURES

According to TRL PPR666, when using paving grade binder, the maximum [mixing] temperature of a WMA, measured according to BS EN 12697-13, shall target:

- ≤140°C (grades 20/30 to 70/100),
- ≤130°C (grades 100/150 and 160/220), or
- ≤120°C (grades 250/330 and 330/430).

However, TRL PPR666 states that when using modified bitumen or hard grade bitumen, additives or premix bitumen, different temperatures may be applicable, which shall be documented and declared.

Apart from using different additives in various WMA production methods which in some cases are significantly different from the production method of HMA, the most noticeable feature of WMA mixtures is their lower production temperatures compared to HMA. In fact, the lower production (mixing and compaction) temperature of WMA compared to HMA, results in the majority of WMA advantages to HMA (i.e. less fuel consumption, less greenhouse gas emissions, reduced paving costs, longer haul distance, etc.) which form the concept and logic behind the invention and production of WMA.

The variety of WMA products is due to the use of a wide range of additives and their production methods. Although all WMA products, according to their general production method, can be categorised into 3 general groups, the production temperature (mixing and compaction temperatures) of each WMA product, even in a group, can be totally unique. This issue refers to the differences between the performance, operation and specifications of various additives used in different WMA production technologies. Therefore, it is not possible and logical to expect a certain production (mixing and compaction) temperature for all WMA products and it is necessary to determine the right temperature range of mixing and compaction for each WMA product individually.

In this respect, usually, the additive suppliers based on the dosage of the additive, promise certain amounts of reduction in mixing and compaction temperatures from the recommended one for the base binder (which could have been used in the reference HMA). It should be

mentioned that the mixing and compaction temperature for an HMA, in general, depends on its bitumen grading. On this matter, based on the penetration grade of bitumen, BSEN 12697-35 recommends certain mixing and compaction temperatures.

Thus, one of the methods to determine the mixing and compaction temperatures of a certain WMA product is to apply the supplier's temperature reduction promises to BSEN 12697-35 recommendations for the mixing and compaction temperatures of the used bitumen grade.

Moreover, attention should be paid to the fact that WMA technologies reduce the mixing and compaction temperature via providing adequate viscosity and/or adhesion for the production of asphalt at lower temperatures through decreasing the binder viscosity, increasing the bitumen-aggregate adhesion, increasing workability, lubricity, compactability, etc.

Therefore, for those WMA products (production methods) which are produced by the use of binder modifier additives (i.e. wax such as Sasobit), a more reliable method to find the proper mixing and compaction temperature is to produce and draw a modified bitumen data line on Shell Bitumen Test Data Chart as shown in Figure 2.28.

Basically, during the mixing and compaction of an asphalt mixture, there are optimum bitumen viscosities. This has been shown on the Shell BTDC presented in Figure 2.27. If the viscosity of the bitumen is too high during mixing, the aggregates will not be properly coated and if the viscosity is too low, the bitumen will coat the aggregate easily but may drain off the aggregate during storage or transportation. For satisfactory coating, the viscosity should be approximately 0.2 Pa.s.

In addition, during compaction, if the viscosity is too low, the mixture will be excessively mobile, resulting in pushing of the material in front of the roller. High viscosities will significantly reduce the workability of the mixture and little additional compaction will be achieved. It is recognised that the optimal bitumen viscosity for compaction is between 2 and 20 Pa.s.

The Bitumen Test Data chart (BTDC) is a system which permits penetration, softening point, Fraass breaking point and viscosity data to be described as a function of temperature on one chart. It was developed in the late 1960s by Heukelom. The chart consists of one horizontal scale for the temperature and two vertical scales for the penetration and viscosity. The temperature scale is linear, the penetration scale is logarithmic and the viscosity scale has been

devised so that penetration grade bitumen with 'normal' temperature susceptibility or penetration indices gives a straight-line relationship.

The BTDC illustrates how the viscosity of a bitumen depends on temperature but it does not take account of the loading time. However, as the loading time for penetration, softening point and the Fraass breaking point tests are similar, these test data can be plotted with kinematic viscosity test data on the BTDC. Since the test results on this chart form a straight-line relationship, it is possible to predict the temperature-viscosity characteristics of a penetration grade bitumen over a wide range of temperatures using only the penetration and softening point.

However, in the case of the binders modified by wax or any other rheological modifier, since the modified binder's viscosity changes nonlinearly with temperature on the BTDC (Figure 2.28), in order to produce the modified binder's data line on a standard BTDC, some extra data points (i.e. the values of binder's viscosity from Brookfield viscometry over an adequately wide range of temperature) are necessary (Figure 2.28).

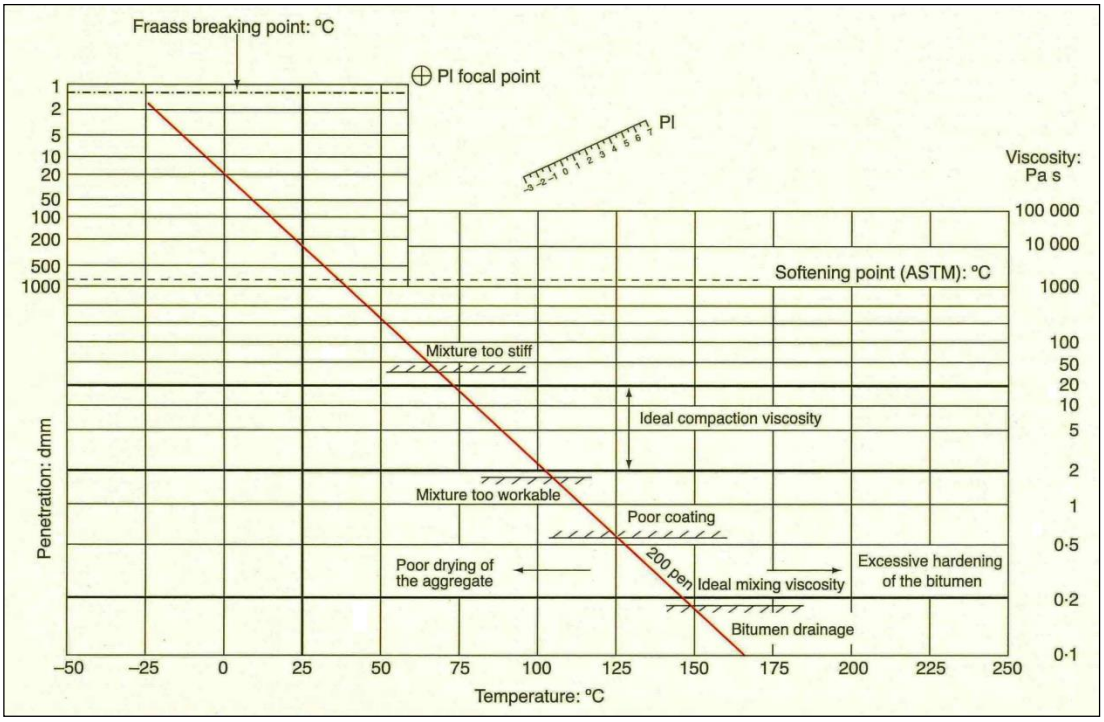


Figure 2.27 : Bitumen Test Data Chart showing 'ideal' bitumen viscosities for optimal mixing and compaction of an asphalt concrete (Whiteoak & Read, 2003)

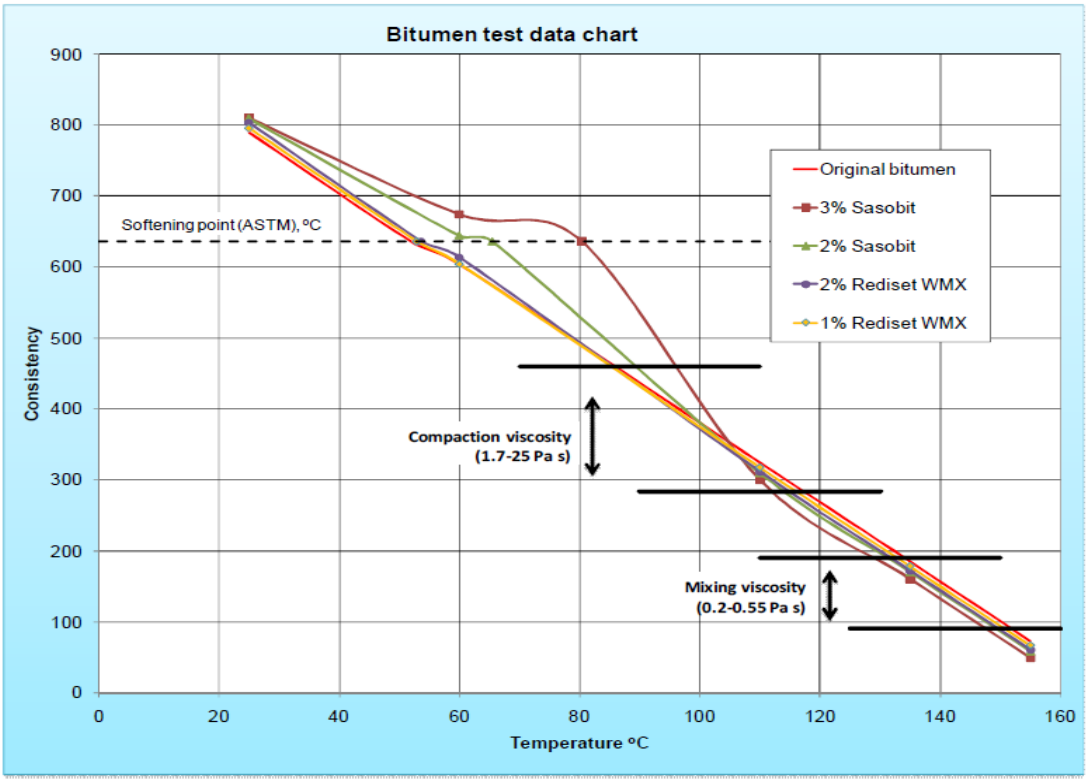


Figure 2.28 : BTDC for some modified bitumen samples (Zaumanis, 2010)

Nevertheless, in the case WMA products (production methods) which are produced by the use of any additive other than binder viscosity reducer (i.e. chemicals such as Rediset LQ, foaming agents such as Advera), other methods are used. These methods are basically comparative-equivalent. According to these methods, the appropriate mixing temperature of a WMA product can be determined as the temperature at which the WMA mixture has the same workability or lubricity as its reference HMA mixture has at its standard mixing temperature. In the same way, the appropriate compaction temperature of a WMA product can be defined as the temperature at which the WMA mixture will have the same compactability as its reference HMA has at its standard compaction temperature. In other words, at the equivalent compaction temperature, the compaction of WMA mixture will result in the same volumetric properties (AV content and bulk density) as its reference HMA which has been compacted at the higher recommended standard temperature.

For the example presented in Figure 2.29, compaction of the reference HMA mixture at its standard compaction temperature of 140°C has resulted in 6.5% AV content. However, this amount of air voids can be developed in a corresponding WMA mixture (which has been produced using the same materials and mix design as the HMA plus WMA additive) at the

lower equivalent compaction temperature of 125°C which can be considered as the appropriate compaction temperature for the particular WMA studied in the example.

The blue data line indicates the AV content versus compaction temperature of the WMA mixture. In order to produce this data base, the WMA samples must have the same mixing temperature but be compacted at different compaction temperatures in such a way that a wide range of compaction temperatures can be covered.

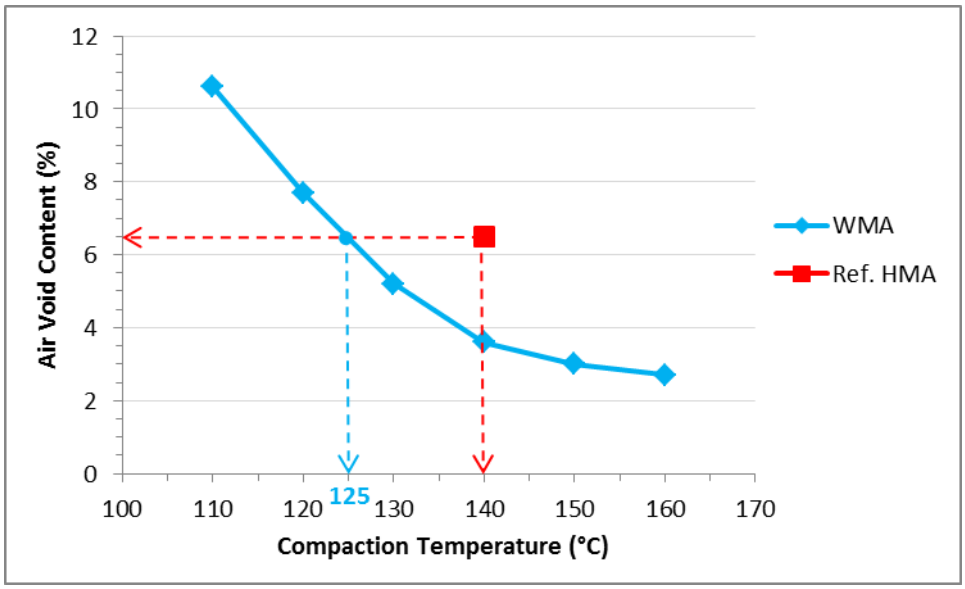


Figure 2.29 : Determining the compaction temperature for WMA according to the air void content of the associated reference HMA

2.11.2. MIX DESIGN

Basically, as Warm Mix Asphalt would be a replacement for conventional Hot Mix Asphalt, it seems that generally there should be no restrictions on the application fields of WMA mixtures. Having a glance at the short history of WMA application in the field, also looking at the multiple research programs on WMA in the US or in Europe, it can be realised that WMA mixtures (regardless of their production technology) have been tried and expected to be used in producing the various types of asphalt mixtures (e.g. Asphalt Concrete, Porous Asphalt, Reclaimed Asphalt, etc.), also to be placed as the different surfacing layers of pavement (i.e. Surface Course and Binder Course) in a variety of thicknesses and under different traffic loads and frequencies. Moreover, they have been tried to be manufactured by the use of different aggregate types and gradations and various bitumen grades. The mentioned research programs were performed by TRB, NCAT, NAPA, EAPA, TRL, etc.

Regarding WMA mixtures, one of the most important issues has always been the lack of a formal mixture design procedure (Bonaquist, 2011). However, due to the nature of WMA which covers a great variety of low temperature production methods of asphalt, basically it has been very difficult to generalise a single mixture design for all its different technologies.

Nonetheless, if WMA is to replace HMA in the future, a particular laboratory mixture design procedure or considerations for WMA should be established. These considerations have to be taken into account to bring equal or better performance than the HMA. For the majority of WMA projects performed in the United States of America to date, the same formula and mixture design as HMA has been used to produce WMA. So far this issue has been logical and reasonable probably based on the definition of WMA.

Several experiments on WMA have been performed and are being conducted in the US and there are many reports available from US Federal HighWay Administration (FHWA) and Departments of Transportation in different states. For instance, Project 9-43 of National Cooperative Highway Research Program (NCHRP), as one of the most comprehensive, recent and applicable research programs on WMA, was sponsored by American Association of State Highway and Transportation Officials (AASHTO) in cooperation with the FHWA.

The main purpose and objective of NCHRP Project 9-43, "Mix Design Practices for Warm Mix Asphalt", was to develop mixture design methods and procedures, which could be applied for the wide range of WMA processes (about 20 different processes at the completion time of the project) for use by engineers and technicians in the public and private sectors. NCHRP Report 691, "Mix Design Practices for Warm Mix Asphalt", fully documents the research leading to the key finding that a stand-alone WMA mix design method distinct from that for HMA is not warranted. Thus, the final product of the research was a proposed appendix to AASHTO R 35, "Standard Practice for Superpave Volumetric Design for Hot-Mix Asphalt (HMA)", titled NCHRP Report 714 "Special Mixture Design Considerations and Methods for Warm Mix Asphalt (WMA)". NCHRP Report 714 provides that proposed appendix in the form of a supplement to NCHRP Report 673: A Manual for Design of Hot Mix Asphalt, produced in NCHRP Project 9-33. Moreover, NCHRP Report 714 became a draft standard practice named Standard Practice for Measuring Properties of Warm Mix Asphalt (WMA) which has been applied for the performance analysis process of the Mechanistic-Empirical Pavement Design Guide Software.

As a framework for WMA mixture design, according to NCHRP, the traditional mix design procedures for HMA can be considered. However, due to the differences between WMA and HMA on the matters of production temperature and additive materials, it seems that some modifications to current HMA mix design procedures is needed to cover the wide range of current WMA production technologies and the ones which may become available in the future.

The European approach for designing HMA and WMA is to somehow different from the US practice. As a matter of fact, for the most commonly used systems, Marshall Method with some regional differences is used in Europe and SUPERPAVE (SUperior PERforming asphalt PAVEment) mix design method is mostly used in the US. The European mix design process tends to be based on asphalt performance tests more than the US mix design process. European standards are being developed to standardise test methods and provide broad definitions of mixture types. The standardisation process is to eliminate the trade barriers between the European countries and developing a common technical language for nations of the European Union. However, individual countries can develop their own national practical documents to specify exactly what they want within the framework of the European standards (D'Angelo et al., 2008).

In the UK, on the matter of WMA mixtures, studies, investigations and attempts for standardisation have begun more recently compared to the European pioneer countries such as Germany. In this respect, it was realised that low temperature asphalts, classified as Warm Mix Asphalt, Half-Warm Mix Asphalt and Cold Mix Asphalt were increasingly being used, but most of the current specifications had been written around Hot Mix Asphalt. However, it was believed that there was no reason why the specifications for HMA could not be modified to become applicable to the various categories of low temperature asphalt. According to the Transport Research Laboratory (TRL), very little modification was required for WMA, with increasing modification being required as the mix temperature departs from that for HMA. Therefore, under a contract with Lafarge Tarmac, TRL published a project report (PPR666) in June 2013 containing the specifications for low temperature asphalt mixtures. In PPR666, the types of specification used for HMA are discussed and a series of documents drafted to cover low temperature asphalt mixtures are attached as appendices. The appendices are modelled on the current European standards, supporting national guidance documents and the Specification for Highway Works clauses.

Table 2.5 : Areas of HMA mixture design and analysis which need modification for WMA according to NCHRP Project 9-43 (NCHRP Report 691)

Step	Item	Special Warm Mix Considerations
Materials Selection	Binder Selection	• Potentially less aging during mixing and construction due to lower production temperatures. • Effect of any warm mix additives and warm mix processing on binder properties.
	Aggregate Properties	• None
	Recycled Asphalt Pavement	• Effect of production temperature on the degree of commingling of recycled and new binders. • Effect of warm mix additives and warm mix processing on the degree of commingling of recycled and new binders.
	Additives	• Warm-mix additive selection. • Effect of lower production temperatures and warm mix additives on anti-strip additives.
Design Aggregate Structure	Nominal Maximum Aggregate Size	• None
	Trial Gradations	• None
	Batching	• WMA process specific
	Mixing	• WMA process specific • Method to determine appropriate mixing temperatures for warm mix processes. • Method to assess workability of WMA.
	Conditioning	• Verify that short-term conditioning per AASHTO R 30 applies to WMA processes.
	Compaction	• Method to determine appropriate compaction temperatures for warm mix processes. • Verification of compaction levels.
	Volumetric Analysis and Criteria	• None
Design Binder Content Selection	Specimen Preparation	• See considerations above for laboratory batching, mixing, conditioning, and compaction.
	Volumetric Analysis and Criteria	• None
Evaluate Moisture Sensitivity	Specimen Preparation	• See considerations above for laboratory batching, mixing, conditioning, and compaction.
	Testing and Analysis	• None
Performance Analysis	Specimen Preparation	• See considerations above for laboratory batching, mixing, conditioning, and compaction.
	Testing and Analysis	• None

2.11.2.2. Aggregate Structure/Gradation

Based on the finding of NCHRP Project 9-43, as can be seen in Table 2.5, aggregate requirements for WMA will not be different from those of HMA mixtures. On this matter, TRL Report PPR666 has similarly recommended the same issue.

2.11.2.3. Bitumen Grade Selection

The production temperature of WMA is at least 20°C lower than HMA. This lower temperature may develop less ageing in WMA bitumen compared to that of a similar HMA bitumen (which has been made using the same bitumen and aggregate) during plant mixing and construction. Therefore, the WMA bitumen should be softer (have less stiffness) than that of the reference HMA which should result in a higher rutting potential. Therefore, a stiffer high-temperature binder grade may be needed for WMA in order to have a satisfactory rutting performance (have similar rut depth as the reference HMA). However, the recovered binder test data from projects sampled and tested under NCHRP Project 9-43 indicated that only extremely low production temperatures had resulted in a significantly lower stiffness of recovered WMA binder compared to HMA. It means that this issue may happen for HWMA (Half Warm Mix Asphalt) and CMA (Cold Mix Asphalt) mixtures due to their significantly low production temperatures and is not expected to be referred to WMA. This means that, high-temperature grade bumping may be necessary only for WMA processes with extremely low production temperatures (HWMA and CMA) to meet the flow number rutting resistance requirements included in the draft appendix to AASHTO R35. Additionally, WMA production temperatures resulted in a minor improvement in the low-temperature grade of the binder. This effect, however, may be offset by the addition of warm mix additives and the effect that these additives and water have on binder ageing.

The draft appendix to AASHTO R35, therefore, recommends that the same grade of binder be used in both WMA and HMA mixtures.

Based on the same rationale, TRL PPR666 states that the ageing of binder during the mixing and placement of HMA, particularly when using batch mixers, in terms of the binder penetration is generally a reduction of the order of 33 %, or one binder grade, which does not occur to the same extent for warm mix asphalt. Consideration should be given to reducing the required binder penetration where equivalence is intended with HMA.

2.11.2.4. Bitumen Content

According to the WMA manufacturers, no instructions have been recommended for changing the bitumen content for WMA production. In fact, due to WMA's lower mixing temperature (compared to HMA), less binder absorption takes place by aggregates which may indicate a necessity to reduce the binder content.

However, overall, until now, most of the researchers have recommended to use the same optimum bitumen content determined for HMA. One reason for such advice can be the concerns of leading the mixture to problems regarding durability, permeability and water susceptibility, if the bitumen content is reduced.

On this matter, TRL Report PPR666 recommends the same binder content as HMA to be considered.

2.11.2.5. Additive dosage

Additive dosage in the mixture is usually determined by the additive supplier as a percentage of either binder or mixture weight (Table 2.1). As mentioned in previous chapters, there are several technologies, each of which uses a particular additive (in some cases within a certain method) to produce WMA.

However, some research may have been performed in order to adjust or determine the proper dosage of some of WMA additives. For instance, according to research conducted by Kilas, Vatikus & Paliokaite (2010), the optimal dosage for Sasobit and Rediset-WMX additives was advised to be 2.0% by the mass of the binder. Using the optimal amount of the mentioned additives allows lowering the production temperatures of the associated WMA mixtures by about 30°C from 150°C to 120°C without a considerable reduction in compaction results.

2.11.3. BINDER PROPERTIES and MIXTURE PERFORMANCE

Bitumen is known as a complex material with a complicated behaviour and response to stress. Bitumen has typically viscoelastic behaviour at normal temperatures. However, its response to loading and stress widely depends and varies over a range of temperatures and the loading frequencies. At higher temperatures and lower frequencies it behaves as a viscous material while at lower temperatures and higher loading frequencies it will show mostly an elastic (brittle) behaviour responding to the loads.

In the case of Wax-WMA and Chemical-Additive-WMA mixtures, bitumen is modified via adding various additives for the purpose of achieving mixtures with similar properties and performance to HMA but at lower production temperatures.

In WMA production technologies, bitumen modification takes place via modifying bitumen's rheological properties (i.e. reducing bitumen viscosity) and/or modifying its Surface Energy characteristics in such a way that by providing either adequate workability, lubricity, compactability, adhesion, coating or wetting, mixing and compacting at significantly lower temperatures than HMA can result in similar mixtures to HMA in terms of performance, behaviour and properties.

For the wide range of WMA processes available, viscosity-based mixing and compaction temperatures cannot be used to control coating, workability, and compactability. The draft appendix to AASHTO R 35 uses direct measures of coating and compactability on laboratory-prepared mixtures. The degree of coating obtained in the laboratory depends on the type of mixer that is used. Several workability devices were evaluated under NCHRP Project 9-43. These devices, which measure the torque or force required to move an auger or blade through the mixture, were able to measure differences between HMA and WMA mixtures, but only when temperatures dropped to the compaction range of WMA. At these temperatures, differences in air voids also were evident in gyratory compacted specimens. The draft appendix to AASHTO R35 uses the change in the number of gyrations to 92% relative density when the compaction temperature is decreased 30°C to characterise the compaction temperature sensitivity of the WMA processes. Increases that exceed 25% indicate that the WMA is more temperature sensitive than HMA. This measure of compactability was sensitive to the compaction temperature, the WMA process and the presence of RAP in the mixture.

It can be stated that bitumen's viscoelastic characteristics will change in production and in-service while being used in WMA production due to the changes in the rheological properties of bitumen due to the action and influence of the WMA rheological modifier additives.

The performance evaluation tests of asphalt, according to NCHRP and BSEN include measuring mixture's stiffness modulus, rutting potential, and resistance to fatigue cracking and thermal cracking.

It is clear that one of the key factors that influence the final stiffness of a mixture is the stiffness of bitumen. This is a significant issue regarding differences between HMA and WMA, because

the stiffness of bitumen in WMA is affected by the differences in temperature of production, mixing process and, possibly, by changes in mixture design.

There is a general concern for WMA rutting performance that is connected with the decreased mixing temperature which may lead to incomplete drying of aggregates and insufficient coating with bitumen. Another aspect that may influence decreased resistance to permanent deformation is the decreased oxidative hardening of bitumen due to lower production and compaction temperature. This may lead to increased rutting potential for WMA and may suggest using harder bitumen in the first place. To evaluate the impact of these potential problem areas a lot of research has been performed to determine WMA resistance to permanent deformation including laboratory evaluation and field tests.

Moisture susceptibility may be an important issue for WMA technologies. If the moisture contained in the aggregate does not completely evaporate during mixing due to low mix temperatures, water may be retained in the aggregate which could in turn lead to increased susceptibility to moisture damage. This is even more critical for WMA technologies that involve foaming as a binder viscosity lowering action, because of residual moisture left behind by the microscopic foaming process of particular WMA technology.

2.11.3.1. Wax in Bitumen and Waxy Additives of Bitumen

Waxes are a class of chemical compounds that are plastic (malleable) near ambient temperatures. Characteristically, they melt above 45°C to give a low viscosity (very fluid) liquid. Waxes are insoluble in water but soluble in organic, nonpolar solvents. All waxes are organic compounds, both synthetic and naturally occurring. Waxes can be divided into Petroleum Waxes and Wax Modifiers. Petroleum waxes naturally exist in bitumen and include (Polacco et al., 2012):

- Paraffin waxes: n-Alkanes with linear Carbon backbone chains and low molecular weight (Carbon chain length < C45)
- Microcrystalline waxes: Aliphatic Hydrocarbon compounds with branched chains, chemically referable to Iso-Alkanes and Cycloalkanes characterised by high molecular weight and carbon backbone chain length > C45
- Aromatics and other molecules with polar functional groups which may crystallise on cooling

Wax modifiers are typically identified as (Polacco et al., 2012):

- Synthetic waxes derived from the Fischer–Tropsch process (e.g. Sasobit)
- Montan waxes (e.g. Romanta-N) and modified Montan waxes
- Functionalized waxes

Petroleum waxes mainly consist of n-alkanes normally crystallise in large, macro-crystalline plates, while waxes of high molecular weight and with long side chains crystallise in small microcrystalline needles (Srivastava *et al*., cited in Edwards & Isacsson 2012)

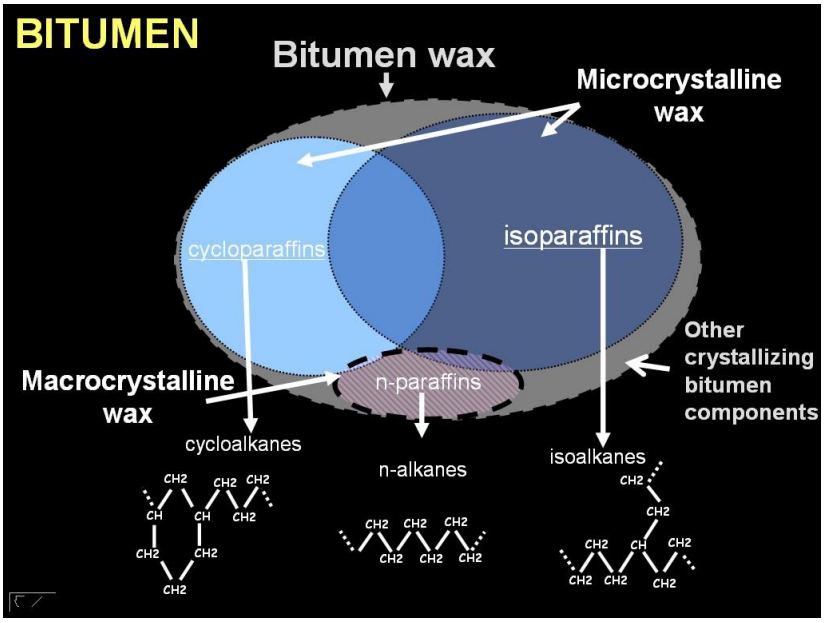


Figure 2.30 : Schematics of various types of wax exist in bitumen (Edwards & Isacsson, 2012)

Regarding the effects of petroleum waxes on the thermal and rheological behaviour of bitumen, according to the widely carried out studies, it has been generally accepted that paraffin waxes, which have a low melting point (generally < 70°C) and form a typical macro-crystalline structure in the process of cooling, are responsible for:

- The reduction of asphalt stiffness at high and intermediate service temperatures; and
- The increase in cracking susceptibility at low temperatures

In contrast, microcrystalline petroleum waxes have a higher melting point (generally > 70°C) (Polacco et al., 2012) and crystallise as small needles, leading to a slight influence on bitumen

performance if their total amount is less than about 3% by the weight of the binder (Polacco et al., 2012).

However, in the case of wax modifiers, the situation is totally different. At asphalt production temperatures, measuring the viscosity of wax-modified binders has confirmed the expected reductions in the required temperatures for mixing and compaction of asphalt mixtures. The results of previous experience indicates that bitumen modification with a Fischer-Tropsch wax (e.g. Sasobit) or a Montan wax (Romanta-N) is significantly controlled by complex interactions and cannot be easily tracked back to the more familiar effects of petroleum waxes (Polacco et al., 2012).

According to the result of a comprehensive study performed by Polacco et al. (2012) towards the structural and rheological characterisation of wax modified bitumens, wax shifted the behaviour of the bituminous binder from sol-type to gel-type. Polacco et al. (2012) state that this issue is due to the presence of wax crystals, which, probably together with the asphaltene molecules, disperse in the bituminous matrix from a solid phase arranged in a continuous network. The properties of the bituminous binder are therefore affected by the network and depend on several parameters, including quantity and quality of the crystals, as well as the strength of the intermolecular bonds formed between the solid particles (asphaltene micelles and wax crystals) also between the particles and bitumen (Polacco et al., 2012).

Amide waxes (i.e. modified Montan waxes), due to their polar functionalities, are expected to have stronger interactions with both asphaltene and the most polar maltene molecules.

Polacco et al. (2012) have presented the conventional properties of the base bitumen and the wax modified bituminous blends of their study in Table 2.6. As expected, waxes have reduced the penetration grade and increased the softening point as well as the penetration index of the blends compared the base bitumen. According to the study, the wax crystals do not behave as dispersed fillers, which would determine much lower effects. In fact they have a strong influence on the whole morphological structure of the blends. It can be seen that the penetration values of all modified binders are very close and comparable together, while significant differences can be observed in the softening points. Among the wax modified binders, B-P1 has the lowest softening point and penetration index, while B-P2 and B-P3 have higher and similar values. The two blends with amidic waxes have the highest values. Blending with waxes P2, P3, A1 and A2 has resulted in a penetration index higher than P1, which is indicative

of 'Gel' where a network of fully interconnected solid particles (in this case asphaltene micelles and wax crystals) exists.

In the study, the pure base binder (B) was a 50/70 penetration grade unmodified bitumen and the five different used waxes were: P1 (a Montan wax produced by Romonta GmbH), P2 (a mix of a Montan wax and a high molecular weight hydrocarbons produced by Romonta GmbH), P3 (a Fisher Tropsch wax made by Sasol Wax), A1 (a mixture of substances on the basis of Montan wax constituents and higher-molecular weight aliphatic compounds with functional groups, manufactured by Romonta GmbH), A2 (a mix of fatty acid derivatives by Clariant).

Table 2.6 : Bitumen/wax blends identification and basic conventional properties (Polacco et al., 2012)

Binder	Wax type (–)	Pen. at 25 °C (dmm)	Soft. Point $T_{r\&b}$ (°C)	Pen. Index PI (–)
B	-	55	50.7	-0.8
B-P1	P1	29	68.1	+1.2
B-P2	P2	26	97.0	+4.7
B-P3	P3	26	95.5	+4.6
B-A1	A1	28	116.8	+6.7
B-A2	A2	24	115.9	+6.3

The rheological study performed by Polacco et al. (2012) basically indicates three temperature ranges over each of which the solid phase influences the blend properties differently. At low temperatures, the bituminous matrix seems to mainly influence the mechanical properties of the modified binder whereas the solid network does not play a significant role in this matter. At intermediate temperatures, the solid network structure starts to limit the mobility of bitumen molecules when they are about to change to liquid state. This issue affects the viscoelastic properties of the binder. At high temperatures, the partial melting of the wax crystals and the weakness of the secondary bonds[1] leads to a complete destruction of the network thus leaving a residual solid phase made of separate particles and again the behaviour of the blend becomes similar to that of the base bitumen (Figure 2.31) (Polacco et al., 2012).

1: Also known as inter-particle, intermolecular, or Van der Waals attractions; are the relatively weak attractions between nearby atoms or molecules that are important in most liquids (especially liquid mixtures) and some solids.

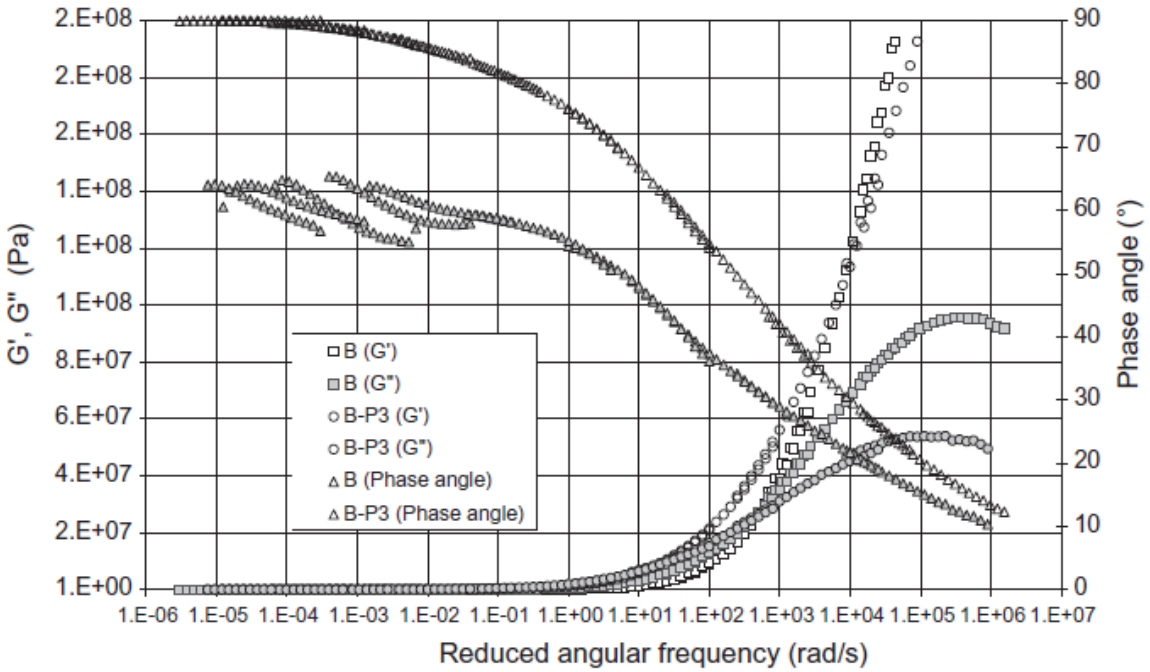


Figure 2.31 : Master curves of moduli and phase angle for B and B-P3. Reference Temperature=20°C (Polacco et al., 2012)

The effect of wax on the viscoelastic properties of bitumen can be studied using a Dynamic Shear Rheometer (DSR). The effect of wax on the complex shear stiffness modulus (G^*) and phase angle (δ) of bitumen has been registered by many authors (Planche et al.; Obertür et al.; Butz et al.; Carbognani et al.; Edwards et al., cited in Polacco et al., 2012).

The most critical influence of wax in bitumen is the sudden decrease in viscosity due to the melting of crystallised wax. If this transition takes place within the operating temperature range it can affect the resistance to permanent deformation of the binder and asphalt pavement (Lu, Soenen & Redelius, 2004).

Regarding the influence of waxes on the performance of bitumen and asphalt mixture, a comprehensive research work has been carried out by Edwards & Isacsson (2012). According to the experimental work, the magnitude and type of wax influence on bitumen rheology depend on the characteristics of the bitumen, the type and dosage of wax and also bitumen composition. Since none of the studied commercial waxes used in this experiment (except for slack wax, which is never used in practice as an additive to bitumen) caused any sudden reduction in the complex stiffness modulus of asphalt at high temperatures, probably they do not affect the rutting resistance in a negative way. Adding commercial waxes (e.g. FT-paraffin,

Montan wax and polyethylene wax) showed no or slightly positive influence on bitumen ageing properties for the tested bitumen samples.

On the matter of the impact of bitumen wax content on its low temperature properties and the performance of manufactured asphalt mixtures (low temperature cracking), Lu, Soenen & Redelius (2004) showed that low temperature properties of bitumen, such as stiffness, performance limiting temperatures, glass transition temperature and Fraass breaking point are not directly related to the content of wax in bitumen. Moreover, according to this study, no simple relationship exists between the low temperature cracking of asphalt mixtures and the wax content of its bitumen. The mixtures fabricated using relatively low pen grade bitumen samples (50/70 or 70/100 pen) with 0 to 4% wax content displayed a small difference in the fracture temperature. For the mixtures manufactured using bitumen samples with the pen grade of 160/220, the fracture temperature might increase by 5 to 10°C when the wax content of bitumen exceeded 3%. It was also shown that there was a significant difference between the bitumen samples with identical wax content but from different sources. In fact, the bitumen sample with low wax content (2.4%) compared to the reference non-waxy bitumen, even showed better resistance to asphalt cracking.

According to (Lu, Soenen & Redelius, 2004), in order to determine the impact of wax on the low temperature properties of bitumen and asphalt mixture, only considering the wax content is not sufficient. In this respect, other factors, such as wax structure and bitumen composition, may also play an important role.

The effect of wax on the low temperature properties of bitumen can, in addition to the traditional determination method of Fraass breaking point, be characterised by Bending Beam Rheometer (BBR) or Direct Tension Test (DTT).

It has been reported in NCAT Report 05-06 that the use of FT-wax (it could apply to all other WMA waxes) for tests with the BBR increases the bitumen stiffness and reduces the relaxing abilities at low temperature regimes (-24°C to -6°C). Accordingly, wax modification leads to a worsening of the low temperature behaviour. A similar problem is reported in NCAT Report Nr 06-02. Changes in PG low temperature performance after production of WMA were compared to the binder used in HMA. While the less short-term aged WMA modified binder performance corresponds to PG 58-28 (where -28 is indicating the low temperature range in °C), the resulting low-temperature properties misses the -28°C grade by about 2 degrees. The

explanation of this problem could be the same as stated above as Sasobit was also used for the experiment.

Wax in bitumen is considered to imply lower ductility (at temperatures from 5 to 25°C) and viscosity than for non-waxy bitumen of the same penetration grade (Plummer *et al*.; Fritsche, cited in Edwards & Isacsson 2012). Paraffin-rich bitumen may lose its ductility and become inhomogeneous as a result of paraffin crystallisation (Obertür *et al*.; Que *et al*.; Lajain, cited in Edwards & Isacsson 2012). The wax crystals restrict plastic deformation which results in earlier failure under ductility testing compared to wax-free bitumen types. However, a number of improved ductility cases have been reported (Lajain, cited in Edwards & Isacsson 2012). In order to study the effect of wax on the cohesive properties of bitumen, a Ductilometer may be used.

According to the rheometer analysis of bitumen/filler mixtures (25%/75%) with waxy bitumen, which was performed by Gastmans (1997) (cited in Edwards & Isacsson 2012), complex modulus and dynamic viscosity, in the case of the chosen test parameters, neither for bitumen nor for bitumen/filler mixtures, could be correlated to bitumen wax content. However, in some cases there was a correlation between the displacement of the test specimen in the rheometer and the associated mixture's wax content (Edwards & Isacsson, 2012).

The possible distresses of asphalt pavements, related to those negative properties of bitumen, which may be due to the bitumen wax content, are listed in Table 2.7, as well as the used bitumen test methods to indicate these problems. Results and experience within this area are based on laboratory studies performed mainly on bitumen samples (Fritsche; King; Que et al.; Obertür et al., cited in Edwards & Isacsson 2012).

Table 2.7 : Possible asphalt pavement problems concerning waxy bitumen (Edwards & Isacsson 2012)

Possible asphalt pavement problems	Negative effect, possibly caused by wax in the bitumen	Test methods used for the bitumen
Cracking at low temperatures	Brittleness of the wax at low temperatures. Low temperature physical hardening.	Flexibility and tensile strength testing: Fraass breaking point, Bending Beam Rheometer, Direct Tension Test.
Rutting at higher temperatures	Low stiffness at high service temperatures and high temperature sensitivity. Decreased viscosity caused by waxes at higher temperature.	Softening point, Complex modulus and phase angle, Zero Shear Viscosity by Dynamic Shear Rheometer.
Laying problems	High temperature sensitivity at laying temperatures. Sudden, viscosity changes for the bitumen in the melting temperature range of the crystalline waxes. Less viscous at higher temperatures as well as more viscous at lower temperatures than bitumen without or with very low wax content. As a consequence of increased viscosity at compaction temperatures, the waxes may contribute to lower compaction of the asphalt mix.	Viscosity at laying temperature, Zero Shear Viscosity. Deviation from Bitumen Test Data Chart.
Loss of aggregate and considerable wear of the wearing course	Loss of adhesion between bitumen and aggregate and reduced cohesion. The ductility of the bitumen may decrease at lower temperatures depending on inhomogeneous material caused by wax crystals. Reduced wetting as a result of hydrophobic character of the wax and predominant hydrophilic character of the aggregate.	(Force)-ductilometer, Pendulum test (Vialit).

Based on NCAT Report 05-06, regarding the evaluation of Sasobit in WMA, it is mentioned that adding Sasobit will decrease the air void content in the gyratory compactor.

2.11.3.2. Sasobit-Modified Bitumen and Sasobit-WMA

It should be mentioned that Sasobit is a product of the Sasol Wax Company based in South Africa. It is a crystalline, long chain aliphatic polymethylene hydrocarbon wax with a general formula of C_nH_{2n+2} in which carbon chain length ranges from C45 to C100 plus. Sasobit results from coal gasification and is a by-product from the synthetic petrol production process called Fischer-Tropsch. Having a melting point of about 100°C, it can be totally dissolved in bitumen at above 115°C. Sasobit can be either in the form of a white powder or granules.

The recommended dosage of Saobit to be added to pure bitumen in the process of producing WMA, according to the Sasobit producer (Sasol Wax) and the recommendations of much research work and field trials, is between 1.5 to 3.0% by the mass of the binder.

According to NCAT Report 05-06, Sasobit could improve the compactability of the mixtures in both the gyratory and vibratory compactors by an average reduction of 0.87% in air void. Improved compaction was noted at temperatures as low as 88°C for the mixtures produced with Sasobit. This report illustrated that while adding Sasobit generally decreased the rutting potential of the mixtures, the rutting potential increased with lowering the mixing and compaction temperatures and this may be related more to less ageing of the binder. However, it was shown that WMA containing Sasobit had less sensitivity (in terms of rutting) to the lowered production temperatures in comparison with HMA. Regarding producing WMA using Sasobit, NCAT Report 05-06 recommends a minimum mixing temperature of 129°C and a minimum compaction temperature of 110°C. If the mixing temperature is below 129°C, then the high temperature grade should be bumped by one grade to counteract the tendency for increased rutting susceptibility with decreasing production temperatures.

A systematic laboratory study of both Sasobit-modified WMA binders and mixtures for the purpose of studying the compatibility of Sasobit WMA technology for Alaskan conditions has been performed by Liu & Li (2012). Through conducting a series of binder tests including BBR, DTT, and ABCD[2] and by performing the IDT[3] test of mixtures along with a thermal cracking analysis to obtain a more confident result regarding the application of this product in

2: Asphalt Binder Cracking Device

3: Indirect Tensile Test

cold weather, this research indicated that the addition of Sasobit significantly impacted the PG of binders and reduced both mixing and compaction temperatures of mixes. The results in this research showed that increasing the Sasobit content will increase the E^* value. In addition, increasing the Flow Number with increasing the Sasobit content indicated a better rutting resistance of mixtures from adding more Sasobit. Moreover, the TSR results in the study indicated that the addition of Sasobit did not contribute to moisture damage of WMA compared to the control hot mixtures. As another important result, the IDT results showed reduced resistance to low temperature cracking of WMA using Sasobit. Although in this research no reason was indicated for such an important defect, it seems to be logical that recrystallising the wax inside the bitumen at the temperatures lower than the melting point of the wax could be a reason for this occurrence.

Through research work including the laboratory simulation of Warm Mix Asphalt binder ageing characteristics, conducted by Gandhi & Amirkhanian (2008), the ageing of different WMA binders including Sasobit-modified ones were simulated in laboratory. This was carried out by preparing asphalt mixtures containing two different binder sources modified with Sasobit. The mixtures were artificially aged in an oven and the binders were extracted for testing. The binders extracted from freshly prepared samples were considered as being short-term aged binders and binders extracted from oven aged mixtures were considered as being long-term aged binders.

Results of several tests presented in the study indicated that the binders extracted from the Sasobit-WMA mixtures had significantly lower ageing index (ratio of the viscosity of extracted binders to original binders) compared to the binders extracted from control HMA mixture. The binders extracted from the Sasobit-WMA showed significantly lower $G^*/\sin\delta$ values compared to binders extracted from HMA. Thus, it could be concluded that the lower mixing and compaction temperatures of the Sasobit-WMA significantly lowered the aging in the binders. The results indicated that the warm asphalt additives did not have any significant effect on the fatigue cracking parameter ($G^*.\sin\delta$) or the creep stiffness of the binders. Moreover, the Sasobit-WMA mixtures used in the study were not more prone to cracking at low temperatures.

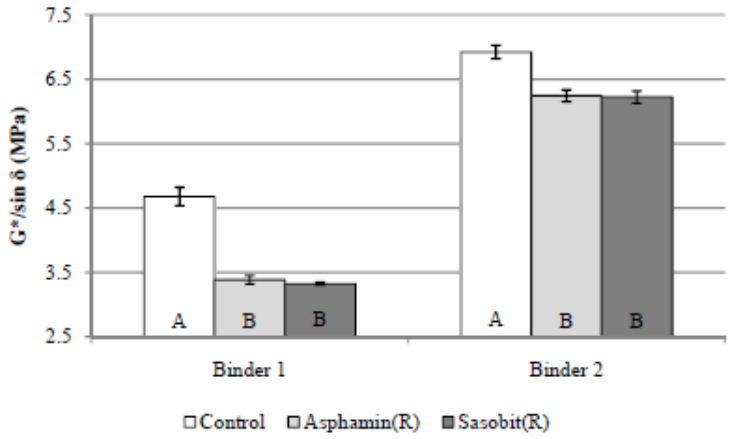


Figure 2.32 : *(G*)/(sin δ)* values of the extracted binders with and without WMA additives (Gandhi & Amirkhanian, 2008)

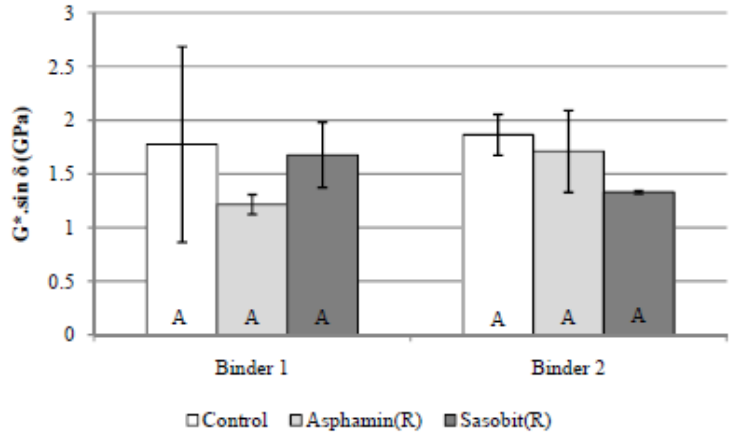


Figure 2.33 : *(G*).(sin δ)* values of the extracted binders with and without WMA additives (Gandhi & Amirkhanian, 2008)

Through the study of Yero & Hainin (2011) the bitumen modification process in the wax production technology of Warm Mix Asphalt by the use of Sasobit as the organic wax modifier has been reviewed. The study involved the determination of penetration grade and softening point and the Brookfield viscometry of bitumen 80/100 pen modified with various dosages of Sasobit (1 to 5% of binder weight).

The study of Yero & Hainin (2011) indicates that Sasobit increases the dynamic viscosity of the binder at low temperature and decreases the kinematic viscosity at high temperatures. The addition of Sasobit significantly reduces the viscosities of the binder at temperatures above 100°C. According to this study, the effect of Sasobit on binder viscosity guarantees an efficient coating of the aggregate by the binder and a good workability of the asphalt mixture at lower

temperatures compared to the conventional Hot Mix Asphalt (HMA). Moreover, Yero & Hainin (2011) concluded that at as low a temperature as 60°C, the higher the percentage of Sasobit in bitumen, the higher the viscosity of the resulted modified binder. The reason for this phenomenon was referred to the nature of wax, which recrystallises in the binder when cooled down, thereby increasing the viscosity of the binder at lower temperatures and enhances the flow of the binder.

Jamshidi, Hamzah & You (2013) have reviewed the performance of Warm Mix Asphalt mixtures containing Sasobit via studying and summarising the findings of laboratory tests and field performance of Sasobit-modified WMA from more than 230 piece of literature on binder and WMA mixture incorporating Sasobit. According to the conclusions of this study, Sasobit has advantages and disadvantages.

On the one hand, it decreases the viscosity of binder at high temperatures, as a result of which, reducing construction temperatures and ageing. It also increases the rutting resistance at intermediate temperatures for a given binder type and source. On the other hand, Sasobit may increase the potential of fatigue failure and low-temperature cracking at intermediate and low temperatures. The study then concludes that it is essential to optimise the performance of Sasobit-modified binders at high, intermediate and low temperature ranges by careful selection of the binder type, source and Sasobit content.

Reviewing several laboratory studies Jamshidi, Hamzah & You (2013) have mentioned that the performance of Sasobit-WMA mixtures depend on construction temperatures, Sasobit content, aggregate type and source, aggregate gradation, filler type, binder type and source, anti-stripping agent type, and the type and amount of waste materials such as RAP (Reclaimed Asphalt Pavement), RAS (Recycled Asphalt Shingles), RCA (Recycled Coal Ash), and crumb rubber (CR).

According to the reviews of Jamshidi, Hamzah & You (2013), no significant differences were observed between Sasobit-WMA mixtures and HMA ones in terms of volumetric properties and optimum binder content. Moreover, since Sasobit improves asphalt binder, the rutting performance of Sasobit-WMA mixtures were often observed to equal or exceed the rutting performance of HMA regardless of the laboratory test method. Aggregate size, source, type, anti-stripping agent type, size of solid anti-stripping particles, and ageing time are factors which affect the moisture resistance of Sasobit-WMA mixtures. Less ageing due to lower construction

temperatures increases the fatigue resistance of Sasobit-WMA mixtures. Use of softer or lower performance-grade binder could increase the resistance of Sasobit-WMA mixtures to fatigue.

According to this research work, the results gained through field studies show that the general performance of Sasobit-WMA mixtures has been satisfactory but more effort is required to assess the long-term performance of Sasobit-WMA mixtures.

Zaumanis & Haritonovs (2010) have conducted a laboratory study to evaluate two different WMA technologies including Sasobit wax and Rediset-WMX chemical additive. The properties of bitumen in this study have been defined through the traditional EN test methods in addition to the determination of the rheological properties of bitumen at intermediate to high temperatures. The compactability characteristics, density, stiffness modulus and resistance to permanent deformation of the produced asphalt mixtures compacted at different temperatures using Gyratory and Marshall Compactors have been determined.

Conforming to other research work, Zaumanis & Haritonovs (2010) have shown that adding Sasobit (2-3%) lowers the viscosity of bitumen at high temperatures and it increases bitumen's viscosity at intermediate temperatures. According to this study, at in-service temperatures, Sasobit provides higher resistance to deformation and improves the elasticity of bitumen. However, addition of Rediset WMX has only a minor effect on bitumen properties.

Zaumanis & Haritonovs (2010) have also shown that adding either Sasobit or Rediset-WMX to bitumen 40/60 pen to produce Stone Mastic Asphalt (SMA) allows reduction of the compaction temperature from 155°C for HMA to 125°C for WMA in such a way that the samples made through both WMA technologies have approximately the same density as the reference HMA. Analysis of the gyratory compaction data in this research showed that in order to produce the WMA samples, less compaction might be required to obtain the same density as HMA and following further compaction effort, even higher density than HMA might be achieved.

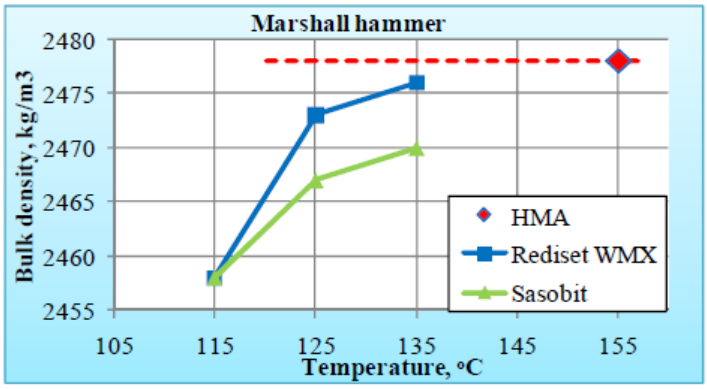


Figure 2.34 : Bulk density at different compaction temperatures for Marshal specimens (Zaumanis & Haritonovs, 2010)

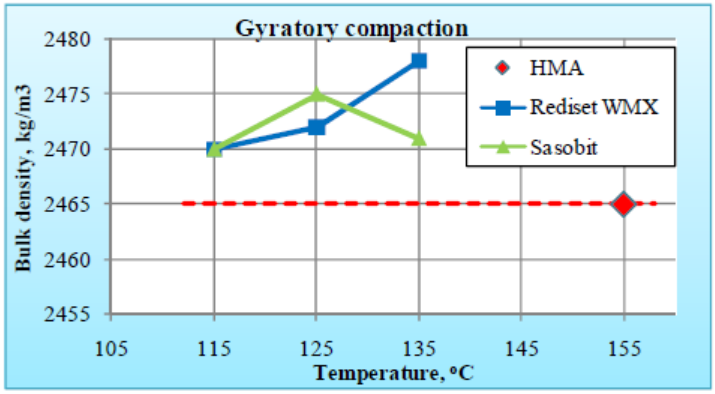


Figure 2.35 : Bulk density at different compaction temperatures for Gyratory specimens (Zaumanis & Haritonovs, 2010)

Moreover, analysing the mechanical properties of asphalt in this research illustrated that reducing the compaction temperature of asphalt to at least 125°C for both WMA products was possible because it still resulted in similar stiffness modulus to the reference HMA without having an increased susceptibility to permanent deformation.

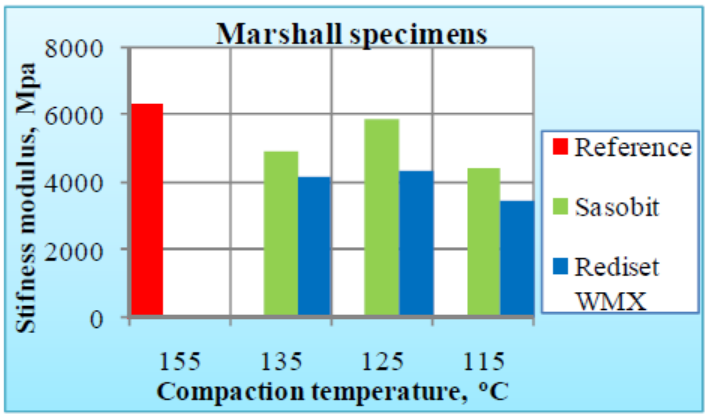


Figure 2.36 : Stiffness modulus test results for Marshal specimens (Zaumanis & Haritonovs, 2010)

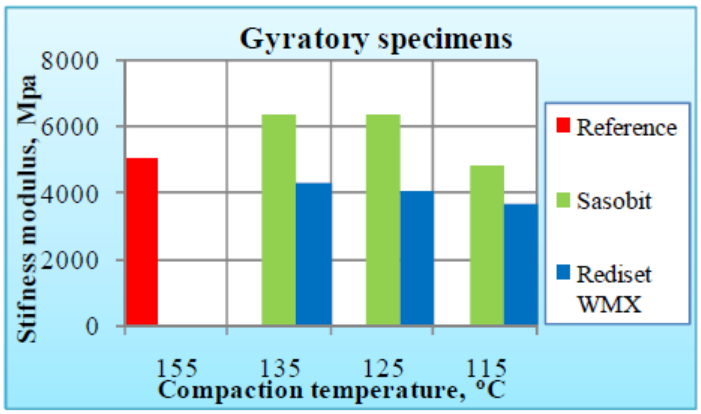


Figure 2.37 : Stiffness modulus test results for Gyratory specimens (Zaumanis & Haritonovs, 2010)

Sebaaly, Hajj & Hitti (2012) have shown that the residual moisture remaining in the aggregates, due to the lower mixing temperature of WMA mixtures could have had a significant negative impact on mixture properties especially their resistance to moisture damage. The additives used in this study to produce WMA mixtures have been Sasobit (wax technology) and Advera (foaming technology). The resistance of the mixtures to moisture damage has been evaluated in terms of the impact of multiple freeze-thaw (F-T) cycles on the dynamic stiffness modulus.

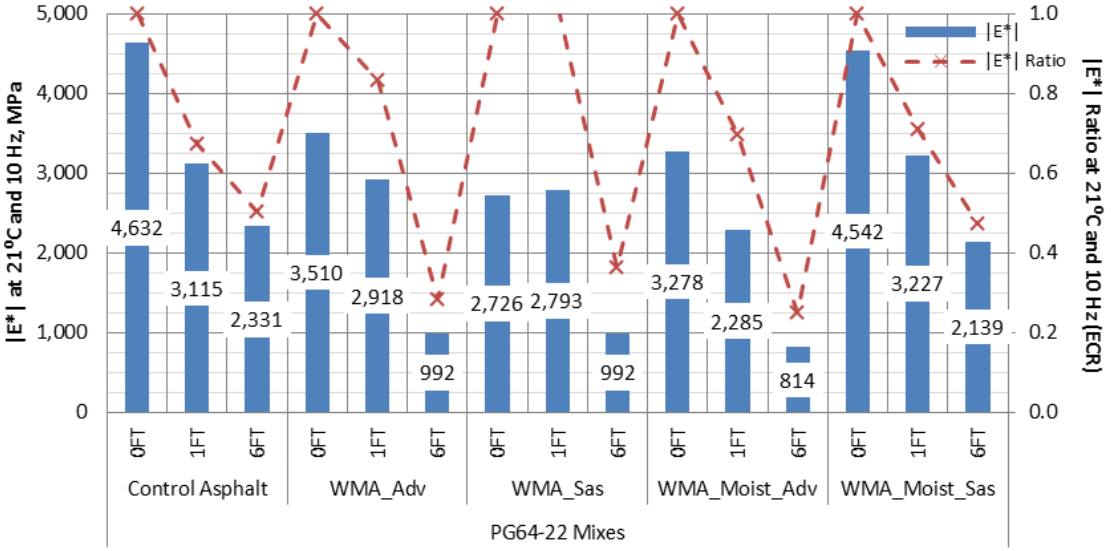


Figure 2.38 : The impact of residual moisture on the dynamic modulus of WMA mixtures (Sebaaly, Hajj & Hitti, 2012)

Moreover, the resistance to permanent deformation has been evaluated referring to the flow number of the Wheel Tracking test. According to this study, the level of the negative influence varies by changing the type of WMA additive and the type of bitumen. It has been highly recommended that the aggregates should be totally dry prior to the mixing process of WMA production so the potential damage to the long-term performance of the pavement is avoided. The research results indicate that the use of anti-stripping additive can improve the resistance of WMA to both short and long-term moisture damage as well as the permanent deformation. However, the results state that in some mixtures, adding the anti-stripping additive has had negative effects on the performance of the mixture in the sense that it had reduced the resistance to permanent deformation. Therefore, it has been recommended that the addition of liquid anti-stripping additive to WMA mixtures should be assessed very carefully prior to its final incorporation in the mixture to avoid the adverse effects on the properties of the mixtures.

You & Goh (2011) have carried out a laboratory evaluation of Warm Mix Asphalt mixtures produced via wax (Sasobit), chemical additive (Cecabase RT) and foaming (Aspha-min and Advera) technologies.

The rheological properties and ageing factor of the binders have been evaluated via measuring the complex shear modulus (G^*). The performance evaluation of the asphalt mixtures including the assessment of rutting potential, fatigue resistance and moisture susceptibility, has been carried out through measuring the complex dynamic modulus (E^*), Flow Number (FN) and

APA (Asphalt Pavement Analyser) Rutting, performing the Four Point Bending Beam fatigue test and evaluating the Tensile Strength Ratio (TSR) respectively. According to the test results, most of the WMA mixtures had higher fatigue life and TSR compared to the reference HMA mixture. This indicated that WMA has better fatigue cracking and moisture damage resistance. However, the rutting potential of most of the tested WMA mixtures was higher than the control HMA. You & Goh (2011) have summarised their findings in a Table as shown in the following page.

Table 2.8 : Summary of WMA performance test results (You & Goh, 2011)

		Asphalt Binder		Rutting			Fatigue	Moisture Susceptibility
		Complex Shear Modulus	Aging Factor[1]	Dynamic Modulus	Flow Number	APA Rutting	Four Point Beam Fatigue	Tensile Strength Ratio
Foaming	Aspha-min®	No Change	Lower	Similar or Higher |E*| Comparable or better rutting resistant	-	Lower Rutting Rutting decrease when mix/ compact temp. increase	-	-
	Advera® WMA	No Change	Lower	Lower |E*| Increase rutting potential	Lower F_N	Higher Rutting	Higher Fatigue Life	TSR value no change or higher; But, lower tensile strength was found
	Water Foaming	No Change	Lower	Lower |E*| Increase rutting potential	Lower F_N	Higher Rutting	Higher Fatigue Life	Higher TSR TSR increase when mix/ compact temp. increase
Organic Additive	Sasobit®	Increase	Lower Samples at 130°C has higher aging factor. Aging factor increase when temp. increase	No Significant Different	No Significant Different	Samples with less Sasobit® have higher rutting.	No Significant Different	No Significant Different Lower tensile Strength was found
Chemical Package	Cecabase RT®	No Change	Lower	Lower |E*| Increase rutting potential	Lower F_N F_N decrease when more Cecabase RT® was added	Samples produced at 100°C have higher rutting. No significant for the rest of the samples.	Higher Fatigue Life	TSR value no change or higher; But, lower tensile strength was found

Part 1 of NCHRP Report 779 presents the analysis of the engineering properties of various WMA mixtures, including Sasobit-WMA, compared to HMA. It also includes the early field performance of WMA and companion HMA test sections built across the United States. According to the report, testing of the recovered binders from the mixtures obtained during construction generally showed that the WMA binders had aged slightly less than the corresponding HMA binders. Moreover, statistical analysis indicated that the Dynamic Complex moduli of WMA mixtures were lower than those of the corresponding HMA mixtures in most cases. On average, the E^* of WMA mixtures have been about 12% lower than those of corresponding HMA, but the differences ranged from about 5% stiffer to 40% less stiff.

In the majority of cases, the tensile strengths of WMA and HMA cores, which were taken immediately after construction from the same project, remained statistically equivalent through at least 2 years.

The study indicated that 82% of the existing and new plant-produced mixtures passed the standard 0.8 minimum TSR criterion of the Tensile Strength Ratio test, which was conducted in accordance with AASHTO T 283.

In terms of rutting potential, in more than 2/3 of the comparisons, the Flow Number test results for the plant-produced WMA mixtures were statistically lower than corresponding HMA mixtures. Hamburg wheel tracking tests were used to assess the rutting potential of the plant-produced mixtures as well as their resistance to moisture damage. As for the rutting comparisons, 59% of the WMA mixes had statistically equivalent Hamburg rut depths to their corresponding HMA mixes, and the other 41% of the WMA mixes had greater Hamburg rut depths than their companion HMA mixes.

Based on the results of a solid research on moisture sensitivity performed by Hurley & Prowell (2006b), in which Sasobit, Aspha-min and Evotherm were evaluated, as shown in Table 5, all of the mentioned additives have lowered the Tensile Strength Ratio (TSR) compared to the control HMA. Only three of the nine tested specimens (three types of additives in different temperature and aggregate combinations) satisfied the Superpave requirement of 0.8 for ratio between tensile strength of saturated and unsaturated samples. The worst results in all cases were shown to be from Aspha-min (water containing technology), which is believed to be connected with the emulsification of binder from the released moisture of the zeolite, causing a cohesive failure.

After this, tensile strength of Sasobit and Aspha-min products with liquid anti-stripping additives were tested, but the results did not show the expected results. Aspha-min resulted in even worse TSR value which may be connected with reduction of binder viscosity from the liquid anti-stripping agent. And whilst Sasobit resulted in acceptable TSR, the actual tensile strength for both saturated and unsaturated samples had decreased more than twice compared to the same mix without anti-stripping additive. Then Aspha-min with an addition of a different amount and also addition of hydrated lime was tested and proved to have a positive effect on TSR.

Table 2.9 : Testing summary of moisture sensitivity (Hurley & Prowell, 2006b)

Aggregate	Mix type	Treatment	Stripping inflection point	TSR
Granite	Control	None	6500	1.16
Granite	Sasobit	None	3975	0.71
Granite	Aspha-min	None	3450	0.67
Granite	Evotherm	None	Not observed	0.96
Granite	Aspha-min	1.5% Hydrated lime	Not observed	0.75
Granite	Sasobit	0.4% antistripping additive	Not observed	0.94
Limestone	Control	None	2500	0.65
Limestone	Aspha-min	None	1700	0.51
Limestone	Sasobit	None	2900	0.91
Limestone	Evotherm	None	2550	0.62

A similar field experiment on moisture sensitivity, which was conducted by Jones, Wu & Tsai (2008) showed some different results and indicated that all types of asphalt are potentially susceptible to moisture damage. Referring to Table 2.10, the water containing additive Advera shows the worst performance in this test. However, the difference in the results was not that significant and the authors of this research believe that there is no considerable difference in moisture sensitivity between control mix and mixes with additives.

Table 2.10 : Test result summary of moisture sensitivity (Jones, Wu & Tsai, 2008)

Specimen	Stripping inflection point	TSR
Control	7 720	0.62
Advera	5 626	0.51
Evotherm	5 069	0.64
Sasobit	9 764	0.57

Similar research was performed by Jones, Wu & Tsai (2008) for evaluating Evotherm (Hurley & Prowell, 2006b). The results showed a decrease in TSR value of WMA compared to reference HMA of more than 50% for all of the different mix compositions that were tested. The HMA control mix resulted in an acceptable TSR of 0.94, but none of the WMA could satisfy the demand of 0.8 for moisture resistance after one freeze/thaw cycle.

The draft appendix to AASHTO R 35 includes an evaluation of the rutting resistance of WMA using the Flow Number test. The test is conducted on specimens that have been short-term conditioned for 2hrs at the compaction temperature to simulate the binder absorption and stiffening that occurs during construction. As lower short-term conditioning temperatures are used for WMA mixtures as compared to HMA mixtures, binder ageing in WMA mixtures is less, resulting in lower flow numbers for WMA mixtures produced with the same aggregates and binder as compared to HMA mixtures. Current criteria for the flow number and other rutting tests for HMA are based on 4 hrs of short-term conditioning at 135°C. The short-term conditioning study completed under NCHRP Project 9-43 shows that this level of conditioning represents the stiffening that occurs during construction as well as some time in service. Since it is inappropriate to condition WMA mixtures at temperatures exceeding their production temperature, the criteria for evaluating the rutting resistance of WMA mixtures were reduced compared to those currently recommended for HMA mixtures conditioned for 4 hrs at 135°C.

Different research to evaluate Sasobit, zeolite and Evotherm for rutting resistance with Asphalt Pavement Analyser (APA) was performed by Hurley & Prowell (2006b). In this research all of the mixes including the control were compacted at four different temperatures. Tests were performed for both, mixes with granite and a limestone mineral skeleton. The test results in Figure 2.39 and Figure 2.40 show that the WMA processes do not increase rutting potential of an asphalt mix. The rutting potential is increased with decreased compaction temperatures for all of the samples, including the control. Therefore reduced resistance to permanent deformation may be related mostly to the decreased ageing of binder than to a particular WMA technology. Moreover, according to the results of this research, mixes containing Sasobit had better rut resistance compared to other mixes.

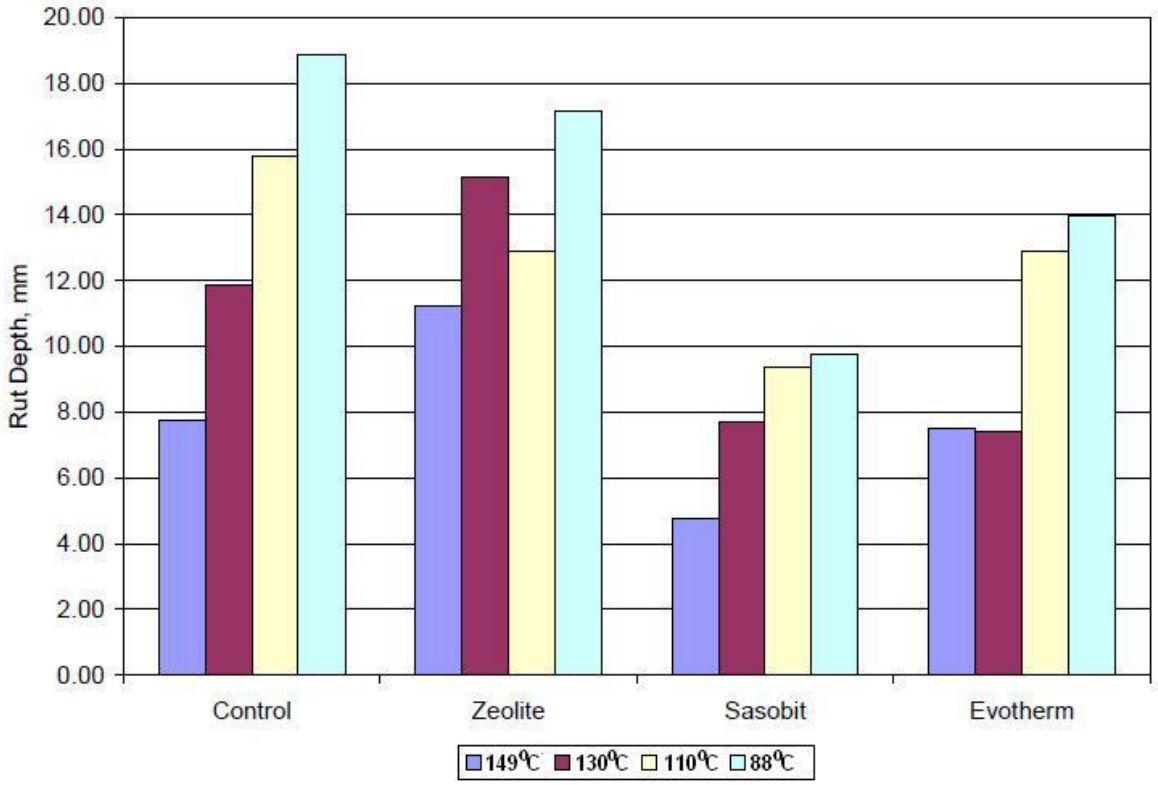


Figure 2.39 : APA rutting results for granite aggregate (Hurley & Prowell, 2006b)

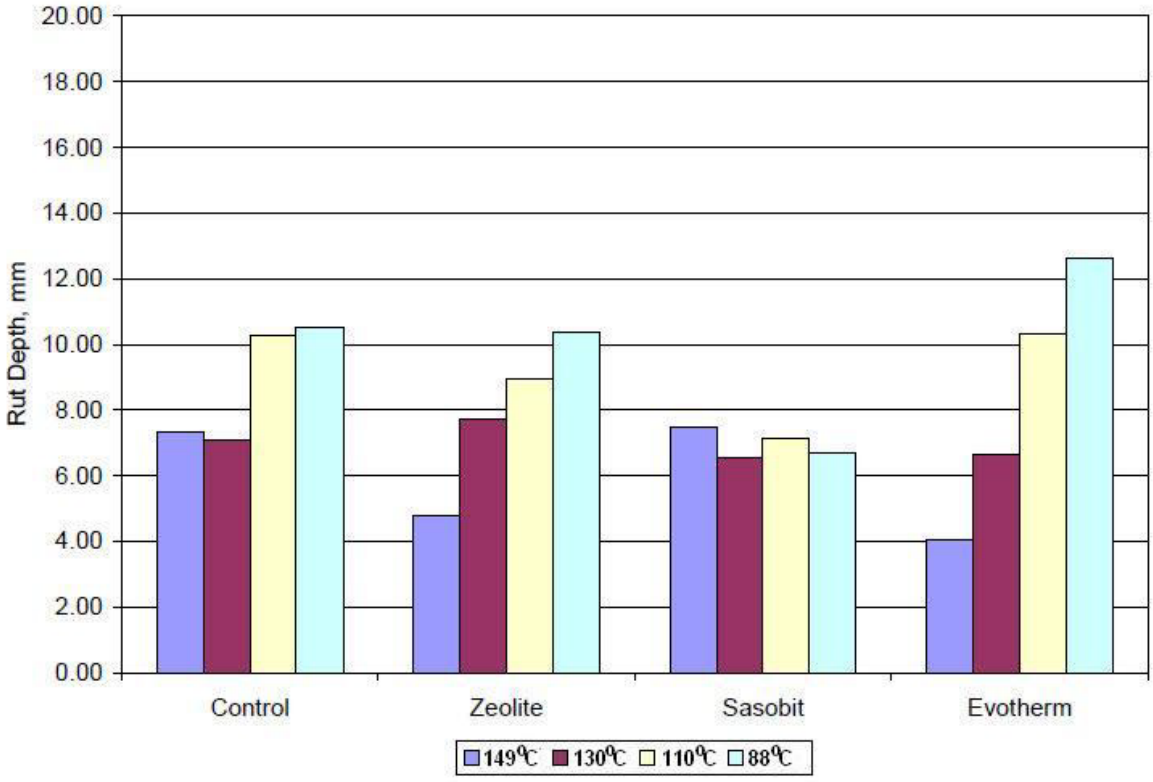


Figure 2.40 : APA rutting results for limestone aggregate (Hurley & Prowell, 2006b)

From the results presented in Figure 2.39 and Figure 2.40, it can be concluded that assessment of resistance to permanent deformation should definitely be a part of WMA evaluation. However, as proved in Hurley & Prowell's research (2006b), the poor resistance of WMA can be connected to a decrease in ageing of bitumen at low production temperatures. The mentioned study believes that this problem can be resolved by initially choosing a stiffer bitumen for production of WMA.

2.11.3.3. Chemical Additives of Bitumen

Chemical additives often include anti-stripping agents. Anti-stripping agents were described in the previous sections briefly. The chemical additives used in Warm Mix Asphalt production do not change the bitumen viscosity (Hurley & Prowell, 2006b). The chemical additives which use surfactants[4], are expected to act as a 'lubricant' and work at the microscopic interface of aggregate and bitumen (Anderson et al., cited in You & Goh 2011). The 'lubricant' reduces the internal friction when asphalt mixture is subjected to high shear rates (i.e. mixing process) and high shear stress (i.e. compaction). This "lubricant" is effective at a certain temperature typically ranging from 85°C to 140°C. Examples of WMA technologies using chemical additives include Cecabase RT, Evotherm, Rediset WMX, Rediset LQ, etc (You & Goh, 2011). Chemical additives may reduce the mix and compaction temperatures by about 20 to 30°C.

Surfactants, in general, are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, adhesion promoters, emulsifiers, foaming agents, and dispersants.

4: Surface Active Agent

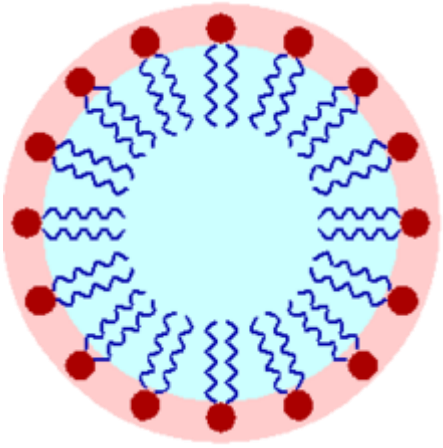


Figure 2.41 : Schematic diagram of a micelle of oil in aqueous suspension, such as might occur in an emulsion of oil in water (Wikipedia, 2016c)

In this example the surfactant molecules' oil-soluble tails project into the oil, while the water-soluble ends remain in contact with the water phase.

The ‘tail’ of most surfactants is fairly similar, consisting of a hydrocarbon chain, which can be branch, linear, or aromatic. Surfactant molecules have either one tail or two; those with two tails are said to be double-chained.

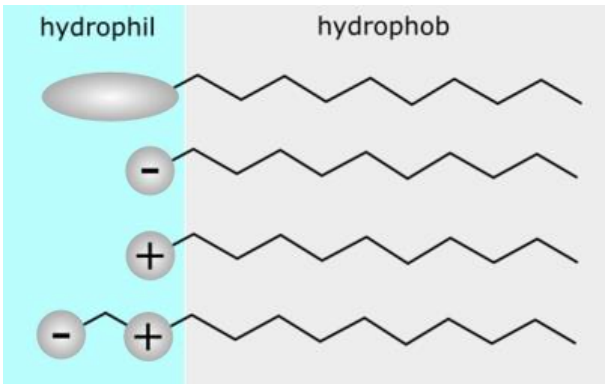


Figure 2.42 : Surfactant classification according to the composition of their head: non-ionic, anionic, cationic and amphoteric (Wikipedia, 2016c)

Most commonly, surfactants are classified according to their polar head group. A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed ‘zwitterionic’.

Adhesion promoters are cationic surface active molecules (cationic surfactants), which concentrate at the bitumen–aggregate interface. Cationic adhesion promoters are fatty amine, amidoamine or imidazoline surfactants (surface active agents). While the positive/hydrophilic head groups on the surface active agents bind strongly to the negative sites on the aggregate surface, the hydrophobic hydrocarbon 'tails' of the molecules (fatty alkyl carbon chain) anchor into the bitumen (AkzoNobel, 2015).

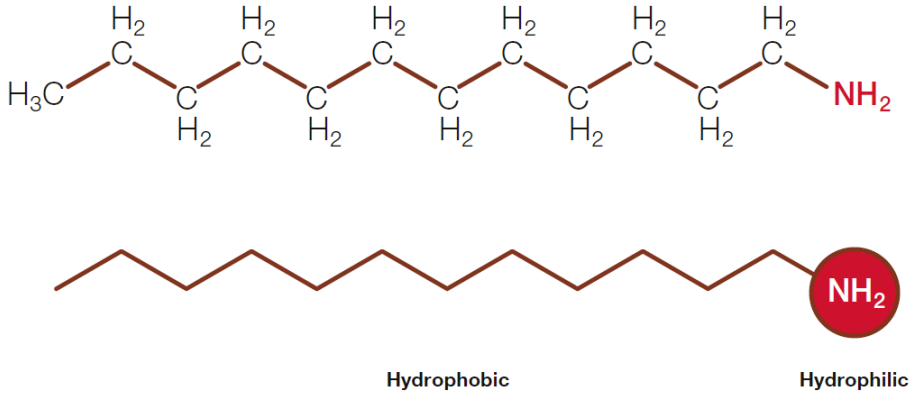


Figure 2.43 : Chemical structure of adhesion promoters (AkzoNobel, 2015)

The adhesion promoter thus acts as a bridge or glue between the bitumen and the aggregate surface which resists the displacing effect of water. Adhesion promoters can be introduced into a system by addition to the bitumen. Although added to the bitumen, adhesion promoter molecules quickly migrate into the bitumen–aggregate interface.

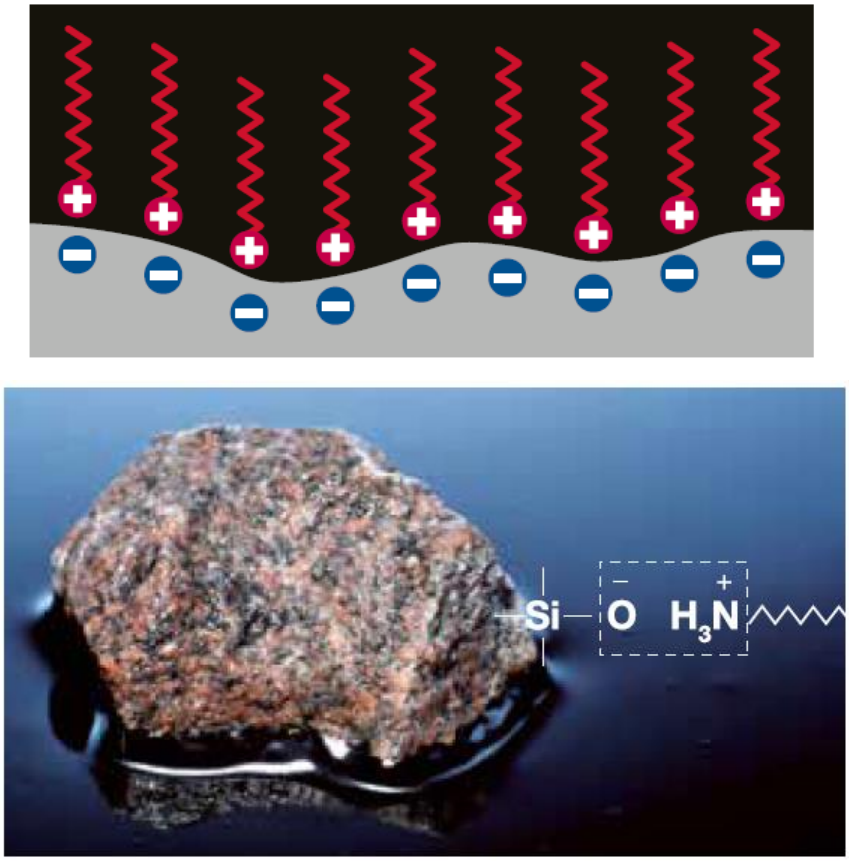


Figure 2.44 : Adhesion promoter molecules act as bridge between aggregate and bitumen (AkzoNobel, 2015)

Aggregates are normally hydrophilic. Under normal circumstances, aggregates have a higher affinity for water than oily substance such as bitumen (AkzoNobel, 2013).

Active adhesion promoters decrease the contact angle (θ) between bitumen and aggregate allowing the bitumen to coat the aggregate (even in the presence of water) whereas passive adhesion promoters create a chemical bond between bitumen and aggregate preventing stripping throughout the service life of the asphalt (AkzoNobel, 2013).

2.11.3.4. RedisetLQ-Modified Bitumen and RedisetLQ-WMA

Rediset LQ, as mentioned previously, is a liquid chemical Warm Mix Asphalt additive which has been invented by AkzoNobel in 2011. According to AkzoNobel (2012), Rediset LQ allows the production and compaction of asphalt pavements at temperatures typically 22 to 33°C (40 to 60°F) lower than conventional HMA. The surfactants in Rediset LQ modify the properties of the binder in such a way that readily allows it to bond with the active sites on the aggregate surface. The surfactants also reduce the surface tension of the binder, which enables efficient

coating of binder on the aggregate surface. This property enables the binder to readily coat the aggregate and eventually increases the workability of the mixture and allows the mixture to be more compactable at lower temperatures. According to AkzoNobel (2012), Rediset LQ will not change the performance grade (PG) of the binder at dosages as high as 0.75% by the weight of the binder. Moreover, a binder modified by Rediset LQ has a higher affinity to the aggregate's surface compared to water. For this reason, it can readily bond with and coat the aggregate surface even if the aggregate is not completely dry (AkzoNobel, 2012).

In summary, Rediset LQ, in asphalt mixtures, is an insurance against stripping, which leads to early pavement failure. Mixtures containing Rediset LQ will have better cohesion after compaction thereby allowing earlier trafficking of roadways after paving compared to HMA. Rediset LQ can be used as a compaction aid and an anti-stripping additive for Hot Mix Asphalt where compaction may otherwise be difficult to attain. Some of these conditions include late season paving, wet aggregate, RAP, mixes containing high levels of RAP and colder weather and night paving (AkzoNobel, 2012).

AkzoNobel (2012) recommends the following table for the dosage of Rediset LQ. It is based on the effective binder weight:

Table 2.11 : Recommended dosages for Rediset LQ by the weight of binder (AkzoNobel, 2012)

Application	Dosage (%)
Warm-mix (standard PG grades)	0.4 – 0.6
Compaction aid	0.3 – 0.5
High-RAP & higher PG binders	0.5 – 0.75
Foam warm-mixes	0.3 -0.5

Probably the most comprehensive study on the performance of RedisetLQ-WMA mixture has been carried out by the producer, AkzoNobel. Various features of RedisetLQ-WMA mixtures have been tested in AkzoNobel's laboratories or have been tested in different research centres. The test results, in addition to the results obtained from field trials, have been made available in Rediset LQ associated documents (e.g. presentation, Bulletin, datasheet, etc.) provided by AkzoNobel.

In this regard, AkzoNobel (2013) has provided a chart (Figure 2.45) illustrating the significantly improved compaction rate and increased compactability of RedisetLQ-WMA

mixture compared to its counterpart reference HMA mixture, at the compaction temperature of 130°C, when adding 0.5% Rediset LQ to bitumen. The improvement has been as much as the Gyration Ratio of 2.0. For both the reference HMA and the RedisetLQ-WMA mixtures, the number of gyrations required to achieve the Target Air Void (TAV) content of 6% at the compaction temperature of 130°C have been extracted, defined and compared.

Figure 2.46, includes a chart provided by AkzoNobel (2013), presenting the above test data in the form of a bar chart besides the results of a similar compaction but this time carried out at 105°C. The results also show a 'gyration ratio' of 2.0. By this means, it has been claimed that firstly even at the compaction temperatures of as low as 105°C, Rediset LQ improves compactability of the asphalt mixture by a Gyration Ratio of 2.0. Secondly, Rediset LQ allows asphalt mixture to be compacted at 25°C below the compaction temperature of conventional HMA while resulting in the same compactability and volumetric properties.

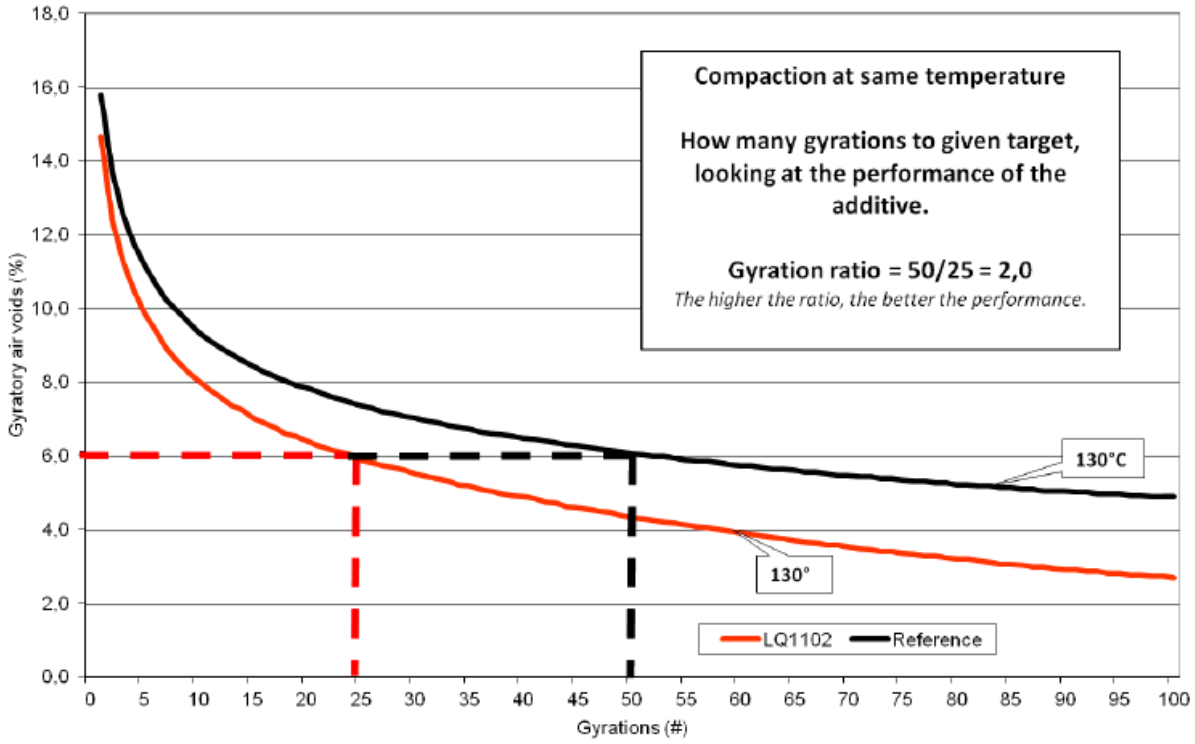


Figure 2.45 : Gyrations to achieve the Target Air Void content of 6% at 130°C (AkzoNobel, 2013)

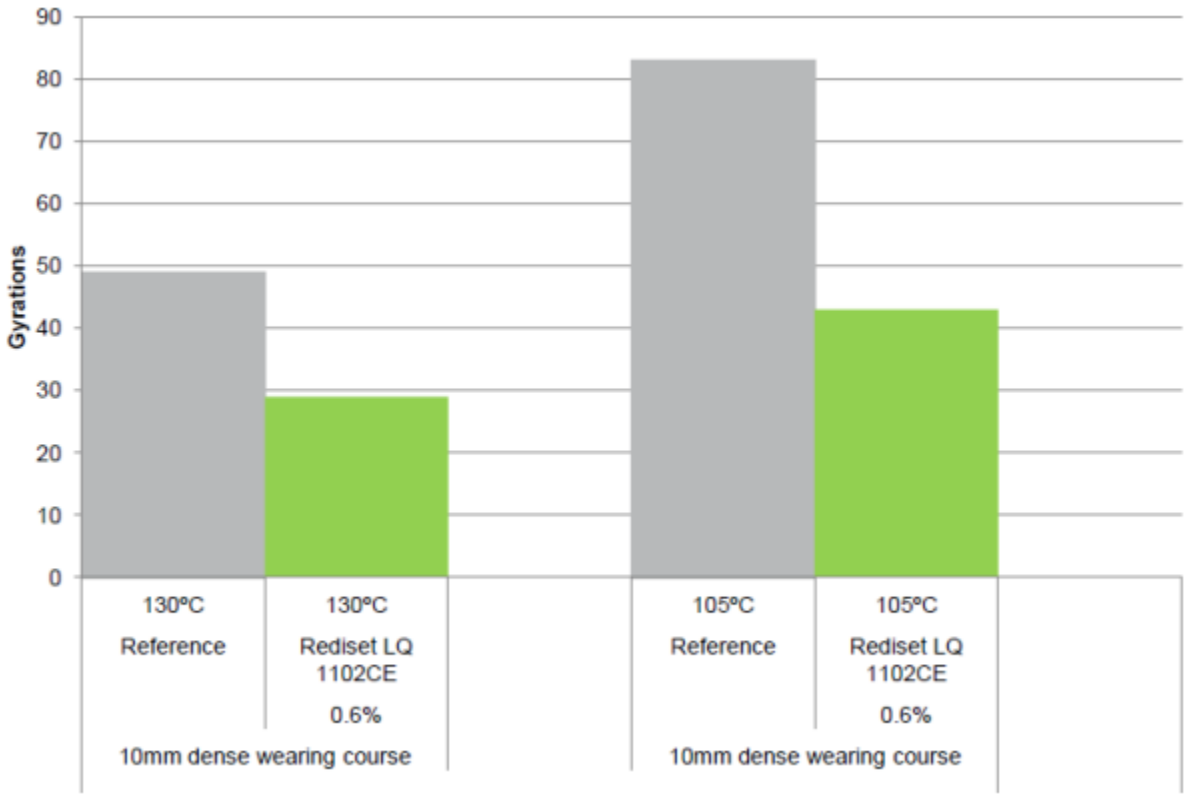


Figure 2.46 : Gyrations to achieve the Target Air Void content of 6% (AkzoNobel, 2013)

AkzoNobel (2012) also claims that the active adhesion provided by the Rediset LQ enables good coating even at the higher moisture levels in the aggregate which can result from the lower mixing and drying temperatures of Warm Mix Asphalt production processes. In this respect, Rediset LQ enables the treated asphalt to displace residual water from the aggregate surface, and creates a strong chemical bond between the aggregate and the bitumen which is resistant to water. Figure 2.47 shows that RedisetLQ-WMA exhibits superior conditioned Indirect Tensile Strength as well as and an improved Tensile Strength Ratio compared with traditional Hot Mix Asphalt (AkzoNobel, 2013).

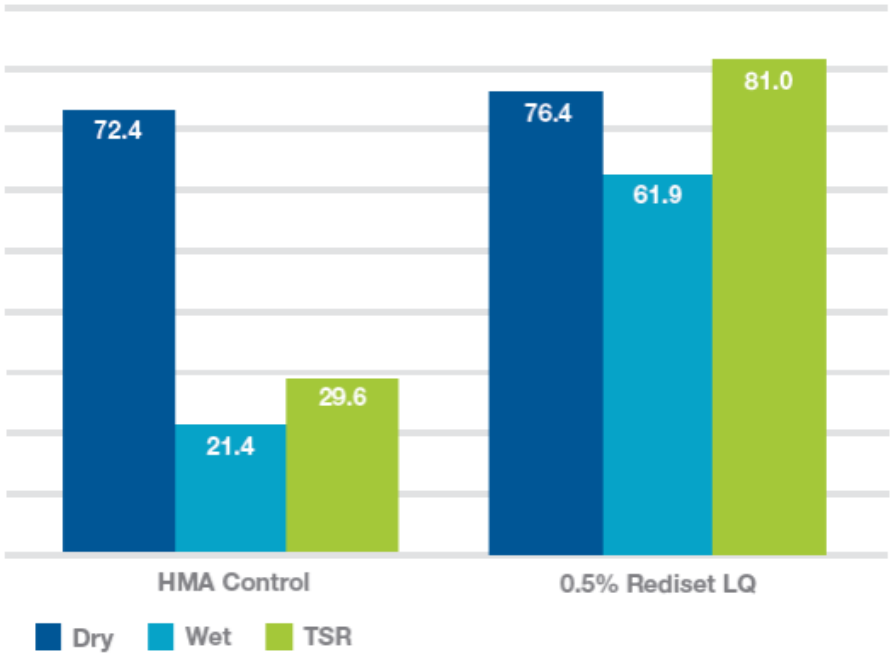


Figure 2.47 : Tensile Strength Ratio (%) in moisture sensitivity test according to AASHTO T 283 (AkzoNobel, 2013)

According to the data provided by AkzoNobel (2013), performance testing in the field and the laboratory confirms that RedisetLQ-WMA mixtures show favourable Hamburg Wheel Tracking test results (Figure 2.48) compared to the Hot Mix Asphalt counterparts indicating strong resistance to moisture damage.

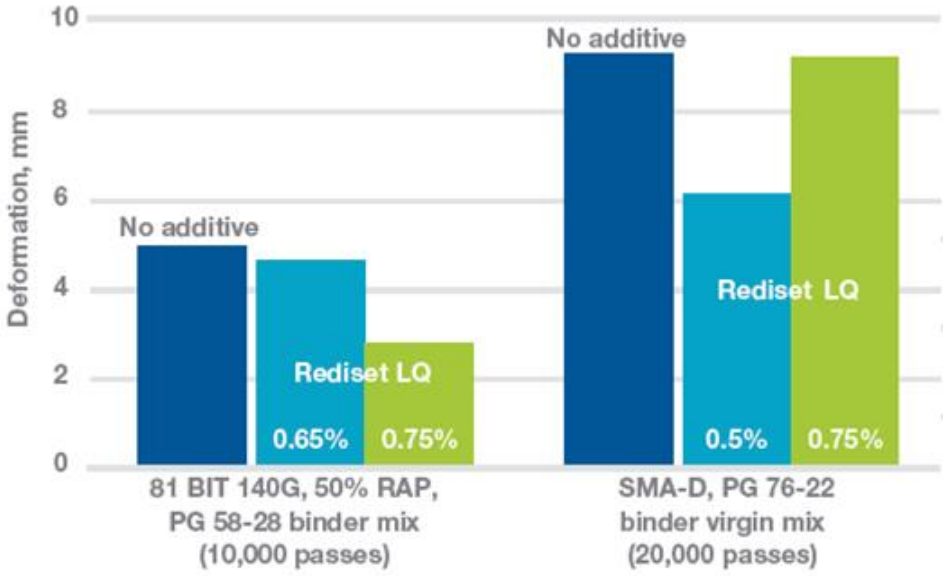


Figure 2.48 : Hamburg wheel tracking test data from Chicago Testing Laboratory Inc. and PaveTex, USA; Testing based on AASHTO T 324 (AkzoNobel, 2013)

Zhang et al. (2012) have investigated the influence of Rediset WMX on the properties of bitumen. This is interesting to look at, as it is also from AkzoNobel. Rediset WMX is the former (initial) generation of Rediset LQ and is very similar, though not exactly the same. The warm mix binder was produced by mixing standard 40/60 pen bitumen with Rediset at two proportions. The dynamic viscosity of the samples was determined using a Dynamic Shear Rheometer (DSR). The results show that adding Rediset WMX can affect the flow behaviour of bitumen. This additive decreases the viscosity of the binders, especially over the temperature range of 100 to 150°C. This study mentions that the contribution of Rediset WMX to the change of viscosity became less with temperature increase from 100°C to 150°C.

Rediset WMX is a multifunctional additive for Warm Mix Asphalt. Rediset WMX comprises a dry chemical additive in solid pelletised form which is added to the bitumen before or during the mixing process (Zhang et al., 2012).

As mentioned before, Zaumanis & Haritonovs (2010) have conducted a laboratory study to evaluate two different WMA technologies including Sasobit wax and Rediset-WMX chemical additive. The results of the study and the charts associated with the behaviour and performance of the RedisetWMX-WMA mixtures have been presented in the previous section (Figure 2.34 to Figure 2.37).

While there is quite a few piece of research carried out on either Rediset LQ or Rediset WMX, looking at the results of studies on other WMA chemical additives (e.g. Evotherm) may be worthwhile to know the general influence of chemical additives on the properties of binder and behaviour of asphalt mixture.

Based on NCAT Report 06-02, regarding the evaluation of Evotherm chemical additive in WMA, it is concluded that adding Evotherm to the mixture decreases the air void content in the gyratory compactor. Moreover, Evotherm improves the compactability of the mixtures in both the gyratory and vibratory compactors due to a reduction of 1.4% in the air void content of the mixtures. The results of evaluating the rutting resistance of the mentioned WMA mixture indicated that using Evotherm would decrease the rutting potential considerably in comparison with the reference HMA. However, for the group of mixtures produced at lower temperatures, rutting potential had increased and this was believed to be related to the decreased ageing of the binder. It was also concluded that the WMA mixtures using Evotherm were less sensitive,

in terms of rutting, to the decreased production temperatures than the control hot mixtures (Hurley & Prowell, 2006a).

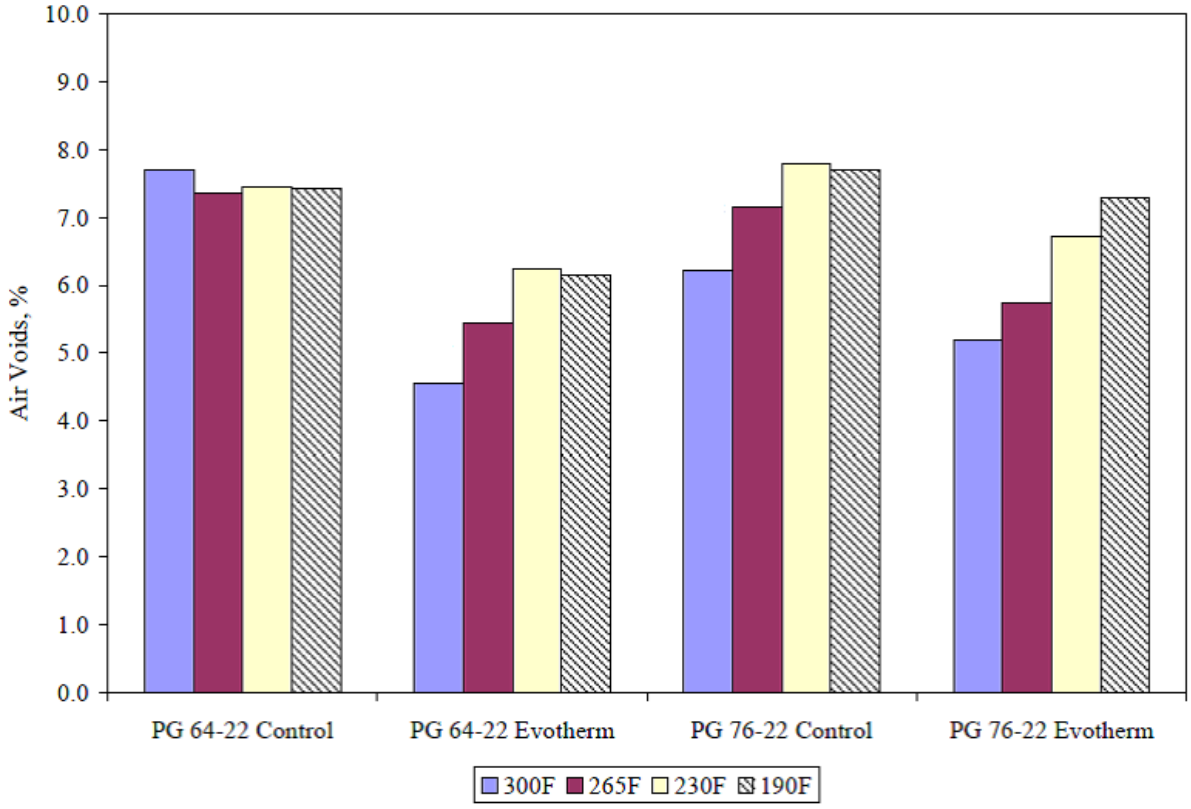


Figure 2.49 : Densification results over range of compaction temperatures (samples made using limestone) (Hurley & Prowell, 2006a)

As an inevitable occurrence, the lower production temperatures can result in incomplete drying of the aggregate which will leave some trapped water in the coated aggregate and may cause moisture damage or possibly a tender mixture. This phenomenon was reported in NCAT Report 06-02 by comparing the TSR value for the mixtures produced at different temperatures.

According to the laboratory compaction and rutting resistant results, NCAT Report 06-02, recommends a minimum mixing temperature of 129°C and a minimum compaction temperature of 110°C to produce WMA using Evotherm. It has also been recommended that in case of a mixing temperature lower than 129°C, the high temperature grade bitumen should be bumped by one grade to neutralise the tendency for increased rutting susceptibility with decreasing production temperatures.

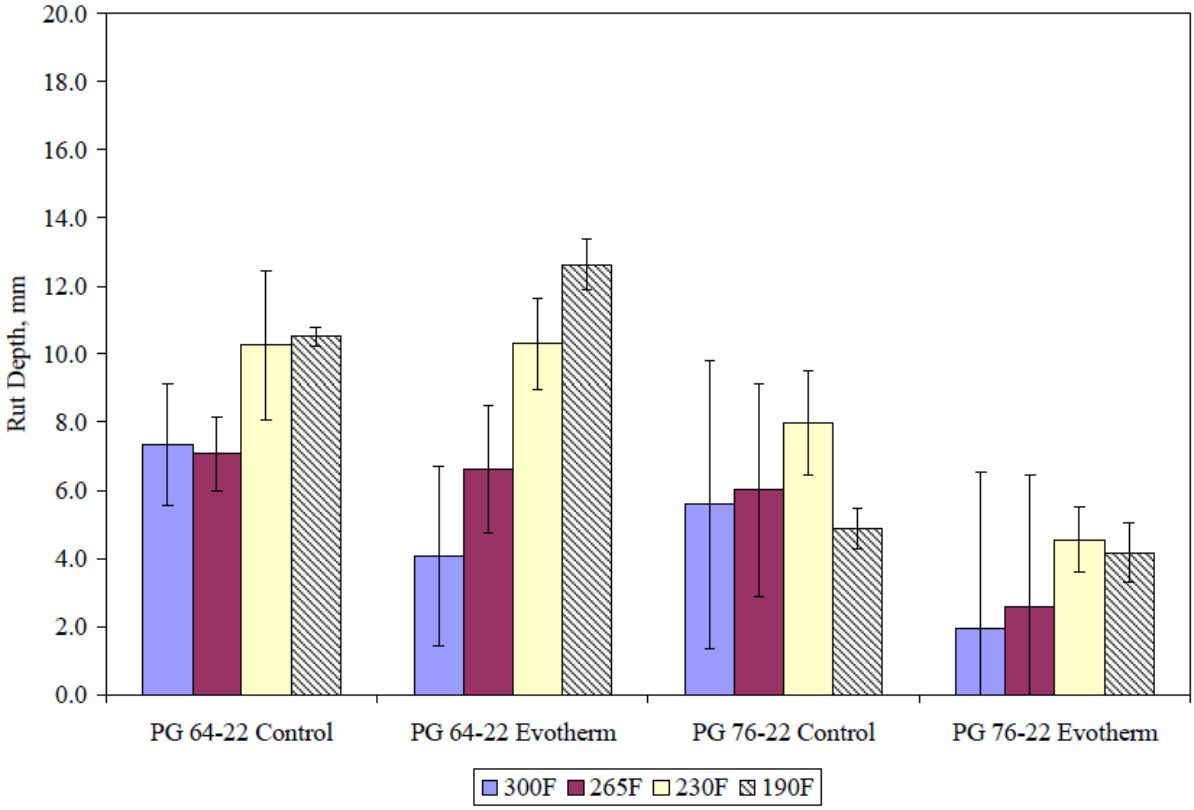


Figure 2.50 : APA rut depth (samples made using limestone) (Hurley & Prowell, 2006a)

2.12.COMPACTION of ASPHALT

Compaction is the process of densification or reducing the volume of a mass of a material. In the case of asphalt mixtures, compaction is a densification process during which air voids are reduced by packing aggregates closer to each other. Compaction locks the asphalt-coated aggregate particles together to achieve stability and provide resistance to deformation (or rutting) while simultaneously reducing the permeability of the mixture and improving its durability.

Bituminous binders are thermoplastic materials and their rheology (e.g. viscosity and shear stiffness) is highly sensitive to temperature. Adequately high temperatures, decrease their viscosity and resistance to flow, making them fluid enough to be able to coat aggregates during the mixing process of asphalt manufacture. Also, bituminous binder still needs to be hot enough to minimise resistance when the binder-aggregate mixture is being compacted in the lab or on the road. This is because moving of the aggregates through the compaction process requires the fluidity of the binder films connecting the aggregates together. In other words, the compaction process of an asphalt mixture is highly influenced by the viscosity of the bitumen

which itself is significantly controlled by temperature. In fact, the higher the binder temperature, the lower its viscosity is, the less it resists flow and the less the resistance to packing during the compaction process and vice versa.

However, serious attention should be paid to the fact that if bitumen is heated too much, the oxidation phenomenon and the volatilization of its lighter fractions may take place at such a high rate that can result in bitumen hardening.

It is logical to conclude that there is an optimum temperature range for asphalt construction. Most importantly, asphalt construction temperatures should not exceed what is needed to achieve sufficient density. In fact, there is a general agreement on the need for 'optimum fluidity temperature' for bitumen with regards to the process of mixing and compaction (TRB Report E-C105, 2006).

Referring to the Shell Bitumen Test Data Chart (Figure 2.27), which presents criteria indicating 'ideal' bitumen viscosities for optimal mixing and compaction of an asphalt concrete, is worthwhile:

2.12.1. LABORATORY COMPACTION METHODS of ASPHALT

Compaction of asphalt mixture is also influenced by the method of compaction (Swiertz, Mahmoud & Bahia, 2010). There are several methods to compact asphalt mixtures in the laboratory (Gyratory compactor, Roller/Slab compactor, Marshall compactor, Vibratory compactor, etc.).

The methods used in the current research were Gyratory compaction (according to BSEN 12697-31) and Roller/Slab compaction (BSEN 12697-33), which will be explained briefly in the following sections.

2.12.1.1. Gyratory Compactor

The Gyratory compactor is one of the most commonly used pieces of apparatus for the compaction of asphalt materials in pavement research laboratories. These devices are able to be set to compact for a certain number of gyrations or until a target mixture density or air void content is reached (Cooper Technology, 2016a).

In this device, compaction is obtained by applying a vertical stress (normally 600kPa) via end platens to a known mass of asphalt mixture, which is poured into a 100 or 150mm internal diameter gyro mould. The longitudinal axis of the mould is rotated (gyrated) at a fixed angle to the vertical whilst the platens are kept parallel and horizontal. During the compaction process, the height of the specimen is automatically measured and both the mixture density and air void content calculated (Cooper Technology, 2016a).



Figure 2.51 : (a) Cooper's Gyratory compactor (Cooper Technology, 2016a), (b) 100mm diameter Gyro mould

Based on BSEN 12697-31-2007, the Gyratory compaction method is considered to be the most realistic simulator of the compaction process that takes place in practice in the placement site. This method allows the aggregate particles to re-orientate themselves under the gyratory loading.

2.12.1.2. Slab Roller Compactor

The Slab Roller Compactor is equipment to compact asphalt mixtures in slab molds in the laboratory. This compactor applies loads which are equivalent to those of full-scale compaction equipment. Asphalt Slab Roller Compaction is considered to be a simulative method for

compacting laboratory specimens and results in slabs of bituminous paving materials with properties which closely simulate those of materials in the highway. The dimensions of the slabs are 305mm x 305mm with 40-100mm thickness (Cooper Technology, 2016b).

The process of compaction is performed by passing the molded asphalt mixture under a steel sector shaped roller load actuator for several times through a reciprocating action on a rail track. The number of passes (variable up to 10 cycles per minute) and the amount of load (30kN over 305mm roll width @ 7bar, 38kN @ 9bar) for each pass can be controlled in order to control the level of compaction. The compactor's roller may also be equipped with a heater to heat up the roller's metal surface in the case that the mixture's temperature is not desired to drop during the compaction due to the heat loss from the material's surface. Moreover, the actuator may be able to provide vibratory action (0-50Hz) along with the compaction. The mechanism can simulate the motion of a full-scale roller on the mixture. However, it is still different from what takes place in the field because the mold edges make the mixture's compaction boundaries confined via preventing the material being infinitively squeezed under the roller actuator. This issue does not happen in the actual field of compaction as there are mostly no barriers, other than the material's bulk itself, to confine the compaction boundary condition by stopping the asphalt being squeezed in front and on the sides of the roller during its motion. The compacted slab shaped sample may be cored for the purpose of having cylindrical specimens.



Figure 2.52 : Cooper's roller compactor; The left photo from Cooper Technology (2016b)

2.12.2. The EFFECT of COMPACTION METHOD on ASPHALT PROPERTIES

According to a study conducted by Hunter, McGreavy & Airey (2009) regarding the effect of compaction mode on the mechanical performance and variability of asphalt mixtures, it was concluded that in general, mould based compaction methods, Gyratory and Vibratory, would produce asphalt mixture specimens with greater stiffness and permanent deformation resistance in comparison with the specimens cored from Roller compacted slabs. This research showed that it was probably due to the boundary conditions of the moulds and their effect on the aggregate-bitumen-voids matrix (internal structure) of the compacted specimen. In addition, the research illustrated that changing the compaction parameters in the Gyratory could affect the mechanical properties of the asphalt mixtures. Regarding the stiffness modulus of the mixtures, in-situ-compacted specimens had mechanical properties that were more aligned with roller compacted specimens than Gyratory or Vibratory compacted specimens. However, on the matter of fatigue cracking resistance, the results of the research indicated that mode of compaction did not significantly affect this mechanical property.

Although this research gave valuable information regarding the effect of compaction methods on the mechanical performance of asphalt mixtures, the results can still be generalised to WMA mixtures because the rationale presented to interpret the results and observations have been totally independent of the mixture's materials and mixing and compaction temperatures.

It is reported in the study of Bonaquist (2011) that WMA has a better compaction potential because of decreased viscosity and less bitumen ageing in the production process. This general specification of WMA results in targeting a particular compaction level through fewer passes of the roller compactor machine and in a shorter compaction time. This can result in saving compaction energy and extending the compaction time which may be especially important for low temperature paving.

According to NCAT Report 05-04 and also a research by Walaa & Mogawer (2008), through a comparison between the compaction methods of the Marshall hammer and the Superpave gyratory compactor, it has been seen that the gyratory compactor manufactures samples with higher density than the Marshall Hammer compactor. However, both methods, in the case of Aspha-min and Sasobit, produced mixtures with slightly higher air void content than the control hot mix which had been compacted at 10°C to 20°C higher temperatures than the corresponding warm mixtures.

2.12.3. The EFFECT of COMPACTION TEMPERATURE on ASPHALT PROPERTIES

Whether in the field or in the laboratory, the temperature of asphalt mixture during compaction is of high importance for the compaction effort required (Bomag GmbH, 2009). During the compaction process, a mixture's cooling causes bitumen to experience progressive stiffening, which means the compaction effort needs to be increased and the lower the compaction temperature the more the compaction effort (Bomag GmbH, 2009).

Bomag GmbH (2009) believe that compaction of asphalt should, as a general rule, be started as soon as possible after the mixing phase in asphalt construction. They also recommend it is better that asphalt compaction takes place at temperatures between 100 to 140°C as according to them this range has been found most favourable for the conventional bitumen types. According to bomag GmbH (2009), compaction should be completed when the temperature has dropped to between 80 and 100°C.

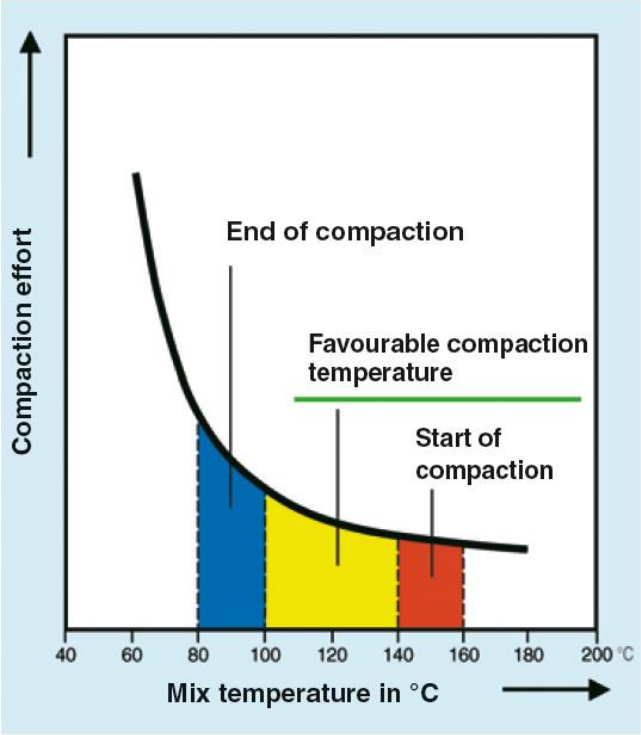


Figure 2.53 : The effect of compaction temperature on the compaction effort (Bomag GmbH, 2009)

According to NCAT Report Nr 06-02, it has been indicated that the gyratory compactor is insensitive to compaction temperatures and as a result, this method of compaction is not

recommended to be used for WMA evaluation. The NCAT report states that the Marshall Hammer compactor and the Vibratory compaction method give reliable results for simulating the service conditions at lower compaction temperatures.

According to the compaction results of the Vibratory compactor in this NCAT report for limestone at different temperatures, as shown in Figure 2.54, it can be found that all the investigated additives including Evotherm, Sasobit and Zeolite have decreased the Air Void content. Even at temperatures below 100°C, the void content for all of the WMA products is lower than that for the reference hot mix at a higher compaction temperature of 148°C. It is concluded that Evotherm has decreased the average air void content by 1.5%, Sasobit by 0.9% and zeolite by 0.8% in comparison with the reference hot mixture.

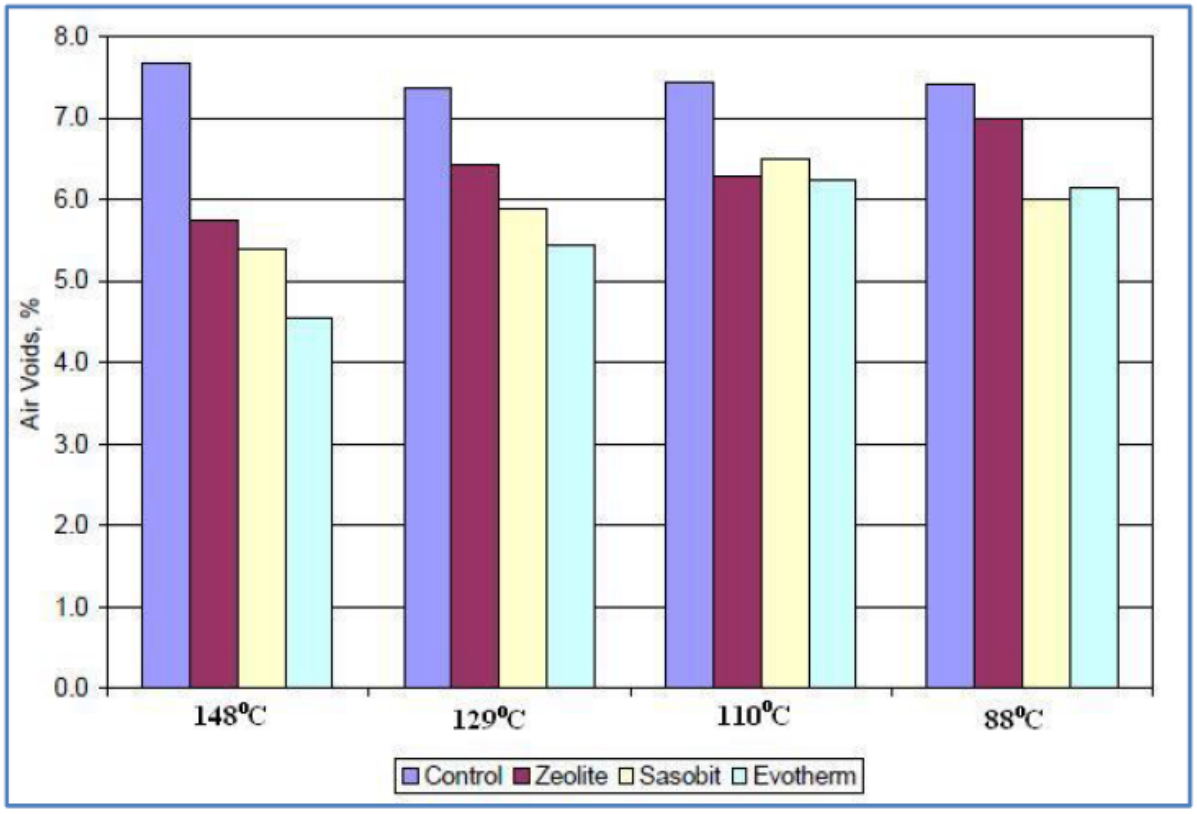


Figure 2.54 : Vibratory compaction results at different temperatures (Hurley & Prowell, 2006b)

Compaction in field trials for a mixture containing 3% Sasobit confirms that above the melting point of Sasobit, the compaction requires less effort and can be done at a lower temperature compared to HMA (Zaumanis, 2010). According to Zaumanis (2010), after only one pass of

the roller machine, a compaction degree of approximately 96% was obtained and with two Roller passes almost the highest possible density was targeted.

Supporting this, NCAT test track, paper No. 07-2514, through research on the Evotherm-modified WMA illustrated that the air voids had reduced by nearly 40% at a compaction temperature which was about 38°C lower than conventional HMA. However, it should be mentioned that the small difference between the aggregate gradation and the higher binder content (of about 1%) used in NCAT research might be partially the reason for such a conclusion.

In contrast with most of the reviewed literature, based on research performed by Kilas, Vatikus & Paliokaite (2010), an increased air void content for WMA in comparison with the reference HMA was reported. In this research, Sasobit, Evotherm and Advera-based WMA mixtures were tested in trial sections. The air void content of the cores from the in situ-mixtures was measured with a mean difference of 1.3% for Sasobit, 1.6% for Advera and 2% for Evotherm greater than measured 6.8% for the reference HMA.

Through field trials with Sasobit (in two sections) and Evotherm (in one section) in Virginia, Diefenderfer et al. assessed the compaction changes via measuring the air void content of the WMA cores during a period of two years from the time of the placement, after 3 months, 6 months, 1 year and 2 years. According to this investigation, although the air void content varied through time, no correlation between time and void content could be established. Moreover, no significant difference between any of the WMA sections and HMA control sections was observed. In addition, no clearly specific conclusions could be extracted regarding the relevance between the air void content of the cores and the location of the coring in terms of being in the wheel path or out of the wheel path. As a conclusion, it was suggested that after initial placement, no significant difference would occur in further compaction between HMA and WMA mixtures (Zaumanis, 2010).

According to the considerable contrast between the mentioned research projects, recommending the right compaction method for WMA, whether generally or for a particular technology and a specific additive, needs more research to be performed on WMA. However, it should be considered clear that different compaction methods have different levels of sensitivity to the compaction temperature and the volumetric properties and density of the mixture depend on the compaction method.

Another research work, which was discussed in the previous sections, also illustrates some aspects of cool/cold compaction on WMA or HMA performance in terms of rutting potential. Research performed by Prowell, Hurley & Crews (2007) evaluates Sasobit, zeolite and Evotherm for rutting resistance with an Asphalt Pavement Analyser (APA). In this research all of the mixes including control were compacted at four different temperatures. The test results in Figure 2.39 and Figure 2.40 show that the WMA processes do not increase rutting potential of an asphalt mix. The rutting potential is increased with reducing compaction temperatures for all samples, including control HMA and for both types of aggregates (i.e. granite and limestone). Therefore reduced resistance to permanent deformation was attributed to the lower ageing of the binders than to a particular WMA technology. Moreover, according to the results of this research, Sasobit-WMA mixtures had higher rutting resistance compared to other mixtures.

Figure 2.45 and Figure 2.46, as explained in the previous sections, include a chart provided by AkzoNobel, showing that firstly even at the compaction temperatures of as low as 105°C, Rediset LQ improves compactability of the asphalt mixture by a Gyration Ratio of 2.0. Secondly, Rediset LQ allows asphalt mixture to be compacted at 25°C below the compaction temperature of conventional HMA while resulting in the same compactability and volumetric properties.

Saedi (2012) performed research for the purpose of assessing the influence of various compaction temperatures on the properties of HMA.

This study indicates that temperature significantly affects the properties of Hot Mix Asphalt mixtures. The compaction method in this research was Marshall Compaction. According to Saedi's study (2012), increasing the compaction temperature up to a certain temperature (145°C in the case of the performed study) increases asphalt mixture's density, whereas at higher temperatures the density follows a declining trend.

The study concludes that increasing the compaction temperature makes the asphalt mixture's stability increase with its maximum rates taking place over the temperature ranges of 115-130°C and 130-145°C. In addition, for any mix designed through the Marshall Method, the study believes in a temperature named the 'Golden Temperature', at which the Marshall samples show the best performance. The Golden Temperature for the above study has been about 145°C. At this temperature, the viscosity of the used bitumen has been 280 centistokes.

Alonso et al. have studied the influence of compaction method and temperature on the mechanical properties of WMA mixtures. According to this study, comparing the two types of compaction (i.e. gyratory and Marshall), the gyratory samples have shown higher Indirect Tensile Stiffness Ratio (ITSR), lower stiffness moduli and lower Air Void content than their Marshall counterparts Figure 2.55 and Figure 2.56). Sanchez, Vega & Castro (2012) have been of the opinion that this issue is due to the increasing trend of the mixtures' AV content by reducing the compaction temperature.

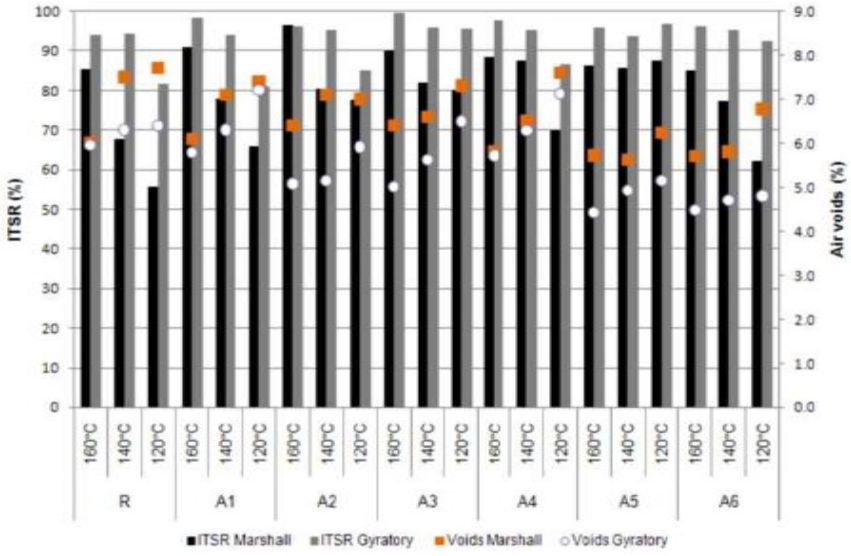


Figure 2.55 : ITSR and AV content of different manufactured mixtures (Sanchez, Vega & Castro, 2012)

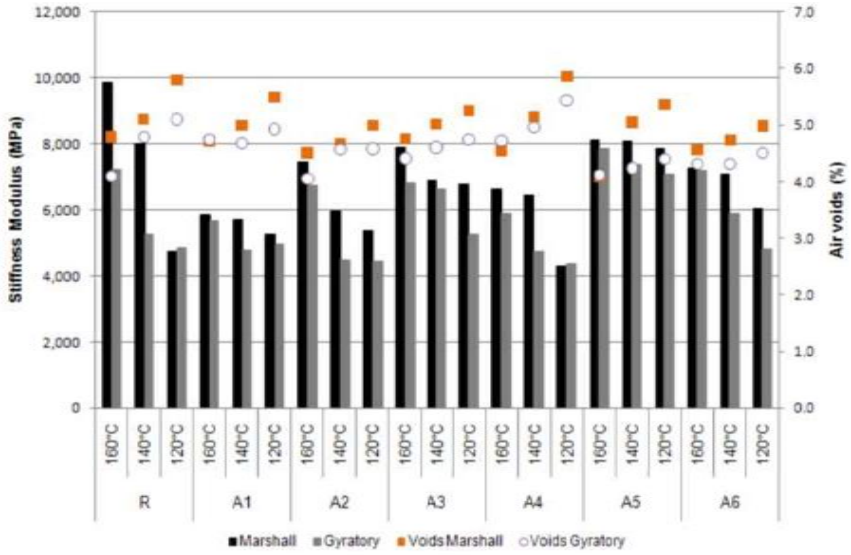


Figure 2.56 : Stiffness modulus and AV content of different manufactured mixtures (Sanchez, Vega & Castro, 2012)

Regarding the influence of compaction temperature, for both compaction methods the ITSR percentages and the stiffness moduli have decreased by reducing the compaction temperature. The study has related this issue to the increase of the mixtures' AV contents by decreasing the compaction temperature.

According to the study, in the case of both compaction methods, the use of additives has improved the ITSR compared to the reference mixture (R) which has experienced the same compaction temperature. The study argues that this issue is due to the improvement of binder-aggregate adhesion in the case of the chemical/surfactant additives (A1 to A4), the stiffening effect of the wax (A5) and the reduction of air void content in the case of zeolite (A6).

Sanchez, Vega & Castro (2012) conclude that in the case of the samples compacted by the Marshall compactor, the WMA samples compared to the reference HMA specimens show less variations in stiffness modulus by changing the compaction temperature. However, in the case of the gyratory samples, except for A5, the stiffness modulus of a WMA mixture group was more similar to that of the reference HMA compacted at the same temperature.

This means that the Gyratory method of compaction neutralises/offsets the effect of additives.

In this study, it was statistically determined and proved that the compaction method affected the mechanical properties of the asphalt mixtures.

Li, Liu & Su (2011) carried out a laboratory investigation on the volumetric properties of Evotherm chemical additive WMA mixtures compacted at seven different compaction temperatures including 170, 150, 130, 120, 110, 100 and 90°C (Figure 2.57 and Figure 2.58). The compaction methods used in the study were the Superpave gyratory compaction and the Marshall compaction methods. Measuring and analysing the volumetric properties as a function of temperature in this study showed that Evotherm could improve the compatability of the produced WMA mixture compared to the HMA reference. Statistics indicated an average reduction of up to 1.6 percent in the air void content of the WMA compared to the traditional reference HMA.

The results illustrate that by decreasing the compaction temperature, the air void content of those WMA specimen which have been compacted by the use of the Marshall Compactor have a more obvious increasing trend compared to the samples manufactured using the Superpave Gyratory Compactor (SGC) Figure 2.57.

On this matter, Li, Liu & Su (2011) are of the opinion that the observed trends indicate that Warm Mix Asphalt is sensitive to the temperature when the compaction method is Marshall. Moreover, they believe that the Marshall compaction method cannot reflect the advantage of WMA additives and according to this statement they conclude that this method of compaction is not suitable to produce WMA in the laboratory for the purpose of research.

However, this conclusion and argument does not seem to be correct as the author has looked at the issue from a prejudged and wrong view point. In fact, they have made their argument presuming that the results of gyratory compactor are correct and the reason for getting good compaction results by the gyratory compactor was the influence of the additives. However, the story should be some different in the sense that the gyratory compactor gave better results as it compacted the material regardless of the compaction temperature and probably additives. And the fact is the results of the Marshal compactor are reflecting what is closer to the performance of the additives at lower temperatures.

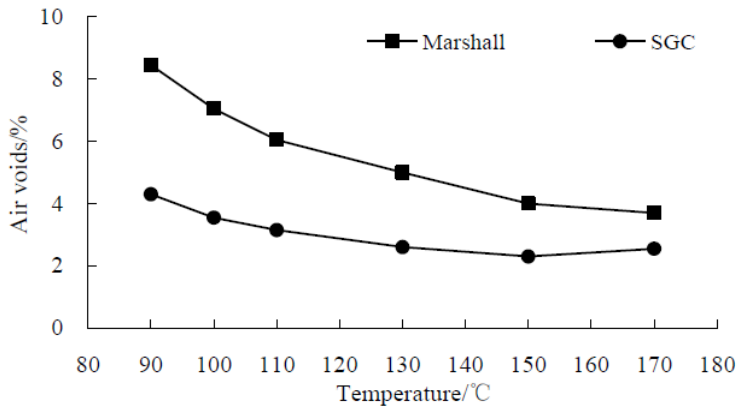


Figure 2.57 : The AV content of WMA samples compacted at different temperatures using two different compaction methods (Li, Liu & Su, 2011)

The results of the study showed that the Air Void content of the Warm Mix Asphalt samples compacted by the SGC very slightly increases by reducing the compaction temperatures from 150°C. In this regard, Li, Liu & Su (2011) suggest that the method of SGC is conducive to dense asphalt pavement for WMA.

The study recommends that the best compaction temperature of Evotherm-WMA is not lower than 125°C. On this matter, it is mentioned that the best compaction temperature of WMA and HMA compacted by SGC are 150°C and 170°C respectively. Moreover, it is recommended

that the compaction temperature of WMA can be more than 20°C below that of the reference HMA.

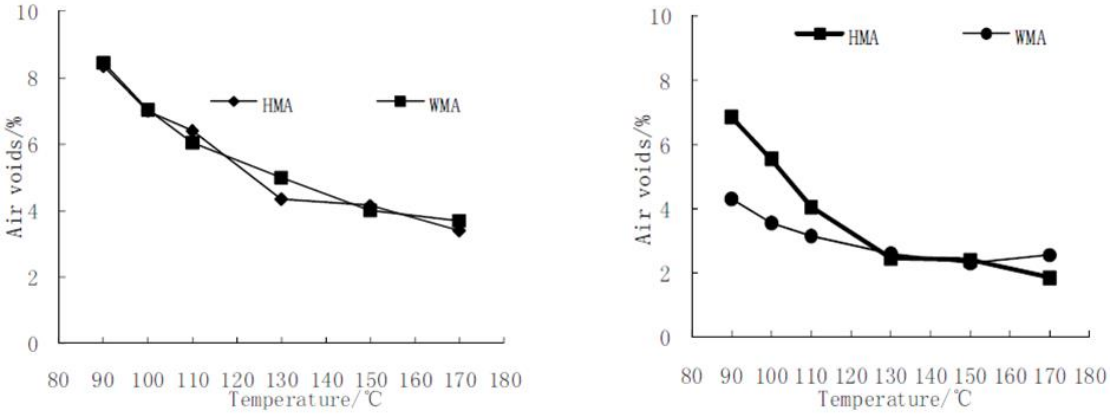


Figure 2.58 : The AV content of HMA and WMA compacted at different temperatures using Marshall Compactor (left graph) and SGC (right graph) (Li, Liu & Su, 2011)

2.13.CONCLUSIONS

Following the comprehensive literature review presented in this chapter, it can be realised that several WMA production technologies have been so far invented, (and still being further developed), which are mostly proprietary-based. All of these production methods can be divided into 3 main production technologies; wax, chemical additives and foaming technologies.

Through studying the literature, it has been understood that nearly all WMA technologies and additives have been developed in industry and the history of research performed on them is much shorter than their history of application in the real field. Moreover, the amount of research performed on studying various behavioural aspects and properties of WMA mixtures are not that considerable compared to other types of asphalt. In fact, it can be said that areas of research on WMA are still untouched and in some cases totally non-existent.

However, through studying the research work on WMA which was relevant to the selected topic of the present PhD research, the following points were found as the gaps which could potentially be covered by the current research:

- Using the gyratory compaction method, Zaumanis & Haritonovs (2010) believe that Sasobit or Rediset-WMX allows reduction of the compaction temperature of SMA from 155°C

for HMA to 125°C for WMA such that the samples made through both WMA technologies have approximately the same density as the reference HMA. Analysis of the Gyratory compaction data in this research showed that in order to produce the WMA samples, less compaction might be required to obtain the same density as HMA and following further compaction effort, even higher density than HMA might be achieved. The problem with Zaumanis & Haritonovs' study (2010) is the fact that the similar compaction results between HMA and WMA could be highly likely because of the use of a gyratory compactor to manufacture the mixtures. Therefore, it looks necessary to use another method of compaction to study the dependency of compaction results to temperature and material (additive). This is what has been performed in the present PhD research. Moreover, there is no cool-compacted or cool-produced HMA to investigate the effect of the presence of additives in mixture's properties when compacted at reduced temperatures. Therefore, in the present PhD research, a devised reference HMA will be used as a Non-standard HMA.

- Limited research such as Sanchez, Vega & Castro (2012) or Zaumanis & Haritonovs (2010) has been conducted on the effect of compaction temperature on the properties of asphalt. The work that has been done has mostly used the gyratory compaction method which is suspected to influence the temperature-dependant properties according to other research work. Therefore, in the current research, asphalt mixtures will be made using two different compaction methods including gyratory and slab roller compaction.

- Moreover, none of the research work on the mechanical performance of asphalt compacted at different temperatures has investigated the test results through fundamental means of study such as surface energy or binder-aggregate interactions. Therefore, SE investigations will be included in the present research as well as studying the results of fundamental tests such as PATTI on binder-aggregate interaction. This is for the purpose of helping with the explanations and reasons for the mechanical test results.

- The moisture sensitivity tests which were performed in the previous research reviewed had mostly been destructive and single phase. In order to increase the possibility of monitoring the behaviour of a certain material over the conditioning phases, a multi-phase non-destructive type of moisture sensitivity test has been devised and will be performed in the current research.

- No surface energy investigation has been performed on WMA additives. Therefore, in order to understand the nature and behaviour of the additive more precisely, this type of study

will be included in the current research. Therefore, in planning the current PhD program, it was seen necessary to:

- Include more than one method of compaction to manufacture the asphalt mixtures (i.e. gyratory and slab roller compaction methods) to more clearly reveal the effect of additives and behaviour of asphalt when compacted at reduced temperatures regardless of the compaction method,

- Accomplish more comprehensive comparisons between WMA and HMA to clarify the effect of additives,

- Perform surface energy investigations on the modified and virgin materials to understand the basics of the influence of the additives in the mixture, and

- Do modified-binder-aggregate interaction studies through mechanical tests.

3. MATERIALS AND TESTS

3.1. MATERIALS in USE

3.1.1. AGGREGATES

The aggregate materials, which have been used in manufacturing the asphalt mixtures in the current study, have generally been limestone. However, the limestone used to manufacture the Gyro specimens was provided from Dene quarry in Derbyshire in the UK, whereas, following the closure of the quarry in the middle of the current research in August 2013, to manufacture the rest of the specimens (i.e. Core specimens from the roller compaction slabs), the limestone aggregate was supplied from another quarry in Derbyshire, namely Tunstead.

Regardless of the aggregate type (in terms of quarry), the aggregate gradation used in the research was 0/14mm specified in accordance with BS EN 13043:2013 as shown in Figure 3.1 and Figure 3.2. The associated aggregate size proportions designed in order to achieve the target gradation for each type of the limestones are presented in Table 3.1.

Table 3.1 : Aggregate size proportions for Dene and Tunstead limestones

	PERCENT WEIGHT (%)	
AGGREGATE SIZE	DENE LIMESTONE	TUNSTEAD LIMESTONE
20 (mm)	0.0	0.0
14 (mm)	40.0	49.0
10 (mm)	0.0	0.0
6 (mm)	17.0	10.0
Dust	43.0	41.0
Sum	100.0	100.0

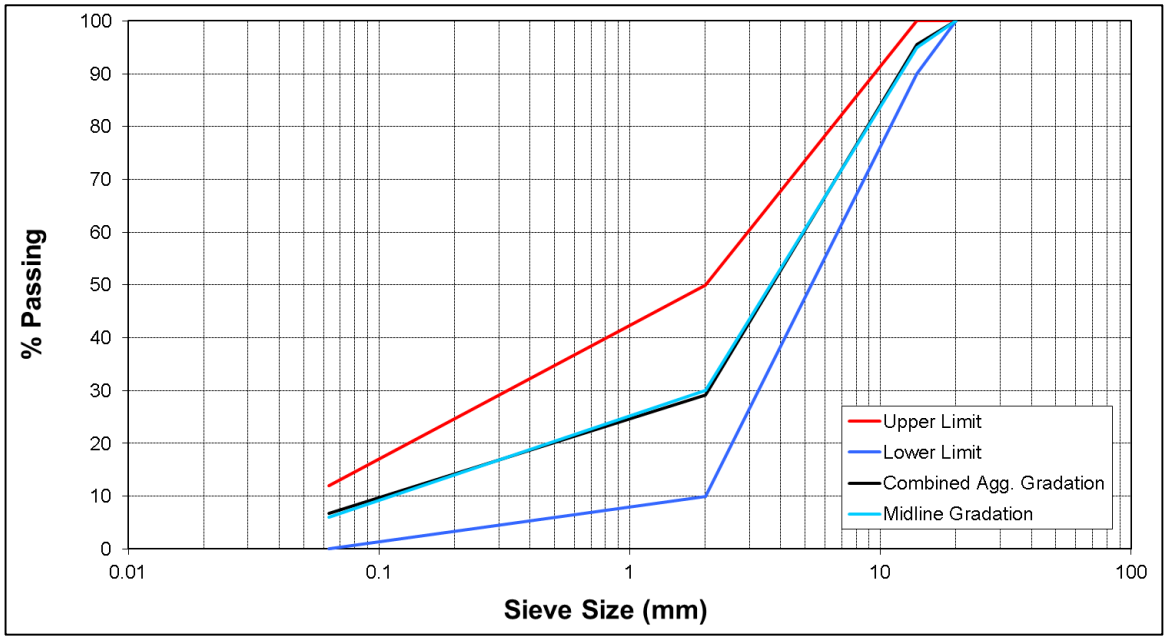


Figure 3.1 : Dene limestone aggregate gradation and 0/14mm size specifications

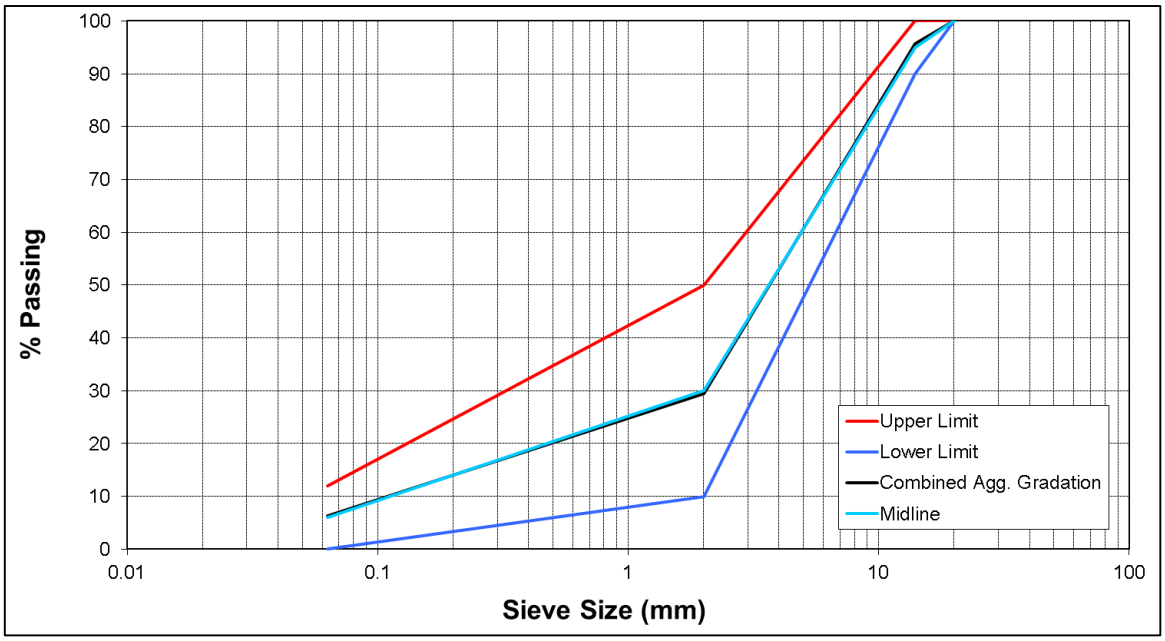


Figure 3.2 : Tunstead limestone aggregate gradation and 0/14mm size specifications

3.1.2. WARM MIX ASPHALT ADDITIVES (BITUMEN MODIFIERS)

In the present PhD research work,

1) **FTWax**, as an organic additive of asphalt, was used to produce Warm Mix Asphalt mixtures with 'wax technology'. In addition to be used to produce the FTWax-WMA mixtures, in order to perform the modified binder characterisation in this study, FTWax

was used to produce the FTWax-modified binders with different dosages (i.e. 2, 3 and 10% by mass of the binder). FTwax and its influence on bitumen characteristics, asphalt properties and performance (from the view point of other research work) have been introduced comprehensively in the previous sections.

Moreover,

2) **CatSurfLq** chemical additive has been used to produce Warm Mix Asphalt mixtures with 'chemical additives' technology. This liquid additive is in fact a chemical package of anti-stripping materials, surfactants (Surface Active Agents) and adhesion promoters. In addition to produce the CatSurfLq-WMA mixtures, in order to accomplish the binder characterisation phase of this research work, CatSurfLq was used to produce the CatSurfLq-modified binders with different dosages (i.e. 0.4, 0.5, 0.6 and 5% by mass of the binder). More information about this chemical additive of WMA and its influence on bitumen properties and asphalt performance, were presented through the previous sections and chapters.

3.1.3. PURE BITUMEN (VIRGIN BINDER) and MODIFIED BINDER BLENDS

The main virgin binder used in this research to manufacture the asphalt specimens was 70/100 pen bitumen made from blending 53.4% 160/220 pen bitumen with 46.6% 30/45 pen bitumen using a shear mixer. The base virgin binders which were used only in the case of supplementary tests were a 160/220 pen as an extremely soft and a 30/45 pen as an extremely hard bitumen. The modified binders in the current research included FTWax-modified and CatSurfLq-modified binders, which had been produced by adding three different dosages of FTWax (2, 3 and 10% by weight of the binder) and CatSurfLq (0.4, 0.5, 0.6 and 5% by weight of the binder) respectively, to each of the three different virgin binders. The overdosed modified binders (i.e. 10%FTWax and 5%CatSurfLq) were produced to have a clearer or an exaggerated effect of the associated additive on the studied property of the tested bitumen.

Among the mentioned modified binders, the 3%FTWax-modified and the 0.6%CatSurfLq-modified ones were chosen to be used in manufacturing the associated WMA mixtures. Therefore, they needed to be produced in the required quantities. Moreover, these two modified binders plus their pure base bitumen (70/100 pen) have been the only binders which were tested through the whole devised Binder Characterisation Test matrix (Table 3.6). The other dosages

and modified binders were only tested occasionally to provide more clarification (as will be realised in the next chapters).

The bituminous blends and modified binders had been prepared and made in accordance with BS EN 12594:2007. However, some modifications were applied to the recommendations for bitumen sample preparation in terms of bitumen's heating temperature and time. Heating time and temperature for the modified binders were considered the same as the virgin binder and not according to their softening point. This was due to the fact that according to the reports, in the current typical asphalt manufacture plants, the same production line for HMA is used to produce WMA and there are mostly no WMA-only asphalt plants that exist independently.

3.2. ASPHALT TEST SAMPLES MANUFACTURE SPECIFICATION

In this section, the specifications of the manufactured asphalt test samples will be comprehensively introduced.

3.2.1. SPECIMENS SPECIFICATIONS

3.2.1.1. Type

In this study, two different methods of compaction have been used to fabricate the asphalt test specimens. As mentioned before in the methodology, this was in order to avoid and understand the undesired likely effects of the compaction methods on the study results. Therefore, the test specimens, based on the compaction method through which they have been fabricated, have been divided into two main types:

1) **Gyratory specimens (Gyros)**, which have been compacted by a gyratory compactor in accordance with BS EN 12697-31
2) **Cored specimens (Cores)**, which are actually the cores taken from 306x306x100mm slab specimens compacted using a slab roller compactor in accordance with BS EN 12697-33

3.2.1.2. Geometry

The geometry of the test specimens in this study was cylindrical with 100mm diameter. They were initially fabricated with 100mm height whether compacted by gyratory compactor or

cored from the slabs of the roller compactor. However, later through the testing program, they were trimmed to 60mm or 40mm thick according to the dimension requirements of the test, which they were chosen for through the mixture testing order matrix (Table 3.8). Later in section 'Mixture Properties and Performance Testing' the reason for choosing the above geometry and dimensions will be explained completely.

3.2.1.3. Volumetrics

The target volumetric properties of the samples including Binder Content (BC) and Target Air Void content (TAV) have been selected in accordance with BS EN 13108-1:2006 as follows:

Table 3.2 : The volumetric specifications of different sample types

TYPE OF SPECIMEN	COMPACTION METHOD	BINDER CONTENT (%)	TARGET AIR VOID CONTENT (%)	TARGET DENSITY (Kg/m^3)	MAXIMUM DENSITY (Kg/m^3)	AGGREGATE TYPE	PARTICLE DENSITY (g/cm^3)
1. Gyratory	Gyratory Compaction	5.0	5.0	2365	2489	Limestone of Dene Quarry	2.689
2. Slab or Cores from Slabs	Slab Roller Compaction	4.6	8.0	2304	2504	Limestone of Tunstead Quarry	2.690

As can be seen in Table 3.2, the TAV value was selected at 8% for Slab specimens while it was 5% for gyratory specimens. This was for the purpose of creating more permeability in the specimens so the moisture sensitivity test could be performed with less difficulty and the effect of air void content on asphalt performance could be more clearly observed. In this respect, it should be mentioned that in practice, the actual AV content of a sample is usually obtained lower than what was targeted. As a matter of fact, as it can be seen in the next chapters, the majority of the gyro specimens manufactured in this research had such low AV contents that the consequent impermeability hardly let water permeate and saturate them during the vacuum saturation phase of the Revised Modified Lottman moisture sensitivity test. Following this experience, for the production of slab specimens, which took place after fabricating and testing gyro specimens, the TAV was increased quite significantly as justified above.

Also, for Slab specimens, the Binder Content was chosen 4.6% whereas for gyro samples it was 5%. This difference is due to the difference between the water absorption (and consequently bitumen absorption) of the two different types of aggregates, which were used to

manufacture the two various types of specimens. slab specimens were manufactured using Tunstead limestone with 0.4% water absorption (according to the aggregate specifications provided by the quarry) while Dene limestone had higher water absorption (i.e. 1.6% for 14mm and 10mm, 1.1% for 6mm and 0.89% for dust). As a result, the binder absorption of Dene limestone was higher than Tunstead limestone. Therefore, in order to have a similar effective binder content in the asphalt mixtures of both types of aggregates, the binder content of Tunstead samples (slab specimens) should be decreased. Following the conventional calculations on this matter, 4.6% binder content was worked out for Tunstead limestone as the equivalent binder content of 5% for Dene samples.

The above process to use equivalent effective binder content for both types of specimens was in order to minimise the negative effect of excessive binder in the mixture on the properties of the resulted samples (e.g. lowering the stiffness modulus) also to provide as much similarity as possible between the two types of specimens.

Regarding Table 3.2, it should be mentioned that for each of the two types of asphalt specimens (i.e. gyros and cores), the Maximum Density has been calculated in accordance with BS EN 12697-5:2009, having the Particle Density of the certain type of aggregate used, having the binder content, binder density (1.030 g/cm^3), aggregate gradation and the proportion of each aggregate size (as presented in previous section). The Target Density has been calculated having the Maximum Density and TAV for each specimen type.

3.2.2. COMPACTION METHODS

As mentioned before, through the laboratory operations, it was noticed that the gyratory compactor compacted the asphalt mixtures almost independently of the compaction temperature. Therefore, it was decided to add another compaction method to the research so the properties of mixtures, which might have been offset by the effect of the gyratory compaction method, could have the chance of revealing themselves.

In fact, this research is investigating the method of compaction along with studying the compaction at reduced temperatures. In this respect, Table 3.3 presents the compaction settings for each method of compaction.

It should be mentioned that in order to obtain the compaction settings, some trial specimens were manufactured to double check and make sure that the target volumetric properties would be achieved while gaining the desired thickness of 100 mm for both gyro and Slab samples.

Moreover, for all samples of a compaction method, the same settings of compaction were applied (i.e. the same number of gyrations for gyro samples and the same number and pressure of roller passes for the slab specimens). This was in order to make sure that the same amount of work would be given to all mixtures to compact them. In other words, the same amount of effort would be done to compact the different mixtures. By this means, the factors influencing the results of compaction at different temperatures became limited just to temperature and material.

Table 3.3 : Compaction settings for different compaction methods

TYPE OF SPECIMEN	COMPACTION METHOD	COMPACTION SETTING(S)
1. Gyratory	Gyratory Compaction	Maximum 300 Gyrations
2. Slab or Cores from Slabs	Slab Roller Compaction	10x25psi + 3x40psi + 90°Rotation + 2x25psi

3.2.3. MIXING and COMPACTION TEMPERATURES

In this research, the mixtures/samples of each compaction method have been fabricated in 10 different groups of samples (‘sample groups’) each of which within 11 specimens per sample group of gyratory compaction and 12 specimens per sample group of slab roller compaction, according to a devised matrix of manufacture temperatures (Table 3.4). The 10 devised ‘sample groups’ have been grouped into 4 main groups of mixtures (Mixture Groups) as follows:

1) Reference Standard HMA mixture group consists of 1 sample group
2) Non-Standard HMA group consists of 3 sample groups
3) FTWax-WMA mixture group consists of 3 sample groups
4) CatSurfLq-WMA mixture group consists of 3 sample groups

Moreover, inside each of the 4 Mixture Groups, in order to narrow down the affecting variables even more to only compaction temperature, the same:

- mixing temperature and
- additive type and dosage (in the case of WMA Sample Groups)

have been used.

A reference HMA mixture group was produced at the recommended temperature according to the recommended mixing temperature (i.e. 150°C) in Table 1 of BSEN 12697-35 in order to provide reference behaviour of a Hot Mix Asphalt mixture so other mixtures can be compared. The reference HMA was compacted at 140°C, according to the Standard recommendations, at 10°C lower than the recommended mixing temperature.

Three different groups of FTWax-WMA (3%FTWax-WMA) mixtures were included in the matrix of manufacture, all of which had the same mixing temperature of 135°C according to the most recommended temperature for this WMA production method in the studied literature. However, their compaction temperatures were different. The compaction temperatures were chosen in such a way that a wide range of temperatures could be covered including a recommended compaction temperature (i.e. 10°C below the mixing temperature) and a series of two reduced compaction temperatures with 20°C intervals (i.e. for FTWax-WMA 125, 105 and 85°C).

By this means, one of the reduced compaction temperatures was positioned at higher than water evaporation temperature i.e. 100°C and the other one was located at below the wax transition point.

As can be seen in Table 3.4, three different groups of CatSurfLq-WMA (0.6%CatSurfLq-WMA) mixtures were included in the matrix of manufacture, as well. All of them mixed at 130°C according to AkzoNobel, the additive supplier, recommendations but compacted at 3 compaction temperatures (i.e. for CatSurfLq-WMA 120, 100 and 80°C) according to the same theory mentioned in the case of FTWax-WMA sample groups.

The Standard HMA will be a reference to have a comparison between HMA and WMA. Moreover, a series of mixtures named Non-Standard HMA has been produced as another reference to study the HMA mixture's properties when manufactured at lower mixing and compaction temperatures. Moreover, the non-standard reference HMA mixture will be a

reference to understand and evaluate the influence of WMA additives on the properties of asphalt mixtures when they are compacted at lower temperatures.

All three non-standard HMA mixtures were mixed at 135°C. With regards to their compaction temperatures, as previously, they were compacted at three different temperatures forming a declining series of compaction temperatures from 125°C to 85°C with 20°C intervals.

In fact, in each Mixture Group, the only difference between the 3 Sample Groups is their compaction temperatures. However, in different Mixture Groups different additives have been used and the production temperatures may also be different. The logic behind such categorisation has been thoroughly explained in the Methodology.

In addition, following another dividing system will necessarily be used frequently in Chapter 6, there are 3 ‘Material Groups’ in this research include:

1) HMA,
2) 3%FTWax-WMA, and
3) 0.6%CatSurfLq-WMA

and 3 ‘Compaction Groups’ also names as ‘Temperature Groups’ include:

1) Hot-compacted (compacted at 140, 125 or 120°C),
2) Mid-range-compacted (compacted at 105 or 100°C), and
3) Cool-compacted (compacted at 85 or 80°C)

Table 3.4 : Grouping the asphalt specimens into the different devised Sample Groups and Mixture Groups

NO.	SAMPLE GROUP NAME	MIXTURE GROUP NAME	WMA ADDITIVE	ADDITIVE DOSAGE (% of BINDER MASS)	BINDER TYPE	MIXING TEMPERATURE (°C)	COMPACTION TEMPERATURE (°C)	NO. of SPECIMENS	
								GYRO	COCSLq from SLAB
1.	StdRefHMAM150C140	Standard Reference HMA	No Additive	N.A.	Pure Bitumen 70/100 Pen.	150	140	11	12*
2.	NStdHMAM135C125	Non-Standard HMA	No Additive	N.A.	Pure Bitumen 70/100 Pen.	135	125	11	12*
3.	NStdHMAM135C105						105	11	12*
4.	NStdHMAM135C85						85	11	12*
5.	3%FTWxWMAM135C125	3%FTWax-WMA	FT Wax	3.0	3%FTWax-Modified Bitumen 70/100 Pen.	135	125	11	12*
6.	3%FTWxWMAM135C105						105	11	12*
7.	3%FTWxWMAM135C85						85	11	12*
8.	0.6%CSLqWMAM130C120	0.6%CatSurfLq-WMA	CatSurfLq Chemical Additive	0.6	0.6%CatSurfLq-Modified Bitumen 70/100 Pen.	130	120	11	12*
9.	0.6%CSLqWMAM130C100						100	11	12*
10.	0.6%CSLqWMAM130C80						80	11	12*

* 2 Slabs per Sample Group and 6 CoCSLq Specimens per Slab

3.2.4. CUTTING/TRIMMING and CORING

The 'coring' operation has included taking cores from the slab specimens, fabricated in the roller compactor, in order to obtain the cylindrical test samples. In this study, six 100mm diameter cores were extracted from each 306x306x100mm^3 slab of asphalt (Figure 3.3).

Since the cored specimens, as well as the gyratory specimens had initially 100 mm thickness, in order to fit them into some of the test frames (e.g. ITSM, RLAT, ITFT, etc.) they needed to be trimmed from both sides so their thickness could be within the standard range of each of the tests. This operation is referred to as 'cutting' or 'trimming'. It should be mentioned that the same thickness has been cut from both ends of each specimen so the sample was taken from as far a distance as possible from the top and bottom of the mould to avoid the end effects. This could guarantee that the sample had been compacted at as a close temperature as possible to that targeted because the centre of the mould was expected to have less temperature loss through the compaction process.

In the case of the cored samples (from slabs), the location of the cores in the slabs of different sample groups was similar so they should have experienced similar compaction conditions. Moreover, the same tests and lab operations were allocated to the same core numbers of different 'sample groups' as presented in Table 3.5.

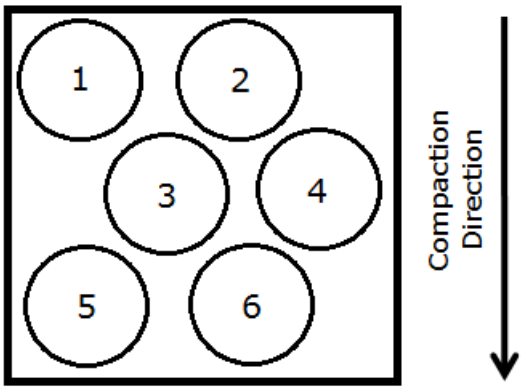


Figure 3.3 : Schematic plan of coring on slab specimens (i.e. No. S1 or S2)

Table 3.5 : Allocation of the lab tests to each coring location

SLAB NO.	LOC. On SLAB	CORE NAME	ALLOCATED LABORATORY TESTS/OPERATIONS
S1	1	C11	Trim60-Dimensions-Volumetrics-ITSM/ITCY-**Rev.Mod.Lottman**
	2	C12	Trim60-Dimensions-Volumetrics-ITSM/ITCY-Trim40-Dimensions-**ITFT**
	3	C13	Trim60-Dimensions-Volumetrics-ITSM/ITCY-Trim40-Dimensions-**ITFT**
	4	C14	Trim60-Dimensions-Volumetrics-ITSM/ITCY-**RLAT**
	5	C15	Trim60-Dimensions-Volumetrics-ITSM/ITCY-Trim40-Dimensions-**ITFT**
	6	C16	Dimensions-**DDCCSM**-Trim-Dimensions-Volumetrics-ITSM/ITCY-**RLAT**
S2	1	C17	Trim60-Dimensions-Volumetrics-ITSM/ITCY-**Rev.Mod.Lottman**
	2	C18	Trim60-Dimensions-Volumetrics-ITSM/ITCY-Trim40-Dimensions-**ITFT**
	3	C19	Trim60-Dimensions-Volumetrics-ITSM/ITCY-Spare
	4	C20	Trim60-Dimensions-Volumetrics-ITSM/ITCY-**Rev.Mod.Lottman**
	5	C21	Trim60-Dimensions-Volumetrics-ITSM/ITCY-Trim40-Dimensions-**ITFT**
	6	C22	Dimensions-**DDCCSM**-Trim-Dimensions-Volumetrics-ITSM/ITCY-**RLAT**

3.3. BINDER CHARACTERISATION TESTING

In order to determine the physical, mechanical and rheological behaviour and behavioural characteristics of the binders and also to study the binding, coating and surface energy properties, a comprehensive matrix of laboratory tests has been devised and performed as shown in Table 3.6.

Table 3.6 : Binder characterisation tests matrix

TEST	STANDARD	DESCRIPTION	APPARATUS	SETTINGS
1. Penetration Grade measurement	BS EN 1426:2007	Determination of Needle Penetration	Penetrometer	Test temperature: 25°C
2. Softening Point determination	BS EN 1427:2007	Determination of the Softening Point- Ring and Ball Method	Ring and Ball apparatus	N.A.
3. Fraass Breaking Point determination	BS EN 12593:2015	Determination of the Fraass Breaking Point	Fraass Breaking apparatus	N.A.
4. Brookfield Viscometry (BSEN-based)	BS EN 13302:2010	Determination of Dynamic Viscosity of Bituminous Binders Using a Rotating Spindle Apparatus	Brookfield Viscometer	Temperature sweep: 90°C to 180°C with 10°C intervals Meter Reading: (50±10)% Spindle size: SC4-34
5. Brookfield Viscometry (ASTM-based)	ASTM D4402 (2012)	Test Methods for Viscosity Determinations of Unfilled Asphalts Using the Brookfield Thermosel Apparatus	Brookfield Viscometer	Temperature sweep: 90°C to 180°C with 10°C intervals Rotational speed: 20 rpm Shear Rate: 6.8 s^{-1} Spindle size: SC4-27
6. Bitumen Wax Content evaluation	BS EN 12606-1:2007	Determination of the Paraffin Wax Content- Part 1: Method by Distillation Part 2: Method by Filtration	Standard laboratory Distillation and Filtration setup	N.A.
7. Complex Shear Stiffness Modulus and Phase Angle measurement using the Frequency-Temperature Sweep test	BS EN 14470:2012	Determination of Complex Shear Modulus and Phase Angle- Dynamic Shear Rheometer (DSR)	Dynamic Shear Rheometer (DSR)	Frequency sweep: 0.1Hz to 10Hz Test temperature range: 10°C to 75°C with 10°C intervals
8. Surface Energy measurement using the Dynamic Contact Angle (DCA) method	NTEC Test Protocol	Dynamic Contact Angle Measurement	Wilhelmy Plate	Test temperature: (23±2)°C Probe liquids: Glycerol, Di-Ionised water, Diiodomethane
9. Adhesive/Cohesive Tensile Strength evaluation using PATTI	ASTM D4541 (2010)		Pneumatic Adhesion Tensile Testing Instrument (PATTI)	Test temperature: 25°C

3.3.1. DETERMINATION of NEEDLE PENETRATION

The penetration grade test was performed in accordance with BS EN 1426:2007, in order to have the basic physical characteristics of the binders and the effect of each additive and their dosages on bitumen properties. According to the Shell Bitumen Handbook (Whiteoak & Read, 2003), the consistency of bitumen is commonly measured by this test, through which a needle of specified dimensions is allowed to penetrate into a sample of bitumen, under a known load (i.e. 100 g), at 25°C for a certain time (i.e. 5 sec). This test can be considered as an indirect

measurement of the viscosity of bitumen at 25°C. The test specifications are as shown in Table 3.6. The test results have been presented in the following chapter.

3.3.2. DETERMINATION of the SOFTENING POINT (RING and BALL METHOD)

The softening point test was performed in accordance with BS EN 1427:2007, in order to have the basic physical characteristics of the binders and the effect of each additive and their dosages on the binders' properties. This is in fact an empirical test used to determine the consistency of bitumen by measuring the equi-viscous temperature at which the consistency of bitumen is between solid and liquid behaviour. In this test, a 3.5 g steel ball is placed on a sample of bitumen contained in a brass ring. This set is suspended in a water or glycerol bath. The bath temperature is raised at 5°C per minute, the bitumen softens and deforms slowly until the ball falls through the ring. At the moment the bitumen and steel ball touch the 25 millimetre base plate below the ring, the water/glycerol temperature is recorded as bitumen's softening point. The test results on the various pure and modified bitumen samples have been presented in the following chapter.

3.3.3. DETERMINATION of the FRAASS BREAKING POINT

Bitumen brittleness plays an important part in many practical applications. The most usual test is the determination of the Fraass breaking point, which can be used to describe the behaviour of bitumen at low temperatures. In this test, a steel plaque (41mm x 20mm) coated with 0.5mm of bitumen is slowly flexed and released. The temperature of the plaque is reduced and recorded at 1°C per minute until the bitumen reaches a critical stiffness and cracks. The temperature at which the sample cracks is termed as 'the Breaking Point' and represents an equi-stiffness temperature. It has been shown that at fracture bitumen has a stiffness of 2.1×10^9 Pa which is approaching the maximum stiffness of 2.7×10^9 Pa. The Fraass breaking point determination tests have been performed in accordance with BS EN 12593:2015. The test results have been presented in the following chapter.

3.3.4. ROTATIONAL/BROOKFIELD VISCOMETRY TEST

In order to study the effect of the additives on the rheological behaviour of the binders, the Brookfield viscometry test was performed on the pure bitumen and modified binders over the temperature range of 90°C to 180°C. This test was accomplished in order to investigate the

viscosity of the binders at high temperatures and to study the changes in binder rheology due to the presence of the WMA additives near to the mixing and compaction temperatures. For this purpose, comparative temperature-viscosity charts for the various used binders were developed (as shown in the next chapter). This was also done to justify or find the correct production temperature of the studied WMA mixtures.



Figure 3.4 : Brookfield viscometer

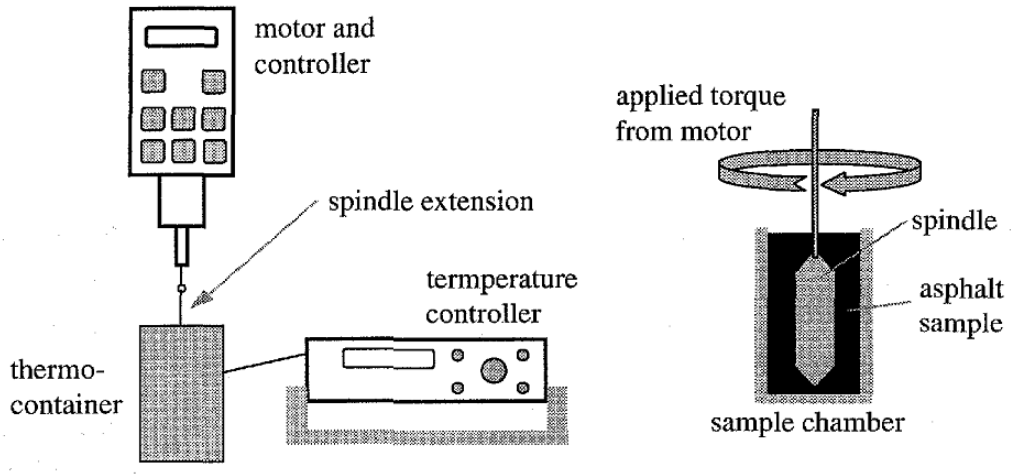


Figure 3.5 : Schematic drawing of a Brookfield viscometer (Osman, 2004)

As shown in Figure 3.4 and Figure 3.5, the rotational viscometer is linked to a digital controller which is used to automatically calculate the viscosity at the test temperature. The spindle is rotated submerged in the bitumen-filled cup at a constant rotational speed. The amount of torque applied by the rotary engine of the apparatus to obtain the constant rotational speed is measured, through which the magnitude of the resistant frictional force applied from the bitumen to the peripheral surface of the spindle is obtained. The resisting tension is developed by and obtained from the viscosity of the binder and this is a general description on how the Brookfield viscometer measures the viscosity of the test liquid (e.g. bitumen).

The Brookfield viscometry test and the associated sample preparation in this research were performed twice, based on two different Standards, BS EN 13302:2010 and ASTM D4402. The reason for this has been the considerable difference between the results of the test based on BS EN 13302:2010 for the FTWax-modified binders, with those of the NCAT Report 05-06, Yero & Hainin (2011) and Liu & Li (2012), which had been done in accordance with the ASTM Standards.

BS EN Standards validate choosing any rotational speed (rpm) for the spindle at which the meter reading remains between 10% and 100%. In the current research, BS EN-based Brookfield viscometry has been performed by using spindle SC4-34. At each temperature, the rotational speed was set to the value at which the meter reading stays between 10% and 100% with a preferred value of about 50(±10)%. However, SUPERPAVE (ASTM) recommends using spindle SC4-21 or SC4-27, rotating at a speed of 20 rpm to apply a shear rate of 6.8 s^{-1}. In this research the SUPERPAVE-based Brookfield viscometry has been performed using spindle size SC4-27. The test results have been presented in the next chapter.

3.3.5. BITUMEN WAX CONTENT TEST

The Bitumen Wax Content test was performed on the base binders in accordance with BS EN 12606-1:2007, because it was predicted that the bitumen might already have been waxy and adding more waxy additive to the existing amount in the bitumen might have no significant effect. In other words, bitumen samples might have been waxy themselves, which could result in decreasing the sensitivity of their viscosity to the extra wax content added in the form of FTWax to bitumen.

3.3.6. FREQUENCY-TEMPERATURE SWEEPS TEST

The rheological behaviour and properties of the pure and modified bituminous binders in this research were also studied by investigating their mechanical characteristics (i.e. *G** and phase angle) over a range of different temperatures (10°C to 75°C) and frequencies (0.1Hz to 10Hz) through performing the Frequency-Temperature Sweeps test using a Dynamic Shear Rheometer (DSR). The test and sample preparation was performed in accordance with BS EN 14770:2012. This oscillatory-type testing is generally conducted within the region of linear viscoelastic shear deformation. The bitumen sample, in the form of a layer, is prepared in accordance with BS EN 14770:2012 and sandwiched between a spindle and a base plate parallel to each other. The spindle is able to be rotated while the base plate is fixed. The temperature of the system can be accurately controlled by means of a fluid bath enclosing the whole environment around the bitumen. The test is performed by oscillating the spindle about its axis such that a radial line through point A moves to point B, then reverses direction and moves past point A to C, followed by a further reversal and movement back to point A (Figure 3.6). This oscillation includes one smooth, continuous cycle, which can be continuously repeated during the test (with different frequencies over a range of temperatures).

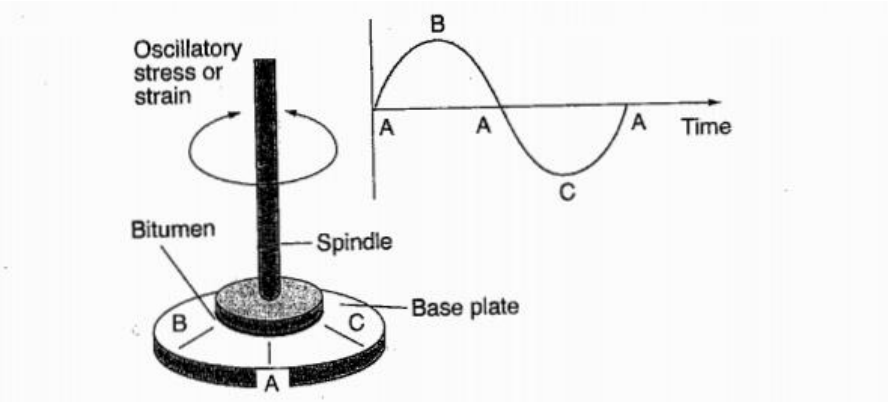


Figure 3.6 : Principles involved in Dynamic Shear Rheometer (Osman, 2004)

The test in this study was performed in strain-controlled mode. The complex shear stiffness modulus (*G**) is calculated as the ratio of shear stress to shear strain. The complex shear modulus, which provides a measure of the total resistance to deformation when the bitumen is subjected to shear loading, consists of an elastic (*G'*) and a viscous (*G''*) component and is defined as a complex number relating the amplitude and phase differences of stress and strain in harmonic oscillation such that:

$$G^* = G' + iG^{"} \qquad \text{Equation 3.1}$$

Where:

G^* = Complex modulus (GPa)

G' = Storage/elastic modulus (GPa)

G'' = Loss/viscous modulus (GPa)

i^2 = -1

The components are related to each other by means of the 'phase angle', which is the phase lag between the applied shear stress and the responding shear strain of the bitumen film during the test.

$$\delta = \tan^{-1}\left(G^{"}/G'\right) \qquad \text{Equation 3.2}$$

Where:

δ = Phase angle

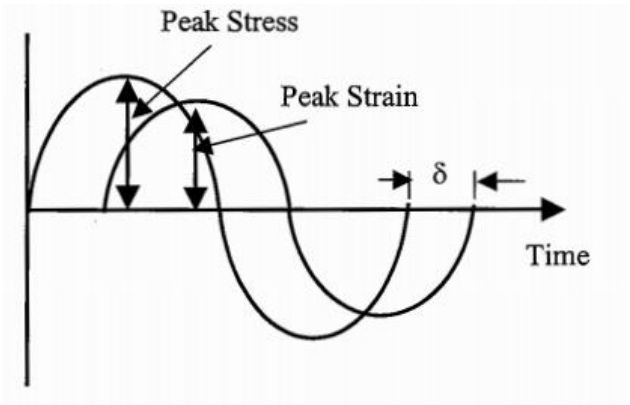


Figure 3.7 : Stress, strain and phase angle schematic definition in one cycle of oscillation (Osman, 2004)

It should be mentioned that the rheological behaviour investigations have been carried out for two main reasons. Firstly, to study the mechanical properties of the binder itself in the presence of additives at different temperatures and loading frequencies and secondly, in order to have sufficient fundamental support to analyse and interpret the mechanical behaviour of the resulting mixtures at the operating temperatures. This will also allow linking the behaviour of

the mixtures to the mechanical properties of their corresponding binders at the mixing and compaction temperatures at which the mixtures mechanical behaviour will be formed.

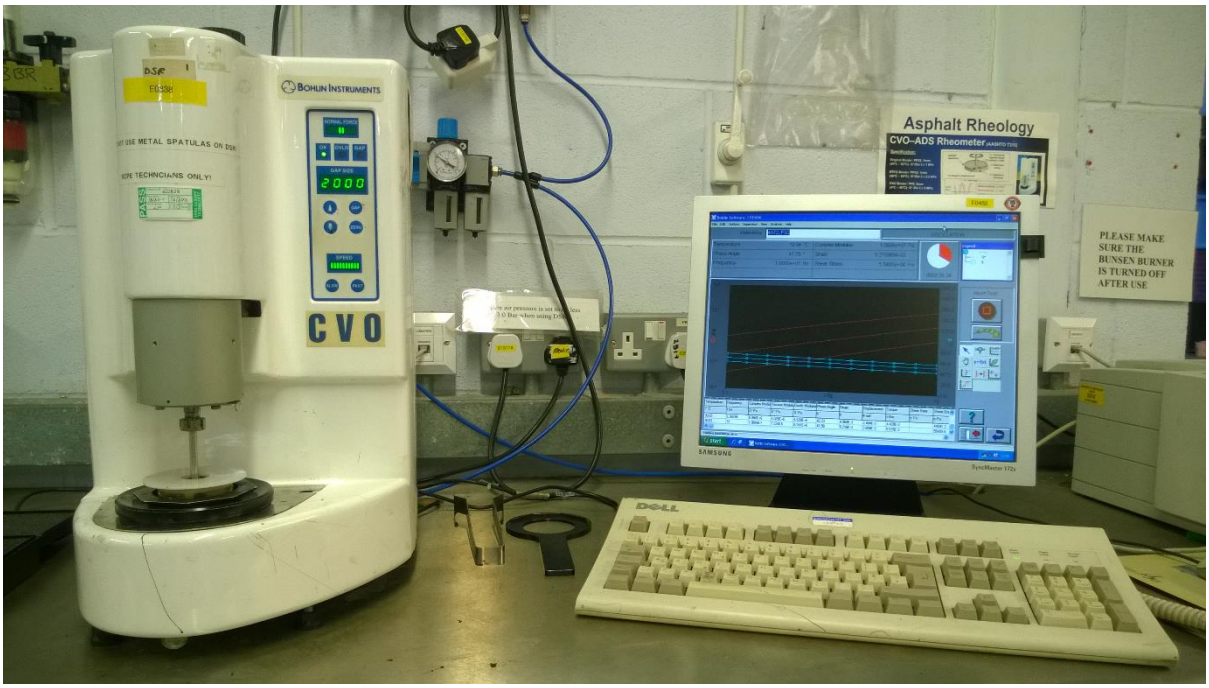


Figure 3.8 : Dynamic Shear Rheometer (left) and the data processor computer unit

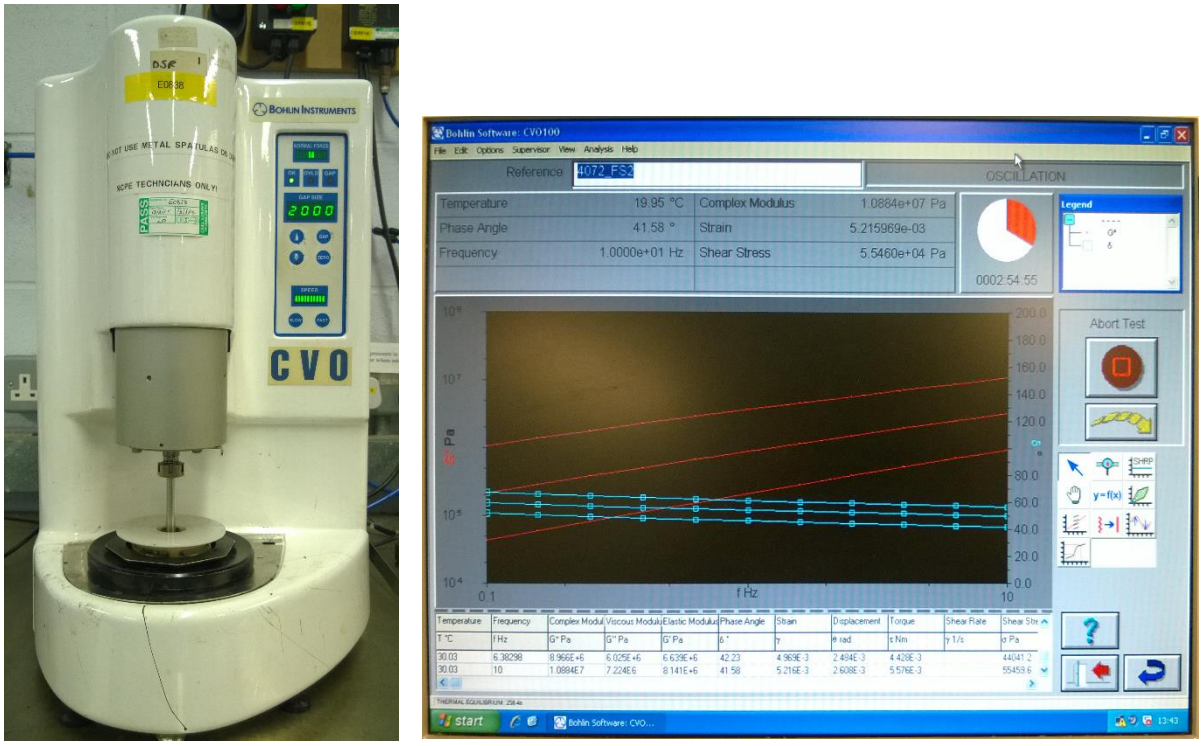


Figure 3.9 : Dynamic Shear Rheometer (left) and the data collector/processor computer unit

3.3.7. SURFACE ENERGY MEASUREMENT via DYNAMIC CONTACT ANGLE (DCA)

This fundamental test was performed to measure the values of the Surface Energy (SE) components of the various bituminous binders (pure and modified bitumen) used in the current research. By this means the influence of the WMA additives on the SE characteristics of the binders was studied. The measured values, combined with the ones of the aggregates (i.e. Dene limestone and Tunstead limestone), were used to calculate the binder-aggregate dry bond strength (Work of Adhesion) according to the basics of Surface Energy presented in the previous chapters. Moreover, having the above data in hand, the work of de-bonding in the presence of water is calculable in order to estimate the moisture sensitivity of the resulting mixtures.

Evaluating the Surface Energy parameters of the binders in the current research was carried out through the Dynamic Contact Angle (DCA) measurement method using the DCA analyser (Wilhelmy Plate apparatus). The test was performed in accordance with NTEC Test Protocol for Measuring the Dynamic Contact Angle Using a Wilhelmy Plate Analyser (cited in Ahmad 2011). In fact, the dynamic contact angle analyser measures the contact angle of the probe liquid with the substrate under dynamic conditions. This method is also referred to as the 'Tensiometric Contact Angle' technique.

In order to perform the test, a clean glass slide is coated by a layer of the test bitumen through dipping the slide into the melted hot bitumen sample. The cooled bitumen-coated glass slide is then hung from the balance of the Wilhelmy Plate apparatus using a crocodile clip. A beaker containing the probe liquid is placed under the glass slide in such a way that the bottom edge of the slide is kept parallel with the surface of the probe liquid (Figure 10). The slide is immersed and then withdrawn from the liquid at a constant speed, as shown in Figure 3.11 and the force involved is continuously measured and recorded.

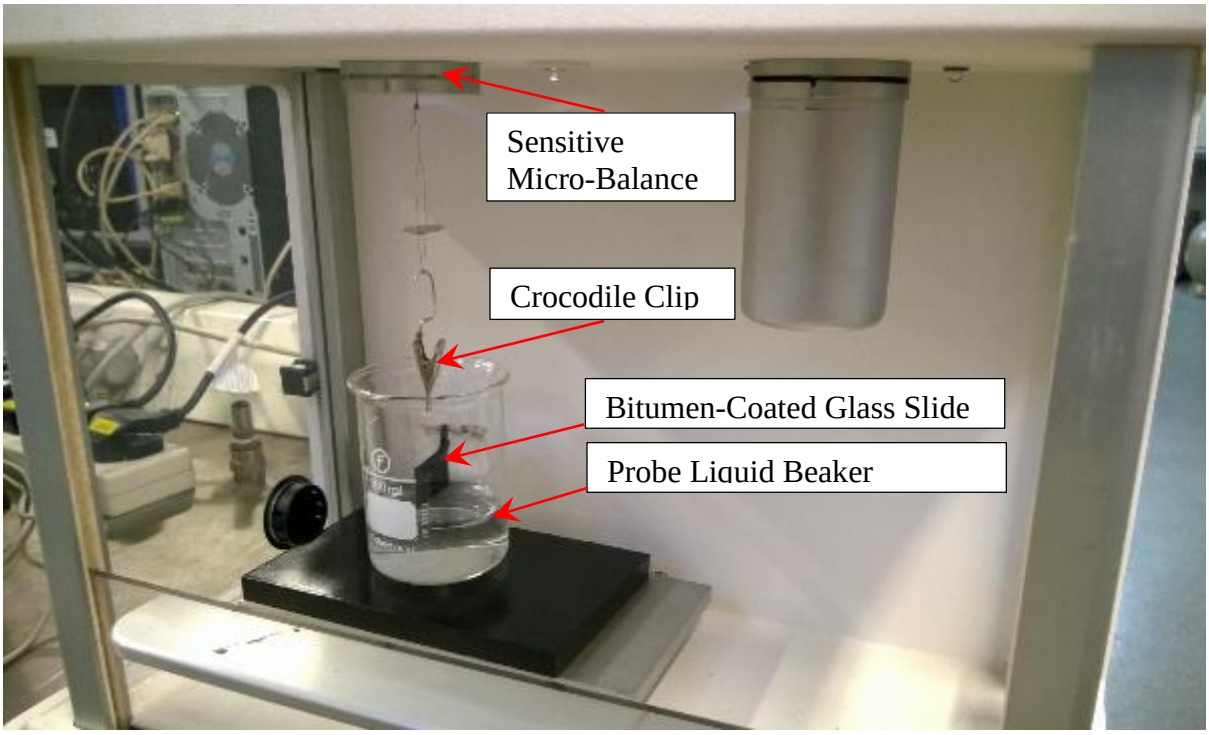


Figure 3.10 : Wilhelmy Plate DCA analyser apparatus

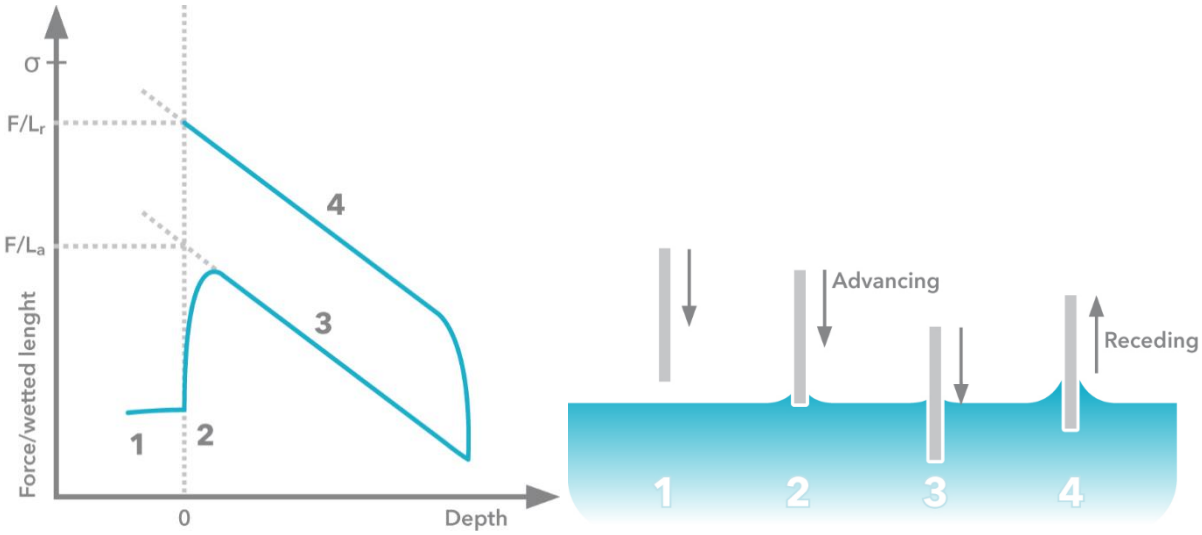


Figure 3.11 : Variation of Wetting Force versus Depth of Immersion during a DCA Test

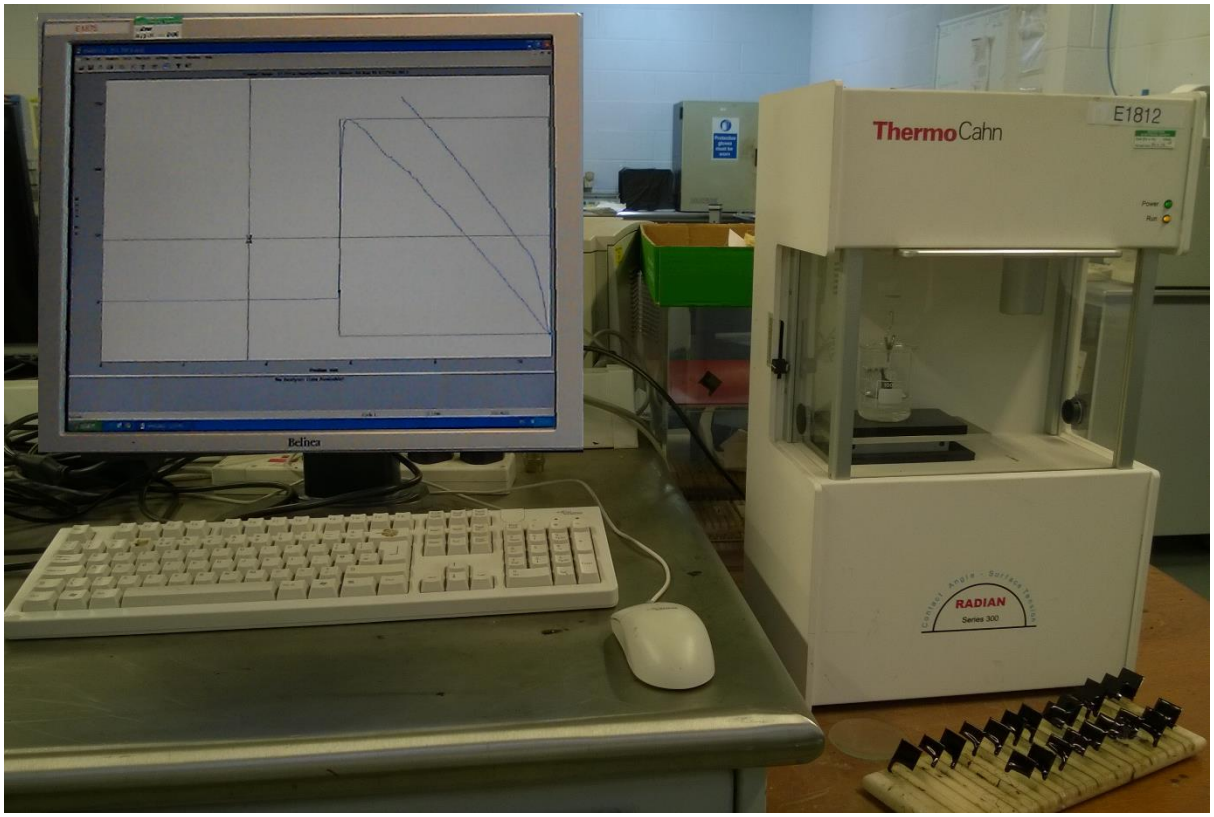


Figure 3.12 : DCA measurement test set; Analyser software (left) Wilhelmy Plate apparatus (right)

The value of force *F* applied during the immersion and withdrawal process is measured from the automatically controlled DCA analyser balance and the contact angle is calculated.

The contact angle value measured during the immersion of glass slide is referred to as the advancing contact angle while the value measured during the withdrawal of substrate is called the receding contact angle. As during the advancing movement the substrate is wetted by the probe liquid, the receding contact angle values are always less than the advancing ones. Therefore, always the advancing values are used in calculations.

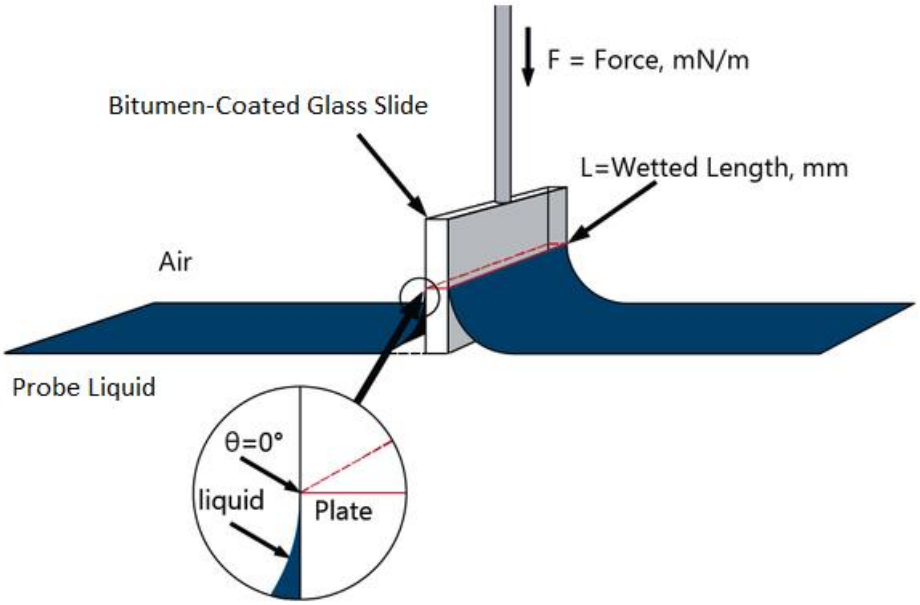


Figure 3.13 : Surface tension measurement using Wilhelmy Plate DCA method (Cahn DCA 315 Operator's Manual, 1999)

The contact angle (θ) values are obtained by using the following equation (Ahmad, 2011):

$$\sigma = F/(L.\cos\theta) \qquad \text{Equation 3.3}$$

Where:

σ= Surface tension

F = Force exerted by the plate

L = Wetted length

θ = Contact angle between the liquid and plate

$$\cos\theta = (\Delta F + V_{im}(\rho_L - \rho_{slide})g)/(P_t.\gamma_L) \qquad \text{Equation 3.4}$$

Where:

θ = Contact angle between the probe liquid and the bitumen-coated glass slide

ΔF = Difference between the weight of slide in air and partially submerged in probe liquid

V_{im} = Volume of the bitumen-coated glass slide immerged in probe liquid

ρ_L = Density of the probe liquid

ρ_{slide} = Density of slide

g = Constant of Gravity

P_t = Perimeter of the bitumen-coated glass slide

γ_L = Total surface energy of the probe liquid

Contact angle values for at least three probe liquids (i.e. water, glycerol and diiodomethane) are measured and applied to the associated equations presented in the previous chapter for the measurement of three surface energy components (i.e. $\gamma^+, \gamma^-, \gamma^{LW}$) of the test bitumen. As mentioned before, 3 equations are produced using the known surface energy components of the three probe liquids. The equations are then written in a matrix form in order to obtain the unknowns. In order to increase the precision of the results, 5 slides were prepared to perform the test on each binder sample. The test results and data have been presented in the next chapter.

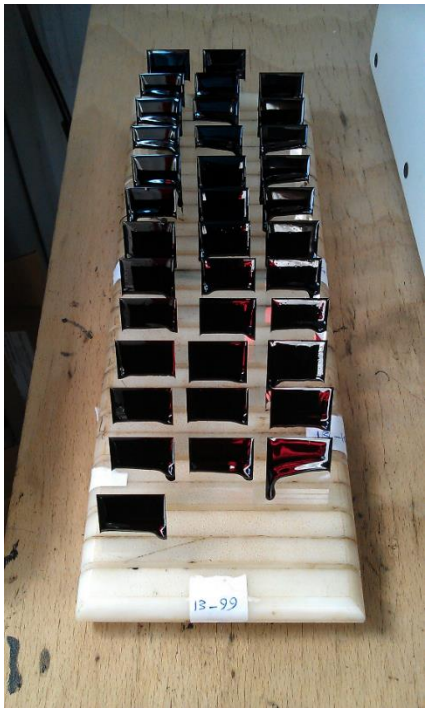


Figure 3.14 : DCA test samples (glass slides coated with bitumen) resting before being tested

3.4. SURFACE ENERGY of AGGREGATES via DVS TEST

It is difficult to use the contact angle technique on high surface energy materials like aggregates (SE values generally > 60mJ/m^2) as the liquids readily spread on high energy surfaces and it is difficult to obtain correct angle values (Ahmad, 2011).

Vapour sorption techniques are normally used for high surface energy materials. For this study a Dynamic Vapour Sorption (DVS) system has been used to measure the surface energy components of the aggregate. Probe vapours with known surface energy components are passed through the aggregate sample, under controlled temperature and pressure conditions, with the help of an inert carrier gas. Normally dry nitrogen is used as the carrier gas. On the basis of the surface characteristics of the aggregate, vapour probes get adsorbed at their surfaces which results in an increase in the mass of the aggregate sample. This technique is termed as gravimetric adsorption technique. The vapour mass adsorbed on the aggregate surface is measured for each solvent with the help of a sensitive balance. The probe liquids that have been used for the DVS testing are octane, ethyl acetate and chloroform (Ahmad, 2011).

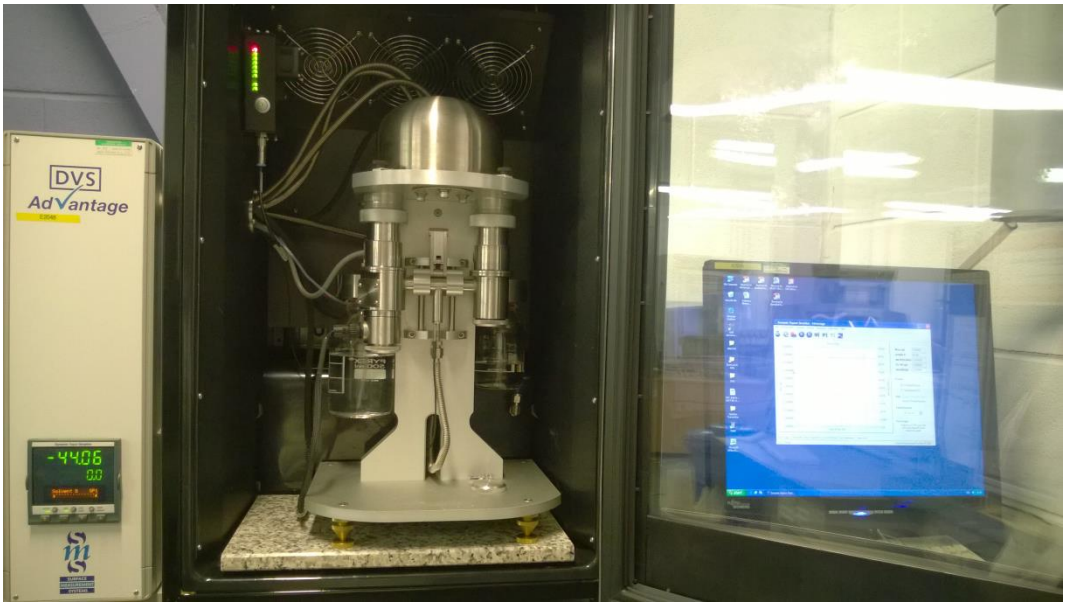


Figure 3.15 : A Dynamic Vapour Sorption (DVS) apparatus

The aggregates to be tested are first washed with deionised water and then dried in an oven. Aggregate fraction passing 5mm and retained on 2.36mm is generally used for the tests however, smaller size fraction can also be used. The upper limit on aggregate size is because of the material holding capacity of the sample chamber. The solvent/probe liquid vapours are passed through the aggregate. The balance measures the quantity of solvent adsorbed onto the surface of the aggregates/sample chamber. This method is comparatively suitable because it considers the irregularity in shape, and surface texture of the aggregates.

Here, the term adsorption means the adhesion of the liquid/vapour molecules on the surface of the aggregate and the specific surface area refers to the surface area per unit mass of the solid.

The specific surface area of the solid is determined by using the Brunauer-Emmett-Teller (BET) approach and is given by Equation 3.5.

$$A = \left(\frac{n_m N_0}{M}\right)\alpha \qquad \text{Equation 3.5}$$

Where:

A = Specific Surface Area of Solid (m^2)

n_m = Monolayer specific amount of vapour adsorbed on the surface of aggregate (mg)

N_0 = Avogadro's number = 6.022 x 10^{23} mol^{-1}

M = Molecular weight of the vapour (g/mol)

α = Projected or cross-sectional area of the vapour single molecule (m^2)

The number of vapour molecules adsorbed and required to from a monolayer on the solid surface is determined by using the Langmuir approach and is given by Equation 3.6:

$$\frac{P}{n(P_0 - P)} = \left(\frac{C-1}{n_m C}\right)\frac{P}{P_0} + \frac{1}{n_m C} \qquad \text{Equation 3.6}$$

Where:

P = Partial vapour pressure (Pa)

P_0 = Saturated vapour pressure of solvent (Pa)

n = Specific amount adsorbed on the surface of the absorbent, (mg)

C = BET constant (parameter theoretically related to the net molar enthalpy of the adsorption)

Adsorption of vapour molecules on the aggregate surface reduces its surface energy. So, spreading pressure as a result of adsorption of the vapour molecules can be expressed as:

$$\prod_e = \gamma_S - \gamma_{SV} \qquad \text{Equation 3.7}$$

Where:

$\prod_e$ = Spreading pressure at maximum saturated vapour pressure or equilibrium spreading pressure (erg/cm^2)

γ_S = Surface energy of aggregate in vacuum

γ_{SV} = Surface energy of aggregate after exposure to vapour

Spreading pressure at maximum saturation vapour pressure, $\prod_e$ for each solvent is calculated by using the following Gibbs free energy equation:

$$\prod_e = \frac{RT}{A}\int_0^{P_0}\frac{n}{P}dP \qquad \text{Equation 3.8}$$

Where:

R = Universal gas constant = 83.14 cm^3bar/mol.K

T = Absolute temperature (K)

By introducing spreading pressure, $\prod_e$, in Young-Dupres's relation, Equation 2.32, the following relationship is obtained:

$$W_{SL} = \prod_e + \gamma_{LV}(1+\cos\theta) \qquad \text{Equation 3.9}$$

As mentioned earlier, the contact angle value for high energy solids is zero, Equation 3.9 can be re-written as:

$$W_{SL} = \prod_e + 2\gamma_{LV} \qquad \text{Equation 3.10}$$

By substituting the above relation in Equation 2.25, the following equation is obtained:

$$2\gamma_L + \prod_e = 2\left(\left(\left(\gamma_B^{LW}\right)\left(\gamma_A^{LW}\right)\right)^{0.5} + \left(\left(\gamma_B^{+}\right)\left(\gamma_A^{-}\right)\right)^{0.5} + \left(\left(\gamma_B^{-}\right)\left(\gamma_A^{+}\right)\right)^{0.5}\right) \qquad \text{Equation 3.11}$$

Spreading pressures from three different probe vapours are measured in order to get the three surface energy components of the solid. It can be seen that regardless of the test method, the basic principle of calculation of surface energy components is the same.

3.5. MIXTURES PROPERTIES and PERFORMANCE TESTING

The asphalt laboratory performance tests in this research have been chosen in such a way that the planned matrix provides a full characterisation of the manufactured mixtures.

In addition, devising the sequence of the mentioned tests in the testing programme has been in such a way that the non-destructive tests were performed earlier in the beginning of the testing program and the destructive tests were accomplished later at the end of the testing spectrum.

By this means, each sample has had the chance of experiencing several performance tests and measurements, passing through the initial non-destructive tests staying undamaged for the later destructive testing. The devised order of testing provided as much characterisation as possible using as few specimens and materials as possible. In fact, by this policy, the results of various tests performed on each specimen were potentially linkable together with more confidence as they all had been performed on one sample through which the response of a given sample to a given test could be interpreted and justified by or traced back to other test results performed on the same sample. This increased the confidence for interpreting and justifying the behaviour of the specimens of a 'sample group' and made them more precise and comprehensive representative of the behaviour of the whole 'sample group' as possible.

In contrast, if the various tests considered to be performed to characterise asphalt mixture (i.e. 'sample group' here) were performed on different specimens of the 'sample group', this would mean the possible deviation of the mixture material's property from one specimen to another might be so significant that it could negatively influence the relation of the various performed tests in a sense that it would develop some uncertainty in linking the various test results.

Then, in order to be able to perform various tests on one sample as reasoned and explained above, the tests should also be chosen in such a way that they were compatible together in terms of their sample geometry and size as a given sample should fit all of them. To resolve this issue, the test types were mostly chosen within the Nottingham Asphalt Tester (NAT) system or other test types which could be performed on samples similar or compatible to NAT/NU14 machines in terms of general geometry and size (i.e. cylindrical with 100 mm diameter).

According to this policy, the following set of asphalt laboratory tests was devised and accomplished on the asphalt samples in the present research.

Table 3.7 : Mixture characterisation tests matrix

TEST	STANDARD	DESCRIPTION	APPARATUS	SETTINGS
1. Bulk density measurement using the Sealed Specimen method (Aluminium foil)	BS EN 12697-6:2012	Test Methods for Hot Mix Asphalt-Part 6: Determination of Bulk Density of Bituminous Specimens	N.A.	N.A.
2. Air Void Content determination	BS EN 12697-8:2012	Test Methods for Hot Mix Asphalt-Part 8: Determination of Void Characteristics of Bituminous Specimens	N.A.	N.A.
3. Indirect Tensile Stiffness Modulus (ITSM) evaluation using the ITSM/IT-CY test	BS EN 12697-26:2012	Test Methods for Hot Mix Asphalt-Part 26: Stiffness	Nottingham Asphalt Tester (NAT/NU14)	Test temperature: 20°C Strain controlled: 5 micron Load pulse Risetime: 124 ms Test mode: ITSM/IT-CY Sample thickness: 60mm
4. Fatigue Resistance assessment using Indirect Tensile Fatigue Test (ITFT)	BS EN 12697-24:2012	Test Methods for Hot Mix Asphalt-Part 24: Resistance to Fatigue	Nottingham Asphalt Tester (NAT/NU14)	Test Temperature: 20°C Load Pulse Risetime: 124 ms Test Mode: Stress Controlled Sample thickness: 40mm
5. Permanent Deformation/ Rutting Potential evaluation using the Repeated Load Axial Test (RLAT)	BS DD 226:1996	Method for Determining Resistance to Permanent Deformation of Bituminous Mixtures Subject to Unconfined Dynamic Loading	Nottingham Asphalt Tester (NAT/NU14)	Test temperature: 40°C Test stress: 100 kPa Loading form: Trapezoidal Rest period: 1 sec Load pulse width: 1 sec Number of load pulses: 1800 Sample thickness: 60mm
6. Complex Stiffness Modulus and Phase Angle measurement using the devised Direct Dynamic Compressive Complex Stiffness Modulus (DDCCSM) test	A devised mode and setting based on AASHTO TP 62-03 (2007)	A devised mode and setting of Standard Method of Test for Determining Dynamic Modulus of Hot Mix Asphalt Concrete Mixtures	Nottingham Asphalt Tester (NU14) with Cooper's Universal software and using RLA test frame and LVDTs	Test Temperatures: 10, 20 (Ref.) and 30°C Test stress: 100 kPa Loading form: Sinusoidal Loading Frequencies: 0.1, 0.5, 1, 5, 10 and 25Hz Sample thickness: 100mm
7. Moisture Sensitivity evaluation using the devised Revised Modified Lottman Water Sensitivity test	A devised mode and setting based on AASHTO T283 (2007)	A devised mode and setting of the Modified Lottman test, Standard Method of Test for Resistance of Compacted Asphalt Mixtures to Moisture-Induced Damage	A set of standard asphalt laboratory apparatus including: Vacuum-saturation pump and facilities, Temperature-controlled circulating water bath, -10°C Freezer, Nottingham Asphalt Tester (NAT/NU14)	Vacuum saturation: @ 35 mbar for 0.5 hr Water bath: @ 60°C for 24 hrs Optional water bath: @ room temperature as Long as getting 60-80% saturation (if necessary) Freezer: @ -10°C for 24 hrs ITSM/IT-CY test temperature: 20°C

Moreover, the chosen asphalt sample tests were performed in accordance with the following devised laboratory testing order schedule.

Table 3.8 : Testing/laboratory tasks order in each sample group

SPECIMEN NO./NAME	ORDER of TESTING/PREPARATION on the SPECIMENS in EACH SAMPLE GROUP (FOLLOWING COMPACTION)								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Gyro: 1, 2 & 3 Core: C11, C17 & C20	Trimming to 60mm thickness	Bulk Density & Air Void Content measurement	Dimension measurement (Average diameter and thickness)	Conditioning @ 20°C for min 6 hrs, Perform the ITSM/IT-CY test	Perform the Revised Modified Lottman Test				
Gyro: 4, 5, 6, 7 & 8 Core: C12, C13, C15, C18 & C21	Trimming to 60mm thickness	Bulk Density & Air Void Content measurement	Dimension measurement (Average diameter and thickness)	Conditioning @ 20°C for min 6 hrs, Perform the ITSM/IT-CY test	Trimming to 40mm thickness	Photography	Dimension measurement (Average diameter and thickness)	Conditioning @ 20°C for min 6 hrs, Perform the ITFT	Photography
Gyro: 9 Core: C14	Trimming to 60mm thickness	Bulk Density & Air Void Content measurement	Dimension measurement (Average diameter and thickness)	Conditioning @ 20°C for min 6 hrs, Perform the ITSM/IT-CY test	Photography	Conditioning @ 40°C for min 6 hrs, Perform the RLA test	Photography		
Gyro: 10 & 11 Core: C16, C19 & C22	Dimension measurement (Average diameter and thickness)	Conditioning @ test temperatures for min 6 hrs, Perform the DDCCSM test	Trimming to 60mm thickness	Bulk Density & Air Void Content measurement	Dimension measurement (Average diameter and thickness)	Conditioning @ 20°C for min 6 hrs, Perform the ITSM/IT-CY test	Photography	Conditioning @ 40°C for min 6 hrs, Perform the RLA test	Photography

3.5.1. BULK DENSITY DETERMINATION (ALIMINIUM FOIL METHOD)

This test has been performed in accordance with BS EN 12697-6:2003, using the Aluminium Foil (sealed specimens) method in order to measure the bulk density of the specimens and their air void content (AV content). The test consisted of the following steps:

- Measure the dry weight of the sample in air
- Measure the dry weight of the Aluminium foil wrapped sample in air
- Measure the Aluminium foil wrapped sample when it is immerged in water
- Measure the water temperature during the test and extract its associated density accordingly
- Carry out the following calculations in order to obtain the bulk density and AV content of the sample:

$$\rho_{bsea} = m_1/\left(((m_2 - m_3)/\rho_W) - ((m_2 - m_1)/\rho_{sm})\right) \qquad \text{Equation 3.12}$$

$$AVC\ (\%) = 100\ (\rho_m - \rho_{bsea})/\rho_m \qquad \text{Equation 3.13}$$

Where:

ρ_{bsea} = Bulk density of the specimen obtained from sealed method (kg/m^3)

m_1 = Mass of dry specimen in air (g)

m_2 = Mass of sealed specimen in air (g)

m_3 = Mass of sealed specimen in water (g)

ρ_W = Density of water at test temperature (kg/m^3)

ρ_{sm} = Density of the sealing material (i.e. aluminium foil) at test temperature (kg/m^3)

AVC = Air Void Content of the specimen (%)

ρ_m = Maximum density of the mixture (kg/m^3)

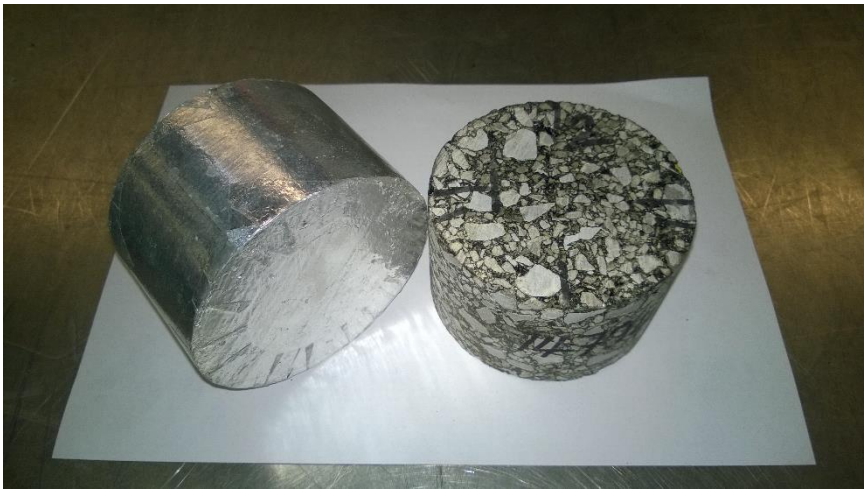


Figure 3.16 : Aluminium foil wrapped and sealed specimen (left)

According to Archimedes rule, the sample, when immerged in water, becomes lighter as much as the weight of the same volume of water as its volume. Therefore, by immersing the specimen in water, the exact volume of the specimens can be measured and calculated. In order to prevent the water permeating the specimen voids replacing the air in samples' voids, they have to be sealed using tight aluminium foil wrapping.

The test results indicate the compactability and permeability of the samples. This test is non-destructive and the samples can be used for other tests. Therefore, the test has been done after manufacture, coring (if necessary) and cutting. In fact, after measuring the sample dimensions, this is the first test which should be done as it is desired to have volumetric information as close as possible to the manufacture time because even performing the non-destructive tests may influence the volumetric properties.



Figure 3.17 : Weighing a sealed sample in water

In this research study, in order to have a complete record of the volumetric properties of all manufactured samples (i.e. Gyro cores and slab cores), this test was performed on all specimens after the coring (in the case of Roller compaction) and cutting stages, when their dimension measurement was finished.

3.5.2. INDIRECT TENSILE STIFFNESS MODULUS (ITSM) TEST

Stiffness modulus is one of the most fundamental properties of asphalt mixtures, which is used as an important input data for pavement design and evaluation of asphalt materials. The term ‘stiffness’ or ‘stiffness modulus’ has been used by Van der Pol to define the stress to strain ratio of bitumen and to avoid using the ‘elastic modulus’ (i.e. Young’s modulus), which is the stress directly proportional to strain and independent of the strain rate for perfect elastic materials.

In order to measure the stiffness modulus of the manufactured asphalt specimens in the present research, as a very commonly used method, the Indirect Tensile Stiffness Modulus test on cylindrical specimens (ITSM/IT-CY) has been performed. The test has been carried out in a

Nottingham Asphalt Tester (NAT/NU14) and in accordance with the criteria of BS EN 12697-26:2012.

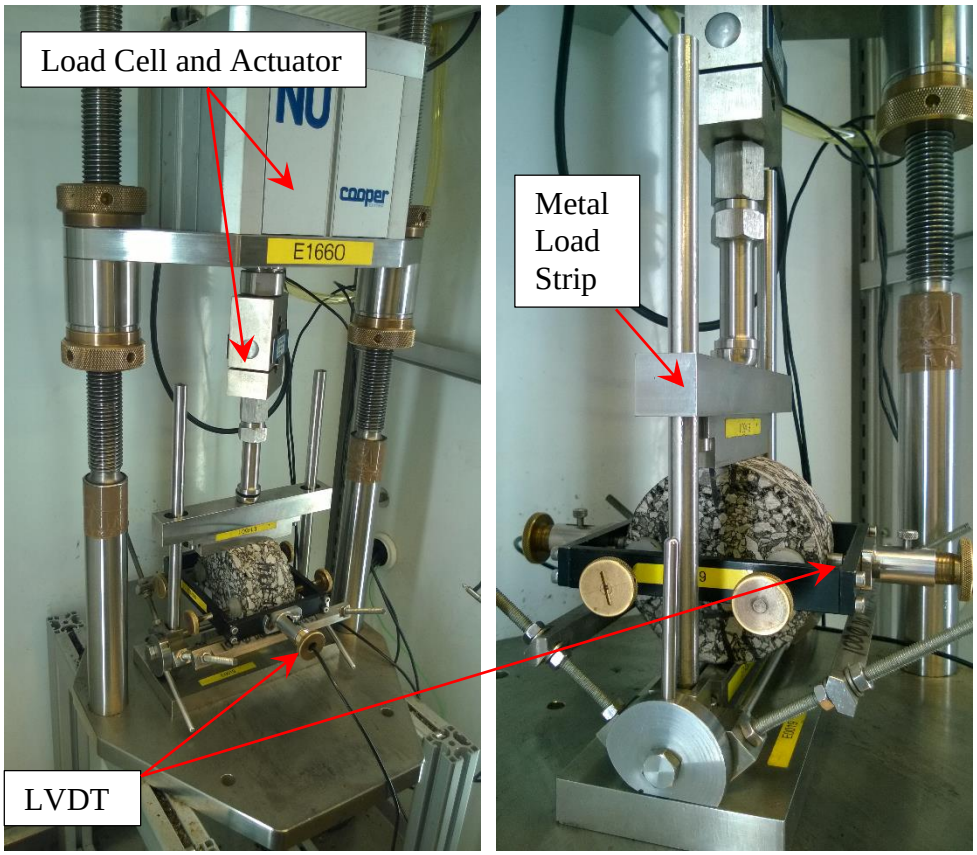


Figure 3.18 : ITSM/IT-CY NU14 test apparatus (left) and sample test frame set (right)

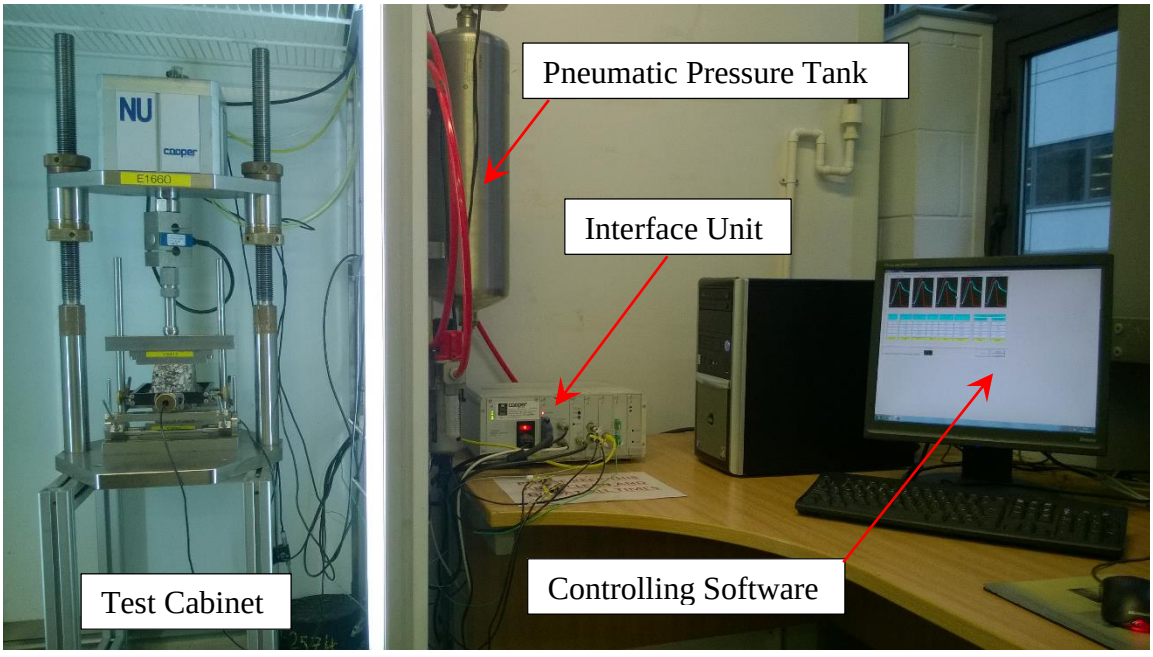


Figure 3.19 : ITSM/IT-CY NU14 test set

Conforming to the shape and dimension criteria of the test standard, the test specimens, whether directly moulded in Gyratory compactor or cored from the Roller compaction slabs, were manufactured in a cylindrical shape with (100±1) mm diameter and trimmed to (60±1) mm thickness. In this test, the specimen is placed on its side on a metal base in the test frame. The load is applied by another metal strip placed on top of the sample. The strips make apply load in the form of uniform tension. The specimen is loaded in the vertical direction due to which a relatively uniform tensile stress is developed in the horizontal direction perpendicular to the vertical plane of loading. The horizontal stress develops horizontal deformation which is measured by two LDVTs installed on both sides of the specimen along its horizontal diameter. Different standards have different criteria for measuring the deformation during the ITSM test (Figure 3.20).

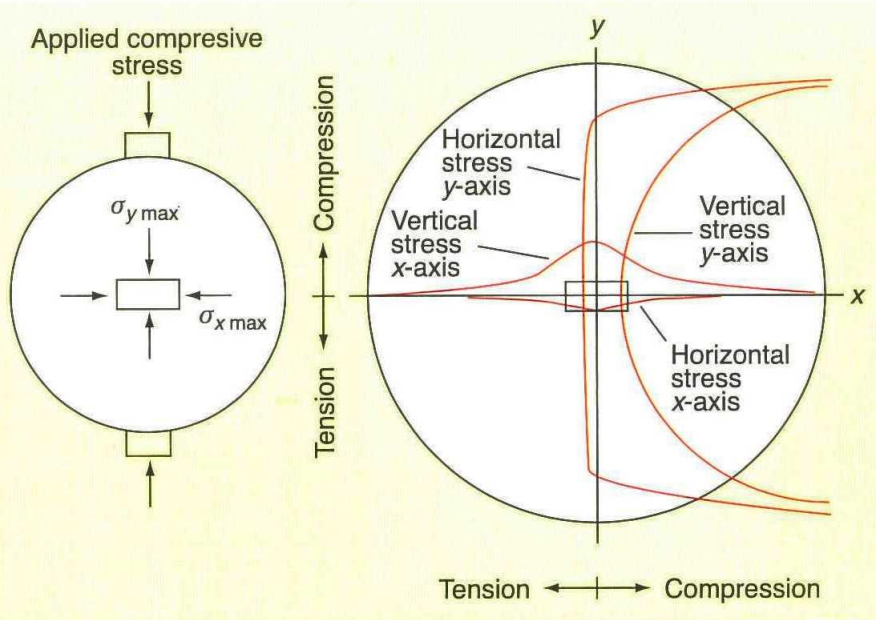


Figure 3.20 : Stress and strain orientations in the ITSM/IT-CY test 0

The horizontal strain can be calculated based on the total deformation (maximum deformation during one loading cycle) or just on the elastic (resilient) deformation or an average of the two. It should be recalled that elastic deformation generally means all recoverable deformation irrespective of whether it is elastic (time independent) or viscoelastic (time dependent).

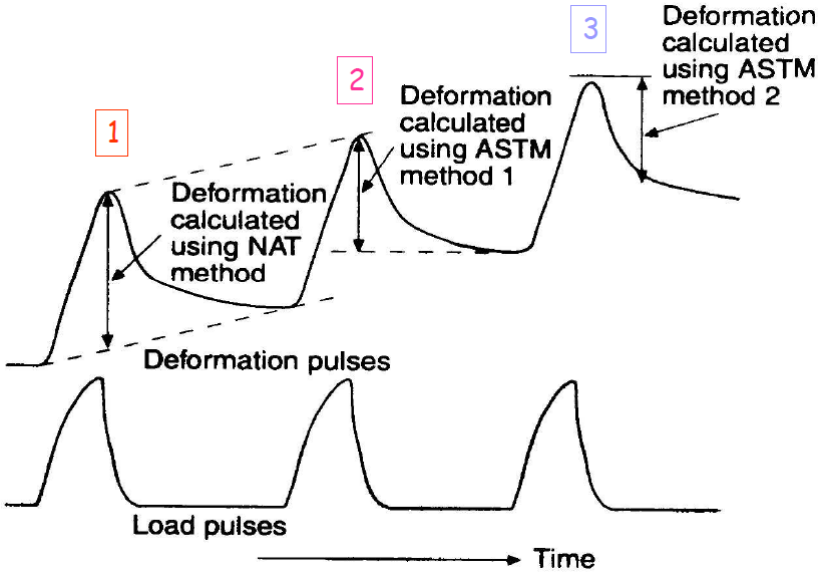


Figure 3.21 : Various methods of measuring the deformation in ITSM test according to different standards

The loading in ITSM/IT-CY is applied in the form of a number of compressive load pulses. In the present research, the ITSM/IT-CY was performed using the following configuration, in accordance with BS EN 12697-26:2012:

Table 3.9 : ITSM/IT-CY test configuration and conditions

ITEM	VALUE
Target Horizontal Deformation (micron)	5
Load Rise Time (ms)	124
Number of conditioning pulses	10
Number of main loading pulses	5
Test temperature (°C)	20
Sample conditioning temperature (°C)	20
Sample conditioning time (hrs)	6

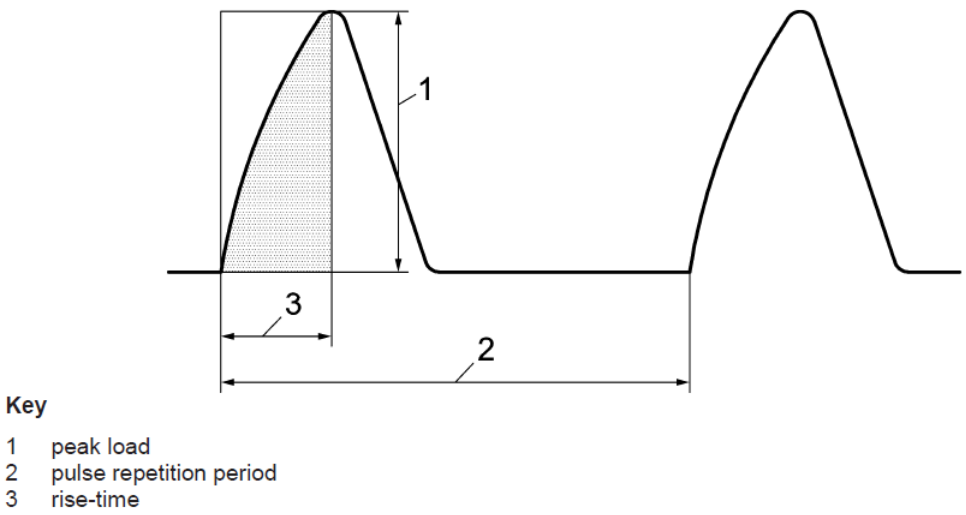


Figure 3.22 : The structure of a single load pulse in the ITSM/IT-CY test (BS EN 12697-26:2012)

The ITSM/IT-CY test is considered to be a non-destructive test. For this reason, the Target Horizontal Deformation is recommended by the standard to be 5 micrometres to ensure that the deformations during the test are so small that the material does not experience the plastic behavioural zone. However, due to the fact that the asphalt material is viscoelastic (within small deformations) also according to some research results, even within such a small amount of strain, the recovery may last several hours (less than a day). Therefore, the test can be non-destructive if enough time is given to the specimens to recover all the recoverable deformation. Ten conditioning pulses are applied before starting the test to make any adaptation for the load needed to produce the target horizontal deformation, also to embed the loading strips correctly on the sample. The system then applies five main load pulses and uses the associated generated horizontal deformation. The test data (vertical load, horizontal stress and strains) is measured and stored automatically and the stiffness modulus is calculated using Equation 7 for the current direction of the sample under the load. Then the sample should be rotated by 90° in the test frame and the same operation is repeated for the new direction. Finally, the test program presents an average of the calculated ITSM in both directions representing the ITSM value of the tested sample.

$$S_m = F \times (\upsilon + 0.27)/(Z \times h) \qquad \text{Equation 3.14}$$

Where:

S_m = Indirect Tensile Stiffness Modulus (MPa)

F = Vertical load (N)

Z = Horizontal deformation (mm)

h = Thickness of the specimen (mm)

υ = Poisson's ratio = 0.35 (For asphalt concrete)

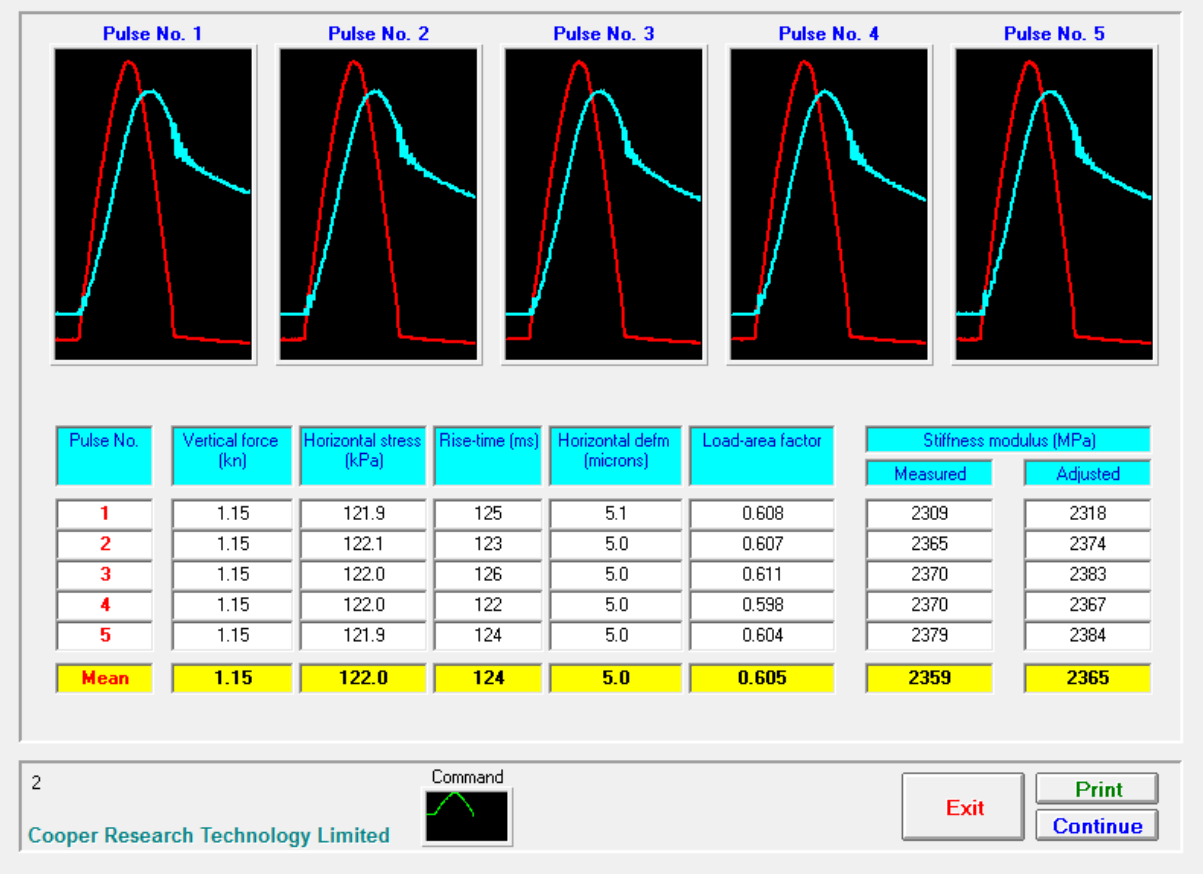


Figure 3.23 : ITSM/IT-CY test load pulses (red curves) and lagged viscoelastic deformation responses (blue curves)

In the present research, the ITSM/IT-CY test has been performed on all manufactured specimens. However, the value, representing the stiffness of a Sample Group, has been calculated considering the removal of the out of range data. The test results on both types of specimens (i.e. Gyros and Cores) have been presented in the form of bar charts in the next chapter, each bar representing 11 samples for Gyratory samples or 12 core samples in the associated charts.

3.5.3. INDIRECT TENSILE FATIGUE TEST (ITFT)

The fatigue resistance of asphalt mixtures is generally defined as their ability to respond to repeated (traffic) loading under the dominant environmental conditions without significant cracking or premature failure being induced (Baburamani, 1999). Damage in asphalt pavements, due to the repetitive stresses and strains, developed whether by traffic loading or the environmental factors can arise in the form of fatigue cracking. Fatigue failure is considered as a main distress mechanism in asphalt pavements and the fatigue characteristic of asphalt is therefore an important pavement structural design parameter. Fatigue resistance of asphalt mixtures is influenced by both (Baburamani, 1999):

- The properties which affect the flexural stiffness (i.e. air void content, binder type and content, bitumen film thickness, binder's rheological properties, aggregate type and gradation), and
- The test method, mode of loading and conditions (e.g. the magnitude and frequency of the stress or strain parameters being controlled during the test, the rest period between the loads, test temperature, etc.)

Under fluctuating or cyclic or repetitive loads and stresses, failure can take place at loads significantly lower than the ultimate tensile or yielding strengths of the material under static loads. Fatigue failure proceeds in three distinct stages:

1) Crack initiation in the stress concentration areas (near the stress raisers).
2) Incremental crack propagation, and
3) Final catastrophic failure, which is the final rapid crack propagation after the crack grows to a critical size.

Crack initiation occurs as a result of deficiencies in the quality of material's surface. Some of the very common sites of stress concentration are micro-cracks, scratches, indents, interior corners, dislocation slip steps, etc.

As a definition, Fatigue Strength is the stress at which the fracture takes place after a specified number of cycles and Fatigue Life is the number of cycles to fail at a certain stress level. The total number of cycles to failure is the sum of cycles at the first and the second stages:

$$N_f = N_i + N_p \qquad \text{Equation 3.15}$$

Where:

N_f = Number of cycles to failure

N_i = Number of cycles for crack initiation

N_p = Number of cycles for crack propagation

In the case of high cycle fatigue, which takes place under small loads, N_i is relatively high. However, with increasing the stress level, N_i decreases and N_p dominates.

In order to evaluate the fatigue resistance of the manufactured asphalt specimens in the present research, Indirect Tensile Fatigue Test on cylindrical specimens (ITFT) has been carried out. The test has been performed in the NAT/NU14 machine and in accordance with the criteria of BS EN 12697-24:2012. According to the standard, the ITFT samples should have a thickness of at least 40 mm and a diameter of (100±3) mm for a maximum aggregate size of 25 mm.



Figure 3.24 : ITFT test cabinet (left) and test frame (right)

In this regard, considering that the maximum aggregate size of the present study is 14 mm, the asphalt specimens, whether Gyros or Cores, have conformed to the shape and dimensions criteria of the test standard because they all had been fabricated in cylindrical shape with (100±1) mm diameter and those which had been allocated for the ITFT test, following the ITSM test, were trimmed to (40±1) mm thickness. In this test, similar to the ITSM/IT-CY test, the specimen is placed on its side on a metal base and under a loading strip in the ITFT test frame which is somehow different from the ITSM/IT-CY test frame. The specimen is loaded in the vertical direction and the strips let the load be applied uniformly to the specimen. Similar to the ITSM/IT-CY test, a relatively uniform tensile stress is developed in the horizontal direction perpendicular to the vertical plane of loading. The horizontal stress results in horizontal deformation. The loading in ITFT is applied in the form of cyclic compressive load pulses. Following the several cycles of loading and unloading, the cumulative unrecovered elastic or plastic horizontal deformation at the centre of the specimen increases so significantly that due to the crack initiation and propagation the specimen starts splitting. However, the criterion to consider the test complete is via measuring the vertical deformation read by the top strip's LVDT, when the vertical deformation exceeds the red line of 9 mm though in reality, the specimens usually fail before that deformation. This may happen suddenly in the case of sudden failures. The accumulation of vertical deformation is plotted with number of load cycles during the test until the final failure takes place.

In the present research, the ITFT was performed in stress-controlled mode with the Load Rise Time of 124 ms. The test was performed at 20°C and the samples needed to rest in a 20°C conditioning cabinet for at least 6 hrs.

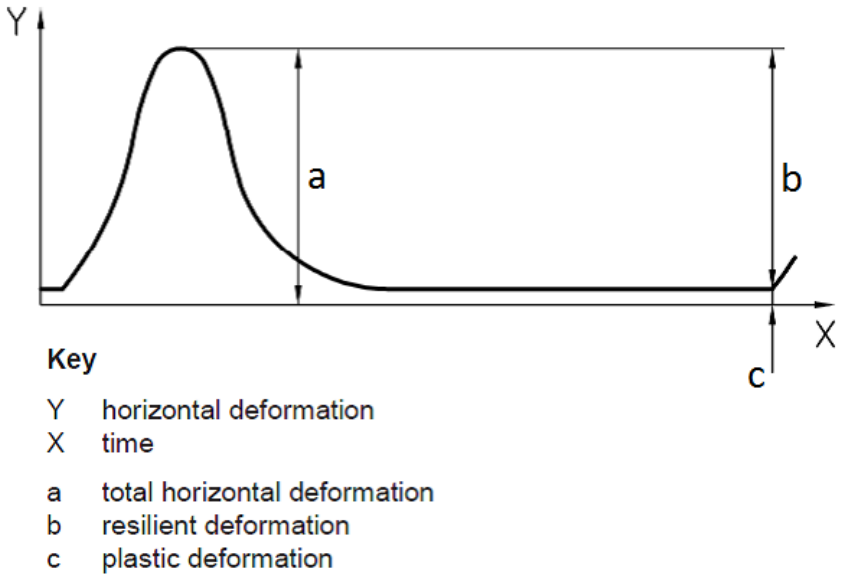


Figure 3.25 : The structure of a single load pulse in the ITFT test (BS EN 12697-24:2012)

Prior to starting the ITFT test, the stiffness modulus of the tested specimen should be measured through an Indirect Tensile Stiffness Test (ITST) using the same stress which will be applied for the associated ITFT. Generally, ITST is very similar to ITSM and is performed in the same test frame of a NAT/NU14 machine. However, ITST, in contrast to ITSM/IT-CY, is a stress-controlled test and also has to be done only in one direction, which is the same direction in which the ITFT is intended to be performed. Five conditioning pulses and five main loading pulses with 124 ms Rise Time are applied in ITST. The horizontal deformation is read by the ITSM/IT-CY LVDTs and the stiffness is calculated automatically by the software in the same way as described for ITSM/IT-CY. The stiffness obtained from ITST is then used to calculate the maximum horizontal tensile strain of each single loading pulse of the associated ITFT using Equation 3.17:

$$F = \sigma_{max} \times \pi \times h \times D/2 \qquad \text{Equation 3.16}$$

$$\varepsilon_{max} = \sigma_{max} \times (1 + 3\upsilon)/S_m \qquad \text{Equation 3.17}$$

Where:

F = Vertical load applied by the actuator (N)

h = Thickness of the specimen (mm)

D = Specimen diameter (mm)

σ_{max} = Maximum horizontal tensile stress at specimen centre (MPa)

ε_{max} = Maximum horizontal tensile strain

υ = Poisson's ratio = 0.35 (For asphalt concrete)

S_m = Stiffness modulus (MPa)

It should be mentioned that the ITST test temperature is the same as that intended for ITFT (20°C for this research) and the samples should rest in a conditioning cabinet at the same temperature for at least 4 hrs.

In the present research, in the case of either of the specimen types (Gyros or Cores), the ITFT test has been performed on 5 out of the 11 (Gyros) or 12 (Cores) manufactured samples of each of the 10 Sample Groups. Due to the fact that ITFT was a destructive test and considering the number of samples needed for the other destructive tests in the present research, the time and material resources, also the practical limitations did not allow providing the recommended number of specimens for producing a single fatigue line. However, the data variations were so small that in all cases, firstly, the fitted fatigue line among the points of failure had an R^2 value of more than 0.9, secondly, the fatigue lines were visually well-fitted through all the points and thirdly, the results could still show a clear and reliable regime between the different Sample Groups. The test results on both types of specimens (i.e. Gyros and Cores) have been presented in the form of scatter charts of fatigue strength versus cycles to failure within fitted fatigue lines on log-log scaled axes in the next chapter. Moreover, a stress-strain chart has been developed using the ITST and ITSM test data to evaluate some kind of stiffness modulus for each of the Sample Groups.

3.5.4. REPEATED LOAD AXIAL TEST (RLAT)

Permanent deformation is the most common mode of failure in road pavement, especially in hot climate areas, particularly those with the maximum pavement temperature of more than 50°C throughout the year. The temperature is the major influencing factor on the permanent deformation mode of asphalt concrete, especially when the temperature rises above 40°C or higher. This is because the asphalt concrete tends to flow out as a viscoelastic material at high temperatures (Aschuri, Woodward & Woodside, 2009). Permanent deformation in asphalt concrete occurs due to the following reasons:

1) Shear deformation in asphalt because of either:

1-1) Plastic shear deformation in binder

1-2) Binder-aggregate debonding

2) Densification and decrease in height in high air void content asphalt, because of insufficient compaction

In this respect, rutting is the accumulated permanent vertical strain due to traffic loading and will be confined only to the top layers when the lower layers are rigid enough. This is non-structural rutting, which will be stopped when faced with a rigid sub-layer in the depth of the pavement. Permanent deformation may happen due to the softness of the lower layers, in which case it is named structural rutting.

Mixtures with well-packed aggregate structure, optimum binder content, low air void content (following sufficient compaction), high interlock (due to angular particles) and rough texture of aggregate (smooth surface texture results in loss of adhesion as well as less interlock) will have less rutting potential.

Table 3.10 : Factors affecting the permanent deformation of asphalt pavement (Gibb, 1996)

	Factor	Change in Factor	Effect of Change in Factor on Rutting Resistance
Aggregate	Surface Texture	Smooth to rough	Increase
	Gradation	Gap to continuous	Increase
	Shape	Rounded to angular	Increase
	Size	Increase in maximum size	Increase
Binder	Stiffness	Increase	Increase
Mixture	Binder content	Increase	Decrease
	Air void content	Increase	Decrease
	VMA	Increase	Decrease
	Method of compaction		
Test / field conditions	Temperature	Increase	Decrease
	State of stress/strain	Increase in tyre contact pressure	Decrease
	Load repetitions	Increase	Decrease
	Water	Dry to wet	Decrease if mix is water sensitive

Laboratory evaluation of permanent deformation of the asphalt test specimens in the present research has been performed through the Repeated Load Axial Test (RLAT), which is performed on cylindrical specimens, in accordance with BS DD 226:1996, and by the use of a NAT machine. RLAT is one of the fundamental methods for measuring permanent deformation (rutting potential) of asphalt mixtures in the laboratory.

The asphalt test samples of this study, whether Gyros or Cores, have conformed to the shape and dimensions criteria of the test standard as they all had been manufactured in cylindrical shape with (100±1) mm diameter and those which had been chosen for the RLAT test, had experienced the ITSM test before, due to which they had been trimmed to (60±1) mm thickness.

In this test, the specimen is placed on its ends between two metal load platens. The specimen is loaded in the vertical direction and the platens let the load be applied uniformly to the specimen. The loading in RLAT is applied in the form of axial repetitive square wave compressive load pulses with the specification mentioned in Table 3.11. Due to the relatively high test temperature and the 1000 ms duration of loading in each pulse, the specimen experiences elastic, plastic, delayed elastic and viscous deformation. However, during the 1000 ms of unloading, it can only recover the elastic and delayed elastic parts whereas the viscous and plastic parts are not recovered. The vertical cumulative viscous and plastic deformations are recorded by RLAT LVDTs sitting on the top platen and stored automatically versus time. In the present research, the RLAT test configuration, in accordance with BS DD 226:1996 was as follows:

Table 3.11 : RLAT test configuration and conditions

ITEM	VALUE
Test stress (kPa)	100
Test period (pulses)	1800
Pulse width (ms)	1000
Time between pulses (ms)	2000
Conditioning stress (kPa)	10
Conditioning period (s)	600
Test temperature (°C)	40
Sample conditioning time (hrs)	6

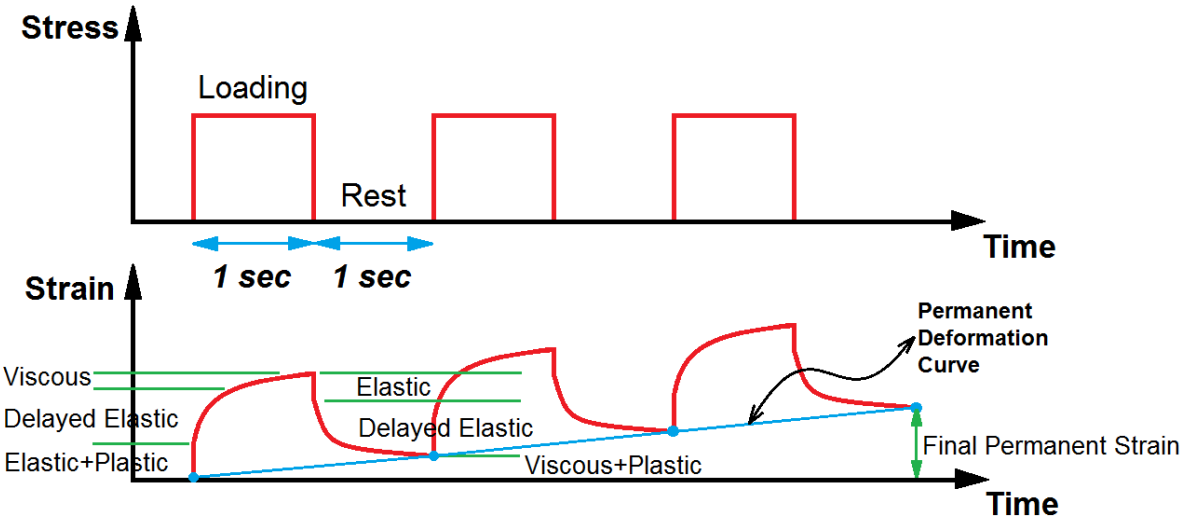


Figure 3.26 : RLAT cyclic loading system and the developed permanent deformation

According to the standard, the following parameters can be extracted from the RLAT results:

$$\varepsilon_{d,(n,T)} = \Delta h / h_0 \qquad \text{Equation 3.18}$$

$$S_{m,(n,T)} = \sigma / \varepsilon_{d,(n,T)} \qquad \text{Equation 3.19}$$

Where:

$\varepsilon_{d,(n,T)}$ = Axial strain caused to the specimen after *n* applications of load at temperature *T*

h_0 = Original distance between the specimens loading surfaces (mm)

h = Axial deformation (change in distance between the specimen loading surfaces) (mm)

$S_{m,(n,T)}$ = Dynamic load stiffness modulus of the mixture after *n* load applications at loading temperature *T* (MPa)

σ = Applied stress (kPa)

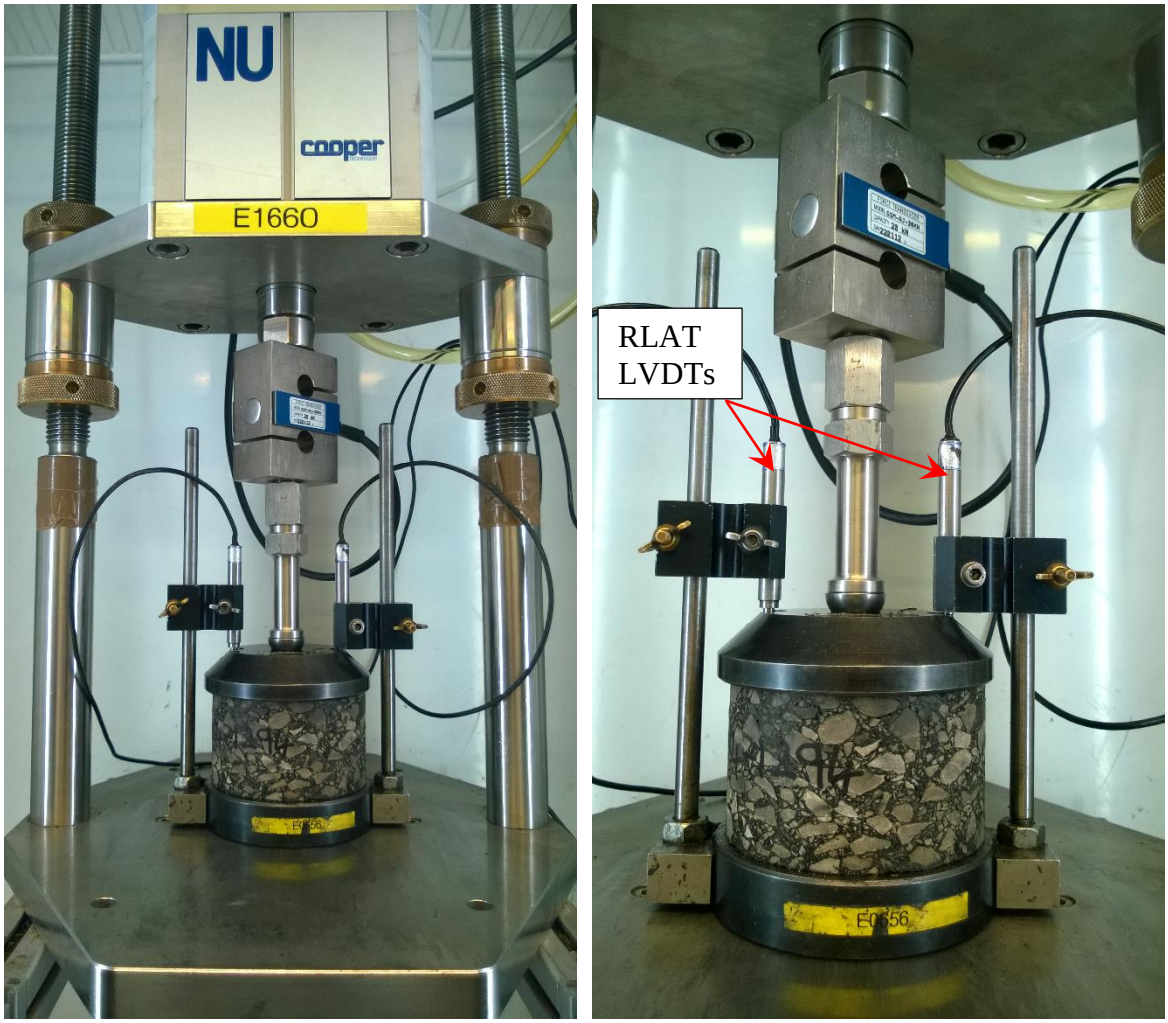


Figure 3.27 : RLAT test cabinet (left) and test frame (right)

In the present research, in the case of either of the specimen types (Gyros or Cores), RLAT has been performed on 3 out of the 11 (Gyros) or 12 (Cores) manufactured samples of each of the 10 Sample Groups. The test results on both types of specimens (i.e. Gyros and Cores) have been presented in the form of scatter charts of permanent deformation versus number of cycles and also the bar chart of dynamic load stiffness modulus.

3.5.5. DIRECT DYNAMIC COMPRESSIVE COMPLEX STIFFNESS MODULUS (DDCCSM)

As mentioned before, stiffness is an essential property of a material which is taken into account through the design process of any structure. In the case of asphalt concrete, similar to any other viscoelastic (visco-plastic) substances (e.g. bitumen, bituminous binders and mixtures/materials), the stiffness changes with temperature and loading frequency and in order to represent the stiffness of the material, the Complex Stiffness Modulus (E^*) is often used.

The complex modulus has an elastic or storage component and a viscous or loss component. The storage (elastic) component is related to the material's ability to store energy, whereas the loss (viscous) component is responsible for the loss of energy and damping in the system. Both the storage modulus, (*E'*), and the loss modulus, (*E"*), change with temperature and the rate of loading (load frequency) and make the complex modulus (*E**) change over the range of temperatures and load frequencies. For purely elastic materials, there is no damping loss and, thus, the elastic component is equal to the overall modulus.

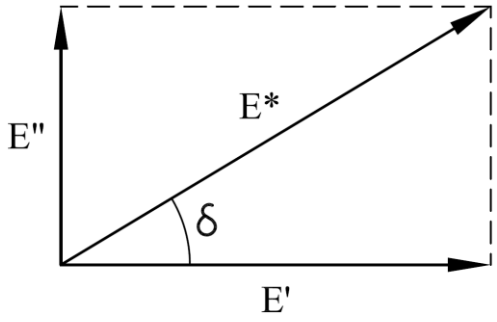


Figure 3.28 : Schematic relationship between Complex Stiffness modulus, Storage modulus and Loss modulus

The Complex Stiffness Modulus (*E**) or the Dynamic Modulus (which is the magnitude of *E**) is one of the most comprehensive representatives of the viscoelastic behaviour of bituminous mixture (asphalt concrete) which whether studied alone or combined with Phase Angle (δ), over the range of various temperatures and frequencies (i.e. in the form of a Master Curve), not only can explain the viscoelastic behaviour of asphalt, but also can represent the mechanical behaviour of asphalt qualitatively and quantitatively. In other words, the results of low temperature behaviour of asphalt (e.g. fatigue resistance) and high temperature characteristics of asphalt (e.g. rutting potential) can be predicted, extracted, justified or interpreted.

In order to determine the Complex Stiffness Modulus (*E**) and Phase Angle (δ) of the asphalt mixtures in the current study, a modified mode of AASHTO TP 62-03 method for Complex Modulus determination in axial compression has been devised by this PhD student to be performed through the research methodology and called Direct Dynamic Compressive Complex Stiffness Modulus (DDCCSM). AASHTO's protocol for dynamic modulus testing, TP 62-03, Standard Method of Test for Determining Dynamic Modulus of Hot-Mix Asphalt Concrete Mixtures (2003) has been developed by the research team of NCHRP 9-19 project (Superpave Support and Performance Models Management).

Recent findings from the NCHRP 9-19 project, also suggest that the dynamic modulus is one of the best indicators for the rutting and fatigue cracking of asphalt mixtures (Pellinen & Witczak, 2002).

The DDCCSM test in this study has been performed in a NAT/NU14 machine using Cooper's Universal software for applying the written test sequences. In this test, the specimen is placed on its ends between two metal load platens. The specimen is loaded in the vertical direction and the platens allow load to be applied uniformly to the specimen. The loading in DDCCSM is applied in the form of an axial compressive sinusoidal wave with the specification mentioned in Table 3.12. The maximum compressive strain has been determined in such a way that the deformations stay in elastic region. In fact, as the test includes measuring the complex modulus of asphalt over a range of temperatures and frequencies, the test should be non-destructive so the same sample can be passed through the test using several combinations of temperatures and frequencies.

The vertical elastic deformations are recorded by the use of RLAT LVDTs sitting on the top platen and stored automatically. Ideally, the values of E^* were calculable and recordable over the range of various frequencies and temperatures through all possible frequency-temperature combinations. However, unfortunately, Cooper's Universal Software had serious errors in processing the raw data and calculating the E^* and Phase Angle. For this reason, a data processor Excel program was developed by the researcher to calculate the Complex Modulus and Phase Angle using the recorded vertical displacement of the top platen and the load values.

Since the asphalt test samples of this study, whether Gyros or Cores, had initially been manufactured in cylindrical shape with (100±1) mm diameter and (100±1) mm height, before being trimmed for any other test (i.e. volumetric determination and ITSM/IT-CY), they had to be tested through the DDCCSM test.

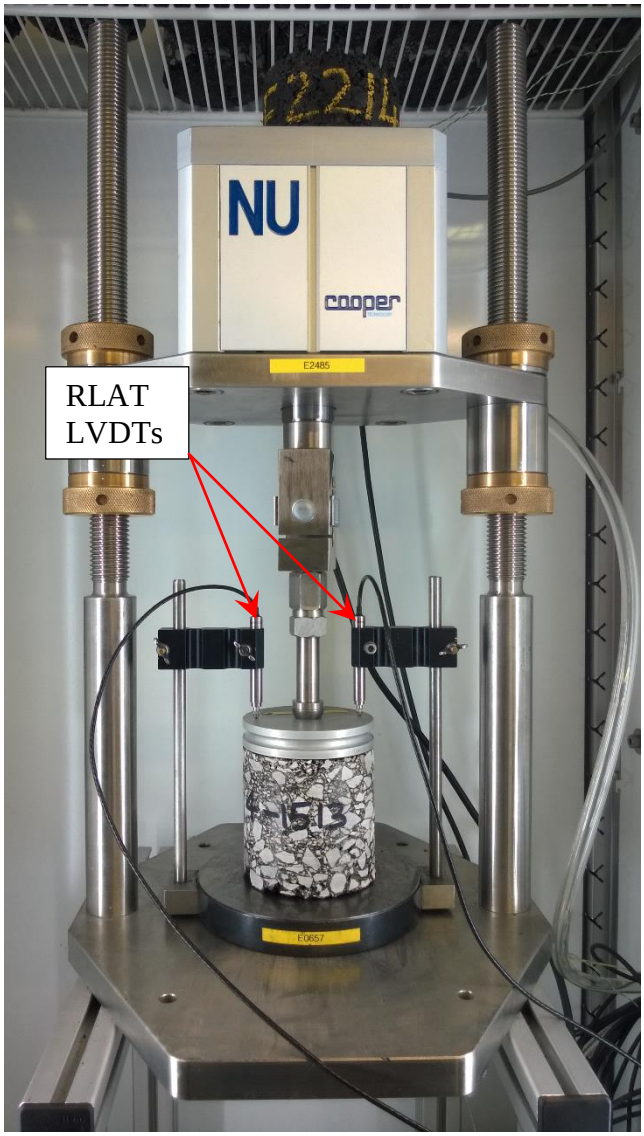


Figure 3.29 : DDCCSM test frame set up

Table 3.12 presents provides a comparison between the devised configurations of DDCCSM and the settings of AASHTO TP 62-03.

Table 3.12 : DDCCSM test configurations and conditions compared to AASHTO TP 62-03

ITEM	**VALUE(S) of DDCCSM**						**VALUE(S) of AASHTO TP 62-03**					
Load pattern	Compressive Sinusoidal						Compressive Sinusoidal					
No. of load cycles applied	15	30	100	150	200	250	15	15	20	100	200	200
for Each Load frequency (Hz)	0.1	0.5	1	5	10	25	0.1	0.5	1	5	10	25
Holding stress (kPa)	5						10					
Peak stress (kPa)	100						200					
Rest between frequencies (min)	5						5					
Test temperatures (°C)	10, 20, 30						-10, 4.4, 21.1, 37.8, 54.4					
Sample Thickness (mm)	100						150					
Sample conditioning time (hrs)	6						-					

The reason for decreasing the height criteria was due to the fact that producing samples 150 mm thickness in either of the compactors used in the project (i.e. Gyratory and Roller compactors) caused a significant dissimilarity or inconsistency in the properties of the produced samples with the ones with 100 mm thickness. This would make the other properties of the two different thickness samples incomparable and unable to be tracked or related to the other properties. In practice, the Gyratory compactor was able to produce 150 mm thick samples but the AV content was far too high (about 15%) which was in no way comparable to the rest of the samples with about 2 to 5% AV content. In addition, fabricating any sample thicker than 100 mm was impossible in the Slab Roller compactor. Therefore, despite the height recommendations of various standards, samples with 100 mm thickness were used to perform the DDCCSM test.

The numbers of load cycles were changed from the AASHTO recommendations due to the fact that NU14 machine used to do the test could not stabilise the maximum requested load value of 100 kPa through the AASHTO recommendations. It might be either due to the accuracy of the operating software or that of the pneumatic loading system. Nonetheless, following a trial and error process, the number of cycles for each load frequency was finalised as presented in Table 3.12 in such a way that the machine could stabilise the load maximum value over the time of load pulses. Regarding the magnitude of the load peak stress, it was decreased having a glance at the ITSM/IT-CY test results in such a way that the amount of strain developed through the test stayed safely in the elastic (viscoelastic) behavioural region.

The temperature was only changed over 10 to 30°C with 10°C intervals as the machine could not go below 10°C with reliable-enough accuracy according to previous experience. In addition, performing the test at temperatures higher than 30°C would increase the risk of being destructive whereas according to the test sequences devised for the research, the DDCCSM samples would be used for other performance tests after trimming. Therefore, it was essential for DDCCSM to be non-destructive. The 5 minute rest between the two frequency tests was to let the material recover the delayed elastic deformation.

The Dynamic Modulus values at various temperature-frequency combinations are used to develop a ‘master-curve’. The development of a master-curve allows the modulus to be determined at any reasonable temperature-frequency combination. The Dynamic Modulus master-curve is based on the concept of the time-temperature superposition (or time-temperature equivalence) principle. According to this concept, the same modulus value of a

material can be obtained either at low test temperatures and long times or at high test temperatures but short times. In other words, the behaviour of a material at high temperatures is the same as that under long loading times or slow loading rates (low load frequencies), and the material behaviour at low temperatures is the same as that under short loading times or fast loading rates (high load frequencies). Although the dynamic modulus test is supposed to be non-destructive following the criteria mentioned in the previous pages, the stress-controlled mode used in the dynamic compression modulus test causes an increase in the mean strain as the test proceeds. Therefore, the testing method needs to be designed so that the testing at the temperature and frequency used in the early sequence of the temperature-frequency sweep has the least effect on the subsequent testing temperatures and frequencies. Based on this theory, the test began at the lowest temperature and proceeded to the highest temperature. Also, at a given temperature, it began at the highest frequency and went to the lowest frequency. This sequence was intuitive due to the stiffening of asphalt concrete at low temperatures and high frequencies.

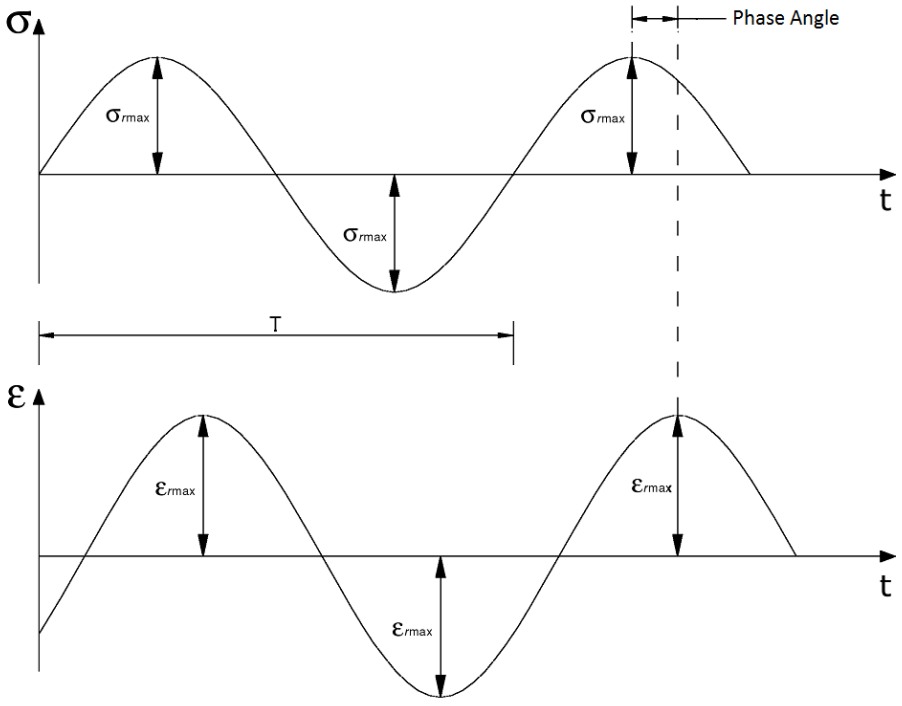


Figure 3.30 : Sinusoidal loading and delayed displacement

The following parameters can be extracted from the test results:

$$P(t) = P_0 \sin(\omega t) \qquad \text{Equation 3.20}$$

$$\omega = 2\pi f \quad \text{Equation 3.21}$$

$$\sigma(t) = P(t)/A \quad \text{Equation 3.22}$$

$$\sigma(t) = \sigma_0 \sin(\omega t) \quad \text{Equation 3.23}$$

$$\Delta(t) = \Delta_0 \sin(\omega t - \delta) \quad \text{Equation 3.24}$$

$$\delta = 2\pi f \Delta t \quad \text{Equation 3.25}$$

$$\varepsilon(t) = \Delta(t)/h_0 \quad \text{Equation 3.26}$$

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t - \delta) \quad \text{Equation 3.27}$$

$$|E^*| = \sigma_0/\varepsilon_0 \quad \text{Equation 3.28}$$

$$|E^*| = ((E')^2 + (E'')^2)^{0.5} \quad \text{Equation 3.29}$$

$$\tan\delta = E''/E' \quad \text{Equation 3.30}$$

$$E^* = E' + iE'' \quad \text{Equation 3.31}$$

Where:

$P(t)$ = Sinusoidal axial load wave (kN)

A = Cross-sectional area of the specimen (m^2)

$\sigma(t)$ = Axial stress (kPa)

Δ = Top platen's vertical displacement (mm)

h_0= Initial height/thickness of specimen (mm)

$\varepsilon(t)$ = Axial strain

σ_0= Peak axial stress (kPa)

ε_0= Peak axial strain

δ= Phase angle (rad)

f= Load frequency (Hz)

Δt= Stress-strain time lag (s)

E^* = Complex modulus (kPa)

E' = Storage modulus (kPa)

E'' = Loss modulus (kPa)

i^2 = -1

In the present research, in the case of either of the specimen types (Gyros or Cores), the DDCCSM has been performed on 3 out of the 11 (Gyros) or 12 (Cores) manufactured samples of each of the 10 Sample Groups. The number of samples should be at least 3 so the test results could be statistically reliable.

As mentioned before, due to a significant problem in Cooper's Universal Software in calculating the *E** and Phase Angle, the whole data process has been performed through a data processor Excel program which was developed by the researcher to calculate the Complex Modulus and Phase Angle. Then, in the first stage, the processed test results of both types of specimens (i.e. Gyros and Cores) were used to produce scatter charts of *E** versus load frequency. Then, the associated master-curves were produced and presented for each of the sample groups as can be seen in Chapter 6 Section 6.5.

3.5.6. THE REVISED MODIFIED LOTTMAN TEST

The presence of water in asphalt pavement is unavoidable and due to the reasons mentioned in the previous chapters, it leads to the moisture damage of asphalt. Asphalt concrete's moisture damage can be defined as the loss of strength and durability in asphalt mixtures due to the presence and effects of moisture (Little & Jones, 2003). In fact, moisture susceptibility in asphalt concrete is a problem that typically leads to the 'stripping' of the asphalt binder from the aggregate. With time passing, the stripping phenomenon, when critical environmental conditions such as freeze-thaw cycles act combined with poor and/or incompatible materials and traffic, develops further and result in ravelling/fretting and the disintegration of the asphalt concrete mixture. This is why the presence of water in asphalt is known as one of the factors that lead to the premature failure of pavements. Moisture damage can happen due to three main mechanisms (Brown, Kandhal & Zhang, 2001):

1) Loss of cohesion of bitumen film
2) Failure of adhesion between aggregate particles and the bitumen film, and

3) Degradation of aggregate particles due to freezing.

Many factors can affect the moisture sensitivity of a mixture. They can generally be divided into three main categories (Williams & Breakah, 2010):

1) Material properties, which include the physical and chemical properties of the involved bituminous binder and the aggregates.
2) Mixture properties, which include bitumen content, bitumen film thickness and the permeability of mixture (AV content and the interconnectivity of the air voids).
3) External factors, which include construction, traffic and environmental factors.

There are six contributing processes, which have been known to cause moisture damage in asphalt mixtures:

1) **Detachment**, which is the separation of bitumen film from aggregate surface from being replaced by a thin film of water without any obvious break in the bitumen film (Majidzadeh & Brovold, 1968).
2) **Displacement**, which takes place at the breaks in the bitumen film on the aggregate surface. A break happens as a result of the incomplete coating of aggregate particles, inadequate coating at sharp edges of aggregates or pinholes in the bitumen film. At these break points, water can permeate and displace the bitumen from aggregate (Tarrer & Wagh, 1991).
3) **Spontaneous emulsification**, which occurs due to the inverted emulsion of water droplets in bitumen mortar (Little & Jones, 2003) through which water diffuses into bitumen mortar, thereby attaching itself to an aggregate and causing a separation between asphalt and aggregate.
4) **Pore-pressure–induced damage**, which can be developed in an asphalt pavement due to the entrapped water or the water moving into air-void systems in vapour form (Little & Jones, 2003). The pore pressure in asphalt concrete can increase due to the repeated loading of traffic and/or increase in temperature. In the case of permeable mixtures, water can escape and flow out, whereas if the mixture is not permeable, the increased pore pressure may surpass the ultimate tensile strength of the mixture via a combination of stripping the bitumen film from aggregate and developing cohesive failure in bitumen, each of which causes micro-cracking (Little & Jones, 2003; Brown, Kandhal

& Zhang, 2001). The rate of micro-cracking is accelerated by an increase in pore pressure and the presence of water in asphalt.

5) **Hydraulic scour**, which happens at the pavement surface and is a result of having repeated traffic tyres on the surface of a saturated pavement. Water is sucked into a pavement by tyre rolling action (Little & Jones, 2003). Hydraulic scour may occur due to the osmosis phenomenon (Williams & Breakah, 2010) in the pavement, as well, which develops a pressure gradient. However, this subject is not the case to be described in this thesis and more explanations can be found through the associated literature.

6) **Environmental effects**, which are factors such as temperature, air and water. They have deleterious effects on the durability of asphalt. Other mechanisms, such as freeze/thaw cycles and the ageing of binder can affect the durability of asphalt, as well (Terrel & Al-Swailmi, 1994). Other considerations, such as construction (segregation and ravelling) and traffic, are also important.

It should be mentioned that not one of the above factors necessarily works alone in damaging an asphalt concrete pavement, as they can work in combination.

One of the most commonly used procedures for determining HMA moisture susceptibility is the modified Lottman Indirect Tension Test (AASHTO T 283), Standard Method of Test for Resistance of Compacted Asphalt Mixtures to Moisture-Induced Damage. This test, itself, is very similar or, in fact, a modified version of the original Lottman test but with a few exceptions. The original Lottman procedure was developed by Lottman at the University of Idaho in the late 1970s (Lottman 1978). AASHTO T 283 was used with Marshall Mix design method. However, following the development of the Superpave mix design method, the modified Lottman Indirect Tension Test was adopted by the Superpave system as the required test for determination of moisture damage in asphalt mixtures with the modification of the compaction method.

In the current PhD study, some modifications have been devised and applied to the mode and settings of the modified Lottman test (AASHTO T 283) by the researcher. The main reason for such modifications has been the fact that the strength evaluation method in the modified Lottman test was the Indirect Tension Test (ITT), which was essentially a destructive test. Therefore, once ITT was performed on a sample, the sample could not be used for any other purpose such as conditioning etc. As a result, the specimens in the AASHTO T 283 test method,

as they are, should be divided into two groups included conditioned specimens and the virgin (unconditioned) ones. This meant that the difference between the indirect tensile strength of the conditioned samples and the virgin ones might not have been solely due to the effect of conditioning on the indirect tensile strength of the samples as it could have been partly as a result of the difference between the initial indirect tensile tension of the two samples, which were compared together, before any conditioning. In other words, there is always some deviation expected between the results of any test (ITT) on different samples taken from a certain mixture. It means that in fact, the ITT results of the conditioned samples might have been initially different from those of the virgin samples regardless of any conditioning. This issue develops some potential errors in the calculated Tensile Strength Ratio (TSR) of the conditioned samples to the virgin ones though, as AASHTO T 283 has considered, increasing the number of test samples in both groups can improve the situation statistically via decreasing the mentioned potential error and deviation. However, in the devised moisture sensitivity test of the current research:

1) Due to the limitation of the material resources (i.e. raw materials, number of samples, time, etc.),
2) For the purpose of avoiding the mentioned potential error in TSR calculation, and
3) In order to be able to track the property changes of the samples over the conditioning stages more realistically, reliably and precisely,

the destructive Indirect Tension Test (ITT) in AASHTO T 283 was replaced by the non-destructive ITSM test in the 'revised modified Lottman' test and the number of samples allocated for this test was decreased to the minimum of three samples to satisfy the minimum number of samples required to statistically credit the test results interpretation.

The 'revised modified Lottman' moisture sensitivity evaluation test, developed by the researcher in the current study included the following stages:

1) Measure the indirect tensile stiffness modulus of all unconditioned samples @ 20°C as S_0 via ITSM/IT-CY

2) Determine the bulk density and air void content of the virgin samples using the Aluminium Foil method

3) Vacuum saturation of the samples @ 35 mbar for 0.5h:

Saturate the samples with water using a vacuum pump. Samples were submerged in a water filled metal tub and experienced a vacuum suction of 35 mbar for 30 minutes.

4) Water bath @ 60°C for 24hrs:

Right after the vacuum saturation, the samples were weighed to determine their saturation percentage via basic volumetric calculations. Then they were placed in a 60°C water bath to rest for 24 hrs.

5) Perform the ITSM/IT-CY test @ 20°C to measure the indirect tensile stiffness modulus of the conditioned samples as S_1:

After the 60°C water bath, the samples were weighed once again to monitor the saturation percentage changes. Then they were placed in a 20°C water bath for about 6 hrs and after that, the ITSM/IT-CY test was performed on them to record their indirect tensile stiffness modulus.

6) Optional water bath at room temperature, for Gyro samples, as long as needed to get 60-80% saturation (if necessary):

In the case of the Gyro specimens, due to their very low air void content and low interconnectivity of the voids, the specimens needed to stay for a long while in a room temperature water bath so they could be saturated as much as 60 to 80%.

7) Freezing @ -10°C for 24hrs:

At this stage, samples were placed in a -10°C freezer conditioner for 20 hrs.

8) Perform the ITSM/IT-CY test @ 20°C to measure the indirect tensile stiffness modulus of the conditioned samples as S_2:

After the freezing phase, the samples were moved into a 20°C conditioner for about 6 hrs to be ready for the stiffness measurement test. Then the ITSM/IT-CY test was performed on them to finalise monitoring their stiffness variations over the conditioning period.

9) The ratios of Pre-Freezing and Post-Freezing indirect tensile stiffness modulus values to the initial value of stiffness, (S_1/S_0) and (S_2/S_0) respectively were recorded in order to study the moisture damage of the specimens. However, in the case of the Gyro samples with the long water bath conditioning stage at the room temperature, the terms,

indices and number of the calculated ratios were some different as can be seen in the test results.

In the current research, for the mixture of each 'sample group', the water sensitivity test has been performed on three samples. In the case of the cored samples (from slabs), the location of the cores in the slabs of different sample groups was similar so they should have experienced as similar a compaction effort and situation as possible.



Figure 3.31 : Test samples in 60°C water bath

The following table shows the main differences between the standard modified Lottman (AASHTO T 283) and the 'revised modified Lottman', which was developed and used in the current PhD research, by the researcher:

Table 3.13 : Revised modified Lottman test configurations compared to AASHTO T 283

ITEM	REVISED MODIFIED LOTTMAN TEST	MODIFIED LOTTMAN TESTAASHTO T 283
Strength test type	Indirect Tensile Stiffness Modulus test (ITSM/IT-CY)	Indirect Tension Test (ITT)
Sequence of the test stages included	1) ITSM/IT-CY 2) AV content measurement 3) Vacuum saturation 4) Saturation% determination 5) Hot water bath 6) Saturation% determination 7) ITSM/IT-CY 8) Freezing 9) ITSM/IT-CY	1) Curing 2) Ageing 3) Vacuum saturation 4) Freezing 5) Hot water bath 6) ITT
Vacuum saturation	0.5 hr @ 35 mbar	As long as 55 to 80% saturation is achieved
Hot Water bath	24 hrs @ 60°C	24 hrs @ 60°C
Freezing	24 hrs @ -10°C	24 hrs @ -18°C
Number of test samples	3	6 = 3 conditioned + 3 virgin
Test mode	Destructive conditioning, Non-destructive testing	Destructive conditioning, Destructive testing
Saturation limit	No limit	70 to 80%
Samples' air void content limitation	No limit	6.5 to 7.5%
Acceptance limit for the strength ratio	80%	80%
Additional conditioning	N.A.	Curing the loose mixture for 16 hrs @ 60°C followed by a 2-hrs ageing period at 135°C

3.6. BINDER-AGGREGATE ADHESION TESTING

3.6.1. ADHESION TENSILE TESTING MEASUREMENT USING PATTI

In this PhD research, as a complementary phase of the research methodology and as a fundamental test to interpret and justify the other mechanical test results, the ultimate tensile strength of binder-aggregate coating system in each of the studied mixtures (i.e. sample groups) has been evaluated by the use of a Pneumatic Adhesion Tensile Testing Instrument (PATTI). This equipment was developed by the National Institute of Standards and Technology (NIST).

Figure 3.32 and Figure 3.34 shows a schematic diagram of the PATTI test set and Figure 3.33 presents a cross-section schematic view of the instrument's operating system.

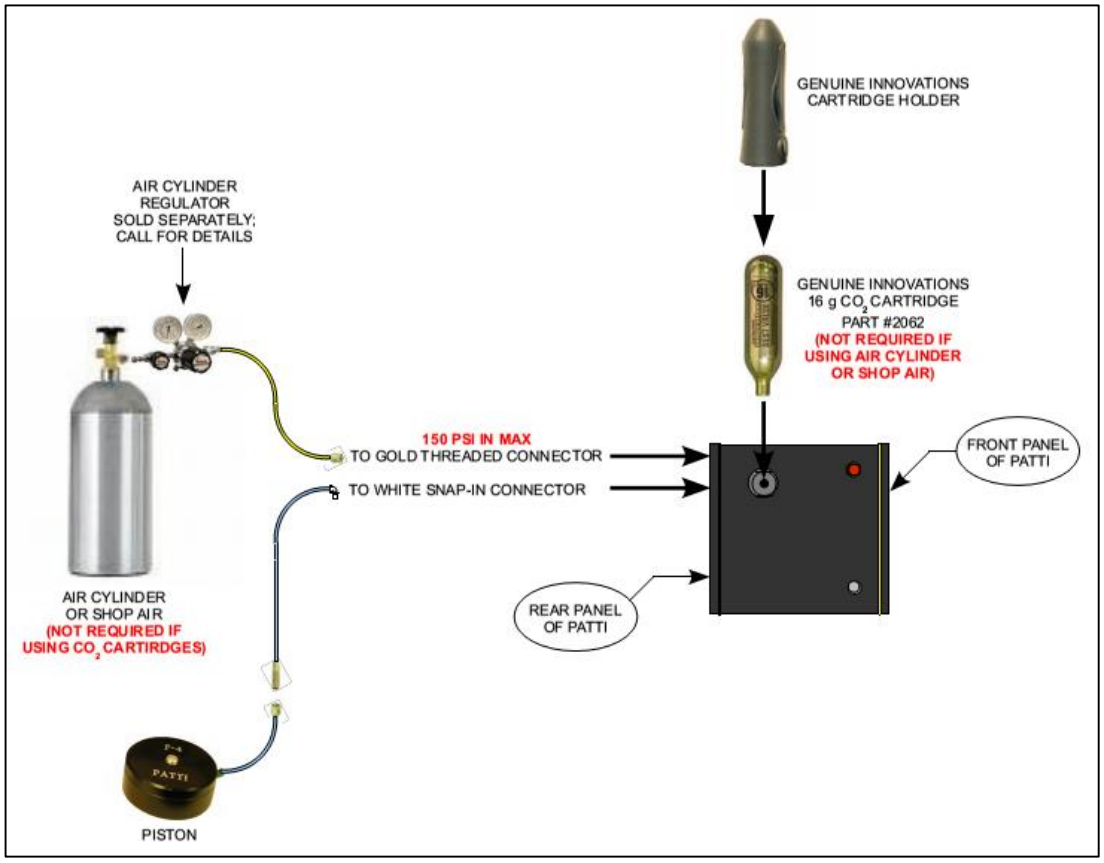


Figure 3.32 : PATTI test set (Quantom Series, 2002)

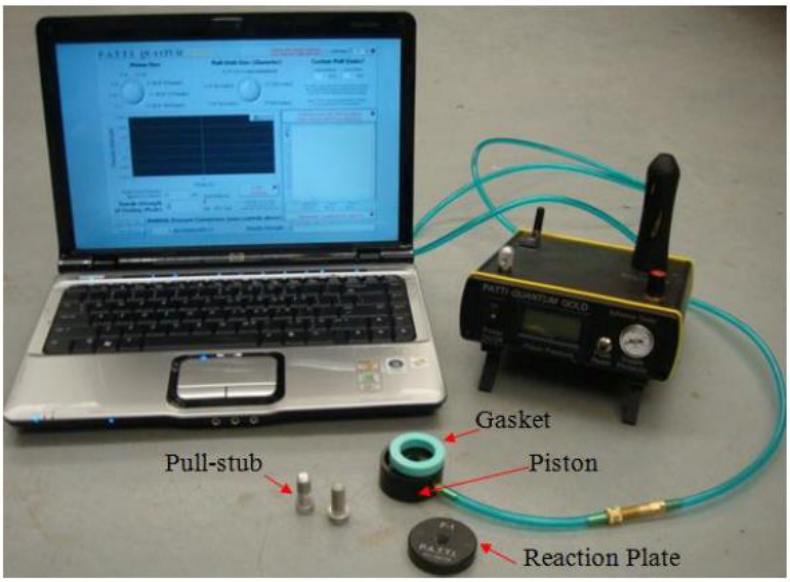


Figure 3.33 : Pneumatic Adhesion Tensile Testing Instrument (PATTI) (Kim, Ban & Pinto, 2009)

A PATTI test sample is fabricated by pouring some hot bitumen onto a prepared aggregate surface (cleaned), then immediately pressing it with a metal pull-stub to establish a good bitumen-aggregate bond. The instrument operates using pneumatic force and is equipped with an air pressure generating system. The air pressure is transmitted to the piston, which is placed over the pull stub and screwed on the reaction plate. The air pressure, on the one hand, applies an upward force to the gasket which has sealed the loading system. The upward force is also applied to the reaction plate and the screwed pull-stub. On the other hand, at the same time, the air pressure applies a downward force to the base plate and consequently to the aggregate surface. As a result, the pull-stub applies an upward stress perpendicular to the coating surface whereas the aggregate substrate exerts the same stress in the opposite direction. Therefore, a constant rate of pulling pressure, which is set in the PATTI pressure control panel, is applied to the coating sample. The test results in the form of tensile pressure versus testing time are recorded by a data acquisition system. The pressure at which the pull stub is debonded from the aggregate surface either by cohesive or adhesive failure is measured and converted to the pull-off tensile strength (Kim, Ban & Pinto, 2009).

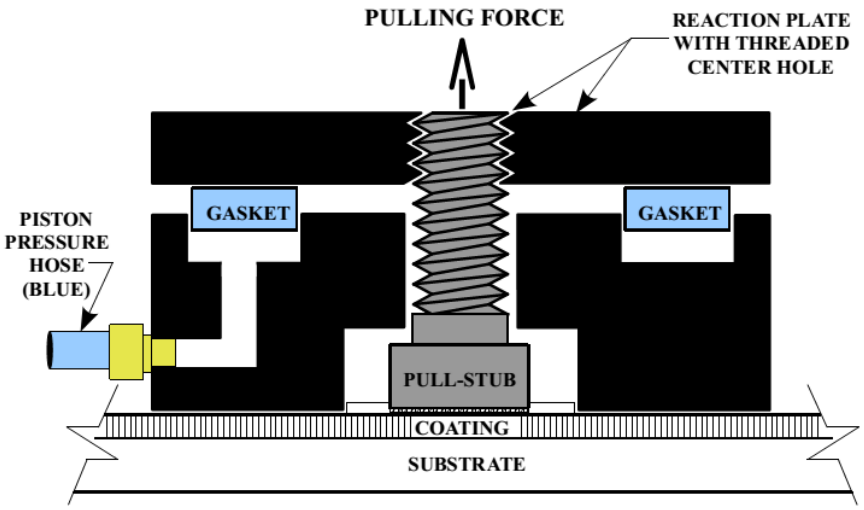


Figure 3.34 : Cross-section view of piston attached to pull-stub (Quantom, 2002)

In fact, each sample of PATTI consists of a coating of bitumen on an aggregate substrate, which together, as a system, experiences a pure increasing tensile stress up to the point of failure. The sample is supposed to simulate the tensile strength of the bitumen-aggregate coating in an asphalt mixture.

It should be mentioned that depending on the type of tensile failure in each test sample (i.e. adhesive or cohesive), the ultimate tensile strength of the coating might refer to either the bitumen-aggregate tensile adhesive bond or the bitumen cohesive tensile strength.

It is needless to remark that the presence of water has a significant effect on the type of failure and the results of pull off tensile strength. In fact, the more the moisture damage the lower the adhesive tensile strength of the bitumen aggregate coating. However, in the current research the samples were produced in such a way that they were not influenced by moisture. Therefore, none of the tensile failures are expected to refer to the moisture damage issue.

In addition to measure the tensile strength of the system quantitatively, the quality of the bitumen-aggregate system under the tensile load has been evaluated through visual investigations via photography or naked eye observations.

Kanitpong & Bahia (2003) stated that the results of the pull off tensile strength conducted using the PATTI had poor repeatability. Moreover, according to the researchers who have so far worked with the PATTI, binder film thickness, loading rate, test temperature, soaking time, bitumen grading and ageing all have significant effects on the pull-off tensile strength value.

The standard PATTI test is performed in accordance with ASTM D4541, Pull-off Strength of Coatings Using Portable Adhesion Testers. However, in the current research, some slight modifications in terms of sample preparation have been devised and applied to the standard method. In the current research, for each of the two types of specimens (i.e. Dene gyro and Tunstead core), to represent the bitumen -aggregate coating quality and tensile strength of each of the 4 ‘mixture groups’, 6 PATTI samples were fabricated. This means 24 PATTI samples for each aggregate substrate (i.e. Dene limestone and Tunstead limestone).

In this research, other than studying the effect of aggregate and bitumen type on the coating quality and tensile strength, it has also been tried to investigate the effect of coating (i.e. mixing) temperature. When fabricating the PATTI test samples representing a certain mixture group, a method was devised to simulate and investigate the effect of mixing temperature on the quality and tensile strength of the bitumen-aggregate coating. Before introducing the binder to the aggregate substrate, both were placed in an oven set at the mixing temperature of the represented mixture group for about an hour, so the coating takes place at the actual mixing temperature. The following table shows how the PATTI samples were supposed to represent the mixture groups:

Table 3.14 : Specifications of the PATTI test samples according to the mixture groups

				REPRESENTATIVE PATTI TEST SAMPLES		
NO.	**MIXTURE GROUP NAME**	**ABBREVIATION**	**MIXING TEMPERATURE (°C)**	**BITUMEN/ BINDER TYPE**	**BITUMEN/BINDER and AGGREGATE TEMPERATURE for INTRODUCTION (°C)**	**SUBSTRATE AGGREGATE TYPE**
1.	Standard Reference HMA	StdRefHMAM150	150	Pure Bitumen 70/100 Pen.	150	1) Dene Limestone 2) Tunstead Limestone
2.	Non-Standard HMA	NStdHMAM135	135	Pure Bitumen 70/100 Pen.	135	1) Dene Limestone 2) Tunstead Limestone
3.	3%FTWax-WMA	3%FTWxWMAM135	135	3%FTWax-Modified Bitumen 70/100 Pen.	135	1) Dene Limestone 2) Tunstead Limestone
4.	0.6%CatSurfLq-WMA	0.6%CSLqWMAM130	130	0.6%CatSurfLq-Modified Bitumen 70/100 Pen.	130	1) Dene Limestone 2) Tunstead Limestone

According to the practical recommendations regarding the PATTI test sample preparation, the film thickness of the coating influences the repeatability of test results. In order to improve the repeatability of the results, the pull-stubs used in this research could control the thickness (0.8 mm) and the uniformity of the binder by the help of four bevels on their edge, as shown in Figure 3.34. The rigid aggregate substrate slices with flat and clean surfaces and about 20 mm thickness were cut from the 83mm diameter cores taken from the associated stone boulders. The PATTI test specimens were prepared through the following steps:

1) Surface pre-treatment:

   The surface of the aggregate substrate and the pull-stub were washed by white spirit, acetone and deionised water (in that order). Then they were left in an oven to be dried properly.

2) Pre-heating the aggregate, pull-stub and bitumen:

   As mentioned in the previous pages, the pull-stub, bitumen and aggregate were placed in an oven to be heated up to the mixing temperature of the represented mixture group for about 1 hour.

3) The aggregate substrates and the binder were taken out from the oven. The liquid bituminous binder was then poured on the surface of the aggregate substrate.

4) The preheated pull-stub was placed on the top of the bitumen layer. Then gentle pressure was applied to the pull-stub perpendicular to the aggregate surface to allow the four bevels of the pull-stub touch the aggregate surface, so as a result, a uniform film thickness was obtained.

5) The excess bitumen at the edge of the pull-stub was removed using a small knife.

6) After trimming, the specimens were left to rest in a 20°C conditioning cabinet to cool down.

7) The specimens were tested after at least 4 hours of their fabrication.

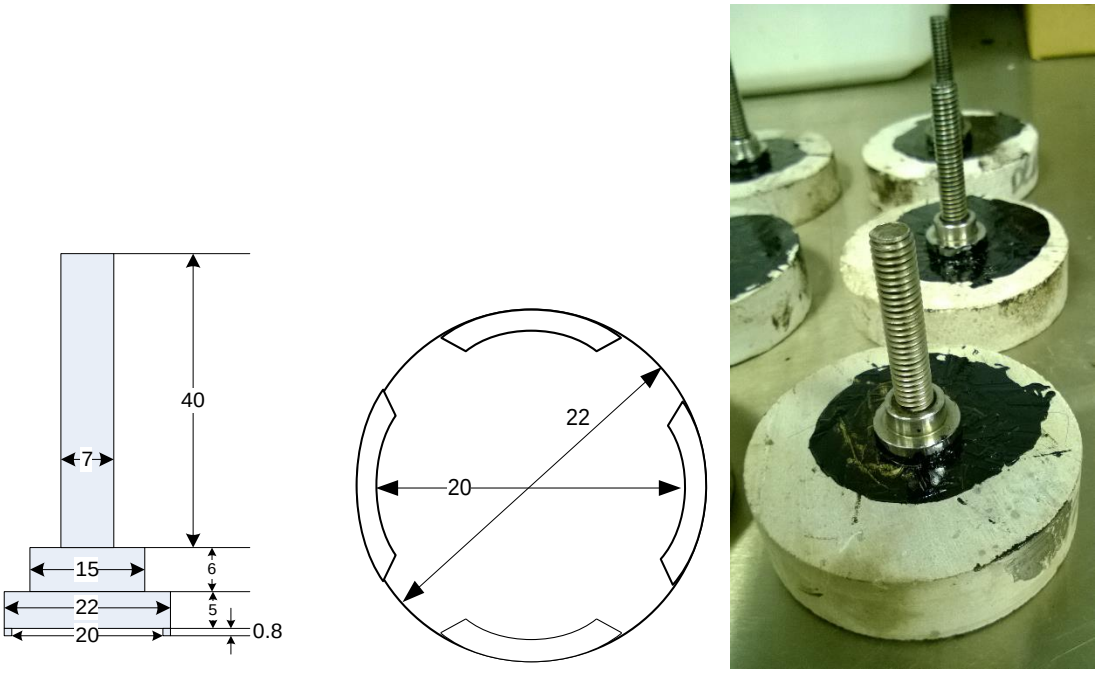


Figure 3.35 : Pull-stub in profile and bottom views

The tensile strength of the coating is calculated through the following equations by the PATTI software.

$$T_{po} = \left(\left(P_b \times A_g\right) - C\right)/A_{ps} \qquad \text{Equation 3.32}$$

Where:

T_{po} = Pull-off tensile strength (kPa)

P_b = Burst pressure (kPa)

A_g = Contact area of gasket with relation plate (m^2)

C = Piston constant (kN)

A_{ps} = Area of pull-stub (m^2)

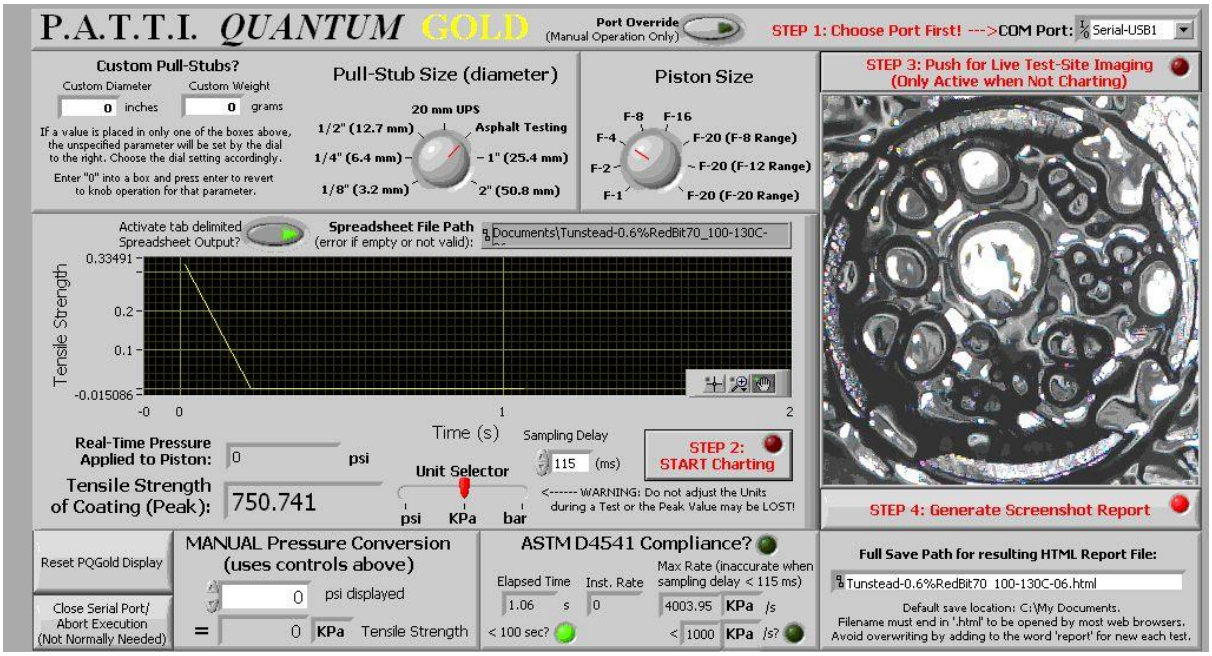


Figure 3.36 : PATTI analyser software's environment

The test results from both types of aggregates have been presented in the form of bar charts in the next chapter.

4. BINDER TEST RESULTS

In the present chapter, the results of the tests which were performed on the pure and modified binders have been presented and discussed.

4.1. PENETRATION GRADE, SOFTENING POINT and FRAASS BREAKING POINT DETERMINATION

The results of penetration grade, softening point and Fraass breaking point determination tests on the samples of all pure and modified binder used in the current research have been presented in Table 4.1 and Table 4.2 as well as schematically in Figure 4.1 and Figure 4.2. It can be seen that while adding CatSurfLq has nearly no effect on penetration grade and softening point of the binders, adding FTWax significantly increases the softening point and decreases the penetration grade and these changes grow by increasing FTWax dosage. In fact, FTWax modifies bitumen's rheological properties whereas CatSurfLq has nearly no influence on this aspect of bitumen behaviour. This can refer to the fact that FTWax develops a crystallised structure in the bitumen bulk when it congeals. The formed crystalized structure acts like a reinforcement for bitumen structure, which increases bitumen stiffness at operation temperatures (e.g. 25°C as penetration grade determination temperature). Moreover, the considerable decrease in FTWax viscosity at the wax transition point makes the modified bitumen viscosity plunge passing the FTWax transition point through the heating up process. Therefore, the FTWax-modified binders have higher softening point compared to their pure base bitumen. However, none of the influences are observed where CatSurfLq is added to bitumen because the chemical additive has been designed and is supposed to affect the surface energy properties of bitumen (and aggregate) and the bitumen-aggregate adhesive bond strength. Looking at the Fraass breaking point determination test results illustrates that both additives more or less increase the Fraass breaking point, which means that both modified bitumen types have become more brittle. The brittleness of the FTWax-modified binders increasing compared to the pure base binder is expectable according to the literature reviewed. FTWax-modified binders have generally higher low-temperature cracking potential. This can be referred to the much lower ductility of FTWax compared to pure base bitumen at low temperatures and the consequent decrease in the ductility of FTWax-modified binders at low

temperatures due to the presence of the crystalized structure of FTWax in bitumen developed through congealing of FTWax in the bulk of bitumen. Later, it will be shown that FTWax decreases the surface tension of the modified bitumen compared to the base binder due to which the ultimate tensile strength of bitumen decreases in the presence of FTWax. This can be another reason for the increase Fraass breaking point of the FTWax-modified binders compared to the pure ones. The same justification can be brought where CatSurfLq is added to bitumen. This chemical additive slightly decreases the surface tension of bitumen to provides more ability to wet the aggregate particles, which should results in decreasing the ultimate tensile strength and the Fraass breaking point of the CatSurfLq-modified binders compared to the associated base binders. It has been described in the Surface Energy Section of Literature Review Chapter that the ultimate tensile strength of a liquid (e.g. bitumen) is another aspect of its 'Work of Cohesion' or cohesive tensile strength and is two times as big as the numerical value of its total surface energy.

Table 4.1 : Penetration grade, softening point and Fraass breaking point determination test results (FTWax-modified binders)

BITUMEN/BINDER	160/220	160/220 +2%FTWax	160/220 +3%FTWax	160/220 +10%FTWax
PEN. GRADE (mm)	200	145	126	57
SOFT. POINT (°C)	37	64.4	75	99.5
BITUMEN/BINDER	**30/45**	**30/45 +2%FTWax**	**30/45 +3%FTWax**	**30/45 +10%FTWax**
PEN. GRADE (mm)	36	27	26	17
SOFT. POINT (°C)	54	67	82.5	102
BITUMEN/BINDER	**70/100**	**70/100 +2%FTWax**	**70/100 +3%FTWax**	**70/100 +10%FTWax**
PEN. GRADE (mm)	90	60	56	34
SOFT. POINT (°C)	44.8	71.6	81	101.5
FRAASS BREAKING POINT (°C)	-12	-13	-13	-8

Table 4.2 : Penetration grade, softening point and Fraass breaking point determination test results (CatSurfLq-modified binders)

BITUMEN/BINDER	160/220	160/220 +0.4%CatSurfLq	160/220 +0.5%CatSurfLq	160/220 +0.6%CatSurfLq
PEN. GRADE (mm)	200	N.A.	186	184
SOFT. POINT (°C)	37	N.A.	37.6	37.6
BITUMEN/BINDER	**30/45**	**30/45 +0.4%CatSurfLq**	**30/45 +0.5%CatSurfLq**	**30/45 +0.6%CatSurfLq**
PEN. GRADE (mm)	36	N.A.	34	34
SOFT. POINT (°C)	54	N.A.	54	54.8
BITUMEN/BINDER	**70/100**	**70/100 +0.4%CatSurfLq**	**70/100 +0.5%CatSurfLq**	**70/100 +0.6%CatSurfLq**
PEN. GRADE (mm)	90	87	87	85
SOFT. POINT (°C)	44.8	44.8	45.2	45.6
FRAASS BREAKING POINT (°C)	-12	-12	-10	-9

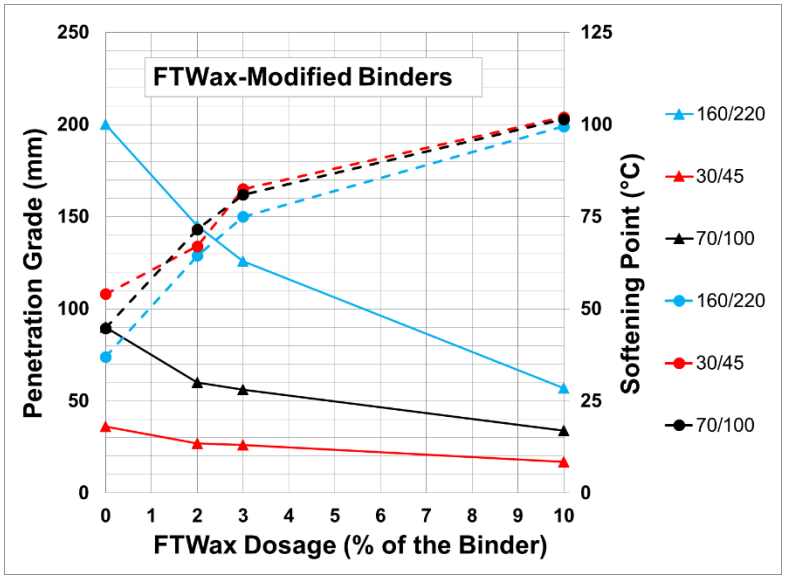


Figure 4.1 : Penetration grade, softening point and Fraass breaking point determination test results (FTWax-modified binders)

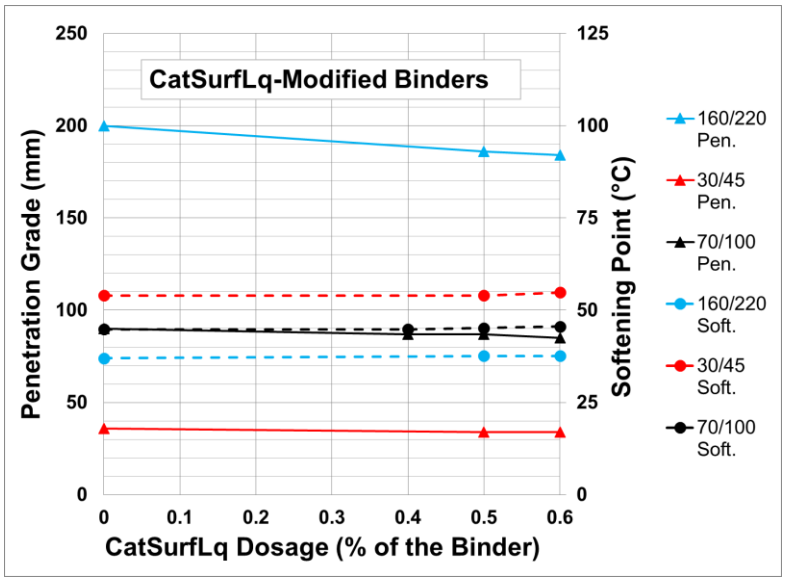


Figure 4.2 : Penetration grade, softening point and Fraass breaking point determination test results (CatSurfLq-modified binders)

4.2. BROOKFIELD VISCOMETRY TEST

From the test results, it can be observed that just after FTWax's melting temperature (transition point), the viscosity of the modified binder drops and the viscosity curve shifts down afterwards. However, it seems that at temperatures lower than the transition point the crystallisation phenomenon in the wax structure results in an increased viscosity of the binder.

As can be seen in Table 4.3, Figure 4.3 and Figure 4.4 according to the Brookfield viscometry test results performed based on BS EN 13302:2010, the viscosity of the 70/100 pen bitumen was not reduced as much as that it could reduce the mixing and compaction temperature by 25°C as promised in NCAT Report 05-06 or even by 15°C as shown by Liu & Li (2012). Even increasing the dosage of FTWax up to 10% by the weight of the binder and also performing the test on both the 30/45 pen and the 160/220 pen binders did not show the promised level of reduction in the viscosity of the binders.

Table 4.3 : BSEN-based Brookfield viscometry test results

		BINDER					
		70/100	70/100 +2%FTWax	70/100 +3%FTWax	70/100 +10%FTWax	70/100 +0.5%CatSurfLq	70/100 +0.6%CatSurfLq
		VISCOSITY (cP) [mPa.S]					
TEMPERATURE(°C)	90	6000.0	5815.0	15837.0	70545.0	5619.0	6539.0
	100	2795.0	2052.0	4042.3	28833.0	2555.0	3034.0
	110	1404.0	1064.0	989.1	775.0	1298.0	1485.0
	120	736.6	601.1	557.9	394.5	712.6	783.8
	130	431.9	344.9	322.3	250.5	394.9	449.9
	140	258.5	211.2	197.4	159.0	240.5	269.9
	150	163.2	142.2	133.2	105.2	158.4	166.0
	160	113.4	96.0	89.1	75.6	104.7	115.0
	170	78.6	66.0	62.1	54.6	72.1	80.0
	180	56.4	48.6	46.5	40.8	53.1	61.0

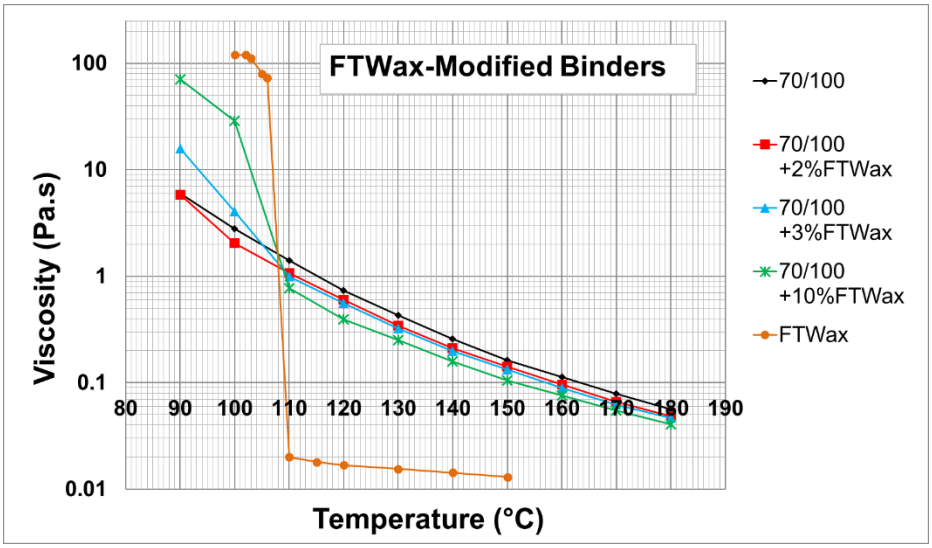


Figure 4.3 : BSEN-based Brookfield viscometry test results (FTWax-modified binders)

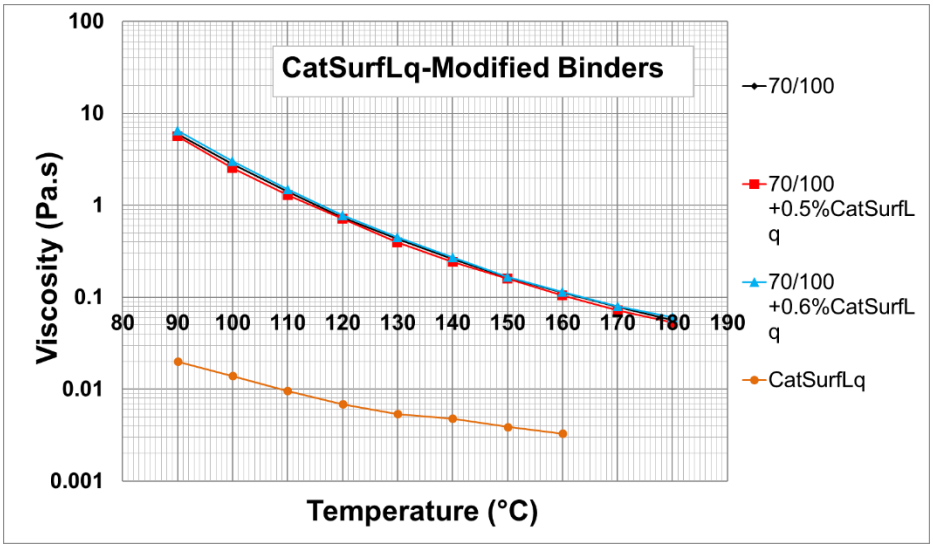


Figure 4.4 : BSEN-based Brookfield viscometry test results (CatSurfLq-modified binders)

Therefore, in order to make sure about the repeatability of the results, the test was repeated again but this time, based on ASTM D4402. Referring to the results of ASTM-based Brookfield viscometry test, as shown in Table 4.4 and Figure 4.5 andFigure 4.6, it can be seen that adding 3% FTWax can decrease the mixing and compaction temperature by up to 10°C, which is still less than the amount reported in the NCAT Report 05-06, work by Liu & Li (2012) and as promised by the producer.

Table 4.4 : ASTM-based Brookfield viscometry test results

		BITUMEN					
		70/100	70/100 +2%FTWax	70/100 +3%FTWax	70/100 +0.4%CatSurfLq	70/100 +0.5%CatSurfLq	70/100 +0.6%CatSurfLq
		VISCOSITY (cP) [mPa.S]					
TEMPERATURE (°C)	90	5565.0	3993.0	3355.0	4968.0	5030.0	4985.0
	100	2336.0	1740.0	1449.0	2275.7	2118.3	2013.3
	110	1176.0	905.7	765.0	1156.0	1077.0	1078.0
	120	647.9	507.3	438.2	596.4	592.8	590.5
	130	364.2	290.6	253.1	333.9	331.6	330.4
	140	217.9	176.9	153.5	202.7	199.2	196.8
	150	144.1	118.3	101.9	132.4	131.6	128.9
	160	96.1	79.7	69.1	92.6	86.7	85.5
	170	66.8	55.1	46.9	63.3	58.6	56.2
	180	49.2	43.4	35.1	45.7	43.4	42.2

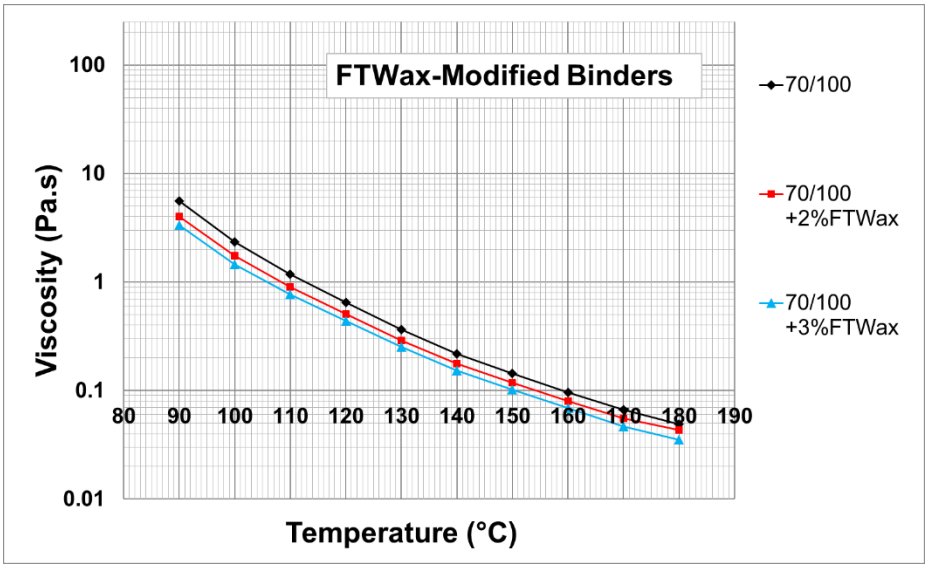


Figure 4.5 : ASTM-based Brookfield viscometry test results (FTWax-modified binders)

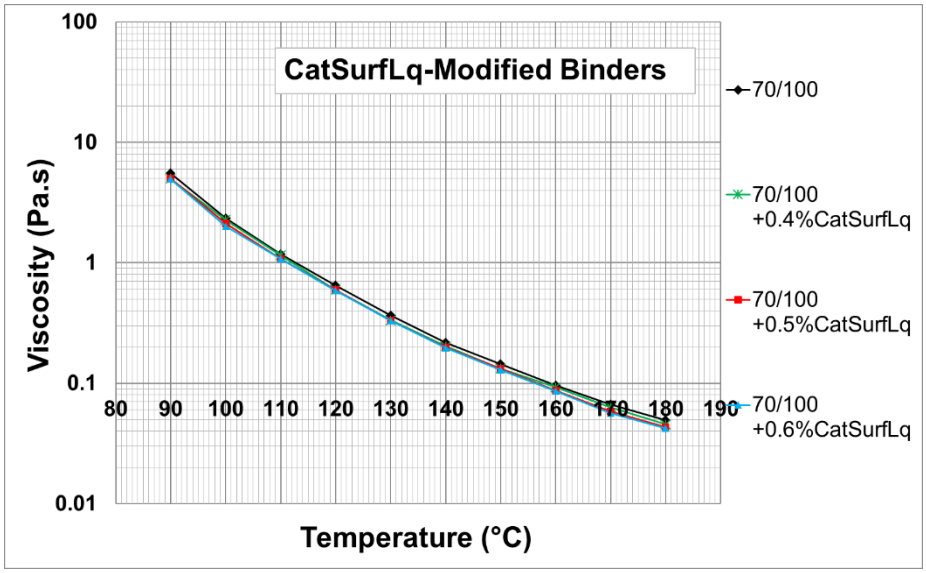


Figure 4.6 : ASTM-based Brookfield viscometry test results (CatSurfLq-modified binders)

In order to justify the difference between the results of the two Brookfield viscometries performed in accordance with two various standards, the recommendation of the Brookfield viscometer manual (2015) was considered stating that "viscosity measurements should be taken under laminar flow conditions, not under turbulent flow conditions". In fact, the ASTM-based Brookfield viscometry has been more reliable at temperatures higher than FTWax transition point. The reason for this expression refers to the higher turbulence of the bitumen flow between the inner wall of the apparatus cup and the surface of the rotating spindle in the BSEN-based tests compared to the ASTM-based ones. It should be mentioned that the BS EN spindle (SC-34) is significantly thinner than the ASTM spindle (SC-27). Therefore, due to the

greater gap between the inner wall of the cup and the surface of the spindle in the BSEN-based test compared to the ASTM-based test, the rotational flow of bitumen around the spindle will be less laminar and more turbulent at high temperatures and rotational speeds. This turbulent flow can result in applying some additional unwanted friction on the surface of the spindle and therefore show a greater value of the binder viscosity than it really is (overestimates the viscosity).

On the other hand, at temperatures about or lower than FTWax transition point, the BS EN spindle was recognised as more reliable. It was observed that using the thick spindle of ASTM setting at temperatures around the FTWax transition point, the wax-modified binder melted at lower temperatures. In fact, as the gap between the spindle and the inner wall of the cup was much smaller in the ASTM-based test compared with the BSEN-based one, the binder layer was much thinner. Therefore, the friction developed through the rotating action of the spindle inside such a viscous binder at such a relatively low temperature probably could have produced extra heat that melted the FTWax all through the thin layer of bitumen at lower temperatures than the BSEN-based test. This means that the FTWax-modified binders' viscosities were underestimated through the ASTM-based viscometry.

Therefore, a combination of BS EN and ASTM settings were used based on the fact that at low temperatures (temperatures about the FTWax transition point) the thin spindle of BS EN and at temperatures higher than that the thick spindle of ASTM was used.

The results of the combination of both ASTM and BS EN Brookfield viscometries combined with the penetration grade, softening point and Fraass breaking point determination test results was used to develop the data lines of the binders (those used in manufacturing the asphalt samples in the current research) on a Bitumen Test Data Chart as shown in Figure 4.7. This chart has been used in the next chapters widely to justify the mixture test results.

However, for the CatSurfLq chemical additive, nearly no effect on the viscosity of the binder can be seen, which was expected from the specifications according to the material producer. This issue also conforms to the other rheological tests.

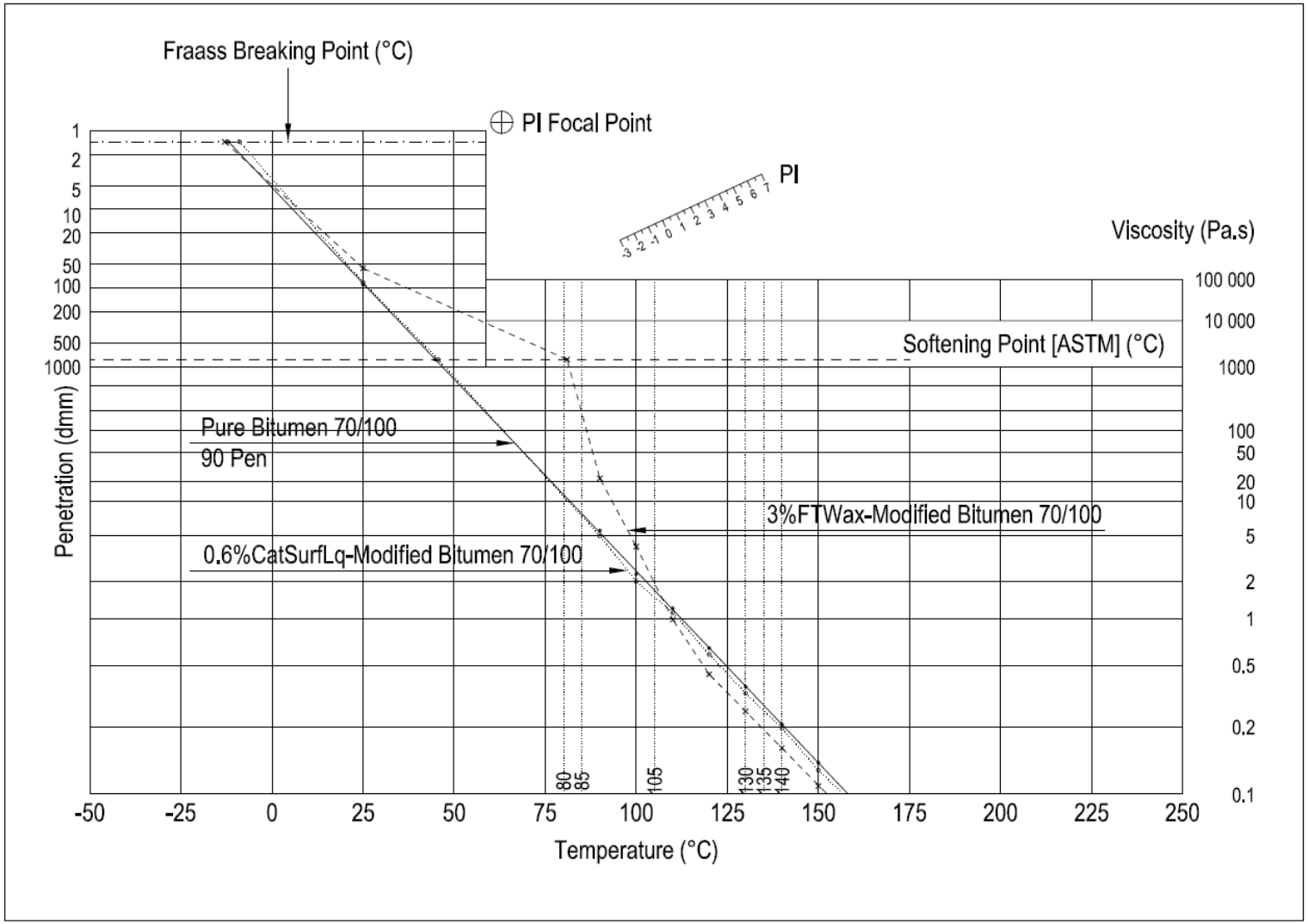


Figure 4.7 : Final data lines/curves of the used bituminous binders on Bitumen Test Data Chart

4.3. BITUMEN WAX CONTENT TEST

The Bitumen Wax Content test showed that the base bitumens were non-waxy types. As they contained no more than 0.06% and 0.02% of Paraffin wax for the 160/220 pen and 30/45 pen, respectively.

Thus, it was initially postulated that the unexpected results (small decrease in the viscosity of the modified binders compared to their pure bitumen) of Brookfield viscometry test might have been because the bitumen samples had nearly no wax initially and due to which, the added FTWax might have been consumed by the non-waxy bitumen to increase its wax content to a normal balanced level.

To check this theory, it was necessary to add more FTWax to modify the pure bitumen samples and 10% FTWax-modified binders were produced. However, performing the same Brookfield viscomety test on the 10% FTWax-modified bitumen grades did not result in any significant decrease in the viscosity of the binders as mentioned in the associated test results interpretations in the previous section.

4.4. FREQUENCY-TEMPERATURE SWEEP TEST

The frequency-temperature sweep test, as mentioned before, was performed in strain-controlled mode applying a maximum strain value of 0.5%, 0.4% and 0.3% for 0%, 2% and 3% FTWax-modified binders respectively to remain within the Linear Visco-Elastic Region (LVER). For the CatSurfLq-modified samples, the LVER has been set to the same value as for the neat binder. The results of the frequency-temperature sweeps tests have been shown in Figure 4.8 to Figure 4.11.

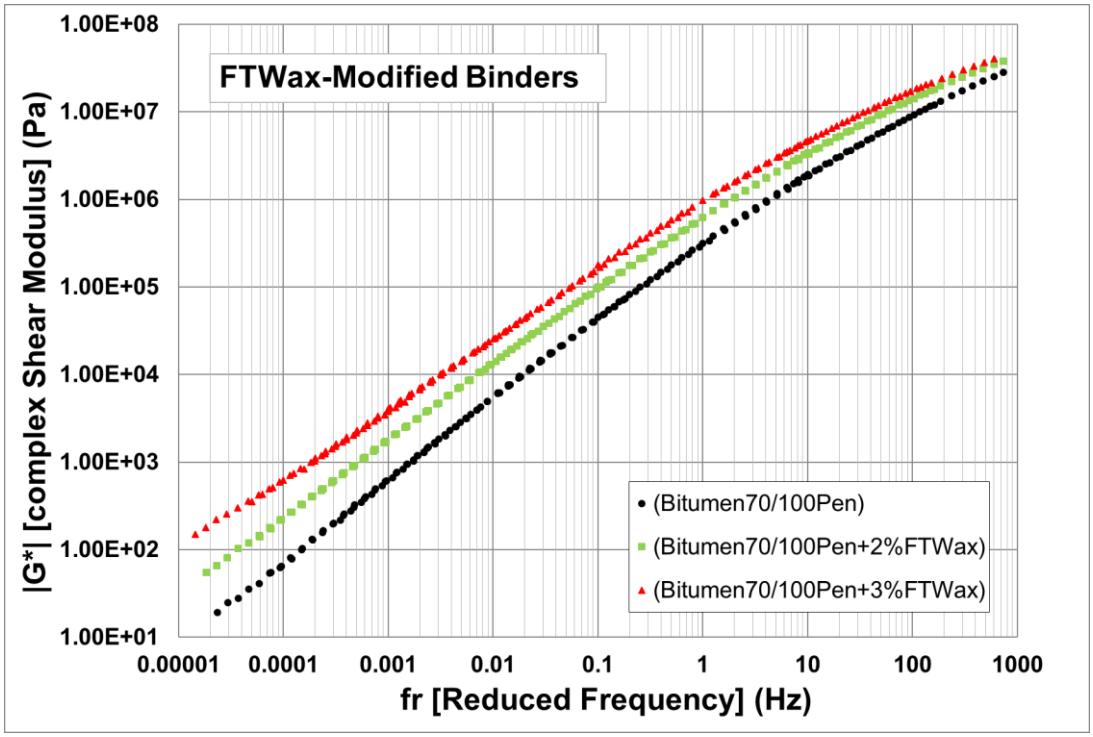


Figure 4.8 : Comparative master curves for the complex shear modulus of the FTWax-modified binders (Reference temperature = 25°C)

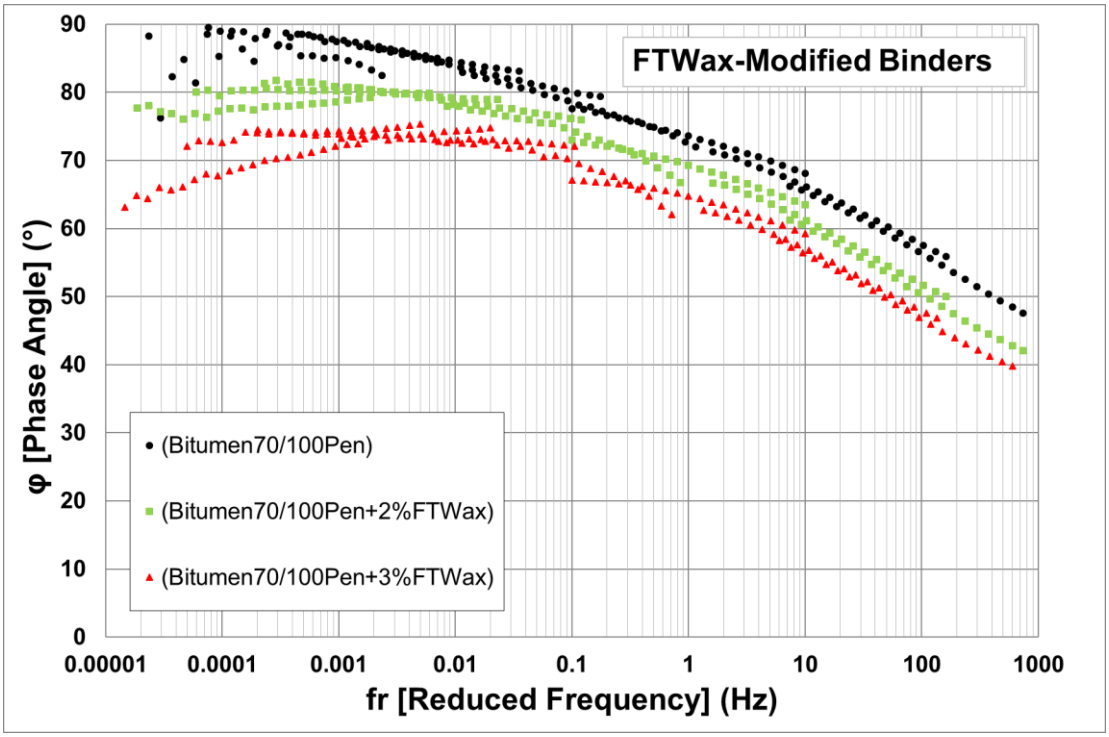


Figure 4.9 : Comparative master curves for the phase angle of the FTWax-modified binders (Reference temperature = 25°C)

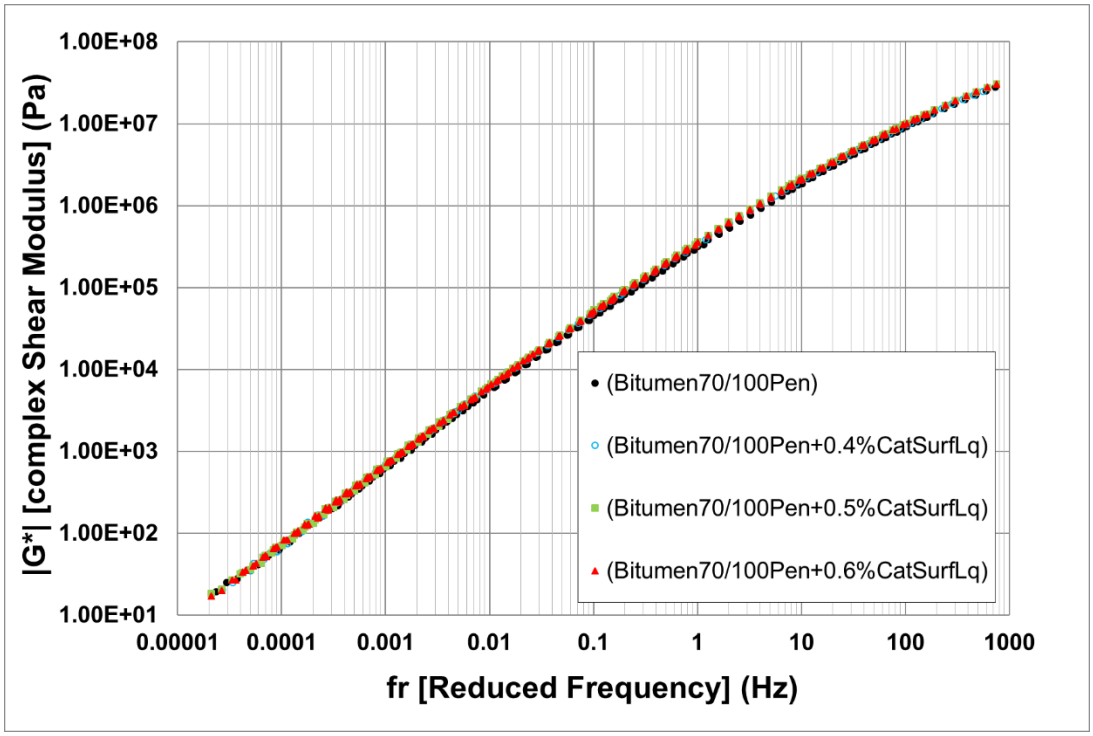


Figure 4.10 : Comparative master curves for the complex shear modulus of the CatSurfLq-modified binders (Reference temperature = 25°C)

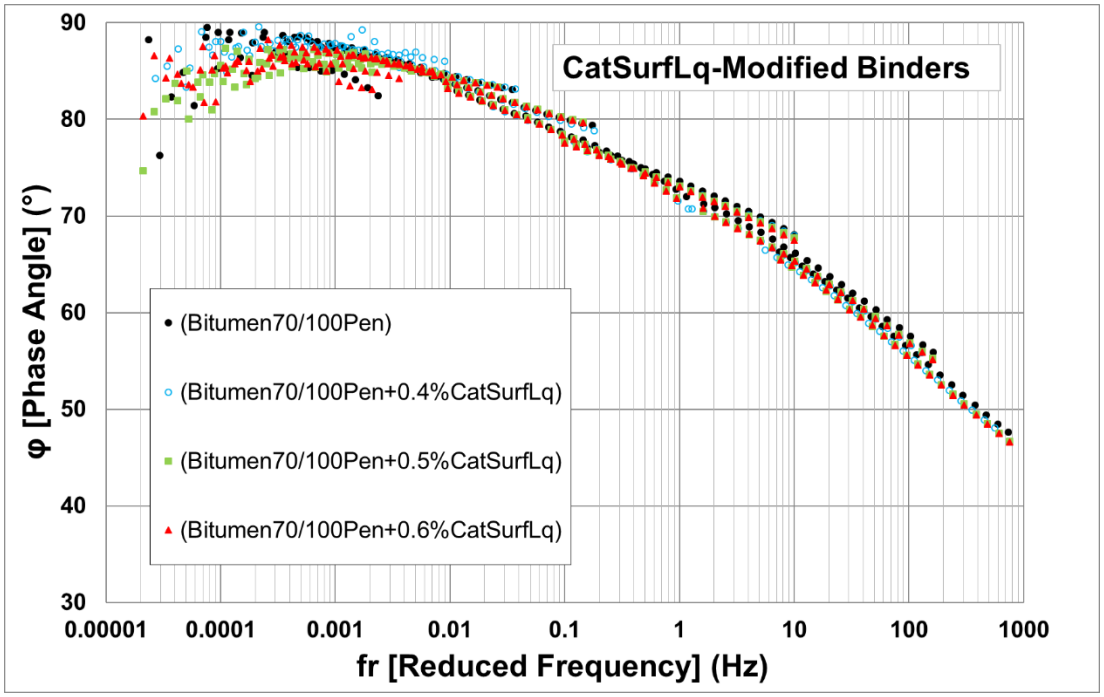


Figure 4.11 : Comparative master curves for the phase angle of the CatSurfLq-modified binders (Reference temperature = 25°C)

From the test results, it can be concluded that adding FTWax increases the complex shear modulus (*G**) and decreases the phase angle of the binders, while the CatSurfLq has nearly no influence on the parameters and mechanical-rheological characteristics.

Adding 3% FTWax to pure bitumen 70/100 pen increases its complex shear modulus by nearly 1.5 times at about 10°C and 8 times at about 75°C. Adding 2% FTWax has increased the complex shear modulus by about 1.5 times at 10°C and nearly 3 times at about 75°C.

Such increase in the shear stiffness of the FTWax-modified binders is due to the structural reinforcement developed in bitumen by FTWax crystallization phenomenon at temperatures below the FTWax transition point. Therefore, higher stiffness moduli for the resulted mixtures are expected. The frequency-temperature sweeps test results have been used to justify the mixture test results in the next chapters.

4.5. SURFACE ENERGY MEASUREMENT via DYNAMIC CONTACT ANGLE (DCA) METHOD

Table 4.5 illustrates the results of surface energy measurement which has been performed through the Dynamic Contact Angle (DCA) method by the use of a Wilhelmy plate apparatus. Referring to Table 4.5, the relatively high values of γ^{LW} component (representative of the Van der Waals non-polar interaction forces) for all binder samples, confirm that all tested bitumens in the current research, whether pure or modified, are more or less non-polar as in a general statement, a bitumen sample is naturally expected to be.

However, in contrast with the slightly acidic behaviour which is usually expected from any pure bitumen (due to the presence of carboxylic acids in bitumen), the higher value of γ^- (basic component) compared to γ^+ (acidic component) indicates that the pure bitumen used in the current research is slightly basic in nature. It means that this bitumen is expected to give better adhesion if it is introduced to acidic aggregates (e.g. normal granite or Dene limestone as it was found to be in this research).

In the case of the FTWax-modified binders, it can be observed that adding FTWax has caused both non-polar and basic surface energy components to decrease compared to the pure base bitumen 70/100 pen. However, the amount of increase in the acidic component is not significant. As a result, it can be stated that FTWax decreases the total surface energy of

bitumen. Therefore, it decreases the ultimate tensile strength of bitumen, which will be discussed in the next chapters. Moreover, it seems that increasing the dosage of FTWax have had a slight reduction effect on the non-polar SE component as well as γ^{Total}.

According to the results reflected in Table 4.5, adding the recommended dosages of CatSurfLq (i.e. 0.4% or 0.6%) has not considerably changed the non-polar component of bitumen's surface energy, whereas it has significantly decreased both γ^{+} and γ^{-}. This means that it has potentially lowered the moisture susceptibility of the associated asphalt mixtures. As a result, the recommended dosages of CatSurfLq to produce WMA mixture also have slightly reduced or not altered the value of γ^{Total} which means that the chemical additive has quite negligibly or not modified the SE (Surface Tension) of the binder. These results do not fully confirm the literature reviewed on this matter and presented in Chapter Literature Review. According to Sections 2.3.2.3, 2.10.5 and 2.11.3.3, the chemical additives of WMA are generally surfactants and adhesion promoters, which are promised to influence both bitumen and aggregate via decreasing the SE of the former (to decrease the contact angle and increase the potential of wetting and being spread) and increasing the SE of the latter (to increase the wettability). In order to do so, the molecules of the surfactants and chemical additives, in practice, move to the surface of bitumen or bitumen-aggregate interface so their polar head positions at the surface of bitumen or attach to the aggregate surface's active points and their hydrocarbon tail stands inwards into the bitumen. This means that as long as bitumen is hot and fluid enough, the dosage of the CatSurfLq should be higher at the bitumen surface or bitumen-aggregate interface compared to the inside of the bulk of bitumen.

As a side conclusion through a study performed by Kino (2014) to compare the Classical Wilhelmy plate method (which has been used in the current research) and Modified Wilhelmy plate method, which has been devised by Kino (2014), it was shown that in the Wilhelmy plate method, the surfactants will adsorb at the interface between the liquid and gas at first and adsorb to the contact line once the plate is touching the interface and will keep on adsorbing until the contact line is full of the surfactants as shown in Figure 4.12. Moreover, it was found that when measuring the surface tension using Wilhelmy plate method, the Langmuir monolayers were formed at the surface of the slide during the measuring process. Especially when measuring the surface tension of the surfactants, this new surface of the monolayers will collect another new layer of the surfactants (Figure 4.12).

Considering the results of this research, one possibility is that the CatSurfLq molecules should have moved to the bitumen surface even in the bitumen layer of the DCA test samples of the 0.6%CatSurfLq-modified bitumen (Figure 4.12). Also, it is possible that in the process of manufacturing the DCA test samples, while dipping the glass slides into the hot bitumen placed in the container, the bitumen samples should have already been collected from the parts with higher CatSurfLq dosage because the CatSurfLq molecules should have moved to the surface of the container (Figure 4.12). Both possibilities indicate that the 0.6%CatSurfLq-modified samples should have a dosage of CatSurfLq higher than the 'nominal 0.6%'. If this postulation conforms to the reality, the test results of DCA on 0.6%CatSurfLq-modified bitumen should simulate a realistic situation and represent the actual SE values of the modified bitumen in a 0.6%CatSurfLq-WMA mixture. In this case, the results of the DCA test on the 0.6%CatSurfLq-modified binder confirm that CatSurfLq does not decrease the SE of bitumen which means that it does not contribute to the adhesion promotion through decreasing the SE of bitumen. This is unexpected, although decreasing the polar components of SE indicates some potential decrease in the moisture susceptibility of the resulting mixtures.

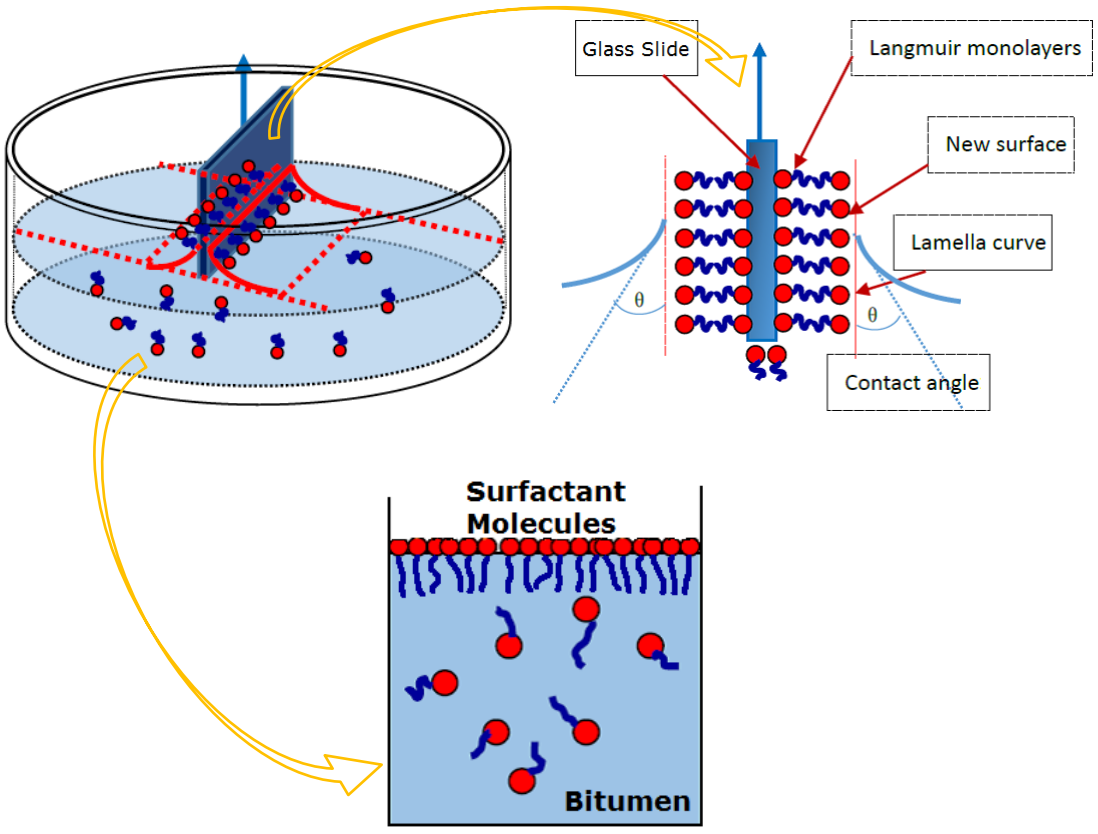


Figure 4.12 : Schematic diagram for the positioning of the surfactant molecules in the CatSurfLq-modified binder's container and DCA sample slide (Kino, 2014)

Another possibility is that, for some reason, the additive molecules have not been moved to the surface of the bitumen layer on the DCA test glass slide sample due to the presence of glass or for some reason such as not collecting the bitumen sample from a proper zone of the hot bitumen container tin (the area with high dosage of the additive). In these cases, the DCA samples manufactured from the 0.6%CatSurfLq-modified bitumen are not reflecting the actual situation of the bitumen sample at the binder-aggregate interface in the 0.6%CatSurfLq-WMA mixtures. This means that the DCA test results for this sample is not acceptable. Therefore, a much-higher-dosage bitumen sample should be tested. For this purpose a 5% CatSurfLq-modified bitumen 70/100 pen sample was produced and its SE components were measured through the DCA method. By this means, it was, in a way assured that even if the CatSurfLq molecules did not move through the modified binder to the surface/interface (for any reason), the dosage of the additive all through the bulk of the modified bitumen sample has become so high that at the surface of the bitumen blend, likewise the surface of the bitumen coating on the glass slides, should be as high as its actual dosage at the binder-aggregate interface in the 0.6%CatSurfLq-WMA mixture. However, looking at the values of SE components for the 5%CatSurfLq-modified bitumen 70/100 pen another unexpected issue arose because they indicated that the high dosage of CatSurfLq (as it was expected to be at the bitumen-aggregate interface) significantly increased the basic (as it contains cationic surfactants) and non-polar SE components as well as the total SE component of the associated modified binder, which meant potentially increasing the contact angle of the CatSurfLq-modified binder on the aggregate surface and decreasing the wetting potential of the aggregate. This meant that either the chemical additive did not work as promised or should be tested in the presence of aggregates, as well. In other words, the DCA test samples might not have properly represented the binder's situation in the CatSurfLq-WMA mixtures.

However, as stated in the next chapter, it is more likely that the SE values for the 0.6%CatSurfLq-modified binder are logical and closer to what is theoretically expected. In order to investigate the effect of the CatSurfLq chemical additive on the aggregates used, the Dynamic Vapour Sorption (DVS) test was seen necessary to carry out on the different aggregates used (modified or pure). The results of Figure 4.13 have widely been used in the next chapters to justify the test results.

Table 4.5 : DCA Test Results

BINDER SAMPLE	PROBE LIQUID	AVERAGE ADVANCING CONTACT ANGLE [θ] (°)	KNOWN SURFACE ENERGY COMPONENTS of the PROBE LIQUIDS (mJ/m2)				CALCULATED SURFACE ENERGY COMPONENTS of the TEST BINDERS (mJ/m2)			
			γ^{LW}	γ^{+}	γ^{-}	γ^{T}	γ^{LW}	γ^{+}	γ^{-}	γ^{T}
Bitumen70/100Pen	Water	97.0	21.8	25.5	25.5	72.8				
	Glycerol	86.9	34.0	3.9	57.4	64.0	33.65	0.13	1.77	34.62
	Di-Iodomethane	51.1	50.8	0.0	0.0	50.8				
Bitumen70/100Pen +2%FTWax	Water	103.8	21.8	25.5	25.5	72.8				
	Glycerol	87.2	34.0	3.9	57.4	64.0	22.26	0.47	0.20	22.87
	Di-Iodomethane	71.1	50.8	0.0	0.0	50.8				
Bitumen70/100Pen +3%FTWax	Water	105.6	21.8	25.5	25.5	72.8				
	Glycerol	91.3	34.0	3.9	57.4	64.0	21.63	0.15	0.34	22.09
	Di-Iodomethane	72.2	50.8	0.0	0.0	50.8				
Bitumen70/100Pen +0.4%CatSurfLq	Water	101.7	21.8	25.5	25.5	72.8				
	Glycerol	87.0	34.0	3.9	57.4	64.0	33.47	0.02	0.30	33.63
	Di-Iodomethane	51.4	50.8	0.0	0.0	50.8				
[Bitumen70/100Pen +0.6%CatSurfLq	Water	99.5	21.8	25.5	25.5	72.8				
	Glycerol	85.2	34.0	3.9	57.4	64.0	34.90	0.02	0.50	35.11
	Di-Iodomethane	48.9	50.8	0.0	0.0	50.8				
Bitumen70/100Pen +5.0%CatSurfLq	Water	68.7	21.8	25.5	25.5	72.8				
	Glycerol	74.1	34.0	3.9	57.4	64.0	40.57	0.56	21.94	47.58
	Di-Iodomethane	38.1	50.8	0.0	0.0	50.8				

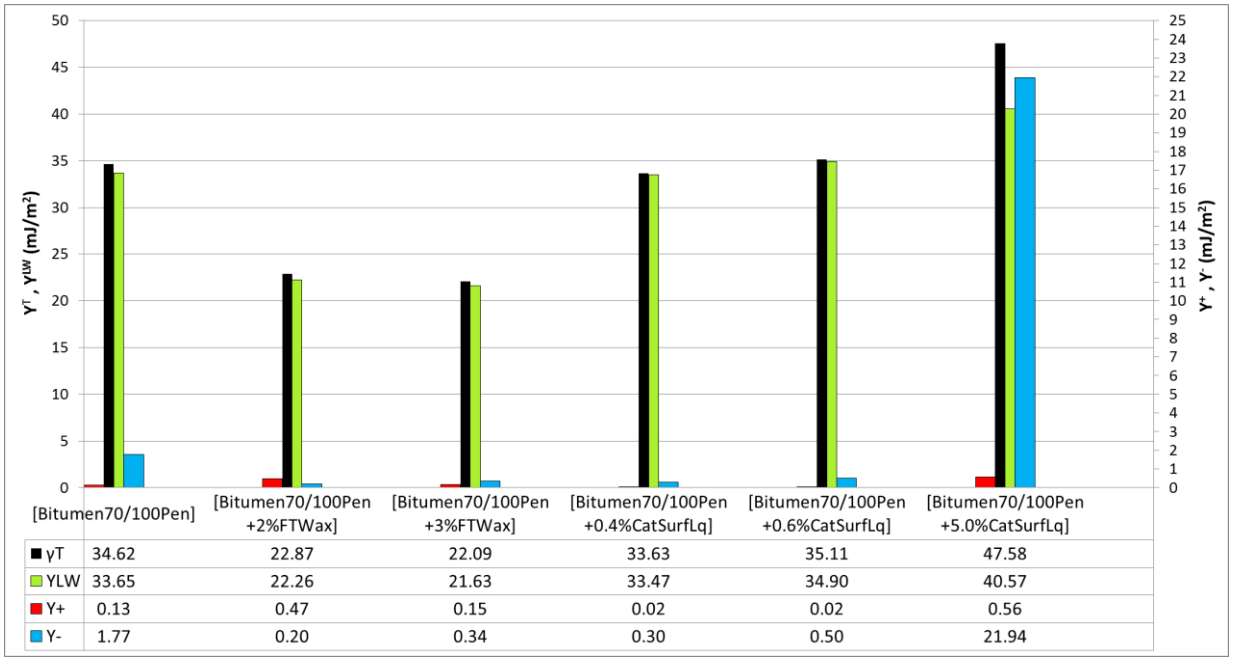


Figure 4.13 : Schematic results of SE measurement through the DCA method

Figure 4.13 illustrates that CatSurfLq has dominantly basic characteristic since adding a large amount (5%) of it to bitumen increases the basic properties of the bitumen significantly.

4.6. CONCLUSIONS

- FTWax, as a waxy additive of WMA, is a rheology and surface energy modifier of bitumen, whereas CatSurfLq, as a chemical additive of WMA, is just a surface energy modifier of bitumen (and, as expected, aggregate modifier), which has no significant influence on the rheological behaviour of bitumen.

- Adding FTWax significantly increases the softening point and decreases the penetration grade and these changes increase by increasing FTWax dosage.

- Adding CatSurfLq has nearly no influence on the penetration grade and softening point of bitumen.

- Just after FTWax's melting temperature (transition point), the viscosity of the modified binder drops and the viscosity curve shifts down at higher temperatures. However, it seems that at temperatures lower than the transition point the crystallisation phenomenon in the wax structure results in a considerably increased binder viscosity.

- The results of the BS EN-based Brookfield viscometry testing do not confirm as much reduction in viscosity as promised by some of the previous researchers, whereas the ASTM-based test nearly confirms the issue, to some extent illustrating that FTWax is able to reduce the production temperature of asphalt up to 15°C.

- FTWax significantly increases the complex shear stiffness of the binder and reduces the phase angle and the higher the dose of FTWax the bigger the changes.

- CatSurfLq does not have any influence on the complex shear stiffness of the binder, nor upon the phase angle.

- FTWax decreases the surface tension of bitumen significantly (about 40%) by decreasing the non-polar and basic polar components. This means that this additive decreases the ultimate tensile strength of bitumen. FTWax, also increases the acidic polar component of the surface energy of bitumen.

- CatSurfLq reduces the surface energy of bitumen via decreasing the polar components. It is expected that this additive increases the surface energy of aggregate so it can work as

promised in the sense that it can increase the dry bond strength of the binder-aggregate interface in asphalt mixture.

- It is thought that the dosage of CatSurfLq or the density of surfactants in the 0.6%CatSurfLq-modified binders is higher at the binder-aggregate or binder-air interface. This phenomenon takes place during preparing and in the bitumen coating of the Wilhelmy plate DCA measurement test samples.

- The high dosage modified binder (with 5% CatSurfLq) does not represent the behaviour of the 0.6%CatSurfLq-modified binder at interfaces as it shows a significant increase in the SE of the modified binder which is not expected.

- Although bitumen is expected to show some acidic properties, the bitumen in this research shows basic tendencies. Therefore, it is expected to develop stronger bonds with acidic aggregates.

5. BINDER-AGGREGATE ADHESION

The results of the binder tests were discussed in the previous chapter. It was mentioned that in order to have a better and more realistic evaluation of binder-aggregate interaction and bond strength, also in order to investigate the effect of the CatSurfLq chemical additive on the aggregates used, the Dynamic Vapour Sorption (DVS) test should be carried out on the different aggregates of this research (modified or pure) so the more realistic and correct values of the surface energy for aggregates are used. Moreover, the results of the PATTI, as a mechanical test for evaluating the binder-aggregate adhesion tensile strength have been presented and investigated in parallel with the SE calculations for 'work of adhesion'.

5.1. DRY BOND STRENGTH

The binder-aggregate 'dry bond strength' of the various binder and aggregate combinations used in producing the different asphalt mixtures in this study was evaluated using the surface energy calculations for 'work of adhesion' (Equation 2.25), combining the values of surface energy parameters of the different binders (Table 4.5) and aggregates involved in the study (Table 5.1 and Table 5.3). As mentioned before, it was carried out as one of the approaches to provide fundamental explanations for the mechanical test results and failure types in this research. Measuring the surface energy values of aggregates was performed through the Dynamic Vapour Sorption (DVS) test.

In this respect, the SE values for the pure (unmodified) Dene limestone had been measured once before using the DVS test through a research conducted by Ahmad (2011) in the Nottingham Transportation Engineering Centre (NTEC) laboratories. Also the surface energy values of the used pure (unmodified) Tunstead limestone were evaluated through another PhD research, which is still in progress, by Zaidi (2014) in the same laboratory. Therefore, no reason was seen to repeat the same test on the same aggregate samples and the values obtained by the above researchers (DVS#1) were used in the associated calculations of the current research (Table 5.1).

Table 5.1 : SE components of the used aggregates (DVS#1)

	SURFACE ENERGY COMPONENT			
AGGREGATE TYPE	γ^{LW}	γ^{+}	γ^{-}	γ
Dene limestone	75.3	108.9	49.7	222.4
Tunstead limestone	65.8	0.98	375.7	104.1

In contrast with the fact that limestone is generally known as a basic aggregate (referring Sections 2.8.4 and 2.8.5), Table 5.1 illustrates that the acidic polar component of Dene limestone is significantly higher than its basic polar component, which means that Dene limestone should show acidic behaviour. Moreover, Table 5.1 confirms that the basic polar component of Tunstead limestone is significantly higher than its acidic component, which means that Tunstead limestone is a highly basic aggregate.

As mentioned before, the chemical additive of WMA is supposed to be adsorbed onto the aggregate surface to increase its surface energy. Therefore, in order to measure the 'work of adhesion' for the CatSurfLq-WMA mixtures, the SE values of the CatSurfLq-modified aggregates should be applied to Equation 2.25.

Moreover, in the previous pages (the last part of the discussion in Section 4.5) it was found that in order to clarify the unexpected DCA test results in the case of the CatSurfLq-modified binders, also to have a more complete understanding of the influence of CatSurfLq on the surface energy properties of the elements in the resulting WMA mixture, investigating the SE of the aggregates in the presence of CatSurfLq was essential (i.e. CatSurfLq-modified aggregates).

The SE values for CatSurfLq-modified aggregates (also for any other modified aggregates) have never been measured through any other testing programs including the DVS test and it has been devised in the current research for the first time as DVS on 'Devised Aggregate Samples' (DAS). In order to measure the surface energy of the CatSurfLq-modified aggregates, the main issue was to modify the aggregates with different dosages of CatSurfLq (0.6% and 5%). For this purpose, two solutions of CatSurfLq in distilled (deionised) water with two different dosages (i.e. 0.6% and 5%) were prepared. Then, each solution was sprayed and introduced to the two different aggregate types used in the research (i.e. Dene limestone and Tunstead limestone), which were precisely graded, thoroughly washed and dried in accordance with NTEC Test Protocol for Measuring the Vapour Sorption of Aggregates using DVS

Advantage System (cited in Ahmad 2011). Once the modified aggregate samples were wetted by the CatSurfLq-in-water solution, they were placed in a 50°C oven to be dried.

The probe liquids chosen for the DVS test were Octane (non-polar), Ethyl Acetate (basic) and Chloroform (slightly acidic) with SE values predefined as follows:

Table 5.2 : SE components of the used probe liquids

	KNOWN SE VALUES (mJ/m2)			
	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}
Octane	21.62	0.00	0.00	21.62
Ethyl Acetate	23.90	0.00	19.20	23.90
Chloroform	27.15	3.80	0.00	27.15

The results of the DVS test, performed in this PhD research, have been presented in Table 5.3 as DVS#2 using Devised Aggregate Samples (DAS). Comparing the SE values of the pure aggregate samples with those measured by Ahmad (2011) and Zaidi (2014) through DVS#1 illustrates a significant decrease in the polar components, which means that unfortunately, the aggregate samples had not been dried thoroughly during the test. This issue was revealed to be due to a problem in the drying system of the apparatus. Nevertheless, the values are still useful and reliable in terms of the general trends. For instance, looking at Table 5.3, Figure 5.2 and Figure 5.3 it can be clearly seen that adding CatSurfLq has significantly increased the basic polar component (by about 10 times) which is totally expected due to the cationic nature of the additive. The additive has also negligibly influenced the non-polar part and left the acidic polar component nearly untouched. Moreover, it can be clearly seen that CatSurfLq influences Dene limestone more than Tunstead limestone. This issue refers to the fact that Dene limestone has been found to be acidic in nature (the opposite polarity as CatSurfLq) and the Tunstead limestone has been basic (the same polarity as the additive).

In fact, once the 0.6%CatSurfLq-modified binder is mixed with the aggregates, the additive moves through the hot bitumen layers towards the active points on the surface of the aggregate particles. As mentioned before, the aggregation of the additive molecules increases the dosage of the additive on the aggregate surface as well as the bitumen surface (i.e. bitumen-aggregate interface).

Putting everything together and considering those postulations which are closer to the expectations, it looks logical that in order to calculate the ‘work of adhesion’ for the

0.6%CatSurfLq-WMA mixtures, the SE values of the 0.6%CatSurfLq-modified bitumen should be combined with those of the 5%CatSurfLq-modified aggregates through Equation 2.25 named in this research as a 'Devised Dry Bond Strength'.

However, in the case of HMA mixtures and the FTWax-WMA mixtures, the SE values of the associated binders combined with those of the pure aggregates (DVS#1) are reliable as reflected in Figure 5.4. Comparing the values of HMA with the FTWax-WMA mixtures, it can be seen that FTWax decreases the binder-aggregate dry bond strength and increasing its dosage has even more decreasing effect. In addition, it is clear that Dene limestone makes stronger bonds with either of the bitumen types compared to Tunstead limestone. The results of this figure have been used in the next chapters to justify the mechanical test results.

In the previous paragraphs it was argued that the values presented in Figure 5.4 for the bond strength of the CatSurfLq-WMA mixtures should not be relied. However, considering the fact that in Equation 2.25 slightly lower SE value of the 0.6%CatSurfLq-modified bitumen 70/100 pen replaces the SE values of the pure bitumen 70/100 pen and significantly higher SE values of the 5%CatSurfLq-modified aggregate replace those of the pure aggregate, it can be concluded that the dry bond strength of the 0.6%CatSurfLq-WMA mixtures can be slightly higher than that of the HMA.

If Equation 2.25 is worked out with the SE values of Table 4.5 and Table 5.3, the following results are obtained which confirm a slight increase in the dry bond strength of the 0.6%CatSurfLq-WMA compared to that of the conventional HMA (Table 5.4).

Following this research, it has been found out that the chemical additive may not be able to significantly increase the adhesion unless it influences the non-polar SE component of the aggregates significantly while decreasing the polar and non-polar SE components of the bitumen at the same time.



Figure 5.1 : DVS test samples stored in a desiccator (pure and modified aggregates)

Table 5.3 : SE components of the used aggregates using DAS (DVS#2)

	MEASURED VALUE OF Π_e (mJ/m^2)			CALCULATED SE PARAMETERS (mJ/m2)			
	Octane	Ethyl Acetate	Chloroform	γ^{LW}	γ^-	γ^+	γ^{Total}
Tunstead Limestone	32.04	44.50	38.24	65.53	4.40	2.25	71.83
Tunstead Limestone +0.6%CatSurfLq	33.54	38.23	20.44	68.17	8.40	0.37	71.68
Tunstead Limestone +5%CatSurfLq	32.07	48.70	53.63	65.58	36.44	3.63	88.58
Dene Limestone	42.10	47.45	19.10	84.22	32.52	0.40	91.40
Dene Limestone +0.6%CatSurfLq	40.10	45.32	10.20	80.31	54.92	0.39	89.61
Dene Limestone +5%CatSurfLq	42.00	47.11	111.00	84.02	320.33	0.36	105.62

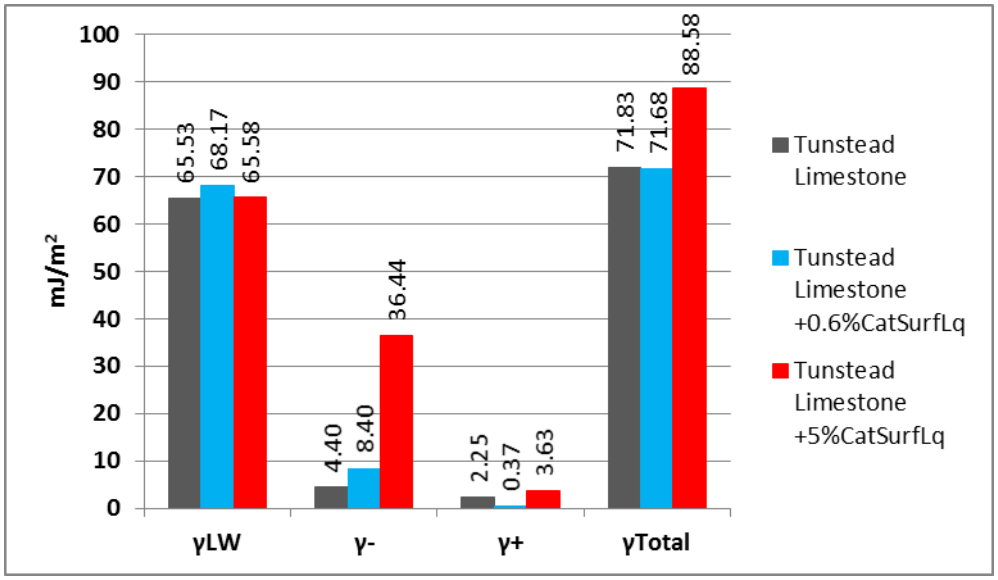


Figure 5.2 : SE values of the DAS CatSurfLq-modified Tunstead limestone

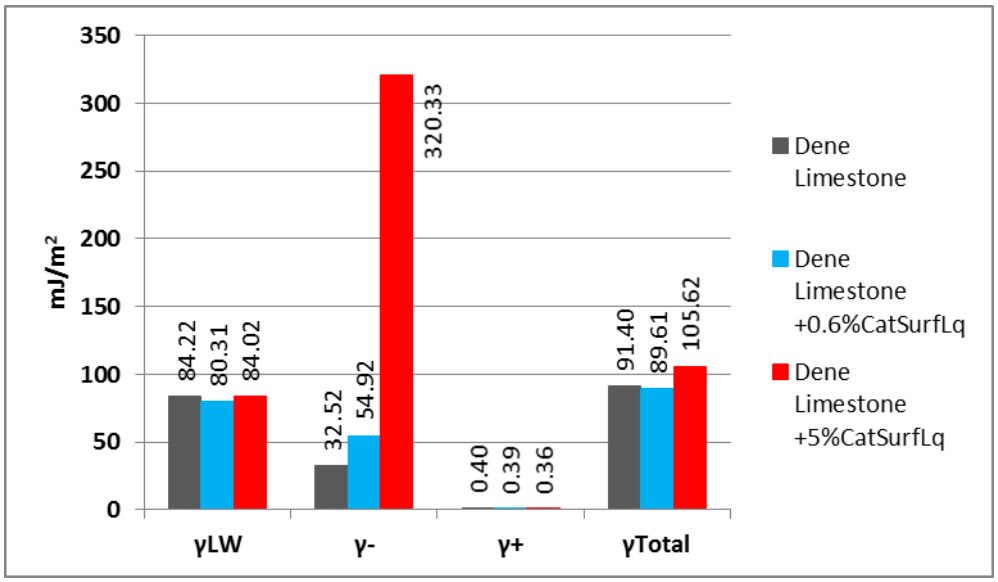


Figure 5.3 : SE values of the DAS CatSurfLq-modified Dene limestone

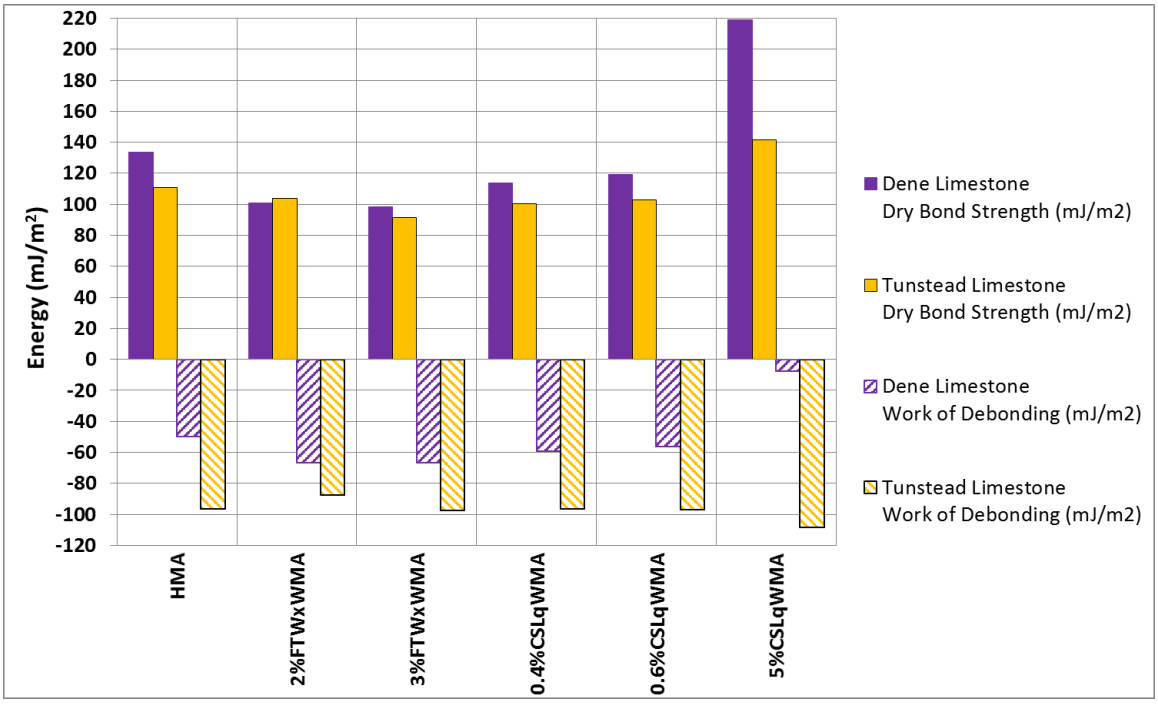


Figure 5.4 : 'Dry bond strength' and 'work of debonding in the presence of water'

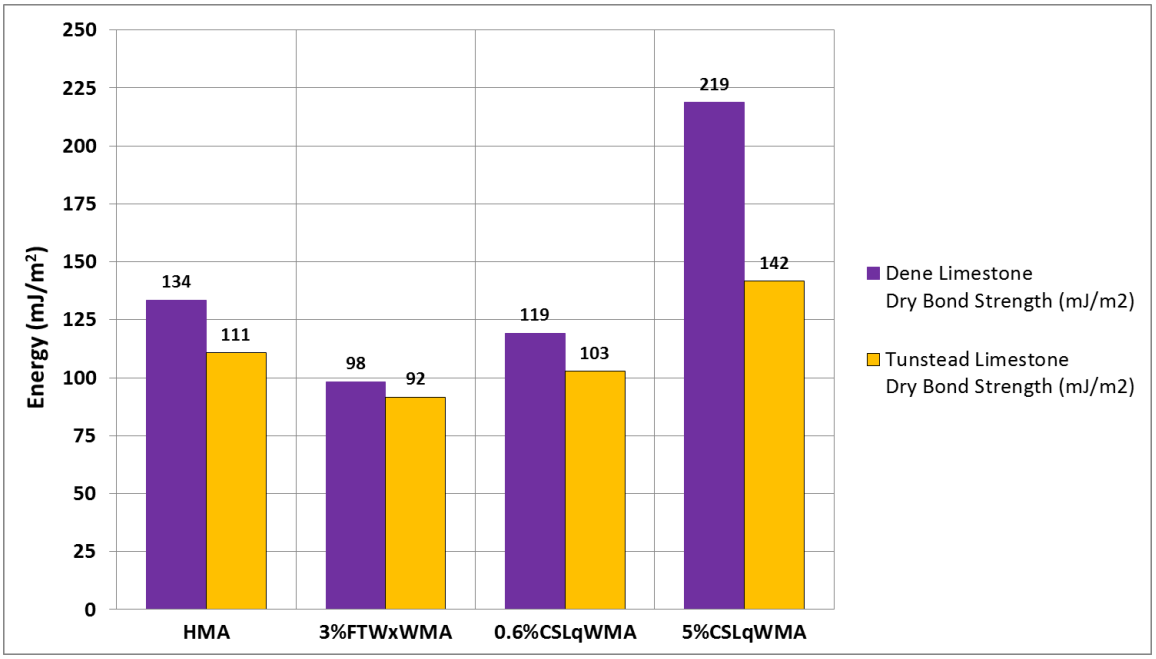


Figure 5.5 : 'Dry bond strength' of the different binder-aggregate compositions

Table 5.4 : 'Devised dry bond strength' of the 3%FTWax-WMA and 0.6%CatSurfLq-WMA compared to HMA

Bitumen Type	Measured SE Values (mJ/m^2)															
	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}
Pure Bitumen 70/100 Pen	33.7	0.1	1.8	34.6					**112.3**				**99.4**			
0.6%CatSurfLq Modified Bitumen 70/100 Pen	34.9	0.0	0.5	35.1	**114.2**				**100.1**							
HMA					84.0	0.4	320.3	105.6	65.6	3.6	36.4	88.6	84.2	0.4	32.5	91.4	65.5	2.3	4.4	71.8
0.6%CatSurfLq-WMA					γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}
					Measured SE Values (mJ/m^2)															
					5%CatSurfLq Modified Dene Limestone				**5%CatSurfLq Modified Tunstead Limestone**				**Dene Limestone**				**Tunstead Limestone**			
					Aggregate Type															

Table 5.4: (Continue)

Bitumen Type	Measured SE Values (mJ/m²)				Aggregate Type							
					Dene Limestone				Tunstead Limestone			
	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}
3%FTWax Modified Bitumen 70/100 Pen	21.6	0.2	0.3	22.1	**90.5**				**78.7**			
3%FTWax-WMA	84.2	0.4	32.5	91.4	65.5	2.3	4.4	71.8				

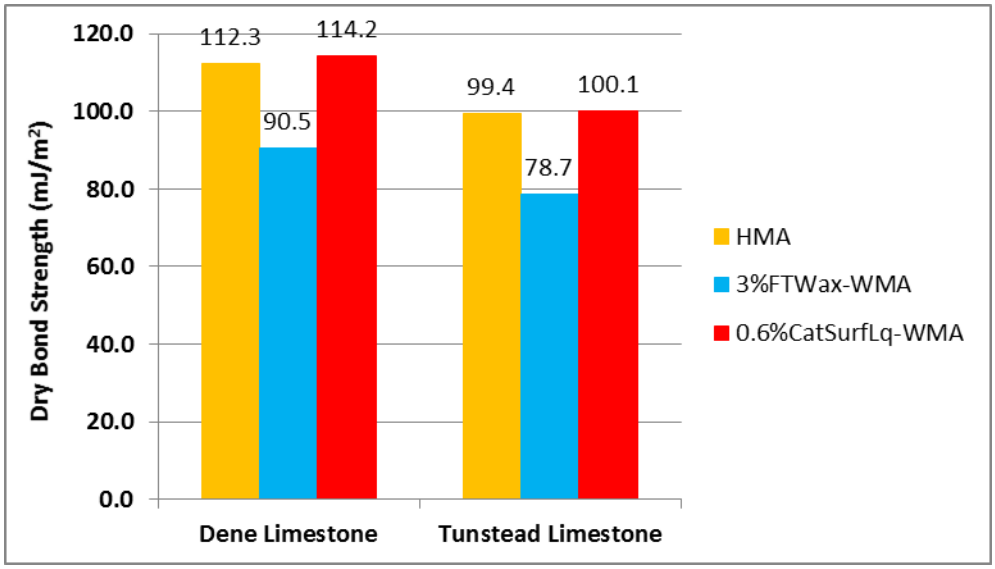


Figure 5.6 : 'Dry bond strength' calculated using Devised Aggregate Samples' SE

5.2. WORK of DEBONDING in the PRESENCE of WATER

The moisture susceptibility of the binder-aggregate bond in the manufactured mixtures were evaluated through the surface energy calculations for 'work of debonding in the presence of water' (Equation 2.36), using the surface energy values of water (Table 4.5), the different binders (Table 4.5) and the aggregates involved in the study (Table 5.1). This was performed for the purpose of providing a fundamental justification or a fundamental evaluation in parallel with the results of the revised modified Lottman moisture sensitivity evaluation mechanical test. Following the same arguments presented in Section 5.1, the results should not be that reliable in the case of the CatSurfLq-WMA mixtures. This is especially because the associated equation (Equation 2.36) is much more complicated than that of 'dry bond strength' (Equation 2.25). Therefore, the results of Table 5.3 (DAS) cannot be used for the rough estimations such as those performed in the case of 'dry bond strength' evaluations.

However, according to Figure 5.4, the moisture susceptibility of HMA and the 3%FTWax-WMA (3%FTWxWMA) is expected to be the same when Tunstead limestone is used in the mixture, whereas when Dene limestone is used, the moisture sensitivity of 3%FTWxWMA is more than that of HMA. Moreover, generally, the moisture susceptibility of the mixtures with Dene limestone (gyro samples) are less than that of the cored specimens which have been manufactures using Tunstead limestone. This issue shows the higher tendency of Tunstead limestone to replace bitumen by water. In fact the higher absolute value of the basic polar component of Tunstead limestone compared to the acidic polar component of Dene is

responsible for this issue (Table 5.1). In addition, it seems that lower dosage of FTWax has slightly lower moisture susceptibility.

5.3. PATTI TEST RESULTS

Figure 5.7 and Figure 5.8 show the results of measuring the tensile strength of coating for various binder-aggregate combinations by the use of a Pneumatic Adhesion Tensile Testing Instrument (PATTI). As mentioned previously in chapter 3.6.1, each group of the PATTI test samples has been devised in order to represent the binder-aggregate adhesion properties of its associated 'mixture group'. In this regard, the associated 'mixture groups' are any of the 'mixture groups' of the present study whose asphalt specimens have been manufactured using the same binder and aggregate and mixed at the same temperature as the binder coating has been introduced to the aggregate substrate. On this matter, it should be mentioned that due to the practical limitations of the PATTI test sample preparation, the effect of different compaction situations, in general, and different compaction temperatures, in practice, could not be included in the sample preparation process. Thus, the presented test results can only reflect the effect of using different materials and different mixing temperatures on the binder-aggregate adhesion properties. Each point of the chart presented in Figure 5.7 represents the tensile strength of one coating sample, whereas each of the bars in the chart of Figure 5.8 represents the average tensile strength of 6 coating samples.

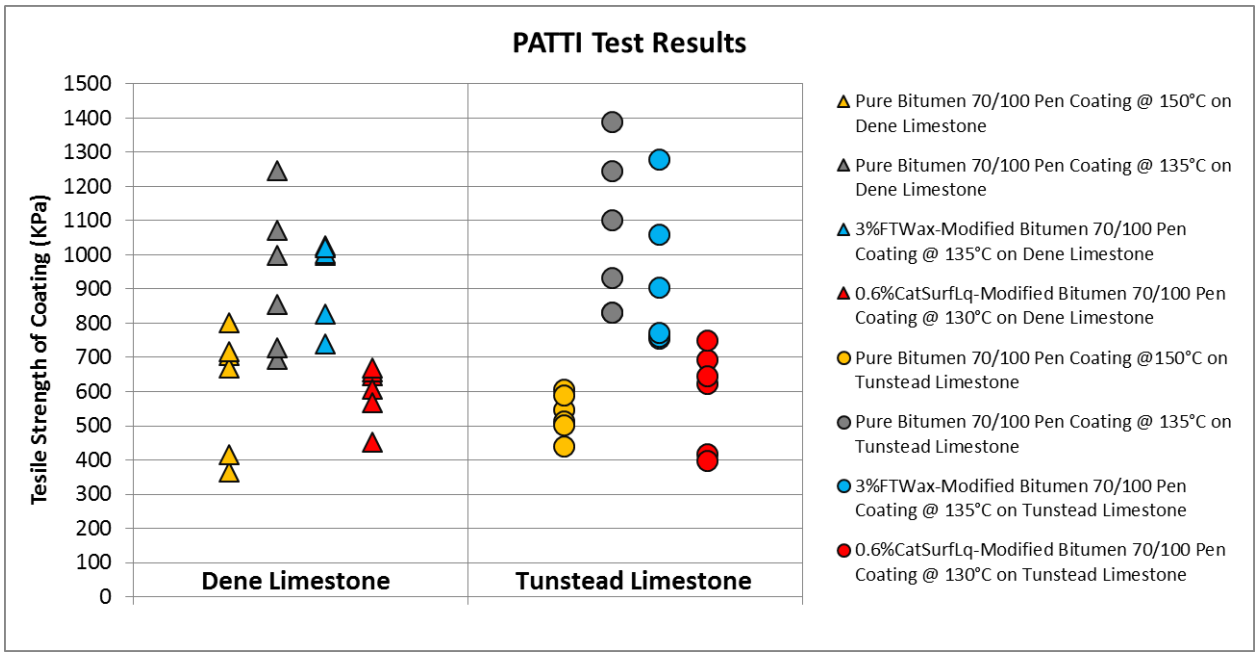


Figure 5.7 : The tensile strength of coating for different binder-aggregate combinations

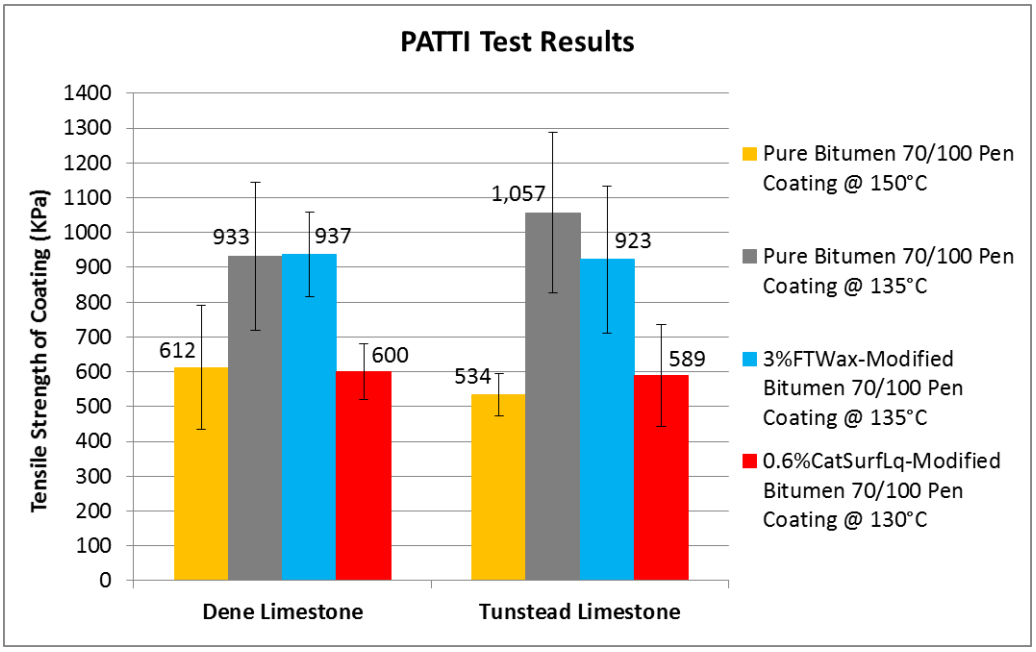


Figure 5.8 : The tensile strength of coating for different binder-aggregate combinations

The PATTI test results of this study have been more complicated to interpret compared to the results of the other tests performed through this PhD project. This has been probably due to the fundamental nature of the PATTI test, the results of which, like any other fundamental test, can possibly be interpreted through theories or should be accepted as they are, if they cannot be interpreted through any known hypothesis.

The first glance at Figure 5.7 and Figure 5.8, in general, shows closely similar values for the tensile strength of each of the 4 tested coatings on both types of aggregate substrates (i.e. Dene limestone and Tunstead limestone). In other words, it seems that the result of the PATTI tests have been almost independent from the type of aggregate and should be mostly dependant on the bitumen coating properties.

The results of naked-eye observations from the post-failure structure of the PATTI samples and visual investigation of the images taken from the failure surfaces through normal camera photography have been reflected in Table 5.5 confirming that the all samples have failed following cohesive tensile failure except to the majority of the FTWax-modified coatings, which have experienced adhesive tensile failure. In fact, it supports the above statements confirming that in the majority of the samples (except to the majority of the FTWax-modified coatings) the substrate had not influenced the test result.

Table 5.5 : Failure type and tensile strength of various coatings

BITUMEN TYPE	SUBSTRATE AGGREGATE	COATING TEMPERATURE (°C)	SAMPLE NO.	TENSILE STRENGTH OF COATING (kPa)	FAILURE TYPE
Pure Bitumen 70/100 Pen	Dene Limestone	150	1	800	100% Coh
			2	707	100% Coh
			3	668	100% Coh
			4	364	100% Coh
			5	718	100% Coh
			6	414	100% Coh
Pure Bitumen 70/100 Pen	Tunstead Limestone	150	1	547	100% Coh
			2	607	100% Coh
			3	513	100% Coh
			4	591	100% Coh
			5	502	100% Coh
			6	442	100% Coh
Pure Bitumen 70/100 Pen	Dene Limestone	135	1	696	100% Coh
			2	998	100% Coh
			3	1071	100% Coh
			4	856	100% Coh
			5	729	100% Coh
			6	1247	100% Coh
Pure Bitumen 70/100 Pen	Tunstead Limestone	135	1	834	100% Coh
			2	933	100% Coh
			3	1391	100% Coh
			4	1247	100% Coh
			5	1104	100% Coh
			6	834	100% Coh
3%FTWax-Modified Bitumen 70/100 Pen	Dene Limestone	135	1	999	85% Coh + 15% Adh
			2	1005	90% Coh + 10% Adh
			3	1027	100% Coh
			4	828	100% Coh
			5	1021	95% Coh + 5% Adh
			6	740	100% Coh
3%FTWax-Modified Bitumen 70/100 Pen	Tunstead Limestone	135	1	756	90% Coh + 10% Adh
			2	762	85% Coh + 15% Adh
			3	905	80% Coh + 20% Adh
			4	1280	50% Coh + 50% Adh
			5	773	90% Coh + 10% Adh
			6	1060	70% Coh + 30% Adh
0.6%CatSurfLq-Modified Bitumen 70/100 Pen	Dene Limestone	130	1	646	100% Coh
			2	657	100% Coh
			3	607	100% Coh
			4	569	100% Coh
			5	668	100% Coh
			6	453	100% Coh
0.6%CatSurfLq-Modified Bitumen 70/100 Pen	Tunstead Limestone	130	1	420	100% Coh
			2	624	100% Coh
			3	696	100% Coh
			4	646	100% Coh
			5	398	100% Coh
			6	751	100% Coh

Figure 5.9 shows the adhesive failure in two of the FTWax-modified coatings.

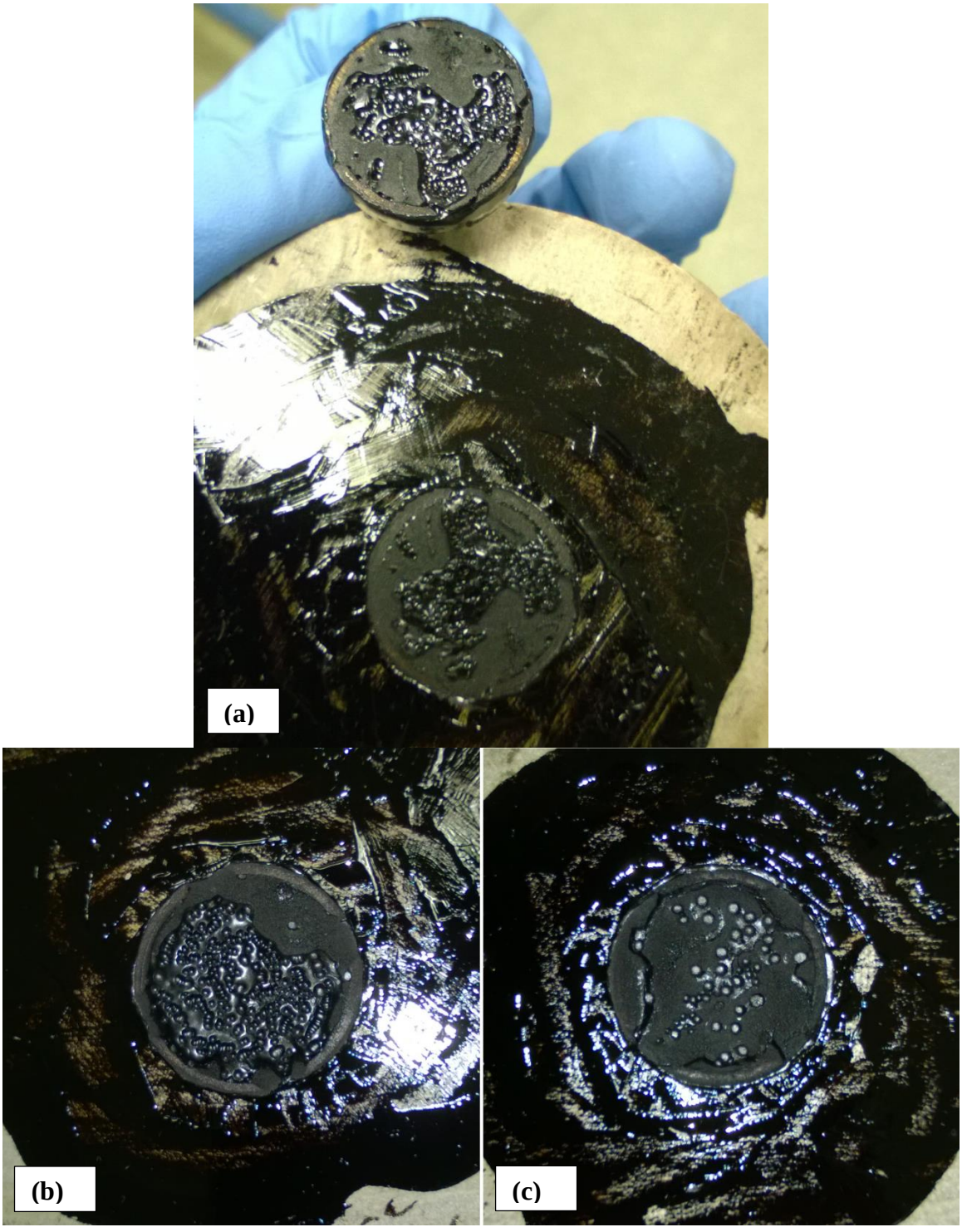


Figure 5.9 : The mixed adhesive-cohesive failure in FTWax-modified coatings (a) sample#4 on Tunstead, (b) sample#6 on Tunstead and (c) sample#2 on Dene substrate

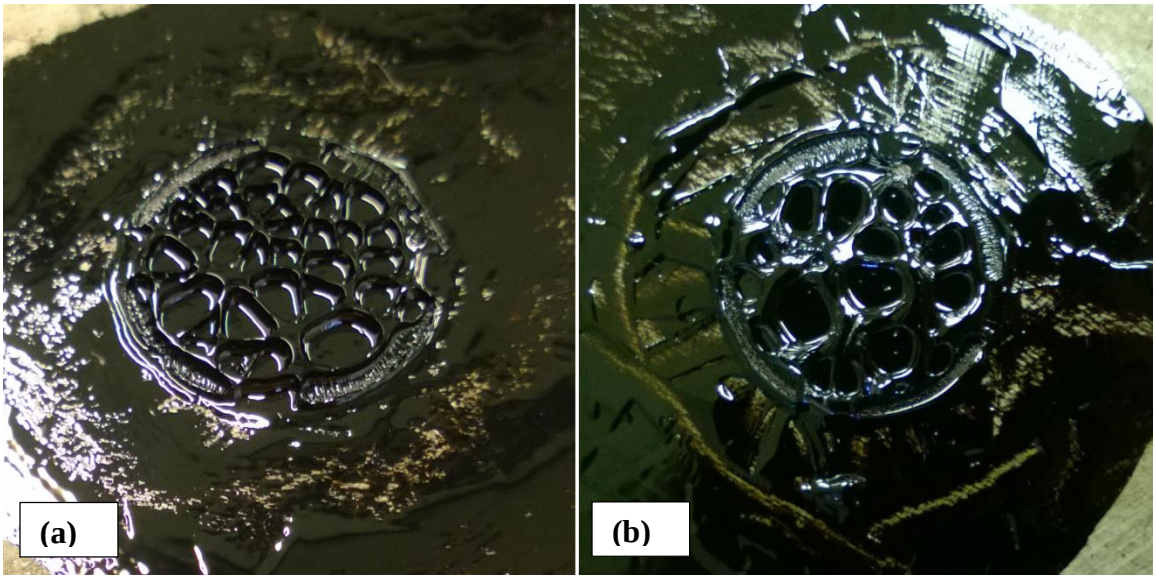


Figure 5.10 : The cohesive failure in (a) CatSurfLq-modified coating on Dene substrate (sample#6) and (b) pure bitumen 70/100 pen coated @ 135°C on Tunstead (sample#5)

From a comparative point of view, according to the general trend of the PATTI test results presented (Figure 5.7 and Figure 5.8), the coating of pure bitumen 70/100 pen introduced to the aggregate substrate at 135°C shows a significantly higher cohesive tensile strength compared to the same coating when introduced to the substrate at 150°C. In fact, the coatings introduced at 135°C have been more effective than those developed at 150°C. In other words, 135°C, compared to 150°C, has been a more suitable temperature to make a coating of pure bitumen 70/100 Pen on the aggregate substrates (Dene and Tunstead limestones). In this respect, considering this fact that the type of failures have been cohesive, increasing the binder-to–aggregate introduction temperature from 135°C to 150°C, has influenced the properties of bitumen in such a way that its cohesive strength has significantly decreased.

Weakening the cohesive strength of a cooled coating due to increasing the temperature of binder-to-aggregate introduction phase could conform to a theory commonly known as ‘The Theory of Weak Boundary Layers’. This theory, as explained in Section 2.10.2, states that the adhesive bonds fail in either the adhesive or substrate, due to the presence of an inter-phase region of low cohesive strength. The cohesive strength of a weak boundary layer can always be considered as the main factor, which influences the level of adhesion. Phenomenological observation indicates that when absorption occurs, the bitumen remaining on the outside becomes hard and brittle (Curtis et al., cited in Jakarini 2012). From the theory of Weak Boundary Layers, it is postulated that a brittle inter-phase will form due to highly associated

polar molecules left behind. This is similar to short-term ageing where volatiles evaporate during the manufacturing and construction process of hot mix asphalt. It is also postulated that in the case that the aggregate substrate is very hot, the small-structure compositions of bitumen are absorbed in the aggregate through the surface voids leaving a brittle layer at the interface. In addition to the formation of an inter-phase region by propagated polarisation, Ross et al. (cited in Jakarini 2012) postulated that high mix temperatures initiate extensive acid-base interactions, altering and most likely the agglomerating of bitumen groups into larger, probably cross-inked assemblies in the boundary region. While the brittleness of this region may form a weak layer if too much cross-linking takes place, the aggregated region can form a seal that may inhibit adhesive failure due to water diffusion to the interface.

Moreover, it may be logical to relate the lower tensile strength of the HMA representative coatings compared to that of the Non-Standard ones to a second issue. This second issue, which does not seem to be as persuasive as the first one (thus it is still a matter of opinion), concerns the difference in the viscosity of the bitumen (coating) at the two different introduction temperatures during the PATTI test sample manufacture. Figure 2.27 shows a Bitumen Test Data Chart devised by Shell indicating the recommended criteria for the ideal bitumen viscosities for optimal mixing and compaction temperatures. According to these criteria, viscosities lower than 0.2 Pa.s, which is the ideal viscosity for optimal mixing, can result in bitumen drainage/flow in the mixture during mixing. In the case of the PATTI test sample manufacture, this researcher postulates that the above fact appears as some kind of bitumen flow on the surface of aggregate substrate when bitumen is introduced to the substrate. This can have negative influence on the quality and adequacy of coating in terms of bitumen film thickness and adhesion strength. In fact, bitumen's low viscosity and its tendency to flow on the substrate, does not let it stay in a static manner to be stable enough while cooling down and develop the adhesion. By this means, the chance of forming a proper coating under the metal stub is lowered. In this regard, according to Figure 4.7, which shows the data lines associated with the different bitumen types used in the current study, the viscosity of pure bitumen 70/100 Pen at the coating temperature of 150°C is about 0.12 Pa.s. This value is less than the mentioned criterion of 0.2 Pa.s and significantly smaller (about 2.5 times smaller) than its viscosity at the coating temperature of 135°C (0.28 Pa.s). Therefore, introducing pure bitumen 70/100 Pen to the aggregate substrates is expected to result in a less effective coating at 150°C compared to 135°C in a sense that the resultant coating will have lower tensile strength.

The PATTI test results illustrate that the coatings of 3%FTWax-modified bitumen 70/100 pen, regardless of the type of substrate, generally have a slightly lower tensile strength compared to those coatings of pure bitumen 70/100 pen, which were made at 135°C. As mentioned before, the 3%FTWax-modified coatings are the only ones, which have experienced some adhesive failure. Therefore, it can be stated that adding 3% of FTWax to pure bitumen 70/100 pen not only lowers its cohesive tensile strength but also reduces its adhesive tensile strength to aggregate substrates to a lower level than the adhesive tensile strength of pure bitumen 70/100 pen. In fact, it seems that 3%FTWax is able to reduce the adhesive tensile strength of the pure base binder to such a low level that some adhesive failure has occurred in parallel with cohesive failure.

This phenomenon is related to the effect of FTWax on the Surface Energy (Surface Tension) of bitumen. Referring to Figure 4.13, Surface Energy measurements and calculations, using the Whilhelmy Plate test results (Dynamic Contact Angle method), illustrate that adding 3% of FTWax to pure bitumen 70/100 pen reduces both the Non-Polar and the Lewis Base Polar Surface Energy (SE) components and consequently the total surface tension of the bitumen.

On the one hand, it means that the total surface tension of the 3%FTWax-modified bitumen 70/100 pen is less than its pure base bitumen 70/100 pen. This fact refers to a principle in Surface Energy, which states that the Work of Cohesion is equal to bitumen's surface tension multiplied by 2:

$$W_C = 2(\gamma^T) = 2\left(\gamma^{LW} + 2\left(\sqrt{\gamma^+\gamma^-}\right)\right) \qquad \text{Equation 5.1}$$

Where:

W_C = Work of Cohesion

γ^T = The total surface energy of binder/liquid

γ^{LW} = The non-polar Lifshitz-Van der Waals surface energy component of binder/liquid

γ^+ = The Lewis acid polar surface energy component of binder/liquid

γ^- = The Lewis base polar surface energy component of binder/liquid

$2\left(\sqrt{\gamma^+\gamma^-}\right)$ = The Lewis acid-base polar surface energy component of binder/liquid

In addition, the cohesive tensile strength of bitumen is actually its Work of Cohesion and is equal to the ultimate stress at which the bitumen will fail in tension. Therefore, the slightly lower tensile strength of the coating of the 3%FTWax-modified bitumen 70/100 pen compared to that of the pure bitumen 70/100 pen, which has been introduced to the aggregate at 135°C, is due to the lower surface energy (surface tension) of the former compared to that of the latter.

On the other hand, the smaller SE components of the 3%FTWax-modified bitumen 70/100 pen cause it to have a lower binder-aggregate dry bond strength compared to the pure bitumen 70/100 pen, when the situation is the same in terms of the type of aggregate substrate and coating temperature. This fact refers to another principle of Surface Energy, indicating that the Work of Adhesion between a solid (e.g. aggregate) and a liquid (e.g. bitumen/binder) is obtained through Equation 5.2 (Bhasin, 2006). In essence, Work of Adhesion is the dry binder-aggregate bond strength or the dry binder-aggregate adhesive strength. According to Equation 5.2, the smaller the SE parameters of either binder or aggregate, the lower the binder-aggregate Bond Strength:

$$W_a = 2\left(\sqrt{\gamma_a^{LW}\gamma_b^{LW}} + \sqrt{\gamma_a^{+}\gamma_b^{-}} + \sqrt{\gamma_a^{-}\gamma_b^{+}}\right) \qquad \text{Equation 5.2}$$

Where:

W_a = Work of Adhesion

γ_a^{LW} = The non-polar Lifshitz-Van der Waals surface energy component of aggregate

γ_b^{LW} = The non-polar Lifshitz-Van der Waals surface energy component of binder

γ_a^{+} = The Lewis acid polar surface energy component of aggregate

γ_a^{-} = The Lewis base polar surface energy component of aggregate

γ_b^{+} = The Lewis acid polar surface energy component of binder

γ_b^{-} = The Lewis base polar surface energy component of binder

Since the adhesive tensile strength of a coating represents its binder-aggregate bond strength, the results of the DCA test and SE evaluations can justify the PATTI test results in a sense that FTWax reduces the surface tension of bitumen, which means it reduces the Work of Cohesion and consequently the cohesive tensile strength of the associated bitumen coating slightly decreases (if Figure 5.7 is considered). It also reduces the binder-aggregate dry bond strength,

which conforms to fact that the 3%FTWax-modified bitumen 70/100 pen has experienced some adhesion failure in contrast with the coating samples of pure bitumen 70/100 pen.

On the matter of the coatings of 0.6%CatSurfLq-modified bitumen 70/100 pen, the story is slightly different because the issue is more complicated. Moreover, as argued in Section 5.1, this researcher believes that the values calculated for the dry bond strength of CatSurfLq-WMA, presented in the bar chart of Figure 5.5, should not fully reflect the proper bond strength in a CatSurfLq-WMA mixture, though the calculation has been performed in accordance with what several published papers had followed. The reason for such statement is the fact that the SE values of CatSurfLq-modified aggregates have not been considered in the associated calculations. However, calculations based on the SE of the modified aggregates were accomplished in this research (Table 5.4) but the values cannot be used to compare with those presented in Figure 5.5 due to the reasons mentioned in the associated section.

It should be mentioned that, referring to the reasons presented in the early pages of this section, all of the coating samples of 0.6%CatSurfLq-modified bitumen 70/100 pen have experienced cohesion failure through the PATTI test.

From the charts presented in Figure 5.7 and Figure 5.8, it can be realised that their average tensile strength is lower than the 3%FTWax-modified bitumen coating samples and the pure bitumen 70/100 pen coatings introduced to the substrate at 135°C. It can also be observed that their average tensile strength is equal to that of the pure bitumen 70/100 pen coatings introduced to the aggregate at 150°C.

In order to interpret the above observations, it may be claimed that the difference in the tensile strength of the two coatings can be as a result of the 5°C difference in the coating temperature of the two different groups of samples.

In order to reject this claim, it looks rational to state that if the 5°C lower coating temperature influenced the coating quality, the coating samples of 0.6%CatSurfLq-modified bitumen 70/100 pen should either show a slightly higher average cohesive tensile strength or probably experience some adhesive tensile failure (according to Section 2.8.2). The higher cohesive tensile strength would be observed if the lower coating temperature reduced the likely weak boundary layer developed through the high temperature coating. With this respect, as described in the previous pages, the lower the coating temperature, the less the weak boundary layer is expected to be developed in the coating adjacent to the substrate. Moreover, the adhesive

tensile failure would be expected if the lower coating temperature did not reduce the bitumen viscosity adequately to make it fluid enough to wet the aggregate effectively and be absorbed by the surface of the substrate adequately in order to let the binder-aggregate bond be developed effectively.

Therefore, the significantly lower average cohesive tensile strength of the 0.6%CatSurfLq-modified bitumen coating samples compared to that of the base binder 70/100 pen coatings should be due to the influence of CatSurfLq chemical additive on the cohesion properties of the pure base bitumen 70/100 pen. In order to clarify the issue, a clear understanding of the mentioned additive's behaviour in bitumen looks necessary.

According to the producer of CatSurfLq chemical additive (AkzoNobel), this material contains surfactants (Surface Active Agents). As explained thoroughly in the previous chapters, surfactants, in general, when added to a liquid, reduce the surface tension of the liquid or the interfacial tension of two-phase systems (i.e. binder-aggregate) due to adsorption at the surface or interface respectively. By this means, they increase the liquid's ability to wet a substrate.

In a similar way, the surfactants in CatSurfLq, are adsorbed at the binder-aggregate interface and by this means, increase the surface energy of the aggregate and reduce the binder-aggregate interfacial surface energy. As a result, the wettability of aggregate is improved. The surfactants are also adsorbed at the surface of the binder and cause the surface tension of binder to decrease (Figure 4.13, the bars associated with 0.4% and 0.6% dosages of CatSurfLq). This issue reduces the binder's resistance to spread over and wet the aggregate surface.

Therefore, the overall performance and advantage of adding adhesion promoters (chemical additives) to bitumen can be summarised as providing adequate and effective aggregate coating (supposing that the bitumen is fluid enough) via decreasing binder's surface tension and increasing the aggregate's Surface Energy (confirmed in Sections 4.5 and 5.1). In addition, as developing improved binder-aggregate bond strength via increasing the Surface Energy of the aggregate.

It should be recalled that the explained behavior of the additive is due to the specific molecular structure of the surfactants in which the hydrophilic (polar) heads of the surfactant molecules adjoins the surface of the aggregate while their hydrophobic (non-polar) tail draws on bitumen.

From the calculation and formulation view point, the changes in the surface energies of the three phases (aggregate, bitumen and bitumen-aggregate interface) is in such a way that results in increasing the binder-aggregate Work of Adhesion according to the following equation, named Dupre's general equation for solid-liquid adhesion:

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \qquad \text{Equation 5.3}$$

Where:

W_{SL} = Solid-liquid Work of Adhesion

γ_{SA} = The total surface energy of solid (aggregate)

γ_{LA} = The total surface tension of liquid (binder)

γ_{SL} = The binder-aggregate interfacial surface energy

Moreover, reducing the surface tension of the binder by the chemical additive can have a negative consequence. According to Equation 5.1, as mentioned previously, it results in decreasing the binder's Work of Cohesion, which itself means that the cohesive tensile strength of the binder reduces.

This should be considered as one of the reasons due to which the coating samples of the 0.6%CatSurfLq-modified binder 70/100 pen have shown lower tensile strength through the PATTI test compared to the pure bitumen 70/100 pen which have been introduced to the substrate at 135°C.

The other reason could be the presence of a weak boundary layer in the coating adjacent to the substrate. In fact, the adsorption of CatSurfLq molecules at the binder-aggregate interface or at the binder's surface increases the additive's dosage at these regions significantly. This means that the additive dosage through the bitumen content should be considerably less than 0.6% while it can be much more than 0.6% at the binder-aggregate interface or bitumen surface. According to the theory of Weak Boundary Layers, a brittle binder-aggregate inter-phase layer is reasonably assumed to be formed due to the congestion of highly polar molecules in a certain region. Therefore, such a weak layer is developed in 0.6%CatSurfLq-modified bitumen 70/100 pen in the vicinity of aggregates' surface, where the polar molecules of the chemical additive have condensed adsorbing to the aggregate.

Therefore, although adding 0.6% of CatSurfLq chemical additive can improve the binder-aggregate bond strength, it can reduce the cohesive tensile strength of the binder due to reducing its surface tension and developing a weak boundary layer in the vicinity of aggregates.

To compare the Saobit-modified coatings with the CatSurfLq-modified ones, it should be mentioned that according to the SE test results, the 'work of cohesion' and subsequently the cohesive strength of the 3%FTWax-modified binder is less than the 0.6%CatSurfLq-modified binder due to the lower SE of the former compared to the latter. However, the stiffness of the FTWax-modifed binder is significantly higher than the CatSurfLq-modified binder. Therefore, the failure of the FTWax-modified coating under PATTI is mostly stress-controlled as the material is more brittle and fails suddenly with an ultimate tensile rupture. Whereas, the failure of the CatSurfLq-modified coating under PATTI is strain-controlled as the sample deforms much more due to its flexibility and fails in the form of yielding. In fact, the significantly higher deformation of the CatSurfLq-modified coating samples under PATTI makes the test sample fail at lower tensile stresses compared to FTWax-modified coatings as well as the other samples.

5.4. CONCLUSIONS

- It looks logical that in order to calculate the 'work of adhesion' for the 0.6%CatSurfLq-WMA mixtures, the SE values of the 0.6%CatSurfLq-modified bitumen should be combined with those of the 5%CatSurfLq-modified aggregates (as explained in Section 5.1).

- FTWax decreases the binder-aggregate dry bond strength and increasing its dosage has an even stronger decreasing effect.

- Dene limestone makes stronger bonds with either of the bitumen types compared to Tunstead limestone. As mentioned before, it refers to the fact that Dene limestone and the used bitumen were from different polarities or acid-base tendencies (means compatible with each other as here: acidic aggregate mixed with basic bitumen), whereas Tunstead had the same polarity as the bitumen (incompatible as both had basic tendencies). This means that before selecting the asphalt materials for fabrication, special attention should be paid to the issue of their polar (acid-base) compatibility.

- The dry bond strength of the 0.6%CatSurfLq-WMA mixtures can be slightly higher than that of the HMA mixture.

- It is thought that the chemical additive may not be able to significantly increase the adhesion unless it influences the non-polar SE component of the aggregates significantly while decreasing the polar and non-polar SE components of the bitumen at the same time.

- The moisture susceptibility of HMA and the 3%FTWax-WMA (3%FTWxWMA) is expected to be the same when Tunstead limestone is used in the mixture, whereas when Dene limestone is used, the moisture sensitivity of 3%FTWxWMA is somewhat worse than that of HMA.

- Generally, the moisture susceptibility of the mixtures with Dene limestone (gyro samples) is expected to be less than that of the cored specimens which have been manufactures using Tunstead limestone.

- Tunstead limestone shows higher tendency to have bitumen replaced by water. In fact the higher absolute value of the basic polar component of Tunstead limestone compared to the acidic polar component of the Dene limestone is responsible for this.

- It seems that a lower dosage of FTWax develops slightly lower moisture susceptibility than the mixture with higher dosage.

- Regarding the PATTI test, increasing the binder-to-aggregate introduction temperature from 135°C to 150°C, influences the properties of bitumen in such a way that its cohesive strength significantly decreases. Weakening the cohesive strength of a cooled coating due to increasing the temperature of binder-to-aggregate introduction phase could be a theory commonly known as ‘The Theory of Weak Boundary Layers’. However, this study suggests an alternative understanding involving some kind of bitumen flow on the surface of aggregate substrate when bitumen is introduced to the substrate. This can have a negative influence on the quality and adequacy of coating in terms of bitumen film thickness and adhesion strength. In fact, bitumen’s low viscosity and its tendency to flow on the substrate, does not let it stay in a static manner to be stable enough while cooling down and develop the adhesion. By this means, the chance of forming a proper coating under the metal stub is lowered.

- FTWax-modified coatings are the only ones which have experienced some adhesive failure. Adding 3% of FTWax to pure 70/100 pen bitumen reduces the surface energy of the binder due to which the cohesive tensile strength of the modified bitumen reduces. FTWax, also, reduces the binder-aggregate adhesive tensile strength to a lower level than the cohesive tensile strength of pure bitumen 70/100 pen. In fact, it seems that 3% FTWax is able to reduce the adhesive tensile strength of the pure base binder to such a low level that some adhesive failure has occurred in parallel with cohesive failure.

- The 'work of cohesion', and consequently the cohesive strength of the 3%FTWax-modified binder, is less than the 0.6%CatSurfLq-modified binder due to the lower surface energy of the former compared to the latter. However, the stiffness of the FTWax-modified binder is significantly higher than that of the CatSurfLq-modified binder. Therefore, the failure of the FTWax-modified coating under PATTI is mostly stress-controlled as the material is more brittle and fails suddenly with an ultimate tensile rupture when. Whereas, the CatSurfLq-modified coating under PATTI is strain-controlled as the sample deforms much more due to its flexibility and fails in the form of yielding. In fact, the significantly higher deformation of the CatSurfLq-modified coating samples under PATTI makes the test sample fail at lower tensile stresses compared to FTWax-modified coatings as well as the other samples.

- FTWax reduces the ultimate tensile strength of bitumen and as it increases the stiffness of the binder, the overall behaviour becomes a stiff but brittle material at asphalt operating temperatures. Therefore, it is expected that FTWax-WMA mixtures will have higher stiffness modulus and their failure under fatigue will be mostly in a brittle form, but at high number of cycles.

- CatSurfLq reduces the surface energy of bitumen but it does not influence the stiffness. Therefore, having the PATTI test results as a background, it is expected that the resulting CatSurfLq-WMA mixtures are of lower stiffness modulus than FTWax-WMA and their failure under fatigue resistance is mostly controlled by the vertical deformation instead of brittle failures. Moreover, they are expected to have higher rutting potential.

6. MIXTURE TEST RESULTS

This chapter provides the results of the performance tests which were accomplished on the manufactured asphalt samples in the present research through two different compaction methods (gyratory and roller compaction) at a decreasing series of 3 different compaction temperatures. The results of the various tests have been tried to linked together and be justified using the results of the binder characterisation and binder-aggregate interaction tests.

6.1. AIR VOID CONTENT USING ALUMINIUM FOIL METHOD

6.1.1. DISCUSSION on the TEST RESULTS

In the beginning, is necessary to state that in order to study the results of the volumetric properties of the manufactured specimens, the graphs of AV content have been seen more applicable for investigation compared to those of bulk density. It was believed that AV content was a more credible and reflective reference for the material's volumetric properties, permeability and durability, which can be more logically related to the other properties studied through the other performance tests.

Looking at the results of bulk density and AV content measurements on the gyro samples (Figure 6.2 and Figure 6.1), clearly illustrates that, there is nearly no difference between their bulk density and AV content. In fact, no clear trend can be found in the volumetric properties of the mixtures which are totally different with each other in terms of additives, mixing temperatures and compaction temperature, even at as low as 80°C. Moreover, the AV contents are very low in such a way that they seem to be highly impermeable.

In a more proper statement, it seems that the gyratory compactor has compacted them regardless of the compaction temperature, materials (additives) and also mixing temperature in such a way that the volumetric properties (AV content and bulk density) of the different gyro samples compacted at different temperatures (even as low as 80°C) do not have any noticeable difference with each other. This issue proves this fact that the gyratory compactor compacts the asphalt mixtures regardless of the temperature (and probably material/additive). In other words, the compaction process in a gyratory compactor will be insensitive to temperature. It is

postulated that this phenomenon happens because through the gyratory compaction process, the combination of the compressive compaction force and the axial angular gyration of the mould, gives enough chance to the materials (aggregates) inside the mould to move as much as and in such a way that they can find the best orientation to be properly interlocked with their neighbour particles.

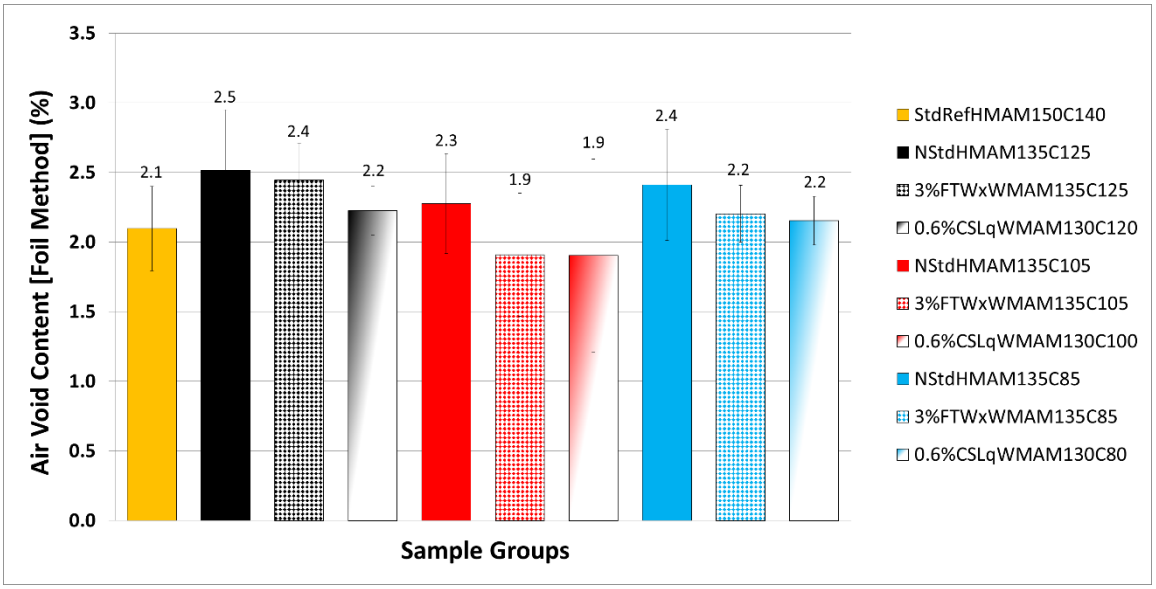


Figure 6.1 : Air Void contents of all manufactured mixtures (gyro samples)

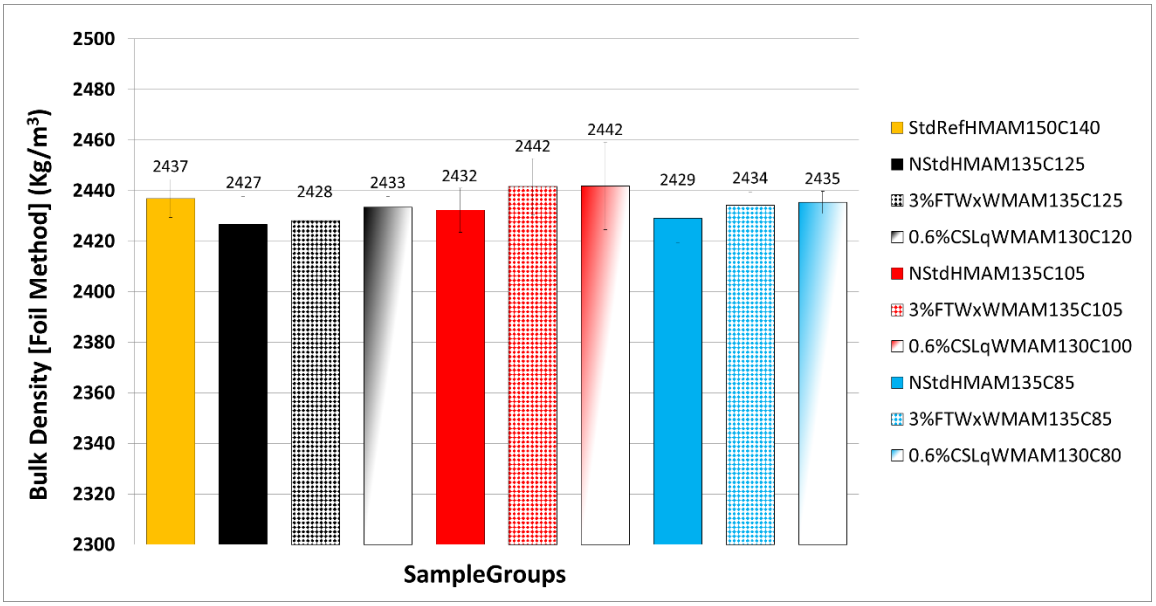


Figure 6.2 : Bulk densities of all manufactured mixtures (gyro samples)

As no more information can be extracted from the above charts, in this section, the main discussion and conclusions will be made on the results of volumetric measurements on the cores taken from the slab specimens.

Comparing the produced graphs for the various studied properties of the manufactured mixtures, it can be stated that the most clear compaction-temperature-dependant trend, can be observed in the bar chart of the volumetric properties of the cored specimens (samples compacted using the slab roller compactor) including the bar chart of the mixtures' air void (AV) content and also that of their bulk density.

Figure 6.3, the bar chart associated with the AV content for all 'sample groups' of the cored specimens, indicates a generally increasing trend in the AV content of the mixtures as compaction temperature decreases. This increasing trend can be seen in each of the 3 'material groups' as well as for each of the 3 'compaction groups'. In other words, in general, regardless of the using additive, the lower the compaction temperature, the higher the AV content of the mixtures. In addition, for each of the 3 'compaction groups', the Non-Standard HMA mixture has the lowest AV Content compared to the Saobit-WMA or CatSurfLq-WMA mixture of that group. The FTWax-WMA itself has lower AV contents compared to the CatSurfLq-WMA mixture. Nevertheless, there are two exceptions, which do not follow this general increasing trend. As it can be seen in Figure 6.3, they are StdRefHMAM150C140 and 3%FTWxWMAM135C105 mixture groups. The former has an AV content higher than expected from the general regime and the latter has an AV content lower than what is expected.

Each bar represents the average value for 12 cores, which have been taken from the 2 manufactured slabs (6 from each slab) for each of the 10 mixture groups. The slabs have been compacted by a Roller compactor. The error bars represent the Standard Deviation of the associated data.

If Figure 6.3, Figure 6.5 and Figure 6.6 are looked at from a statistical point of view, considering the error bars, it may be mis-concluded that some of the mixture groups essentially have the same AV content (within a certain probability) though their representative bars have, apparently, different lengths. But, if the associated raw test data are looked at, it will be realised that the high scatter of some data are due to the relatively big difference between the average AV values of the two associated slabs. Basically, not only in the case of the volumetric measurements, but also in the case of most of the mixture characteristics, the test results are

totally consistent within the 6 samples of each of the two slabs of a sample group, whereas from one slab to another, the average value has changed to such an extent that a high overall scatter is recorded.

In addition, practical evidence such as comparing the mass of absorbed water by the specimens of the different mixture groups during the various conditioning phases of the Revised Modified Lottman Water Sensitivity test (Figure 6.40) confirms that the bars of AV content are significantly different because the bars in both charts mostly have similar relative heights compared to each other. On the other hand, the higher the AV contents the more the absorbed water (Figure 6.39). This issue will be discussed in details later in Section 6.6. Thus, in spite of having error bars with considerable overlaps, the differences between the heights of the bars in the AV content bar chart are not negligible as according to the mentioned evidence, they indicate values that are significantly different.

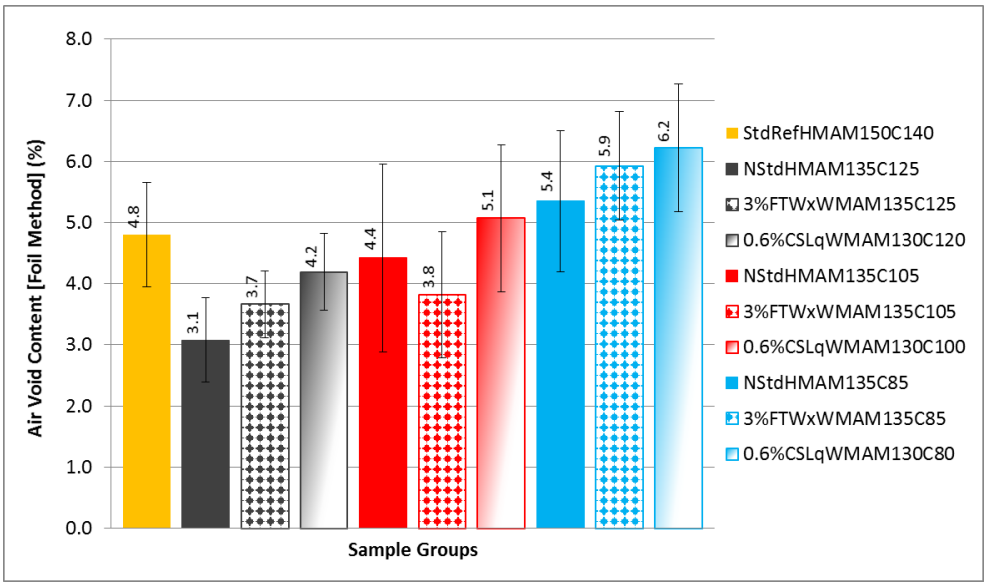


Figure 6.3 : Air void contents of all manufactured mixtures (cored samples)

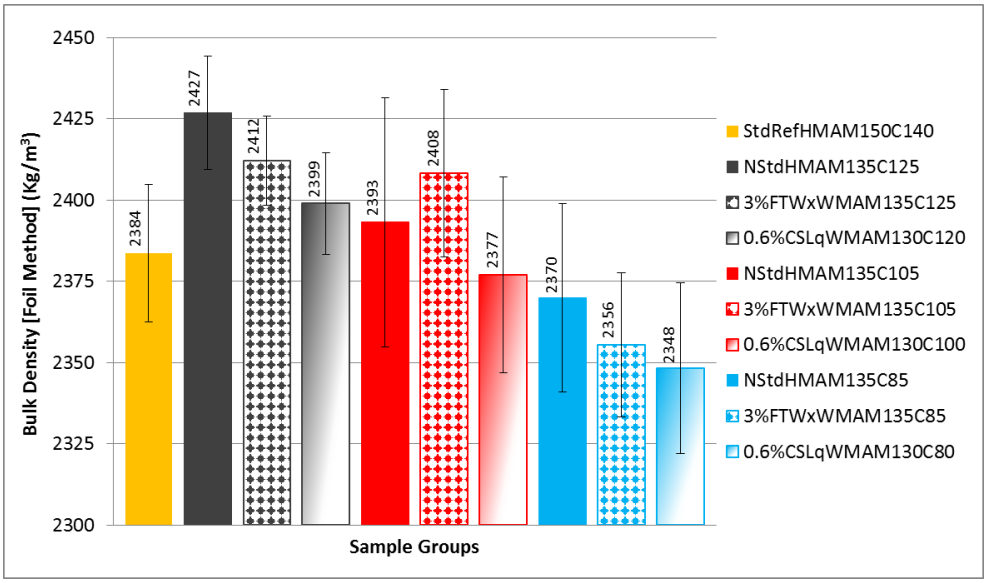


Figure 6.4 : Bulk densities of all manufactured mixtures (cored samples)

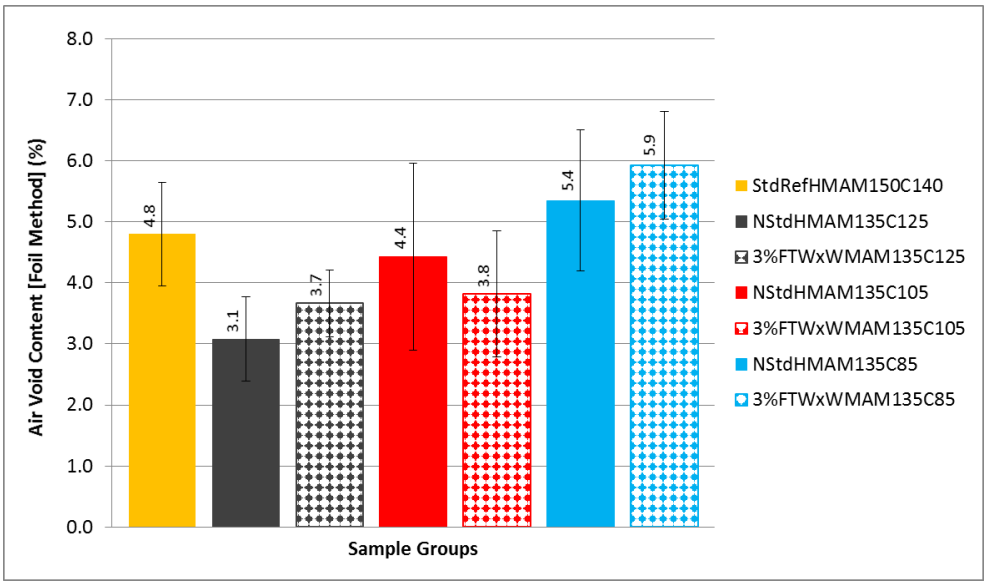


Figure 6.5 : Air void contents of the FTWax-WMA and the reference mixtures

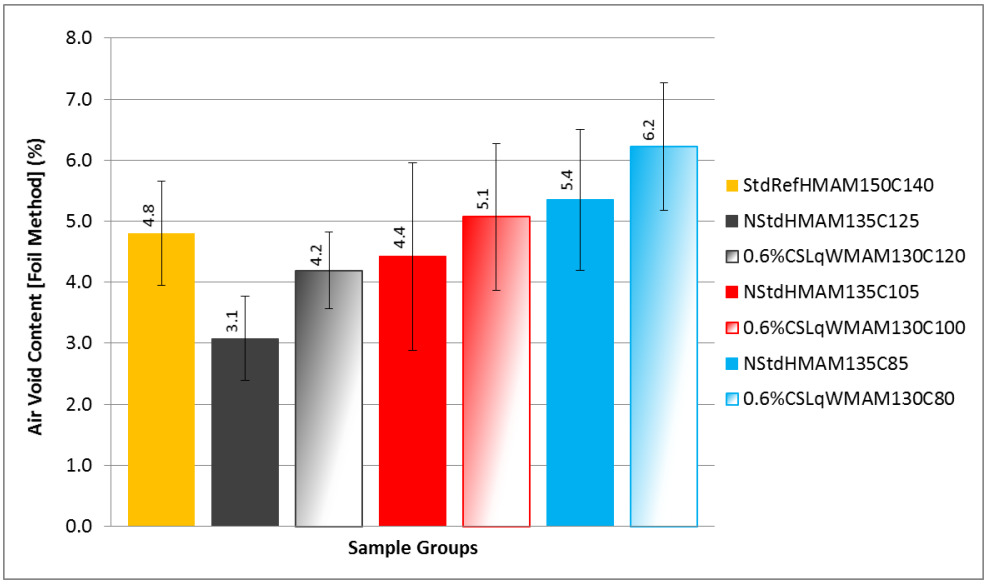


Figure 6.6 : Air void contents of the CatSurfLq-WMA and the reference mixtures

The overall trend of AV, as revealed in the bar charts, indicating "the lower the production temperature of asphalt, the higher the AV content of the resulting mixture", generally conforms to the findings of other researchers as mentioned in Chapter Literature Review with regards to compaction of asphalt. However, in order to interpret the exception points, the Shell Bitumen Test Data Chart (BTDC) (Figure 2.27) has been used.

The Shell BTDC presents the ideal bitumen viscosities for optimal mixing and compaction of asphalt. Thus, the data curve of each of the used bitumen types was plotted on the Shell BTDC (Figure 4.7). This provides the viscosity of each of the used bitumen types at their mixing and compaction temperatures. As the data charts of each bitumen require Fraass Breaking Point, Penetration Grade, Softening Point and viscosities (over the high temperature range of 90 to 180°C), these tests were performed on each bitumen.

According to the Shell BTDC criteria (Figure 2.27), the ideal viscosity of bitumen in order to have an adequate coating is 0.2 Pa.s. Lower viscosities will result in bitumen drainage and higher viscosities will decrease the coating quality, poor coating occurring at viscosities higher than 0.5 Pa.s. Moreover, compaction can be considered 'optimal' when bitumen viscosity is between 2 and 20 Pa.s. Viscosities lower than 2 Pa.s will result in a mixture which is too workable to compact and viscosities higher than 20 Pa.s are not suitable for compaction as the bitumen becomes too stiff. Obviously, as the binder viscosity increases from 2 to 20 Pa.s, the materials' workability for compaction will decrease. Moreover, as long as the mixture is too

workable for compaction, it seems logical to say that the compactability cannot be influenced significantly through viscosity changes.

Figure 6.3, Figure 6.5 and Figure 6.6 illustrate that the specimens of Reference HMA mixture group (StdRefHMAM150C140) have higher AV contents compared to the specimens of the similar mixture whose mixing and compaction temperatures have both been lowered by only 15°C (NStdHMAM135C125). In other words, using bitumen 70/100 Pen, if the HMA mixture's production temperature is reduced by 15°C, a denser mixture will result. This practical result seems to contradict the general common sense statement about the relation between an asphalt mixture's porosity and its production temperature as it was believed that decreasing the compaction temperature should have logically increased the AV content, which means being more permeable and porous.

As mentioned before in Section 3.2.3, the production temperature of StdRefHMAM150C140 has been chosen according to BSEN 12697-35, where the appropriate mixing and compaction temperatures for bitumen 70/100 Pen have been recommended to be 150°C and 140°C respectively. However, looking at Figure 2.27, Figure 4.7 along with a glance at Figure 6.39, shows that 150°C, may not be a suitable mixing temperature where bitumen 70/100 Pen is used because the bitumen's viscosity is much lower than 0.2 Pa.s. According to Shell BTDC, this means that bitumen drainage will happen in the mould resulting in the collection of bitumen at the bottom of the mould. Thus, in the case of StdRefHMAM150C140 the bitumen content of the sample will decrease in the main body of the slab and consequently in the associated cored samples. This could be the reason why compared to NStdHMAM135C125, the cored samples of StdRefHMAM150C140 have significantly higher AV contents. In fact, in the case of bitumen 70/100 Pen the appropriate mixing temperature to have adequate coating without drainage is 140°C. Therefore, in the case of NStdHMAM135C125, which has experienced a mixing temperature of 135°C, no bitumen drainage may have happened as the viscosity of bitumen 70/100 Pen at 135°C is higher than 0.2 Pa.s. This means that the bitumen content of the samples of NStdHMAM135C125 should be more than the ones of StdRefHMAM150C140. In other words, the samples of NStdHMAM135C125 should be denser than the ones of StdRefHMAM150C140, which should be more porous due to the bitumen drainage. This explains why in the associated bar charts of volumetric measurement test, the AV content of StdRefHMAM150C140 is significantly higher than that of NStdHMAM135C125.

However, although the mixing temperature of StdRefHMAM150C140 is quite enough to provide adequate coating (regardless of the bitumen drainage), in the case of NStdHMAM135C125 the coating may be slightly poorer due to the higher viscosity of bitumen at the mixing temperature of 135°C compared to 150°C. According to the Shell BTDC, the closer the viscosity is to 0.5 Pa.s, the poorer the coating provided.

On the matter of compaction, both 140°C for the StdRefHMAM150C140 (providing 0.2 Pa.s) and 125°C of NStdHMAM135C125 (providing 0.5 Pa.s) will, according to the Shell BTDC viscosity criteria, produce too-workable materials for compaction. In fact, for pure bitumen 70/100 Pen, it seems that the proper mixing and compaction temperatures should be 140°C and about 100°C respectively.

When talking about mixing and coating, it seems obvious that the viscosity of the binder, the binder-aggregate Surface Energy properties and their compatibility should be considered altogether. A proper coating needs compatible binder and aggregates to be introduced together but it will not happen in practice unless the binder is fluid enough to flow, wet and coat the aggregate highly depend on aggregate's surface energy. This part is directly influenced by the viscosity of the binder, which is a temperature-dependant characteristic. In other words, neither viscosity of the binder nor binder-aggregate compatibility can by itself guarantee an adequate coating. Both factors need to be at sufficient levels.

However, on the matter of compaction, the influencing factors vary. It may appear to be logical to state that insufficient compaction (high AV content) is mainly a consequence of a material's resistance against compaction. In fact, the compaction consists of moving the mixture's particles to the point of interlocking to a certain level. Thus, any resistance against this operation (compaction) should include some kind of resistance against moving the particles. This may be due to a mixture's internal friction, which resists particle relocation and compaction. An asphalt mixture includes aggregate and binder. Therefore, the internal friction should just be related to:

1) The friction between the aggregate particles (inter-particle aggregate friction),
2) The adhesion between the binder and aggregate (which can be considered as a sort of friction in a sense that it works against their movement into each other), and
3) The internal friction of the binder (viscosity).

The friction between the aggregate particles can be introduced as aggregates' angularity or inter-particle aggregate friction, which should not change if the aggregate type, gradation and moisture are kept constant. The more angularity the aggregates have, the more the internal friction and the more the resistance against compaction, which means the less the compactability.

The friction between binder and aggregate can be referred to the binder-aggregate adhesion, which is actually the adhesive force between the two elements. In fact, the greater the binder-aggregate adhesion is, the more the internal friction and resistance against compaction develops, which means the less the compactability is achieved. In fact, the adhesion promoter chemical additive molecules, such as the ones used in this research (CatSurfLq), as mentioned previously (Section 'Literature Review'), are attracted to the surface of the aggregate particles through the bitumen. This issue affects (increases) the binder-aggregate bond strength in all structural scales of the mixture including mastic and mortar. Thus, the internal friction of the elements in mastic/mortar is increased. This means the lubricity of the mixture is lowered. In fact, the internal resistance of the mentioned scales of the mixture against compaction increases and the workability of the materials for compaction decreases. In other words, it can be resulted that using an adhesion promoter additive, such as the one which has been used in this research (CatSurfLq), decreases the compactability through decreasing the lubricity and decreasing the workability of the mixture for the purpose of compaction. Looking at Table 5.4 shows how a high dosage CatSurfLq-modified bitumen 70/100 has stronger bonds with two different aggregates. It should be mentioned that although CatSurfLq has been added to the bitumen by 0.6% of the weight of the binder, the actual dosage of the additive for SE and bond strength calculations should be considered significantly higher. As mentioned in Section 4.5, this is because the additive is attracted to the aggregate particles in the mixture due to which the dosage of the additive in the neighbourhood of the aggregate particles, where the adhesion occurs, increases.

Looking at Figure 5.5 also shows that FTWax has less binder-aggregate bond strength, through which the lubricity of the mixture is more than the two other types of mixtures. This does not necessarily mean that the workability will be increased since the factor of viscosity should be considered in parallel in the case of FTWax (FTWax affects the viscosity in contrast with CatSurfLq which has no effect on the viscosity of the binder).

The internal friction of the binder appears in the form of a well-known characteristic namely viscosity. The higher the viscosity of the binder is, the more the resistance against compaction and vice versa will be. On this matter, referring to the Shell BTDC (Figure 2.27), it should be mentioned that viscosities lower than 2 Pa.s make the mixture too workable for compaction which means the material will squeeze under the compactor actuator. This phenomenon may result in moving the aggregate inside the mixture through the bitumen in such a way and level that some kind of segregation happens. It can also result in damaging the mixture through some kind of over compaction. Meantime, viscosities higher than 20 Pa.s are considered as too high for the purpose of compaction since the material will become too stiff to be compacted. In fact, the viscosities between 2 and 20 Pa.s are recommended as ideal for compaction considering this issue that over the mentioned range, the higher the viscosity, the lower the compactability.

In fact, it should be stated that FTWax increases the lubricity (decreases the internal friction) of the mixture through two different ways. One way (temperature-dependant) is to decrease the viscosity of bitumen at temperatures higher than FTWax's transition point. This action decreases bitumen internal friction and mixture's resistance to compact through increasing the lubricity. The other way (temperature-independent) is to decrease the surface tension of bitumen, which decreases binder-aggregate adhesion. This action decreases that part of mixture's internal friction as well as resistance for compaction which is due to the binder-aggregate interaction (adhesion). Increasing the lubricity provides more workability for compaction.

The above gives a reasoned interpretation of the data but, before it could be accepted as a valid explanation of the dominant trend of the AV content it is also necessary to explain the exceptions as, otherwise, these would undermine this interpretation.

The samples of both NStdHMAM135C125 and 3%FTWxWMAM135C125 mixture groups have been compacted at 125°C. Referring to Figure 2.27 and Figure 4.7 , at this temperature, both mixtures are too workable for the purpose of compaction as their binders' viscosities are as low as about 0.5 Pa.s and 0.33 Pa.s for NStdHMAM135C125 and 3%FTWxWMAM135C125 respectively, which are much lower than the minimum criteria of 2.0 Pa.s as recommended by Shell. Therefore, the compaction situation should have been the same for both mixtures and it should not have made the any difference to the AV content. Thus, for the proposed general explanation to be valid, there should be another factor that would explain the different AV contents of the mentioned mixture groups.

Looking at Figure 4.7, the curve for 3%FTWax-modified bitumen 70/100 Pen presented on a BTDC indicates that the ideal mixing viscosity for this type of modified bitumen is obtained at just below 135°C. Thus, in the case of the samples of all the 3%FTWax-WMA mixture groups, some bitumen drainage might have happened since their mixing has taken place at 135°C with about 5°C tolerance. This issue does not happen in the case of the Non-Standard Reference HMA mixtures since their binder viscosity at their mixing temperature (135°C) is about 0.3 Pa.s which is far enough above the limiting viscosity for drainage to be an issue. Thus, the higher AV content of 3%FTWxWMAM135C125 compared to its corresponding Non-Standard Reference HMA mixture (NStdHMAM135C125) may be as a result of some bitumen drainage in the mould of the FTWax-WMA mixture due to its critical binder viscosity.

In addition, regarding the FTWax-WMA mixtures, it should be mentioned that their bitumen content is less than the Reference Non-Standard HMA mixtures because of replacing 3% of the bitumen's mass by FTWax. FTWax is completely soluble in bitumen. Thus, the bitumen content of the 3%FTWax-WMA mixture is 3% less than the other mixtures. This can be another reason due to which the 3%FTWax-WMA mixture in each of the three compaction groups has a higher than average AV content than the Non-Standard HMA mixture.

Regarding the quality of coating, it should be mentioned that it is highly influenced by the viscosity of binder during mixing since a binder's surface tension is low/lowered through heating and the potential of coating is increased supposing that binder and aggregate are compatible in terms of polarity. The surface tension of a binder can also be reduced by the use of additives. Referring to the Surface Energy measurements presented in Figure 4.13 and the associated explanations in Section 4.5, this is what happens after adding FTWax to the pure bitumen. FTWax decreases the surface tension of bitumen and increases the lubricity of the mixture. However, regarding the binder's viscosity during the mixing phase, referring to Figure 2.27 and Figure 4.7, regardless of any bitumen drainage, which may happen at viscosities lower than 0.2 Pa.s, StdRefHMAM150C140 mixtures should have adequate coating quality as well as all of the FTWax-WMA mixtures since they all have experienced the same mixing temperature of 135°C.

However, all Non-Standard HMA mixtures, regardless of their different compaction temperatures, might have inadequate coating since, from the same Figures, their binders' viscosity at the mixing temperature of 135°C will have been more than the ideal viscosity for mixing (>0.2 Pa.s). The same is true of all the CatSurfLq-WMA mixtures, regardless of their

different compaction temperatures. For these groups of mixtures, the coating quality is expected to be even less than the Non-Standard HMA mixtures since 0.6%CatSurfLq-modified binder's viscosity at 130°C (mixing temperature) is more than the that of pure bitumen 70/100 pen. at 135°C (the mixing temperature of the Non-Standard HMA mixtures).

From the viewpoint of ideal viscosity for compaction, referring to the Shell BTDC in Figure 2.27, the mixture of 0.6%CSLqWMAM130C120, just like NStdHMAM135C125 and 3%FTWxWMAM135C125, is considered too workable for compaction because its binder viscosity is significantly lower than the bottom limit of 2.0 Pa.s at the compaction temperature of 120°C. However, referring to Figure 4.7, at 120°C the binder viscosity of 0.6%CSLqWMAM130C120 is more than those of NStdHMAM135C125 and 3%FTWxWMAM135C125. In addition, compared to NStdHMAM135C125 and 3%FTWxWMAM135C125, it should still have lower workability for compaction due to its stronger binder-aggregate adhesion, which increases the internal friction of the mixture resisting the compaction effort. In the case of the CatSurfLq-WMA mixtures, regardless of their compaction temperature, the lubricity of the mixture is at a lower level, which results in less workability under compaction (less compactability). The reason for such a statement was discussed in the previous pages.

This issue, as Figure 6.3 and Figure 6.6 confirm, should have caused the mentioned mixture's specimens to have higher AV contents compared to the ones of the other two mixture groups (i.e. NStdHMAM135C125 and 3%FTWxWMAM135C125). On this matter, the lower mixing temperature can guarantee that no bitumen drainage may have happened. It just indicates that aggregate coating may not be as good as NStdHMAM135C125 and 3%FTWxWMAM135C125.

Since the mixing temperatures of the 3 compaction groups of each of the 3 material groups (i.e. Non-Standard HMA mixtures, FTWax-WMA mixtures and CatSurfLq-WMA mixtures) was the same, the quality of aggregate coating and the amount of binder drainage (if it happens) in the compaction groups of each material group should be the same, regardless of their different compaction temperatures.

The samples of 3%FTWxWMAM135C105 mixture group have been compacted at 105°C as well as the ones of NStdHMAM135C105. However, according Figure 4.7, the 3%FTWax-modified binder's viscosity meets the ideal criteria for optimal compaction at lower

tempertures than the pure bitumen 70/100 Pen. This has happened because the 3%FTWax-modified binder is passing through the FTWax Transition Point temperature from 110°C down to 100°C, over which range the FTWax congeals quite suddenly. The sudden congealing rapidly increases FTWax's viscosity by which the FTWax-modified binder's viscosity increases sharply over the mentioned range of temperature. The increased viscosity of 3%FTWax-modified binder exceeds the viscosity of pure bitumen 70/100 while cooling down from 110°C. Figure 6.3 and Figure 6.5 illustrate that the average AV Content of 3%FTWxWMAM135C105 is nearly as low as that of 3%FTWxWMAM135C125. In other words, at 105°C, the FTWax-WMA mixture is nearly as compactable as it is at 125°C though its binder is about 7 times more viscous than it is at 125°C.

From another point of view, the binder viscosity of 3%FTWxWMAM135C105 is nearly equal to that of NStHMAM135C105 but its average AV content is less than the one of NStHMAM135C105. It is clear that 105°C is an optimal compaction temperature for the 3%FTWax-WMA mixture but it does not seem to be easy to justify it. The only possible phenomenon which may have influenced the compaction process is what happens in FTWax at this temperature. Probably, passing through the liquid-to-solid transition phase provides some kind of suitable situation which increases the compactability of the mixture. This may also refer to the lubricity of the mixture in this situation. In other words, 105°C may be an ideal temperature in terms of lubricity, workability and compactability altogether.

As a merely theoretical guess, it can be referred to the congealing process of FTWax, which causes a crystallisation-form restructure to be produced inside the bitumen. This phenomenon may develop a contractile tension inside the mixture which increases the compactability neither via lubricity nor workability. However, the fact that compaction of the 3%FTWax-WMA mixture at 105°C has resulted in the lowest AV content could not be justified with more definite reasons as stated above.

For the same reason as stated through the previous pages, with the CatSurfLq-modified bitumen (with lowered lubricity) in the mixture during compaction, the compactability of the CatSurfLq-WMA mixture is less than the other two mixtures. Moreover, according Figure 4.7, the viscosity of the CatSurfLq-modified binder at the compaction temperature of 100°C is more than the viscosities of Pure Bitumen 70/100 Pen and 3%FTWax-modified Bitumen at 105°C. These two reasons have caused the CatSurfLq-WMA mixture to be compacted with more

difficulty and resulted in higher AV contents compared to NStdHMAM135C105 and 3%FTWxWMAM135C105 mixtures.

Compaction of the samples of 3%FTWxWMAM135C85 and NStdHMAM135C85 mixture groups was also performed at 85°C. Referring to Figure 4.7, the viscosity of pure bitumen 70/100 Pen is in the recommended range of ideal viscosities for optimal compaction (2 to 20 Pa.s). However, since it is approaching the top limit of 20 Pa.s and the binder has become stiffer consequently, following the same roller passes, the average AV content of NStdHMAM135C85 has become higher than the one of NStdHMAM135C105. In fact, the mixture of NStdHMAM135C85 is relatively less workable and stiffer for compaction. Referring to Figure 4.7, at 85°C, the 3%FTWax-modified binder's viscosity is about 200 Pa.s due to widely congealing of FTWax at temperatures below 110°C, which produces a very stiff structure of crystallised wax inside bitumen. According to Figure 6, this value is much higher than 20 Pa.s, thus the mixture is far too stiff for compaction with a significantly lowered workability. In addition, as mentioned before, as in all the 3%FTWax-WMA mixtures, the small probable amount of bitumen drainage, which might have happened during placing the mixture in the mould at 135°C, can be another reason for the higher AV content of the 3%FTWxWMAM135C85 as compared to the NStdHMAM135C85 mixture.

At 80°C, which is the compaction temperature of the 0.6%CSLqWMAM130C80, the viscosity of 0.6%CatSurfLq-modified bitumen 70/100 is higher than the viscosity of pure bitumen 70/100 Pen, which results in a stiffer mixture for compaction. This issue decreases the workability of 0.6%CSLqWMAM130C80 mixtures compared to NStdHMAM135C85 mixtures for compaction. Moreover, the CatSurfLq-mixture's lubricity has been lowered due to the presence of the chemical additive, as argued previously. Having less workability and lubricity compared to NStdHMAM135C85 mixture, has resulted in having a higher average AV content for the same number of roller passes.

Regarding the reason why the average AV content value of 3%FTWxWMAM135C85 samples is smaller than the one of 0.6%CSLqWMAM130C80, it should be mentioned that it may be due to the higher lubricity of the FTWax-modified mixture at binder-aggregate interface, which may have neutralise the negative effect of its higher binder viscosity.

It can be mentioned that in order to obtain optimal mixing and compaction for an asphalt mixture, the suitable manufacture temperatures must be chosen in accordance with the criteria

of Shell Bitumen Test Data Chart indicating the ideal viscosities for asphalt manufacture. In order to approach this purpose, the associated binder's data line must be drawn on the BTDC.

6.1.2. CONCLUSION

All in all, the more general, clear and dominant trend, which can be extracted from the produced bar charts of average AV Contents of mixture groups (Figure 6.3, Figure 6.5 and Figure 6.6), can be stated as the lower the compaction temperature of asphalt (regardless of mixture type, production technology or used additive) the higher the Air Void Content of the mixtures. On this matter, the AV content of the Reference HMA mixture is a remarkable exception, as it does not follow the mentioned trend.

In fact, it seems that adding the additives, to some extent, has worsened the compactability of the mixtures since the AV Content of the Non-Standard HMA mixture in each of the 3 compaction groups has the lowest AV Content compared to the Saobit-WMA or CatSurfLq-WMA mixture. The FTWax-WMA itself has lower AV Content compared to the CatSurfLq-WMA mixture. In other words, it seems that neither the 3%FTWax-WMA mixture nor the 0.6%CatSurfLq-WMA mixture can be as good as their counterpart Non-Standard HMA mixture in terms of the volumetric properties (AV content, bulk density, compactability and etc.). Thus, at least in terms of the volumetric properties, neither FTWax nor CatSurfLq can help their associated WMA mixture to be even as good as their reference HMA mixture.

On this matter, compaction of 3%FTWax-WMA at 105°C produces an exceptional case, which is 3%FTWxWMAM135C105 and has lower AV Content than its counterpart Non-Standard Reference HMA (NStdHMAM135C105) and even than the FTWax-WMA which has been compacted at 125°C (3%FTWxWMAM135C125). The reason for this issue has not been defined although some possible justifications were postulated.

From the viewpoint of Target Air Void (TAV) Content, which has been 8% for Slab specimens, it can be stated that all of the manufactured mixtures are acceptable as their AV Content are significantly lower than the TAV of 8%. On this matter, it should be mentioned that compaction of asphalt (whether HMA or WMA) can take place at temperatures as low as 80°C only if the base binder is soft enough such as 70/100 pen bitumen and its modified derivative. In a more general form, it can be stated that the softer the binder, the lower the practically possible compaction temperature.

6.2. INDIRECT TENSILE STIFFNESS MODULUS (ITSM/IT-CY)

6.2.1. DISCUSSION on the TEST RESULTS

Among the various tests, which have been performed commonly on both cored and the gyratory specimens, the most similar trend can be found between the Indirect Tensile Stiffness Modulus (ITSM) test results. Regarding the results of the other tests, except the RLAT, such a clear trend is hardly observable.

It should be mentioned that in the case of the ITSM test results for the cored samples taken from the slab specimens (Figure 6.7), each bar represents 12 specimens while in the case of the ITSM Bar chart of the gyro samples (Figure 6.10), each bar represents 11 specimens. In this section, first, the results of the ITSM/IT-CY test on the cored specimens will be discussed and then those of the gyro samples will be investigated.

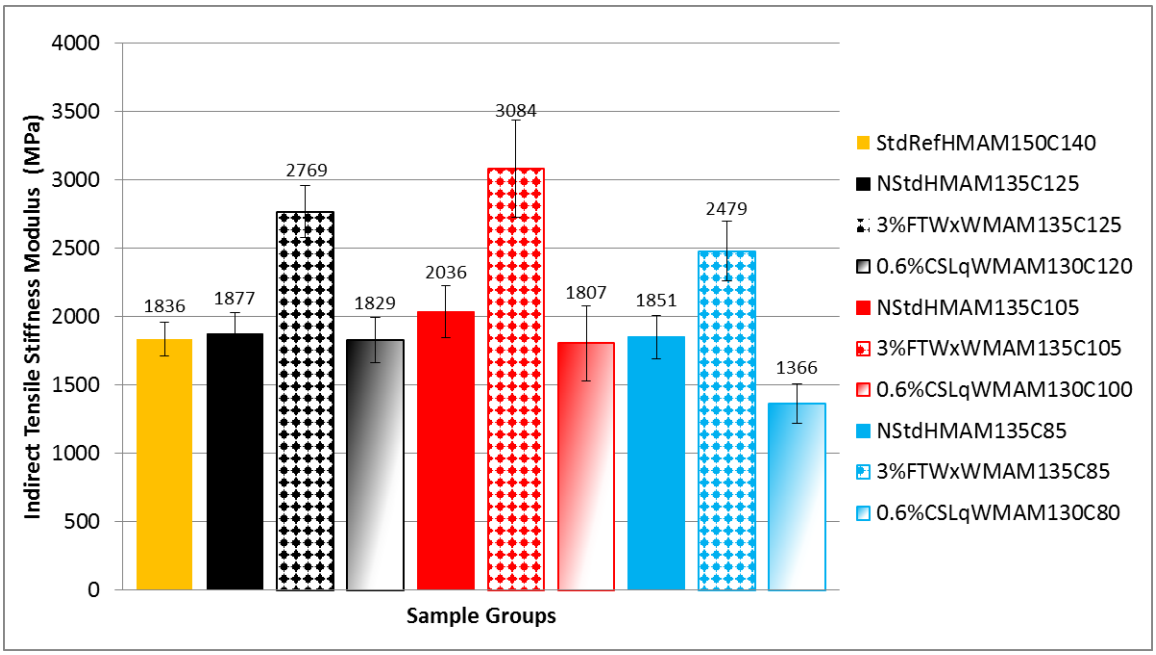


Figure 6.7 : ITSM/IT-CY test results of the cored specimens (all sample groups)

Looking at Figure 6.7, which is the bar chart of the ITSM test results of the cores taken from the slab specimens, illustrates that generally there is not any considerable difference between the average ITSM values of the Reference HMA, the Non-Standard HMA and the 0.6%CatSurfLq-WMA mixture groups (maybe a slightly declining regime). Considering this graph, NStdHMAM135C105 sample group with a slightly higher average ITSM value and 0.6%CSLqWMAM130C80 mixture group with a quite significantly lower average ITSM value

are two exceptions. From another viewpoint, the average ITSM value associated with the Reference HMA mixture is nearly the same as that of NStdHMAM135C125. It means that in the case of a standard HMA mixture (or at least in the case of the one which has been produced in this research using bitumen 70/100 Pen, mixed at 150°C and compacted at 140°C), without using any additive, it is possible to lower the production temperatures (mixing and compaction temperatures) as much as 15°C, whilst no negative influence on the Indirect Tensile Stiffness Modulus of produced samples occurs.

Moreover, comparing the ITSM values of the 3 different Non-Standard HMA sample groups (i.e. NStdHMAM135C125, NStdHMAM135C105 and NStdHMAM135C85) all of which have been mixed at the same mixing temperature of 135°C, shows that reducing the compaction temperature even to as low as 85°C has nearly no negative influence on the Indirect Tensile Stiffness of asphalt. In other words, from the view point of Indirect Tensile Stiffness of an HMA which has been produced by the use of pure bitumen 70/100 with no additive, a 15°C reduction in mixing temperature and a 55°C decrease in the compaction temperature is allowable. In fact, a slight increase in the ITSM value can be observed if it is compacted at 105°C. This shows that 105°C can be a more ideal compaction temperature for an HMA with bitumen 70/100 Pen bitumen as binder.

Comparing the test results of the three 0.6%CatSurfLq-WMA mixture groups (with the same mixing temperature of 130°C and different compaction temperatures of 120, 100 and 80°C) show that reducing the compaction temperature down to 100°C does not affect the ITSM value. Whereas compaction at 80°C has quite a significant 24% decreasing effect on the Indirect Tensile Stiffness Modulus.

In each of the 3 compaction groups, comparing the average ITSM values of Non-Standard HMA mixture with 0.6%CatSurfLq-WMA mixture it can be said that applying the chemical additive does not positively influence the mixture's ITSM unless the 5°C decreased production temperature is taken into consideration. Moreover, it seems that adding 0.6% CatSurfLq can negatively affect the ITSM value at the low compaction temperature of 80°C.

Figure 6.7 indicates that in each of the 3 compaction groups, the 3%FTWax-WMA mixture is in the possession of the highest average ITSM value compared to the Reference HMA, the Non-Standard HMA and the 0.6CatSurfLq-WMA mixtures. Comparing the average ITSM value of all 3%FTWax-WMA mixture groups with that of all Non-Standard HMA mixture

groups illustrates that adding 3% of FTWax to pure bitumen 70/100 Pen has significantly (about 45%) increased the Indirect Tensile Stiffness Modulus of the resultant asphalt. It should be mentioned that in each compaction group, the mixing and compaction temperatures of the 3%FTWax-WMA mixture are the same as those of the Non-Standard HMA mixtures. Meanwhile, Figure 6.7 shows that over the relatively wide range of compaction temperatures (125, 105 and 85°C), the average ITSM value of the 3%FTWax-WMA mixture has clearly increased (by about 10%) when it is compacted at 105°C (mixture group 3%FTWxWMAM135C105). However, if the compaction temperature of the 3%FTWax-WMA mixture is lowered to 85°C (3%FTWxWMAM135C85), according to the test results, the average ITSM value decreases (by about 20%) to an even lower value than that of the 3%FTWax-WMA mixture which was compacted at 125°C (3%FTWxWMAM135C125). Therefore, it can be said that 105°C should be considered as the ideal compaction temperature for 3%FTWax-WMA mixture (manufactured using 70/100 Pen bitumen) in order to obtain the optimum ITSM value.

In order to justify the stated interpretations, and also to find the rational reason behind the described trends, it seems necessary to look at ITSM as one of the mechanical properties of an asphalt mixture from a more analytical viewpoint through studying the more basic properties of the mixture which can influence the ITSM value.

Theoretically, the ITSM value shows the Indirect Tensile Stiffness Modulus of a cylindrical sample in the centre of the sample, in the perpendicular direction to the loading ordination.

An asphalt mixture consists of bitumen and aggregate. Thus, any stiffness property of asphalt such as ITSM should be related to the stiffness of the aggregates, that of the bitumen and the bond strength between the bitumen and aggregates. The higher the value of aggregate stiffness, bitumen stiffness or bond strength, the higher the value of the resultant asphalt mixture. As long as the same type and gradation of aggregates for the mixtures is used, it is logical to state that the difference between the ITSM values of different mixtures refers to the difference between the bitumen properties and the difference between the binder-aggregate bond strength of the mixtures.

In fact, Shell's nomograph for predicting the stiffness modulus of asphalts (Figure 6.8) confirms that in the same situation in terms of bitumen content (volume), aggregate content (volume) and aggregate type and gradation, asphalt mixtures with higher stiffness of their

bitumen will have higher stiffness modulus. In addition, the nomogragh can confirm that supposing having equal bitumen stiffness, asphalt samples with higher AV content (lower volume/content of bitumen or aggregate or both) will have lower stiffness modulus.

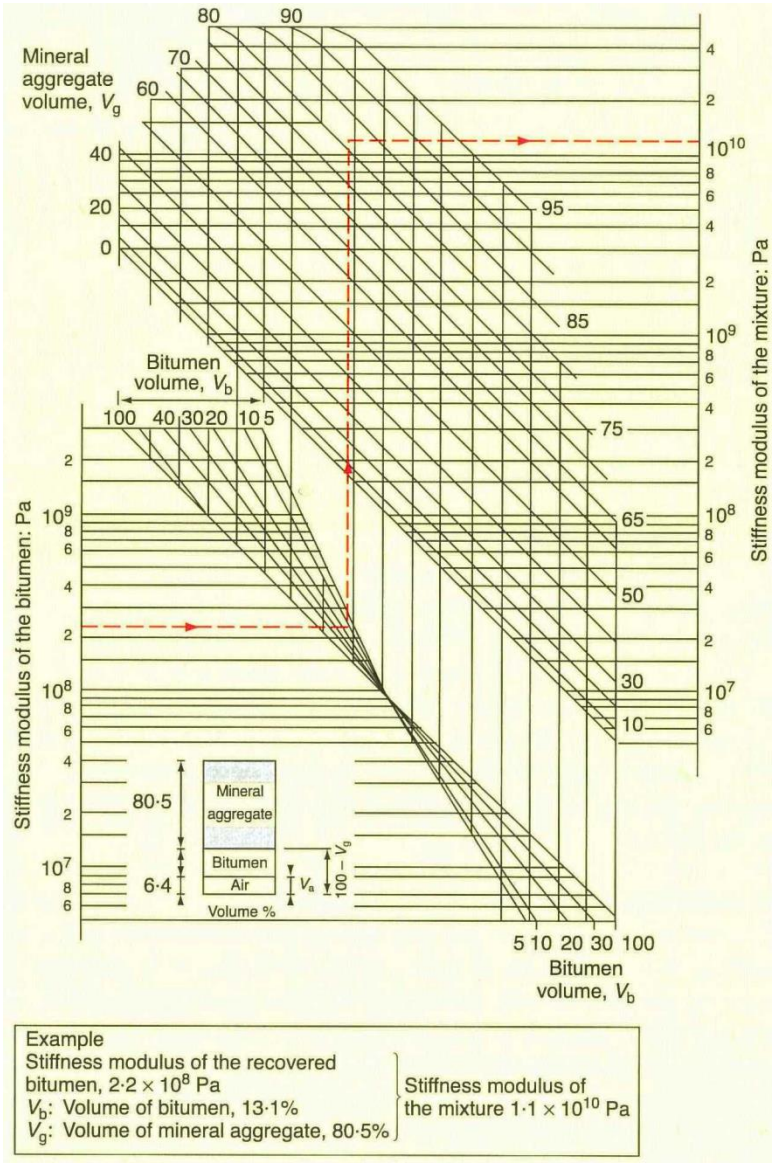


Figure 6.8 : Nomograph for predicting the stiffness modulus of asphalt (Whiteoak & Read, 2003)

Nevertheless, supposing that the whole composite structure of a typical asphalt specimen can be simulated as a simplified 3-element equivalent model consisting of an equivalent aggregate element, an equivalent bitumen element and an equivalent bitumen-aggregate interface element, which can deliver the same total stiffness modulus as the main specimen together, the three elements should be arrayed in a series order (not parallel with each other). This way lets

the global stiffness of the simulating system be truly related to the stiffness of each of components. In fact, through this array of the elements, while higher values of the components results in increasing the total stiffness value, the total value is smaller than the value of each component individually. On this matter, the thousand-times smaller stiffness modulus of any typical bituminous specimen (not necessarily the samples of the current study) compared to that of its aggregate components can be a supporting argument.

According to the basic definitions of the fundamental Mechanics of Materials, the relationship between E (Young's elasticity modulus), G (shear stiffness) and ν (Poisson's ratio) is as follows:

$$E = G \times 2(1 + \nu) \qquad \text{Equation 6.1}$$

The above formulation states the higher the shear stiffness (G) the higher the stiffness modulus (E). In fact, G represents E. Overall, it is logical to conclude that the bigger the Shear Stiffness of bitumen the higher its stiffness modulus as well as the stiffness of the resultant mixture.

Figure 4.10 and Figure 4.8 show the results of the Frequency-Temperature Sweep DSR test on pure bitumen 70/100 pen, FTWax-modified and CatSurfLq-modified bitumen 70/100 Pen. As described in Section 4.4 it can be seen that while there is nearly no difference in the Complex Shear Stiffness of the CatSurfLq-modified binders compared to their base 70/100 Pen bitumen, the FTWax-modified binders have significantly higher G^* values compared to their base 70/100 Pen bitumen. Following the previously mentioned arguments, using the same type and gradation of aggregates can make asphalt's stiffness merely dependant to its binder stiffness and binder-aggregate bond strength.

Putting Figure 4.8, Figure 4.10 and Figure 6.7 together and comparing the ITSM values of the asphalt samples and complex shear stiffness modulus of their associated binders, confirms that the equal Shear Stiffness of 0.6%CatSurfLq-modified binder and its base pure bitumen 70/100 has resulted in the very close (nearly equal) stiffness modulus of their associated mixtures regardless of their compaction temperature (except to the cold compacted group i.e. 0.6%CSLqWMAM130C80 and NStdHMAM135C85). Moreover, the significantly higher G^* of 3%FTWax-modified binder compared to its pure base binder 70/100 Pen is the main reason for the ITSM value of the 3%FTWax-WMA mixtures to be considerably higher than that of the Non-Standard HMA or the Reference HMA mixtures regardless of their compaction temperature.

On the matter of the influence of binder-aggregate bond strength on the ITSM value of the mixture, comparing Figure 6.7, Figure 5.5 and Figure 5.6 together causes some complications in the sense that although higher bond strength is logically expected to result in the higher stiffness modulus of the resultant mixture. However, it seems that in practice, or at least in the case of the materials used in the current research, the effect of binder-aggregate bond strength variation in changing the ITSM value of an asphalt mixture is negligible even if the same aggregate type and gradation and bitumen stiffness is used.

As can be found out, looking at Figure 6.7 and Figure 5.6 together, the higher bond strength of the 0.6%CatSurfLq-WMA to HMA has not caused the ITSM of 0.6%CatSurfLq-WMA mixtures to be higher than that of the Non-Standard or the Reference HMA mixtures. Moreover, the lower bond strength of the 3%FTWax-modified binder (Figure 5.5) compared to the other binders has not caused the ITSM of the 3%FTWax-WMA mixture to be less than that of the other two types of mixtures though it may have had some negative influence.

This may be due to the non-destructive nature of the ITSM test during which no de-bonding takes place. Thus, the binder-aggregate bond issue never arises no matter how big it is. That may also relate to the way that it contributes to ITSM calculations which is not the subject of the current research and may be worth being studied through further research.

Nonetheless, it is clearly found that the Indirect Tensile Stiffness Modulus of asphalt is highly related to the shear stiffness of the binder.

6.2.2. CONCLUSION

FTWax increases the ITSM of mixture via increasing the stiffness of binder while CatSurfLq has no effect on mixture's ITSM since it does not vary the binder's stiffness. If 3%FTWax-WMA is compacted at 105°C (while they have been mixed at 135°C), even better stiffness can be resulted compared to those which have been compacted at 125°C. If the compaction temperature is lowered to 85°C, the stiffness modulus becomes slightly smaller than that of the 3%FTWax–WMA mixture which has been compacted at 125°C. The same decrease can be seen in the 0.6%CatSurfLq-WMA which has been compacted at 80°C while the other two 0.6CatSurfLq-WMA mixtures with higher compaction temperatures have roughly the same ITSM values. However, this matter cannot be seen in the case of the Non-Standard HMA mixtures. It means that if the Non-Standard HMA mixtures are compacted even at 85°C, no

decrease can be seen in their ITSM value though there may be some increase in the stiffness value at the compaction temperature of 105°C.

It means that using the additives may have made the mixtures more susceptible to temperature decline. In the case of FTWax-WMA mixtures, this may be due to the crystallisation of FTWax at temperatures below the FTWax transition point, which as discussed in Section 2.3.2.2 and 2.11.3.1 makes the mixture too stiff for compaction and also should have made the FTWax-modified binder's structure brittle at the compaction temperature of 85°C. Therefore, the FTWax-modified binder's brittle structure may have been damaged to some extent under the cold compaction at 85°C in such a way that the mixture's ITSM value has decreased.

Regarding the reason why CatSurfLq makes the mixture's ITSM more sensitive to temperature decline, no reasonable argument can be stated through the available data.

In the case of the Gyro samples, the results are quite similar to the cores in terms of the trends, but not the values. However, at the compaction temperature of 105°C, the FTWax-WMA has experienced a slight decrease in its ITSM. Nonetheless, the FTWax-WMA mixtures are still in the possession of the highest ITSM values which conforms to the results of the cores and can be justified and interpreted through the same arguments and discussion. Moreover, following the cool compaction (compaction at 85°C or 80°C), the same ITSM drop as that of the cored specimens is observable but in all types of the manufactured mixtures including the Non-Standard HMA mixture. It means that the hypothesis regarding damaging the brittle structure of bitumen at the mentioned compaction temperatures should have taken place in the case of all types of mixtures.

Figure 6.9 shows the relationship between the ITSM values of the cores from the manufactured Slab specimens versus their AV contents. In this Figure, there is a general downward trend in the ITSM values of the samples of each mixture group by increasing their AV Contents. In other words, for a particular mixture group, the higher the AV Content of the samples, the lower their ITSM values. This trend can mostly be seen in the mixtures which have been compacted at low temperatures (i.e. 105, 100, 85 and 80°C). Nonetheless, this issue, as mentioned in the previous pages, conforms to what Shell's nomograph for predicting the stiffness of asphalt states regarding the relation of AV Content and stiffness of asphalt.

Looking at Figure 6.9 along with comparing Figure 6.7 with the bar chart of the AV contents (Figure 6.3) leads to the issue that the higher ITSM of 3%FTWxWMAM135C105 samples

may be related to their lower AV Contents compared to 3%FTWxWMAM135C125 and 3%FTWxWMAM135C85.

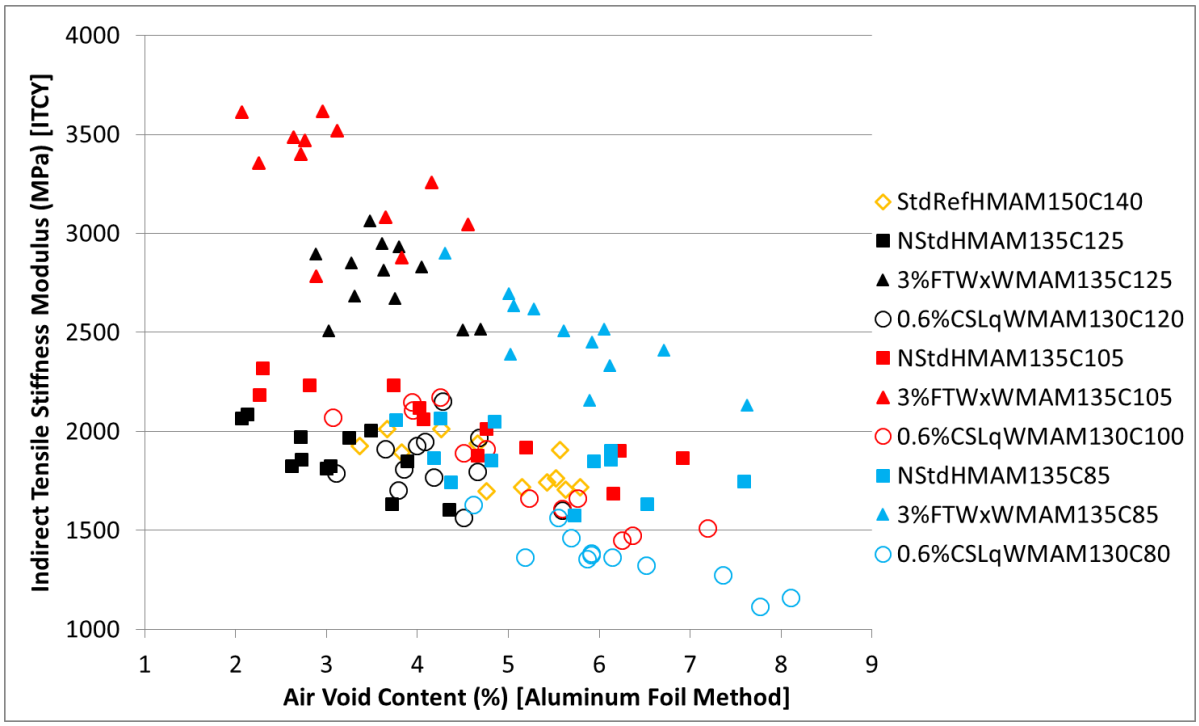


Figure 6.9 : ITSM values vs AV contents of the samples (Cores)

Figure 6.9 also illustrates that lowering the compaction temperature produces higher scatter in the AV Content values of the specimens while the scatter of the ITSM values are nearly the same in different mixture groups.

Regarding the ITSM/IT-CY test results on the gyro specimens, with a comparative glance at Figure 6.10 with Figure 6.7, it can be realised that almost a similar general slightly declining regime dominates both of them. In other word it seems that reducing the compaction temperature has had the same influence on the ITSM variations of both gyro and cored samples and the compaction method, as well as the aggregate type has influenced the magnitude of the absolute values of the stiffness modulus.

However, it can be realised that in the case of the gyro sample groups 0.6%CSLqWMAM130C100, NStdHMAM135C85 and 0.6%CSLqWMAM130C80 a noticeable decrease takes place in the ITSM value. This issue can be referred to the reduced temperature which they have been compacted. It can also be seen that in the case of the NStd-HMA mixtures and the 0.6%CatSurfLq-WMA mixtures a lightly declining regime dominates

the bar charts indicating that the stiffness of the mentioned 'material groups' decreases by reducing the compaction temperature. Considering the fact that the AV content of the gyro samples have not increased over the declining compaction temperature, the reduction in the ITSM values should not relate to the volumetric properties. Therefore, the reason may relate to the fact that reducing the compaction temperature made the binders stiffer with more viscosity such that the mixtures' lubricity and workability have declined significantly. This has increased the internal tension of the moulded materials considerably in such a way that the aggregates have been crushed through the temperature-independent gyrations of the gyratory compaction process. Following this issue, the internal resistance of the materials to tensile stress should have reduced which resulted in decreasing their indirect tensile stiffness modulus.

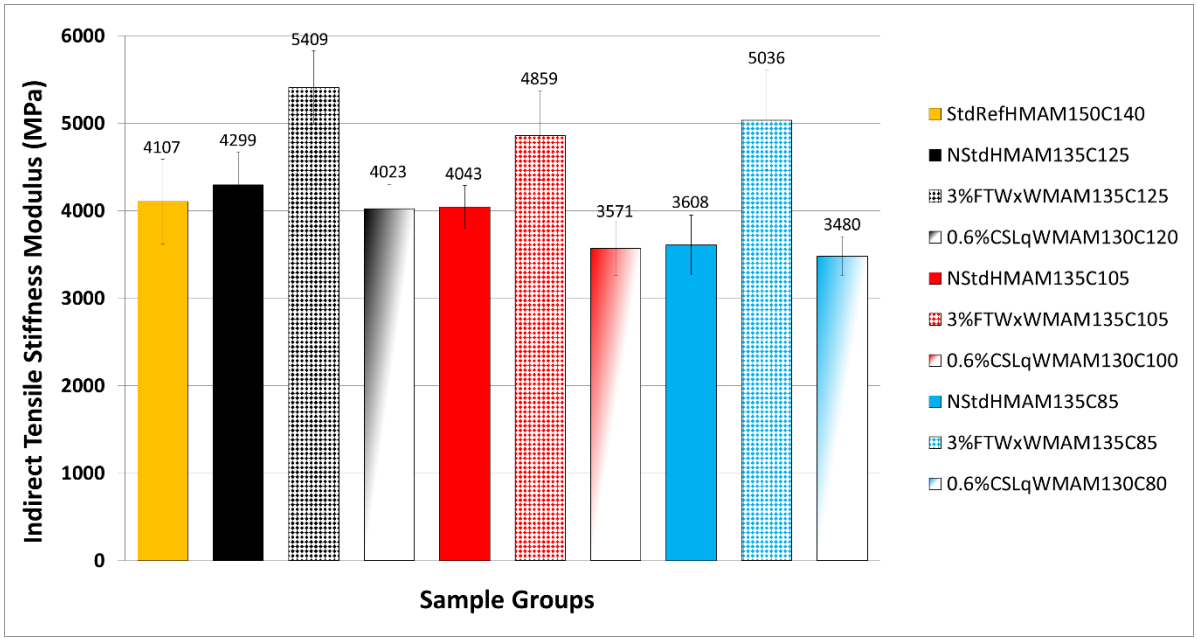


Figure 6.10 : ITSM test results of the gyro specimens (all sample groups)

6.3. RESISTANCE to FATIGUE FAILURE under ITFT

6.3.1. DISCUSSION on the TEST RESULTS

Figure 6.11 presents the fatigue life lines, which have been produced from the results of the stress-controlled Indirect Tensile Fatigue Test (ITFT) made on the cores taken from the slab specimens. Each line has been produced from 5 points each of which represent the test result on one core.

On this matter, it should be mentioned that the recommended minimum number of samples to produce each point is 3 and each fatigue line should be drawn by the use of at least 11 points. However, in practice, due to the time and material limitations as well as the inevitable limitations of the research framework, as long as a trend line's reliability stayed over 90% (as happened for all fatigue lines of the current research), using 1 sample per point and 5 points per line was recognised as acceptable.

Regarding interpreting the fatigue life lines of the stress-controlled fatigue tests, it can be stated that the higher (can also be the longer) the fatigue life line in the graph, the higher the materials resistance to fatigue failure (indicating the failure of materials at higher numbers of loading-unloading cycles under a certain loading stress). Moreover, it can be said that the further the fatigue lines' distance to the horizontal axis, the higher the resistance of the material to fatigue distress (indicates failing under a higher load stress at a certain number of loading cycles). Also, the smaller the slope of the fatigue line, the higher the materials fatigue resistance (indicating the failure of materials at higher numbers of loading cycles under a certain loading stress).

The graphs shown in Figure 6.14 have been produced using the combination of ITST and ITSM test results. It is in fact comparatively showing the Stress-Strain relationship of the mixtures. The slope of each line represents the average Indirect Tensile Stiffness of different samples in a mixture group, tested at different stresses.

A comparative glance at Figure 6.11, Figure 6.14 and the ITSM bar chart of the cores taken from the slab specimens (Figure 6.7) confirms that the higher the Indirect Tensile Stiffness Modulus of samples, the more their resistance to fatigue failure or the longer their fatigue line life. The same relationship can be found between the ITFT and ITSM test results of the gyro

samples though the values of ITSM are totally different from those of the cored specimens as well as the fatigue line characteristics.

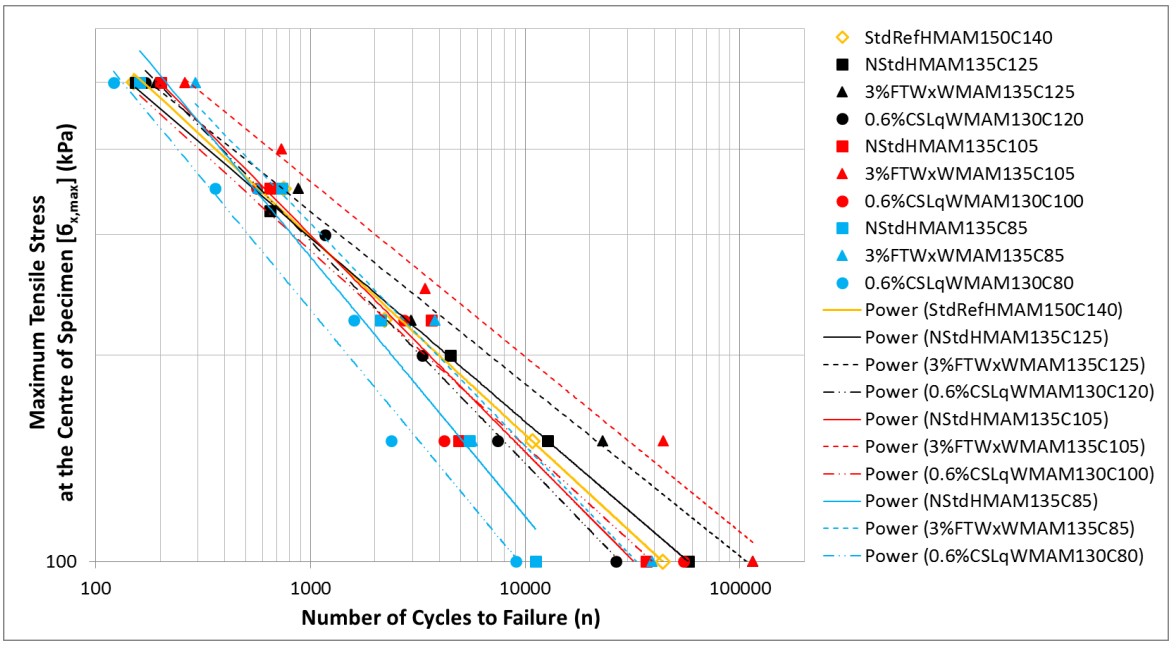


Figure 6.11 : ITFT results for the cored specimens (all sample groups)

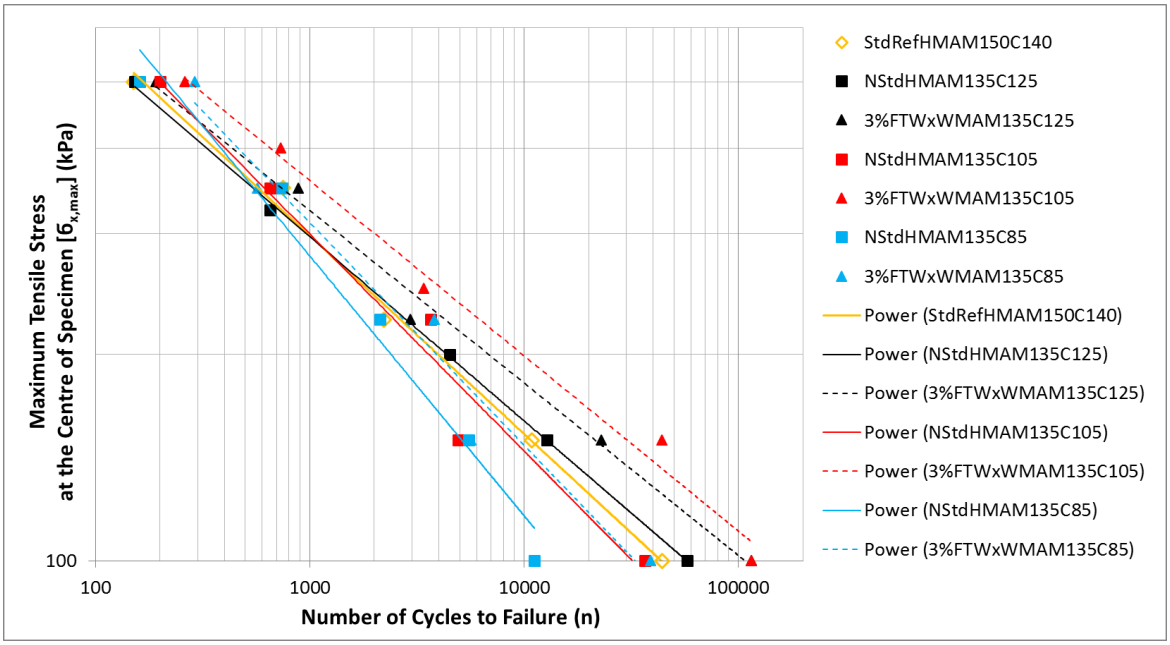


Figure 6.12 : ITFT results for the cored specimens (FTWax-WMA, NStd-HMA and StdRef-HMA)

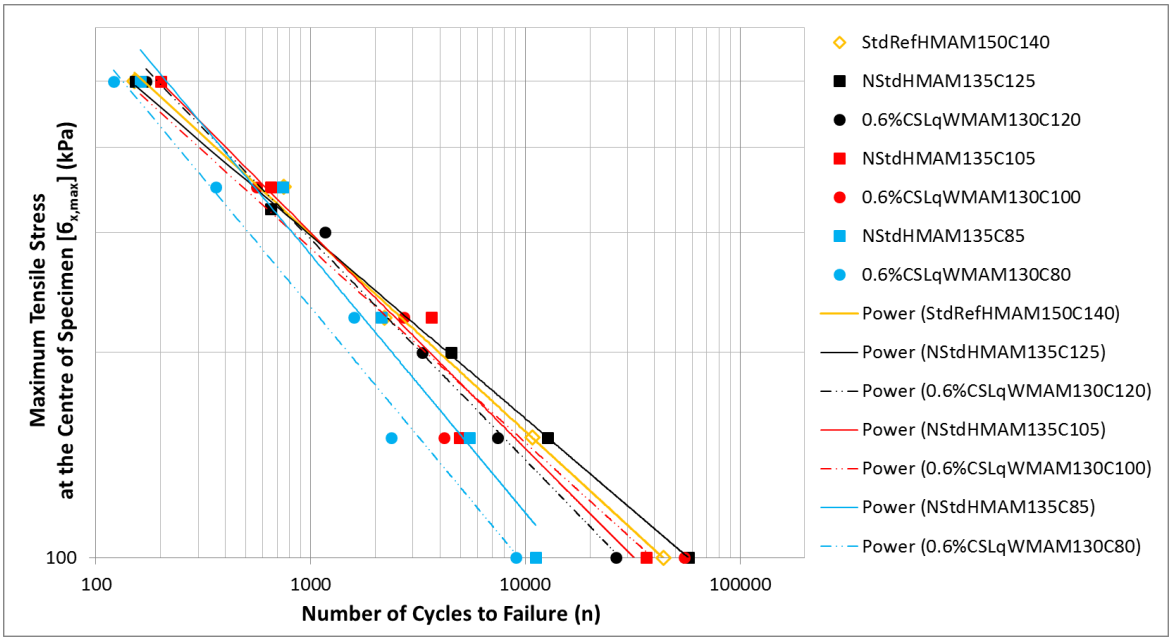


Figure 6.13 : ITFT results for the cored specimens (CatSurfLq-WMA, NStd and StdRef-HMA)

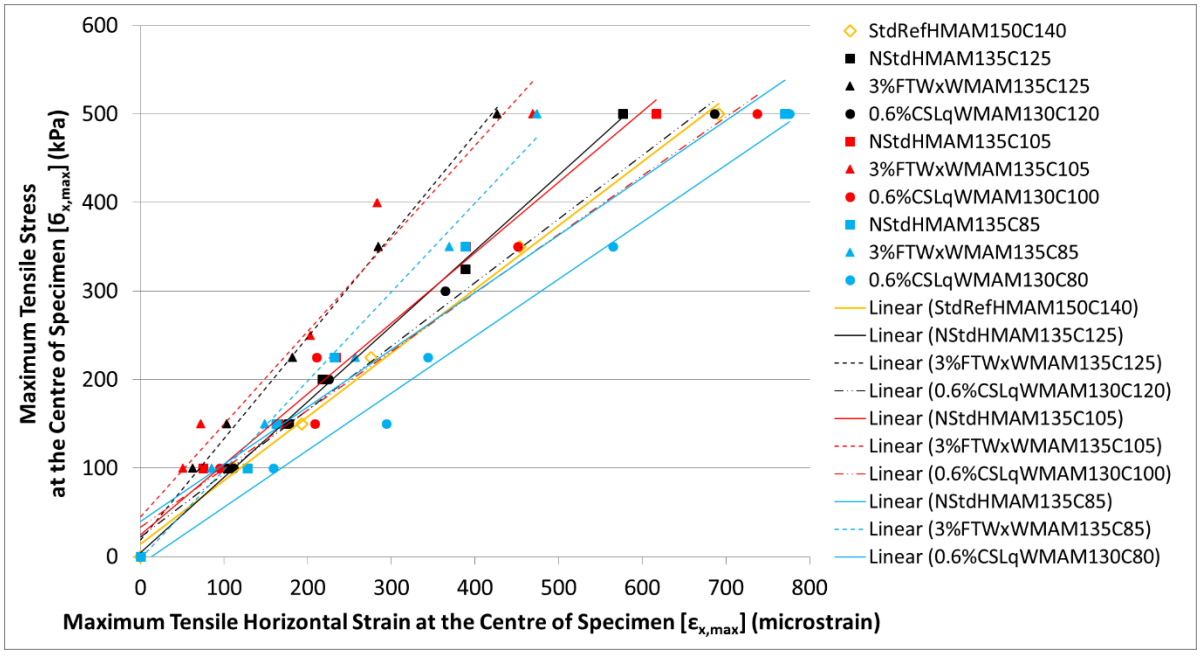


Figure 6.14 : Stress-strain graphs for the cored specimens (all sample groups)

Figure 6.11 can generally confirm that in each of the 3 compaction groups, the 3%FTWax-WMA mixtures have significantly higher resistance to fatigue failure compared to the Standard Reference HMA, the Non-Standard Reference HMA and the 0.6%CatSurfLq-WMA mixtures.

In addition, in each of the 3 material groups, the lowest level of fatigue resistance is in the sample groups with the lowest compaction temperature (i.e. NStdHMAM135C85, 3%FTWxWMAM135C85 and 0.6%CSLqWMAM130C80).

While the samples of the Standard Reference HMA mixture stand in the middle of the spectrum of the fatigue resistance lines (Figure 6.11 and Figure 6.14), Figure 6.12 illustrates that the 3%FTWax-WMA mixtures have generally higher resistance to fatigue failure compared to the Non-Standard HMA and the Standard Reference HMA mixtures. Meanwhile, Figure 6.13 shows that the 0.6%CatSurfLq-WMA mixtures have generally less resistance to fatigue failure compared to the Standard and Non-Standard HMA mixtures.

Figure 6.11 indicates that compaction of the 0.6%CatSurfLq-WMA mixtures at 120 and 100°C (0.6%CSLqWMAM130C120 and 0.6%CSLqWMAM130C100) can result in producing asphalt mixtures, which behave similar to the conventional HMA mixture StdRefHMAM150C140 in terms of fatigue failure resistance. This can result through compaction of the 3%FTWax-WMA mixtures at 85°C (3%FTWxWMAM135C85) and compaction of the Non-Standard HMA mixtures at 125 and 105°C (NStdHMAM135C125 and NStdHMAM135C105).

On this matter, Figure 6.11 shows that compaction of the 3%FTWax-WMA mixtures at 125 and 105°C (3%FTWxWMAM135C125 and 3%FTWxWMAM135C105) can produce materials with a significantly higher performance in terms of resistance to fatigue failure compared the conventional HMA mixture StdRefHMAM150C140. In this regards, the one which has been compacted at 105°C shows the highest Fatigue resistance which as mentioned before conforms to its higher ITSM value compared to those of the other mixture groups.

However, according to Figure 6.11, it seems that the negative effect of cold compaction arises in the case of the Non-Standard HMA mixture when it is compacted at a relatively low temperature such as 85°C (NStdHMAM135C85) and in the case of the 0.6%CatSurfLq-WMA mixture when it is compacted at the relatively low temperature compaction of 80°C (0.6%CSLqWMAM130C80). In other words, due to the negative effect of cold compaction, NStdHMAM135C85 and especially 0.6%CSLqWMAM130C80 show much lower levels of resistance to fatigue failure compared to the rest of the mixture groups.

Looking at the ITFT results on the gyro specimens (Figure 6.15 to Figure 6.18) reveals that more or less the same regime of ITFT test results of the cored samples dominates them, as well.

Still FTWax-WMA mixtures are of the highest fatigue resistance, the Reference HMA and the Non-Standard HMA mixtures are in the mid-range and the CatSurfLq-WMA mixtures are of the lowest fatigue resistances. Also the results are more or less compatible with the results of ITSM/IT-CY indicating the issue that the higher the ITSM value, the longer the fatigue line or the higher the fatigue strength. However, due to the significantly higher stiffness modulus of the gyro samples compared to the cored ones, the associated fatigue life lines are much longer and the fatigue strengths are significantly higher in the case of the gyro samples compared to the core samples. Moreover, the fatigue lines of different are much closer together in such a way that they should be considered to have the same resistance to fatigue. Therefore, in order to have a more reliable judgment on the relativity of the fatigue resistance of the various manufactured test mixtures to their compaction temperature, the test results of the cored specimens have mainly been considered for conclusion.

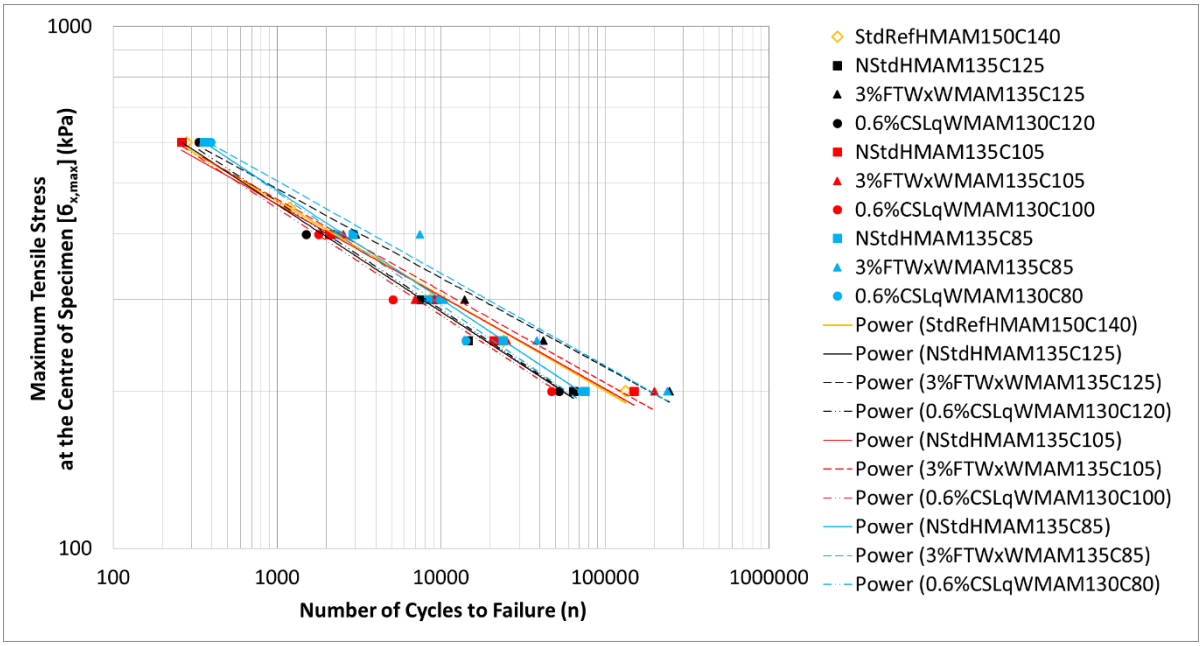


Figure 6.15 : ITFT results for the gyro specimens (all sample groups)

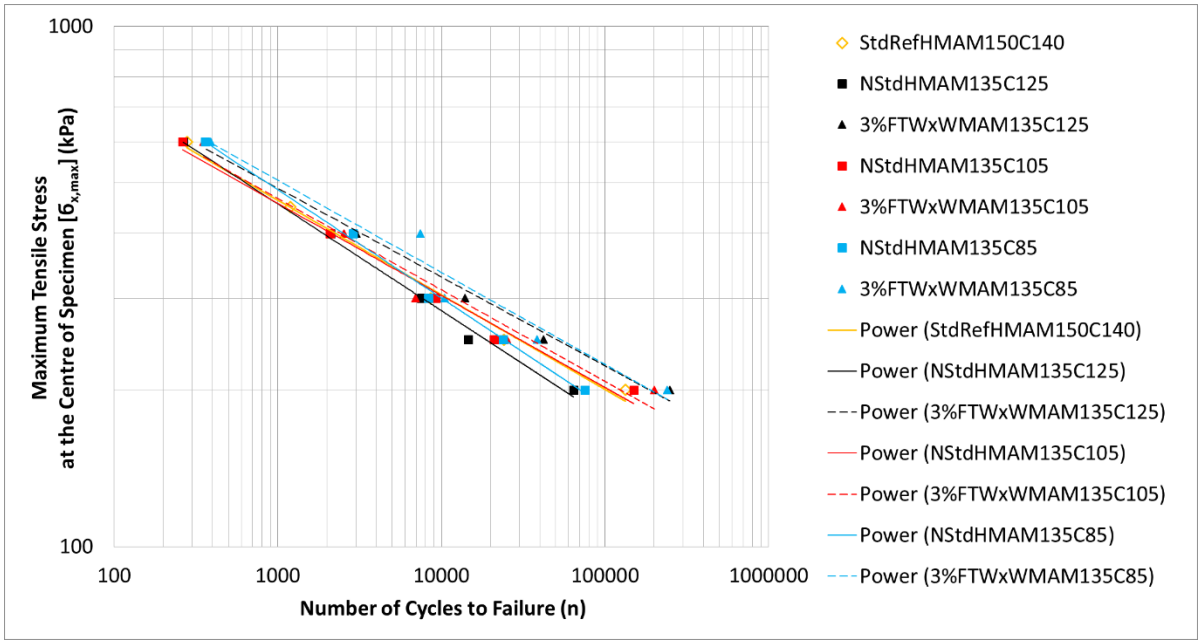


Figure 6.16 : ITFT results for the gyro specimens (FTWax-WMA, NStd-HMA and StdRef-HMA)

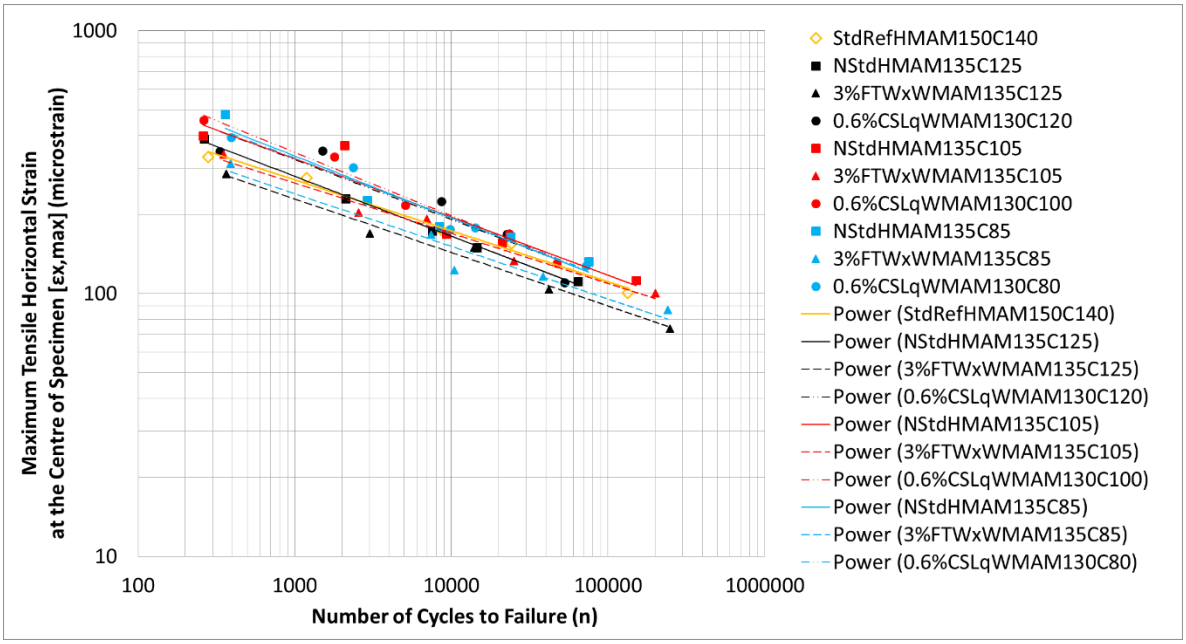


Figure 6.17 : ITFT results for the gyro specimens (CatSurfLq-WMA, NStd and StdRef-HMA)

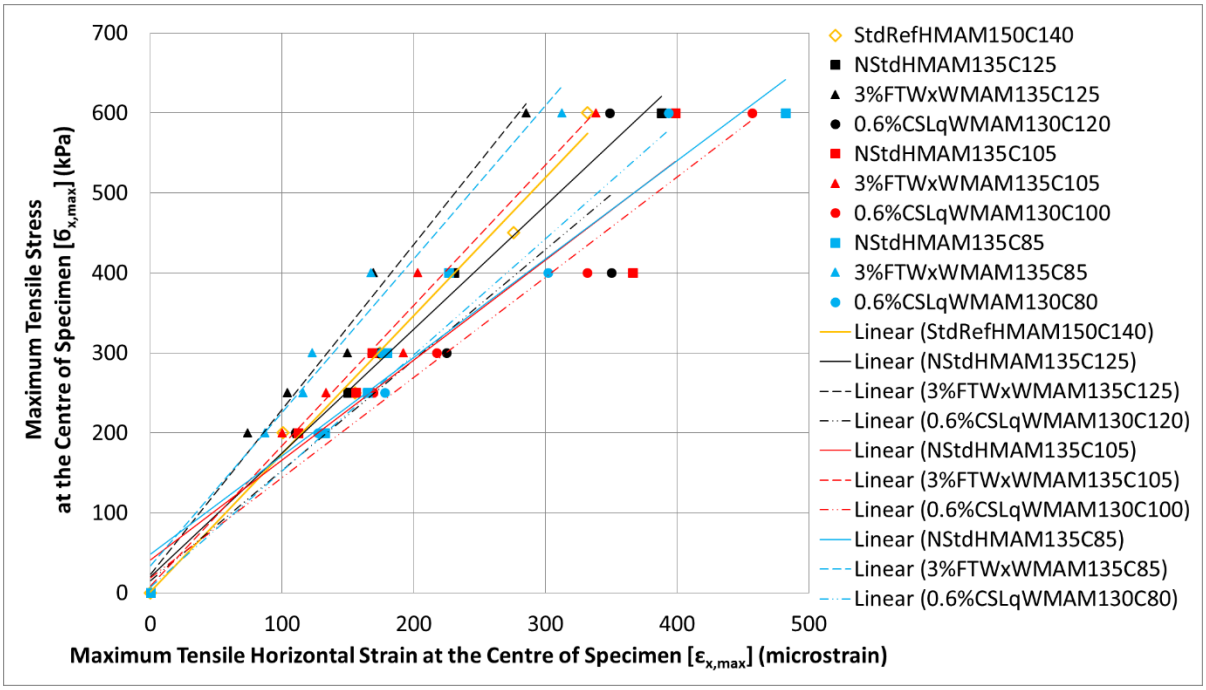


Figure 6.18 : Stress-strain graphs for the gyro specimens (all sample groups)

6.3.2. CONCLUSION

Putting everything together, it can be stated that FTWax significantly increases the mixture's resistance to fatigue failure in such a way that even compaction of a 3%FTWax-WMA mixture at as low as 85°C produces specimens which last as long as their corresponding Standard HMA specimens under the ITFT. Meanwhile, CatSurfLq does not have any positive effect on the fatigue resistance of the derivative mixtures since they perform nearly the same as their corresponding Non-standard specimens (as long as the compaction temperature is not reduced to as low as 80°C).

Generally, it seems that fatigue resistance of the studied asphalt mixtures, at least in the laboratory scale, is not that sensitive to the compaction temperatures around and above 100°C. It significantly decreases when the compaction temperature is as low as 80°C and increases at any of the studied compaction temperatures if FTWax has been added to the mixture.

Referring to the matter of fatigue failure phenomenon, it is a structural failure resulting from a deficiency of the construction material, which happens under a repetitive loading situation including cycles of loading (tensile) and unloading through which the maximum applied stress does not exceed the ultimate strength for the load bearing material. In general, the mechanism

of fatigue includes crack initiation at weak points, crack propagation and finally total failure each of which requires a number of loading cycles.

As a matter of fact, inside any load bearing material, due to reasons such as imperfect manufacture, in-homogeneity, etc., several inevitable weak points exist at which the local strength of the section is less than what is assumed for the whole system. In addition, for the same reason as stated above, depending on the situation through the manufacturing process, several micro or even macro cracks are expected to be produced or left inside the material. Crack edges and section corners are stress concentration points, at which the tension increases and the presumed uniform distribution of the applied load changes to non-uniform.

Under the applied repetitive tensile load, the cracks can initiate from any of the above-mentioned weak points at which the tensile stress exceeds the tensile strength of the material. Then the cracks propagate gradually all throughout the structure and the total failure of the system takes place once the section becomes so small that can no longer bear the applied load.

Following the above description regarding the fatigue failure mechanism, it is expected that the higher the AV Content, the greater the number of stress concentration points within the asphalt specimen, and the less the resistance to fatigue failure.

If micro cracks are expected to be produced inside the specimens through a cold compaction process, it can result that the colder the compaction temperature, the lower the material's resistance to fatigue failure.

Thus, cold compaction of asphalt, in each of the 3 material groups has produced a higher AV content, some of which are likely to be in the form of cracks. This has decreased the fatigue resistance of NStdHMAM135C85, 0.6%CSLqWMAM130C80 and 3%FTWxWMAM135C85 compared to their similar mixtures with higher compaction temperatures. In addition, the relatively lower fatigue resistance of the 0.6%CatSurfLq-WMA mixtures compared to their corresponding Non-Standard HMA mixtures can be due to their higher AV content. This is why the fatigue life lines of the 0.6%CatSurfLq-WMA mixtures lie generally below those of the Non-Standard HMA and the Reference HMA specimens.

Moreover, as another obvious result of describing the fatigue failure mechanism, it is logical to state that the higher the Indirect tensile stiffness of the asphalt specimens, the smaller the deformation under the tensile load. This means the higher the resistance to crack initiation and

propagation, the higher the resistance to fatigue failure. This conforms to the relationship between the bar chart of ITSM and the results of ITFT as stated at the beginning of this section. In fact, the higher the stiffness of the binder is, the higher the fatigue resistance of the mixture.

Following these interpretations, on the one hand, the similar fatigue resistance of the Non-Standard HMA mixtures and their counterpart 0.6%CatSurfLq-WMA specimens (except the cold compacted mixtures) can be referred to the fact that their binders are of the same stiffness. In fact, CatSurfLq does not change the structure of the binder since it is mostly absorbed to the surface of the aggregates to improve the binder-aggregate adhesion properties. In fact, it is an adhesion promoter more than a rheology and stiffness modifier.

On the other hand, FTWax improves bitumen's stiffness and produces a uniform crystallised structure. This increases the resistance of the 3%FTWax-WMA specimens to fatigue failure.

Overall, it should be stated that the fatigue resistance of a mixture is highly controlled by the stiffness of the binder and the AV content of the mixture. The former can be controlled by the use of additives and the latter through the compaction temperature.

Moreover, the starting point of the fatigue life line is usually a failure under a high stress which is influenced by the ultimate tensile strength of the mixture/binder. However, as long as the test stress decreases, the fatigue life becomes more dependent on the stiffness modulus as the failure will be mostly following the propagation of the initiated cracks which. This process is stiffness-dependant. FTWax-WMA mixtures, as well as their FTWax-modified binders have significantly high stiffness modulus. However, FTWax-modified binders should have less ultimate tensile strength due to their reduced surface tension. This issue may have reduced the ultimate tensile strength of the FTWax-WMA, as well. Probably these facts are the reason why the fatigue lines of the FTWax-WMA mixtures are close to those of the other sample groupes at high stresses, where the fatigue life is highly affected by the ultimate tensile strength.

6.4. PERMANENT DEFORMATION under RLAT

6.4.1. DISCUSSION on the TEST RESULTS

According to Table 3.10, it is expected that, in the current research, mixtures with higher AV content have more permanent deformation and those with higher stiffness modulus (i.e. ITSM value) have less permanent deformation under the RLAT. The other factors mentioned in Table 3.10 have been more or less the same in all the mixtures manufactured in the current research. As mentioned in Section 3.5.4, permanent deformation in asphalt concrete takes place due to some defined reasons as follows:

1) Shear deformation in asphalt because of:
   - Plastic shear deformation in binder
   - Binder-aggregate debonding
2) Densification and decrease in height in high air void content asphalt, because of insufficient compaction

Looking at Figure 3.26 illustrates that the RLAT curves are formed by a series of points, each of which represents the accumulated viscous and plastic (permanent) parts of the deformation of the sample under each load pulse from the beginning of the test. The general shape of a permanent deformation curve is as shown in Figure 6.19 and consists of 3 different parts as Primary, Secondary and Tertiary.

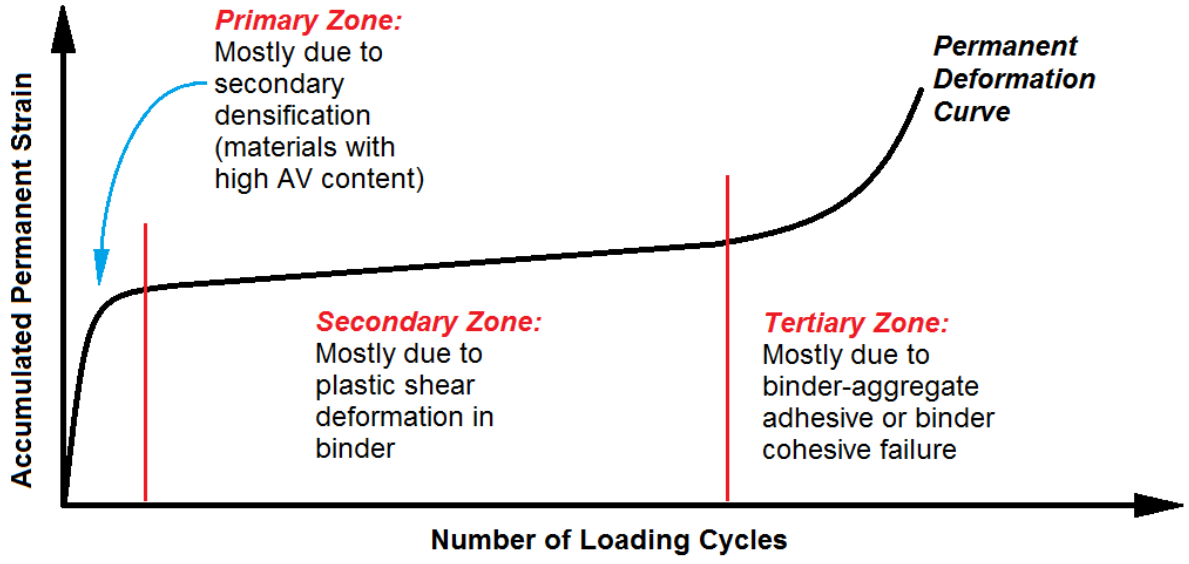


Figure 6.19 : Typical permanent deformation curve

As shown in Figure 6.19, the accumulated permanent strain in each zone on the permanent deformation curve is mostly due to a certain type of deformation. The Primary part mostly includes the secondary densification of the material which especially takes place in the case of the specimens with high AV content. The secondary zone is mostly due to the plastic shear deformation of the binder and the tertiary part is mostly because of the adhesive failure of the binder-aggregate bonds or the cohesive failure of the binder. The number of loading cycles at which the permanent deformation curve turns into zone 3 is usually called the 'Flow Number'. The material experiences its total failure in zone 3.

As shown in Figure 3.26, the final permanent strain of an asphalt specimen at the end of the Repeated Load Axial Test (RLAT) consists of the accumulated plastic and viscous components of deformation. As the viscous component of deformation is related to binder, the secondary zone should mostly consist of viscous deformation. However, zones 1 and 3 should mostly include plastic deformation. Figure 6.20 illustrates the final axial permanent strain of the cored samples taken from the slab specimens and Figure 6.21 shows that of the gyro specimens.

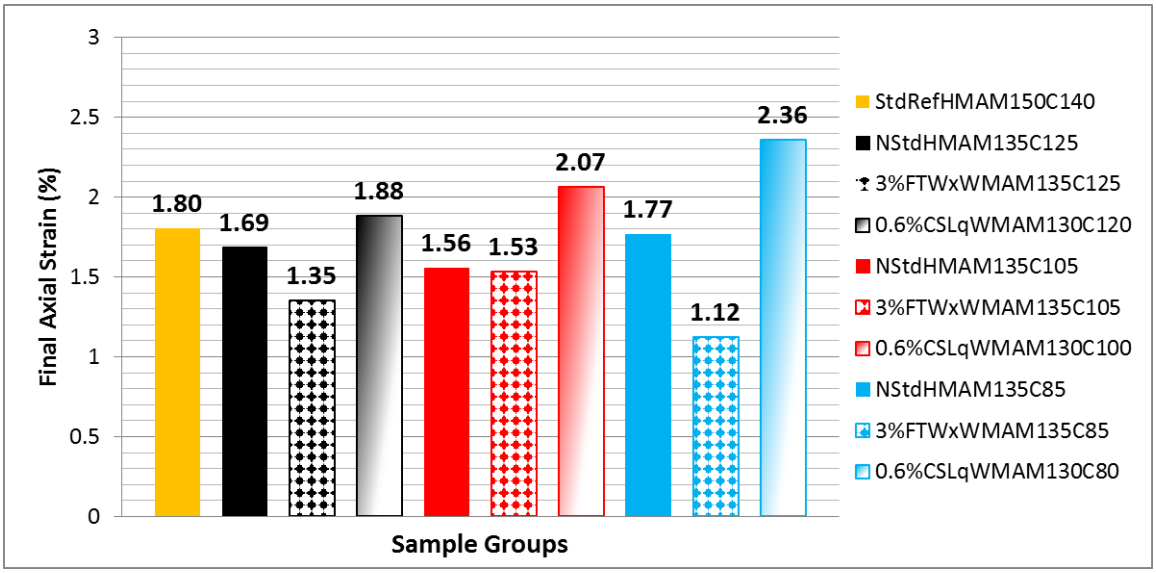


Figure 6.20 : The final axial strain values of RLA test on the cored specimens

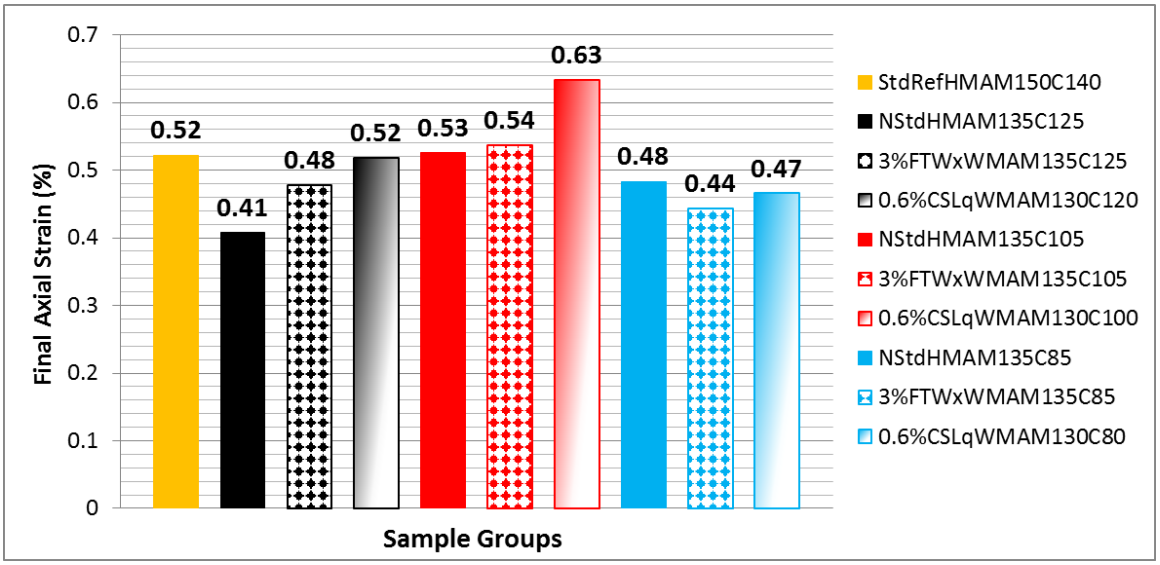


Figure 6.21 : The final axial strain values of RLA test on the gyro specimens

The first comparative glance at both figures reveals the values of the final permanent deformation of the gyro samples are generally much smaller than those of the cored samples. Looking at Figure 6.19 it can be realised that a high proportion of the final permanent strain under RLAT test is because of the primary zone of deformation which takes place due to the secondary compaction. It is clear to state that the higher the AV content of a specimen, the bigger the primary permanent deformation due to more densification (if the stiffness is almost the same). In Section Figure 6.1, the results of measuring the volumetric properties showed that the gyro samples had significantly lower AV contents compared to the cored specimens. Such low AV contents (which are very close together, as well) in gyro samples has not allowed any further compaction to take place in the form of secondary compaction during the RLAT. As a result, the final permanent deformation of the gyro samples has missed a significant part of its components and that is one of the reasons that caused the gyro samples to have much smaller permanent deformation under RLAT compared to the cored specimens. The other reason referring to Table 3.10 should be the significantly higher stiffness of the gyro samples compared to the cored ones. Samples with higher stiffness should have less secondary densification. Since the stiffness of the mixture is highly influenced by its binder stiffness, samples with stiffer binder are expected to have less secondary permanent deformation due to less plastic shear deformation in their binder. These are other reasons why the gyro samples have low final permanent deformations compared with the cored samples. Moreover, looking at the results of binder-aggregate dry bond strength (Figure 5.5 and Figure 5.6) shows that the Dene limestone used in gyro samples has made stronger bonds with the binders compared to

Tunstead limestone which has been used in manufacturing the cored specimens. Therefore, the tertiary zone of deformation is expected to be observed in fewer gyro samples than would be observed in the cored specimen.

To support this expectation, performing visual investigations on the post-RLAT structure of the samples by the naked eye revealed that none of the gyro specimens have experienced adhesive or cohesive cracks and failure whereas a number of cored specimens (0.6%CSLqWMAM130C80) have had such adhesive/cohesive cracks. This issue will be discussed later in the current section.

As a result of what is mentioned above, the permanent deformation in gyro samples should have been mostly due to the plastic shear deformation of their binder. Overall, the amounts of final permanent deformation in gyro samples were so small that made it too difficult to differentiate between different samples and find a relation between their compaction temperature, additives and RLAT results. In this regard, the permanent deformation of NStHMAM135C125 seems to be the smallest one and that of 0.6%CSLqWMAM130C100 can be considered as the highest one, however for this no reasonable justification was found.

All in all, due to the reasons stated, it was realised that the gyro specimens could not provide much information with regards to the effect of compaction temperature on the resistance to permanent deformation (Figure 6.32). Thus, the conclusion and judgement on this matter was performed based on studying the results of RLAT on the cored samples.

Looking at the final axial strain of the cores along with visually investigating the post-RLAT failure structure of the cored specimens illustrated that in each temperature group, the biggest final axial strain occurs in the CatSurfLq-WMA mixtures. According to the facts mentioned through the previous pages, CatSurfLq-WMA mixtures had lower stiffness modulus than the FTWax-WMA mixtures and nearly equal to the Non-Standard-HMA ones. That is why they experienced much bigger permanent strains than FTWax-WMA mixtures. However, referring to Figure 6.3, CatSurfLq-WMA mixtures had the highest AV content in each ‘Temperature Group’. Therefore, they should have had the biggest primary permanent strains compared to the others, which have resulted in the biggest final permanent strains in each ‘temperature group’, as well.

Moreover, by decreasing the compaction temperature, the permanent deformation in CatSurfLq-WMA mixtures increases. This issue conforms to the increasing regime of their AV

contents through decreasing their compaction temperature which increases the permanent strain of the primary zone.

In addition, due to the nature of the CatSurfLq chemical additive, as proved through the DCA SE measurements, the CatSurfLq-modified binders should have lower cohesive tensile strength. This is why the tertiary zone of the permanent deformation curves can be seen only in the case of these types of mixtures, which, as visual investigations confirm, indicate the occurrence of cohesive failure in their binder. It should be mentioned that the tensile cracks can only be seen in the CatSurfLq-WMA cores not in any of the other sample groups even in FTWax-WMA mixtures with the lowest SE values (Figure 6.22 to Figure 6.31). The reason is the primary and secondary zones of deformation for the FTWax-WMA mixtures have been much smaller due to their lower AV content and significantly higher stiffness modulus. With the same argument, in the case of the CatSurfLq-WMA mixtures, the higher primary and secondary zones of permanent deformation, results in experiencing the tertiary zone of strain at significantly fewer numbers of load cycles compared to the FTWax-WMA or NStd-HMA or the StdRef-HMA mixtures. It means that the CatSurfLq-WMA mixtures should have adhesive failures in addition to the cohesive failures as can be seen in Figure 6.29 to Figure 6.31.

The plastic shear deformation part of the curves is flatter in the case of FTWax-WMA mixtures regardless of their compaction temperature. This is because of the significantly higher shear stiffness modulus of their FTWax-modified binders compared to the CatSurfLq-modified or the pure bitumen.

Sample group StdHMAM150C140 has a higher final permanent strain than NStdHMAM135C125. This can be due to the significantly higher AV content of the former than the latter.

Sample group 3%FTWxWMAM135C125 has lower final permanent strain compared to NStdHMAM135C125. This issue should be due to the significantly higher stiffness modulus of the former than the latter though the FTWax mixture had higher AV content.

Sample group 3%FTWxWMAM135C105 has nearly equal final permanent deformation to NStdHMAM135C105 while it was expected to have lower permanent deformation due to its relatively lower AV content and significantly higher stiffness modulus. No justification was found in this respect.

Sample group 3%FTWxWMAM135C85 is in the possession of the smallest final permanent deformation of all sample groups, which is strange and unexpected to some extent as this sample group has had one of the highest AV contents though its stiffness modulus was relatively very high.

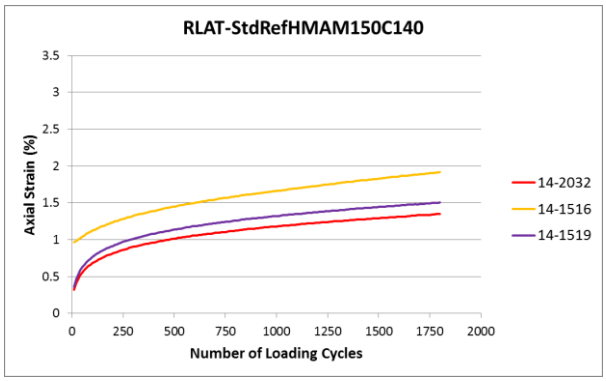


Figure 6.22：Permanent deformation curves of the StdRefHMAM150C140 cored samples

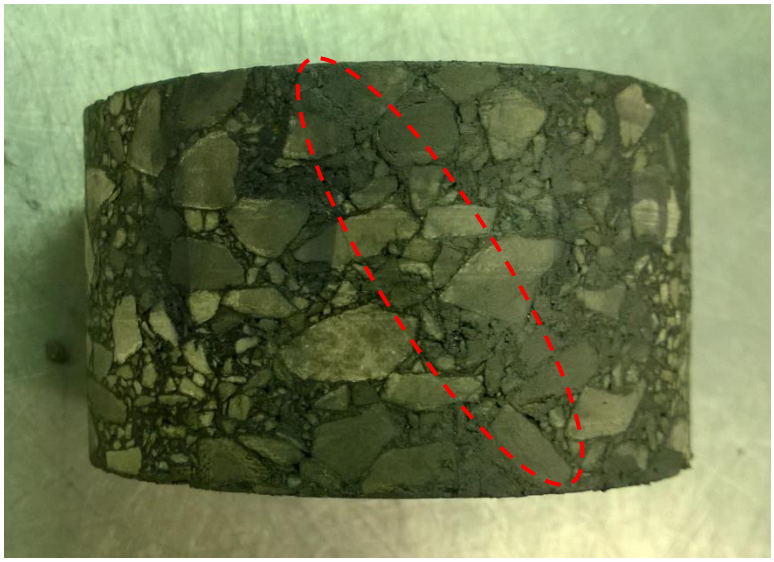


Figure 6.23：Shear crack in a StdRefHMAM150C140 cored sample (specimen 14-1516) after RLAT due to the plastic shear deformation/failure of the binder

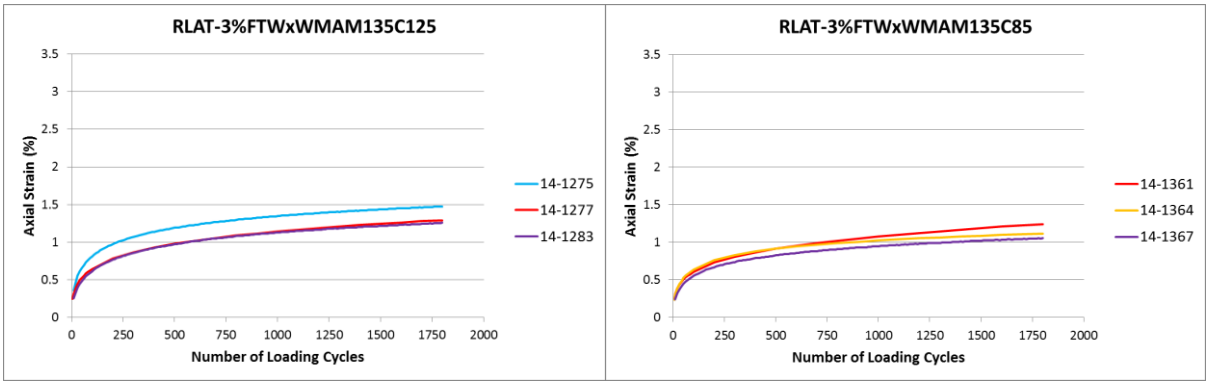


Figure 6.24 : Permanent deformation curves of the 3%FTWxWMAM135C125 and 3%FTWxWMAM135C85 cored sample groups with very flat secondary zones

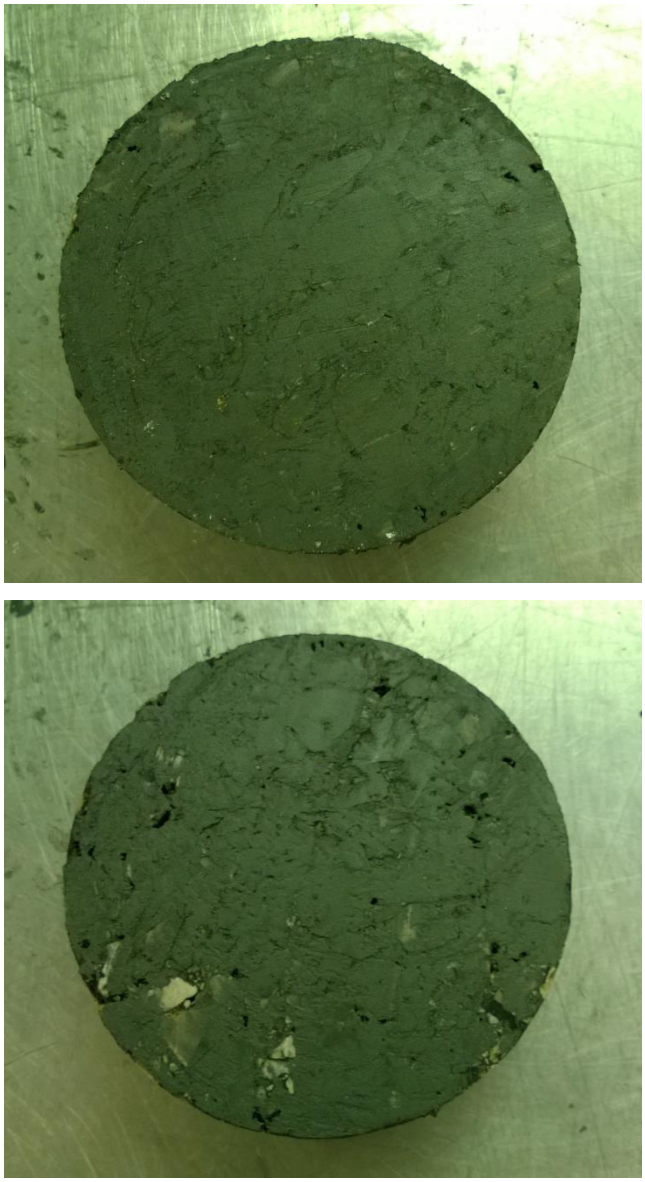


Figure 6.25 : Post-RLAT feature of two 3%FTWax-WMA cored samples (specimens 14-1277 and 14-1361) with no adhesive/cohesive or shear failure

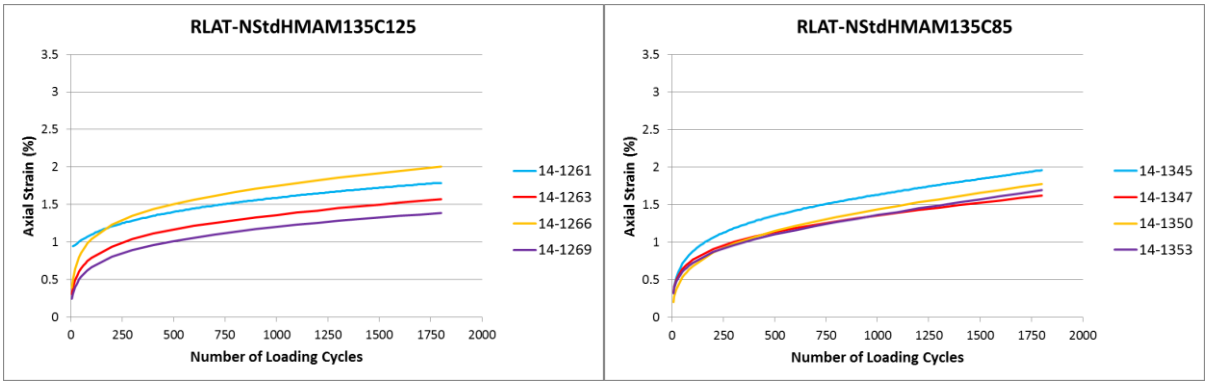


Figure 6.26 : Permanent deformation curves of the NStdHMAM135C125 and NStdHMAM135C85 cored sample groups

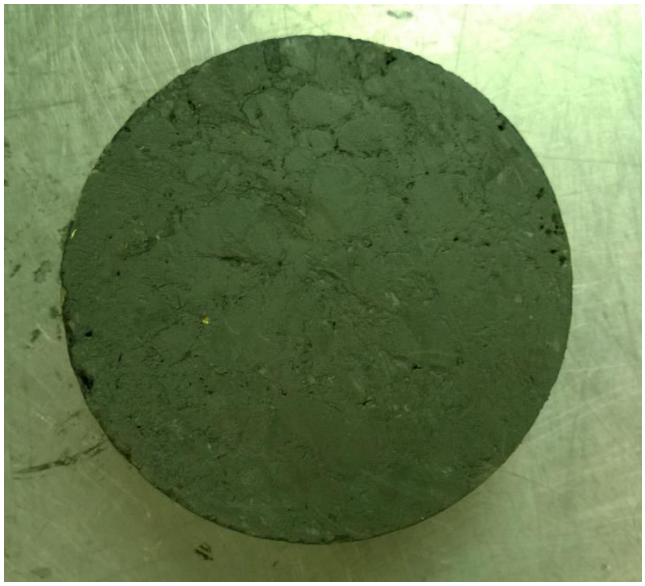


Figure 6.27 : Post-RLAT feature of a NStdHMAM135C125 cored sample (specimens 14-1263) with no adhesive/cohesive or shear failure

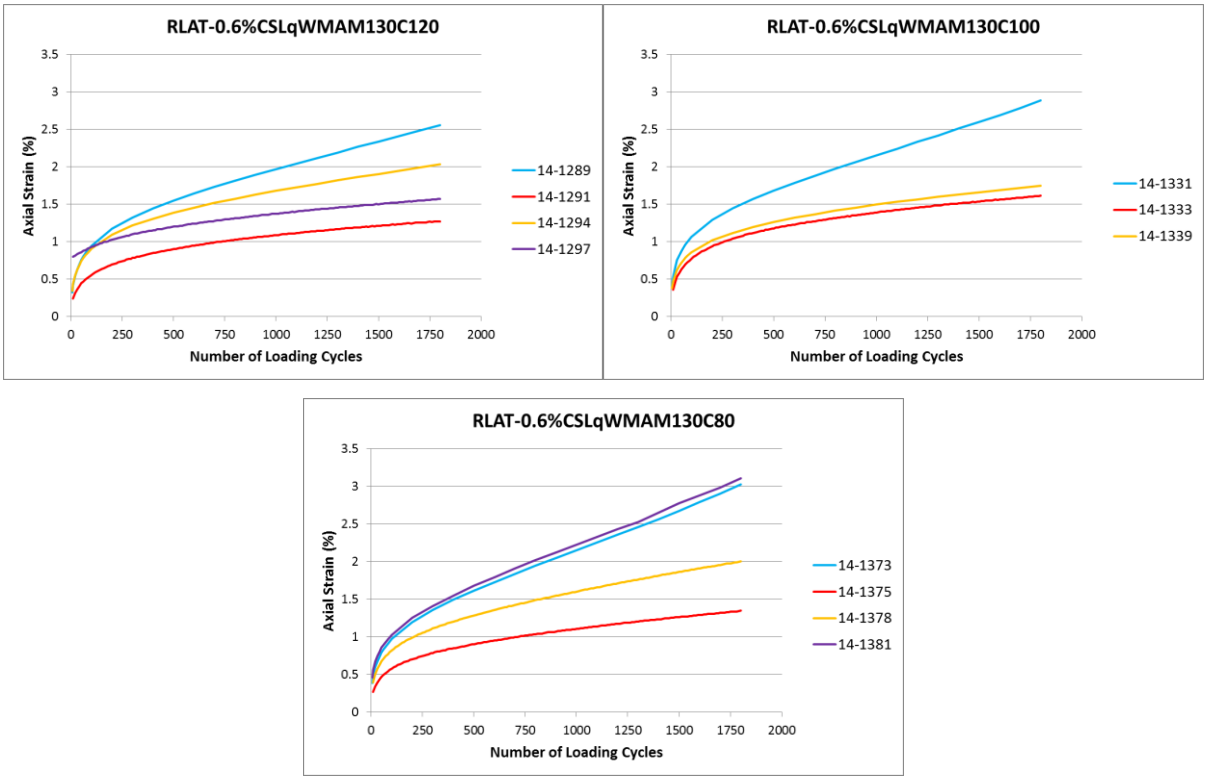


Figure 6.28 : Permanent deformation curves of the 0.6%CatSurfLq-WMA cored samples

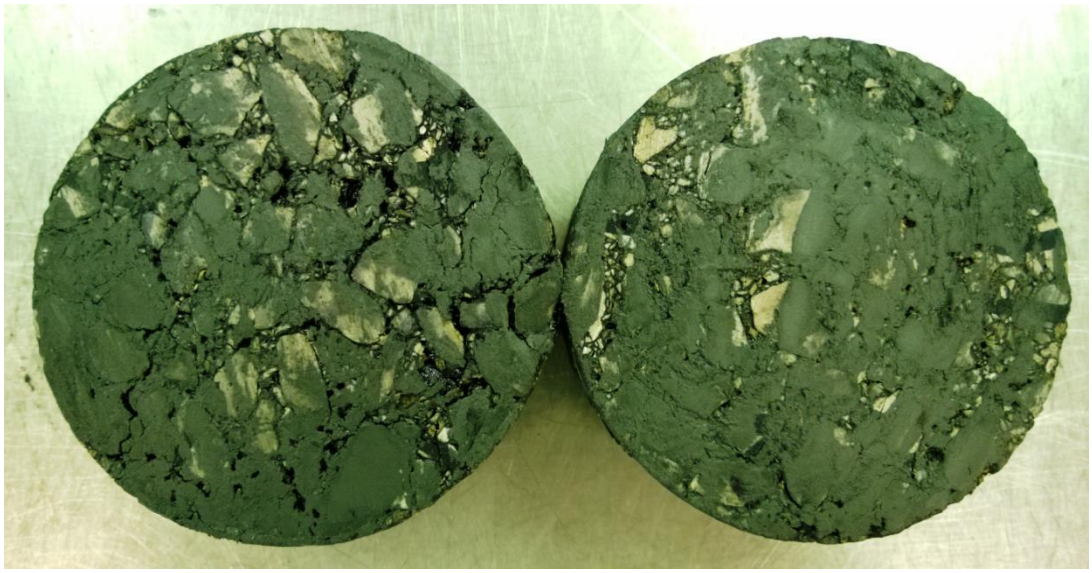


Figure 6.29 : Post-RLAT feature of a 0.6%CSLqWMAM130C80 cored sample (specimen 14-1373) with a network of cohesive and adhesive failures (left) compared with a NStdHMAM135C85 cored sample (specimen 14-1345) with no adhesive/cohesive or shear failure (right)

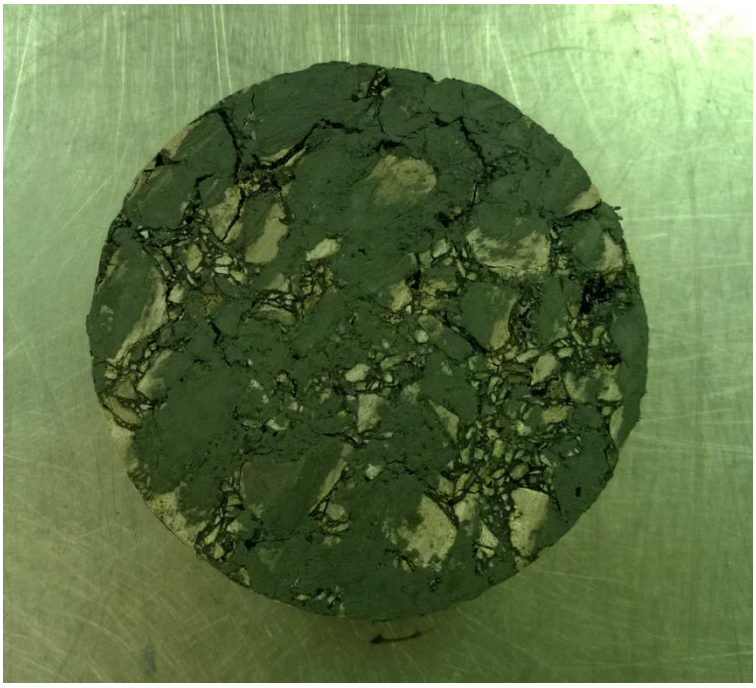


Figure 6.30 : Post-RLAT feature of a 0.6%CSLqWMAM130C100 cored samples (specimen 14-1331) with a network of cohesive and adhesive failures



Figure 6.31 : Post-RLAT feature of a 0.6%CSLqWMAM130C80 cored sample (specimen 14-1381) with a network of cohesive and adhesive failures

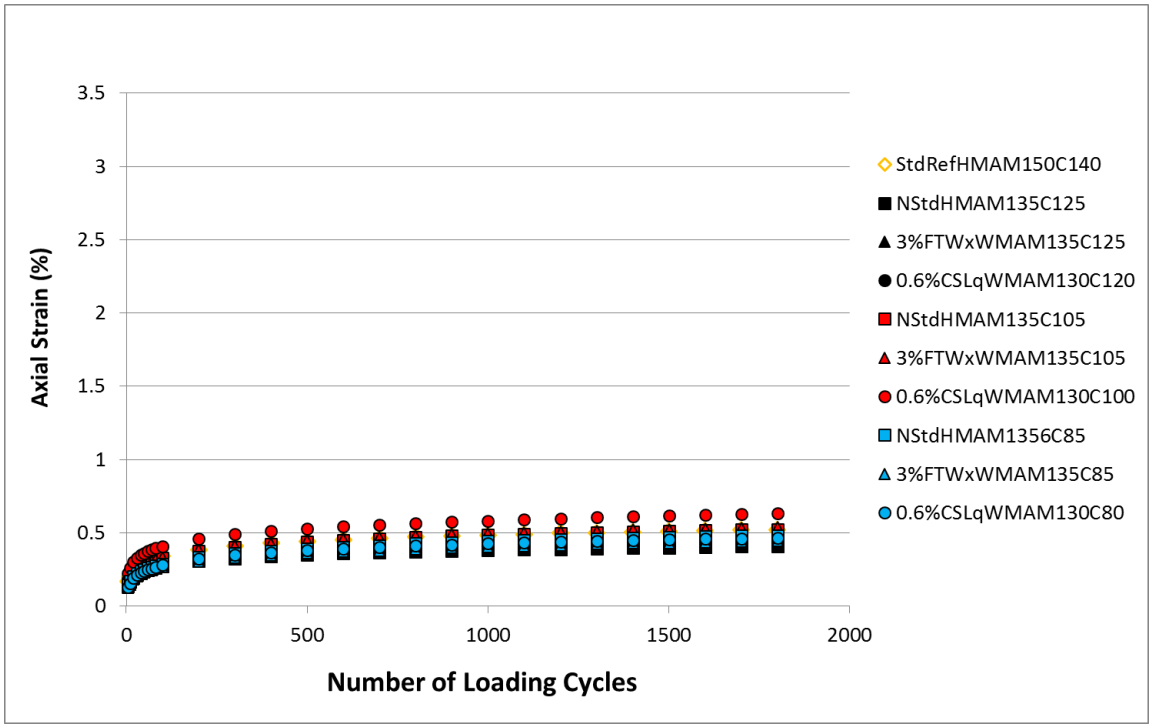


Figure 6.32 : Permanent deformation curves of all sample groups of gyro specimens with very small primary zones, very flat secondary zones, no tertiary zones and very small difference in final permanent strains

6.4.2. CONCLUSION

Overall, it can be mentioned that the resistance of the 3%FTWax-WMA mixtures to permanent deformation under RLAT, in general, has been as much as or much more than the standard reference HMA or the Non-Standard HMA mixtures considering that this resistance was not influenced negatively by decreasing the compaction temperature. However, the resistance of the 0.6%CatSurfLq-WMA mixtures to permanent deformation was quite remarkably less than their counterpart non-standard HMA and FTWax-WMA mixtures as well as the standard HMA mixture. Moreover, this resistance was significantly decreased by reducing the compaction temperature. Also the mechanism of cohesive failure was seen only in CatSurfLq-WMA mixtures due to the mentioned reasons.

6.5. DIRECT DYNAMIC COMPRESSIVE COMPLEX STIFFNESS MODULUS

6.5.1. PRINCIPLES

According to what was mentioned in Section 3.5.5 with regards to the application of the results of this test (i.e. *E** and phase angle), DDCCSM was used as a support or proof for the results of the other mechanical performance tests and to predict the viscoelastic behaviour of the manufactured mixtures at various temperatures and loading frequencies.

Figure 6.34 illustrates the comparative charts of *E** master curves produced using the results of the DDCCSM test on the various sample groups of the manufactured cored specimens.

It is known that the complex stiffness modulus (*E**) consists of an elastic/storage modulus component (*E'*) which represents the elastic behaviour of the material and its ability to store energy and a viscous/loss modulus component (*E"*) which represents viscous/damping behaviour of the material and its ability to dissipate energy in the form of heat or etc. Both *E'* and *E"* are influenced by temperature as well as loading frequency. The former can be considered as in-phase stiffness whereas the latter can be seen as lagged/delayed stiffness. *E'* is the real component of stiffness which as expected for pure elastic materials, decreases with increasing the temperature as well as decreasing load frequency. Although it is the direct compressive stiffness modulus of the specimen, as it is still representing the materials strain under the applied stress, it is logical that it can be (at least qualitatively) related to the other types of stiffness such as indirect tensile stiffness modulus. *E"* is the imaginary component of the complex stiffness modulus. It initially increases by decreasing the temperature (increasing the frequency) but passing a certain point (which depends on the material), it starts decreasing. So at very low temperatures (very high frequencies) the material has only the elastic modulus forming the complex modulus. In fact, at temperatures which the material behaves more viscous, *E"* is higher than *E'* whereas at temperatures which material behaves more elastic, the elastic component becomes bigger than the imaginary one. Therefore, the curve of *E'* and *E"* versus temperature or loading frequency normally should have a crossing point as shown in Figure 6.33.

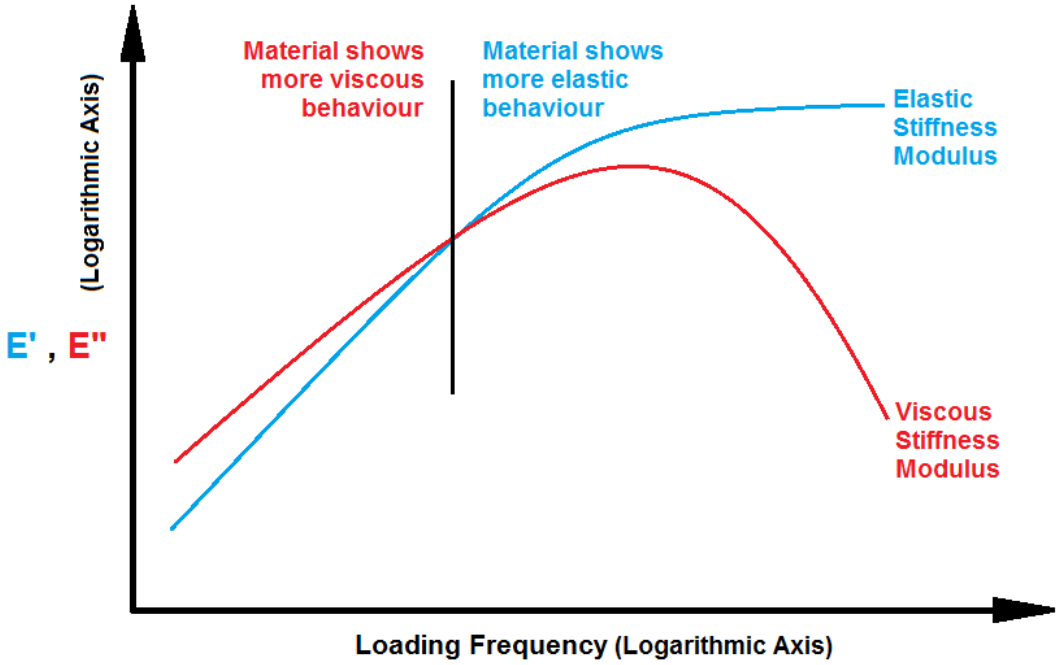


Figure 6.33 : Variations of elastic and loss modulus of stiffness over loading frequency

The changes of *E'* and *E"* over temperature or frequency, as shown in Figure 6.33, causes the ratio of *E"/E'* to decrease by decreasing the temperature and vice versa. This ratio, as mentioned in Section 3.5.5 represents the phase lag between the stress applied to the material and the strain which takes place as materials response.

In the current research, due to the problems mentioned in Section 3.5.5, to calculate the values of E* from the raw data collected from the test software (Universal Software), the values of phase angle could not be calculated as precisely and reliably as they should be in this study. Therefore, the values of *E** are the only outputs of performing the devised DDCCSM test in this research.

6.5.2. DISCUSSION on the TEST RESULTS and CONCLUSION

Looking at Figure 6.34 and comparing the results with the results of AV content measurement (Figure 6.3) illustrates that the lower the AV content, the higher the *E** value and vice versa. While the indirect tensile stiffness modulus of the cored samples seems to have no clear or noticeable relation with their AV content (the regimes of the associated bar charts were not similar), it seems that the direct compressive stiffness modulus of the cored asphalt samples are more clearly influenced by their air void content. In fact, it can be justified through the fact that the AV content influences the direct compressive stiffness modulus of asphalt in the sense

that higher AV contents result in more flexibility/elasticity of the asphalt mixture and lower direct compressive stiffness, which means lower *E'* and consequently lower *E** of the sample.

In fact, it can be mentioned that the complex stiffness modulus of the cored specimens, representing their viscoelastic behaviour, is highly influenced by the AV content of the samples as a result of the material being influenced by the compaction temperature.

However, in the case of the FTWax-WMA mixtures, the values of *E'* have been highly influenced by the values of *G** in such a way that the difference in the AV contents of the various FTWax-WMA mixtures has not resulted in their *E** to be significantly different. It means that reducing the compaction temperature, does not change the *E** and viscoelastic behaviour of the FTWax-WMA mixtures.

As mentioned in Section 3.5.5, from the right zone of the *E** master curves (high frequencies or low temperatures) the low temperature behaviour of the mixtures (such as fatigue resistance) should be evaluated. Moreover, from its left zone (low frequencies or high temperatures) the potential of mixtures' permanent deformation should be compared. Such evaluations do not seem to be reliable in the case of the *E** graphs in the current research as comparing the *E** master curves does not fully conform to the results of the actual RLAT and ITFT tests performed on the samples.

In fact, the potential of the mixtures for permanent deformation is somewhat difficult to be understood from the left zone of the graphs though the vertical axis has not been drawn in logarithmic scale. However, except for the results of the FTWax-WMA mixtures, it seems that in the case of the other sample groups, the dominate regime on the ITFT results conform to those of the DDCCSM. This may relate to the issue that FTWax-WMA mixtures have stiffer binders which cause them to show less viscous behaviour. This means having smaller phase angles under sinusoidal loads which may decrease the value of *E**.

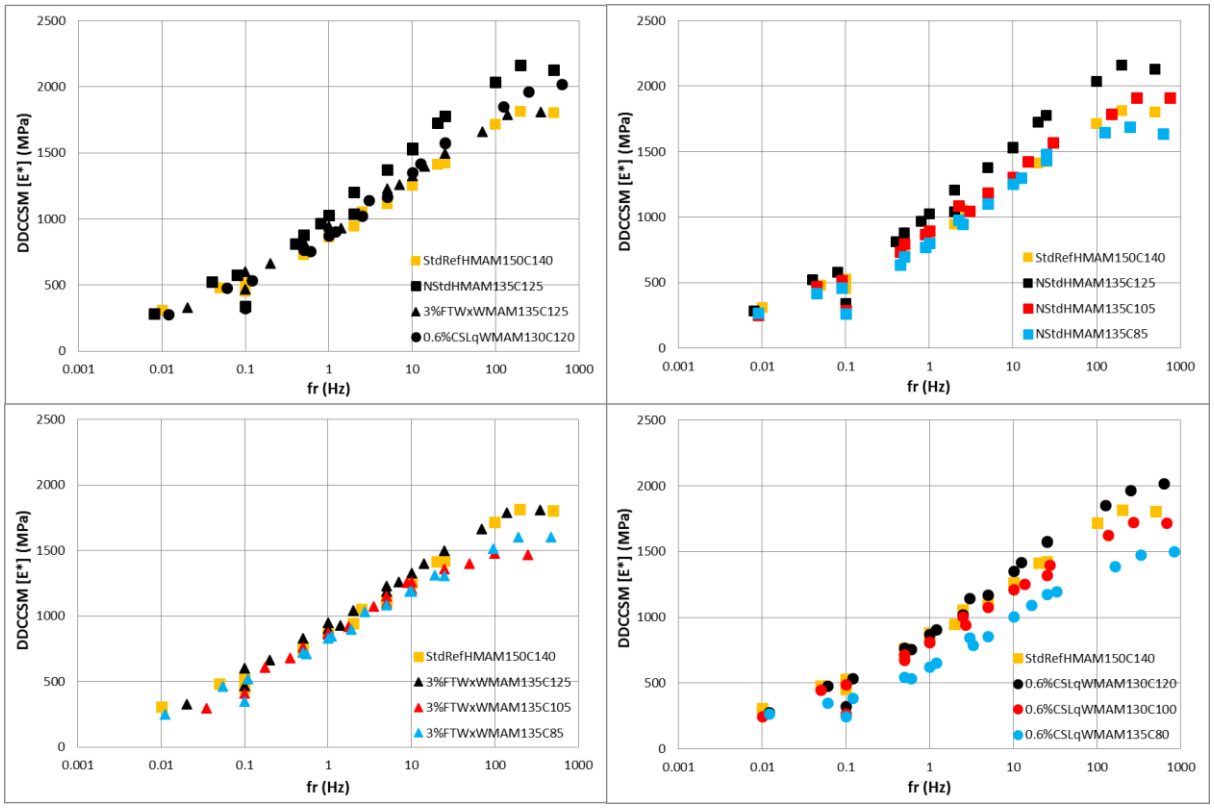


Figure 6.34 : Comparative charts of the master curves of *E** for the various manufactured sample groups of cored specimens

Figure 6.35 shows the comparative charts of *E** master curves produced using the results of the DDCCSM test on the various sample groups of the manufactured gyro specimens. Although the curves have less overlap and are more distinguishable from each other compared to the cored samples, it seems that no clear or logical regime conforming to the other test results can be extracted from them. In fact, as mentioned before, the gyratory compactor has influenced the volumetric properties of the gyro samples in such a way that all of them had been compacted to an extreme point nearly equal to each other. Moreover, the results of the ITSM do not conform to the results of the DDCCSM in the case of the gyro samples. As mentioned before, the gyro samples are suspected to be damaged by the gyratory compactor in the sense that the aggregates might have been crushed to some extent. This issue could have influenced the elasticity of the resulted samples and this may be why the DDCCSM test results look generally strange and possibly unreliable.

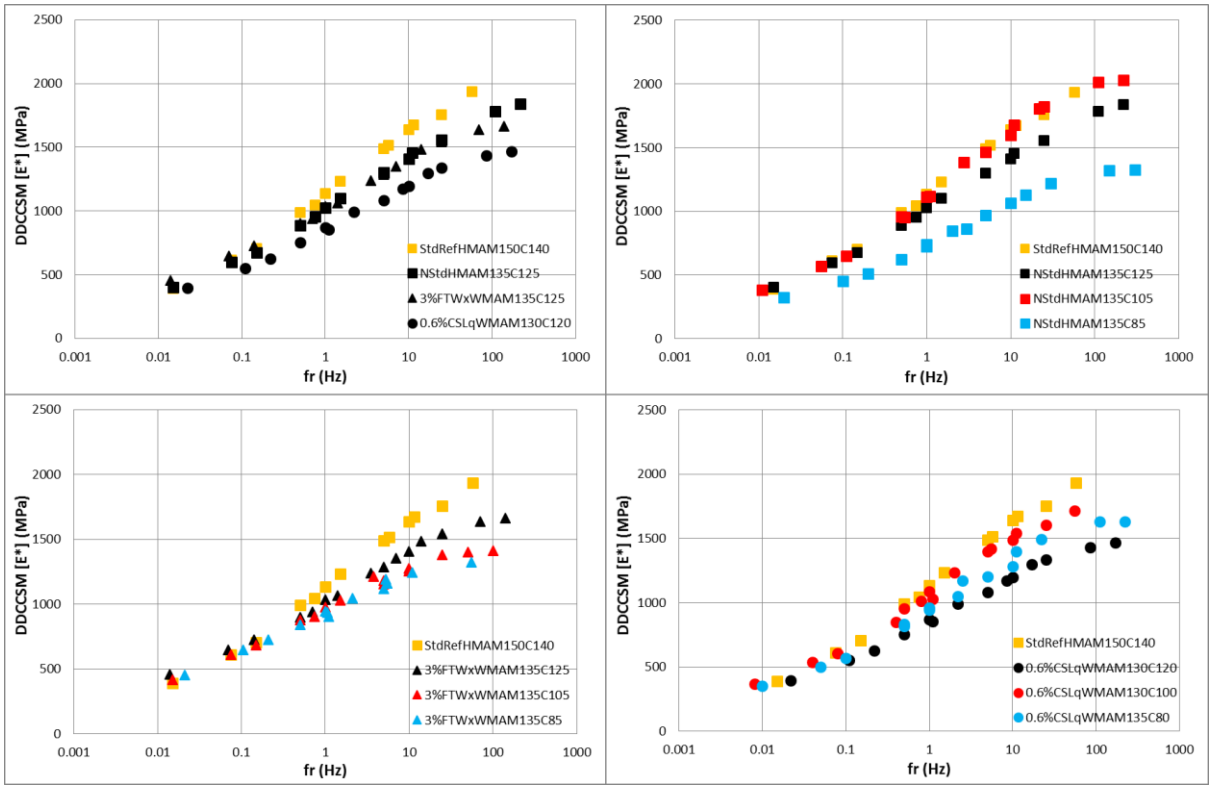


Figure 6.35 : Comparative charts of the master curves of *E** for the various manufactured sample groups of gyro specimens

6.6. MOISTURE SENSITIVITY (REVISED MODIFIED LOTTMAN TEST)

6.6.1. DISCUSSION on the TEST RESULTS

As mentioned previously in Section 3.5.6, in the first conditioning phase of the newly devised 'Revised Modified Lottman' water sensitivity test, the specimens have experienced a 35 mbar vacuum saturation for half an hour. The level of specimens' saturation was calculated through the basic volumetric formulations having the initial volumetric properties of the specimens and also their weight, just after the vacuum saturation phase. The same measurement was performed right at the end of each conditioning phase in order to monitor the specimens' saturation percentage over the test period.

Graphing the amount of saturation versus the air void content of specimens gives a relatively true idea of the quality of air voids connectivity or even distribution inside the specimens. For instance, if the material has a high AV content but low saturation level, it means that either there may be a big insulated air void or a large number of disconnected air voids which have

not been filled by water (low permeability). High AV content and high saturation indicates the vast-connectivity of the voids whereas low AV content and low saturation says that the material is very dense with a low permeability. It is also logical to say that low AV content and high saturation indicates that either the material is basically highly permeable or the air voids are mostly concentrated in a small area which the water is able to access or the voids are mostly near the surface of the specimens (this does not seem logical for cored specimens but may be true in the case of the gyro specimens). Basically, the higher the amount of saturation, the more the air voids linked together which means the more the permeability of the samples. Knowing the quality of air voids distribution inside the specimens can be useful for interpreting the materials behaviour when introduced to water. Figure 6.36 shows the saturation percentage of the cored specimens versus their AV content. It has to be notified that here, the terms 'low' and 'high' explain the quantities relatively.

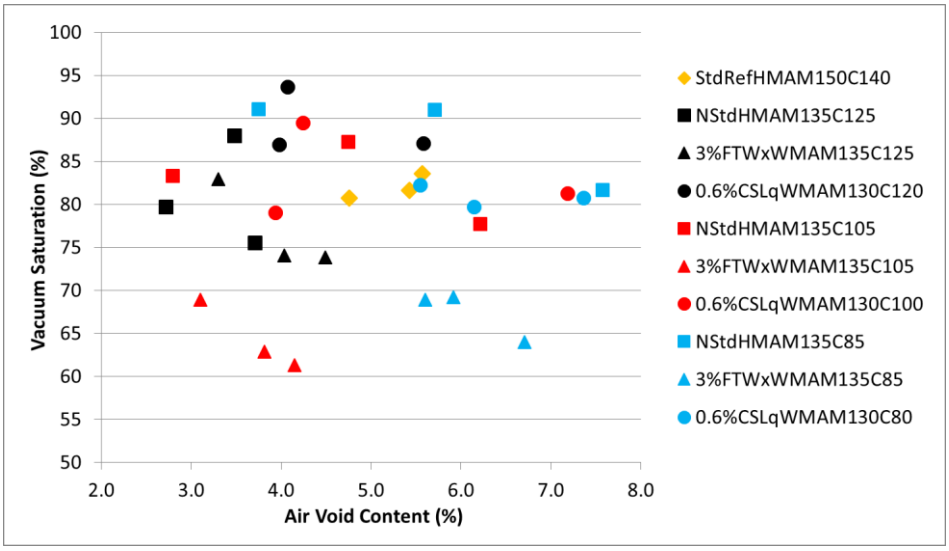


Figure 6.36 : Vacuum saturation vs AV content (cored specimens)

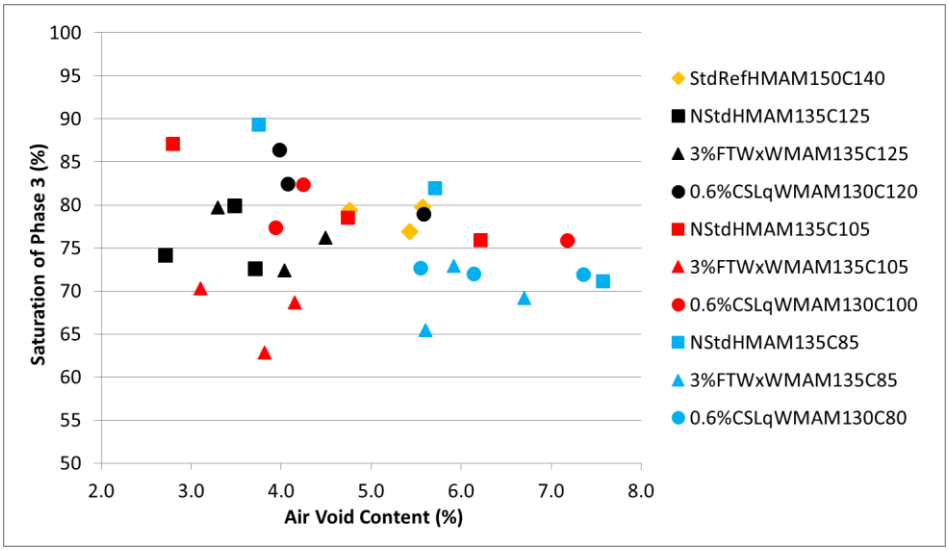


Figure 6.37 : Saturation at phase 3 (cored specimens)

Figure 6.38 indicates the ITSM ratio at three different phases of conditioning to its initial value for the cored specimens. Each bar represents 3 specimens which had been cored from the same location on the slabs of each mixture (location 1 from the first slab and locations 1 and 4 from the second slab of each mixture group). Thus, it is quite likely to have specimens with rather different AV contents in each sample group. This can result in having high scatter around the average value of the group which should not be considered as the indicator of having out of range data. It should be mentioned that the error bars represent the Standard Deviation of each group.

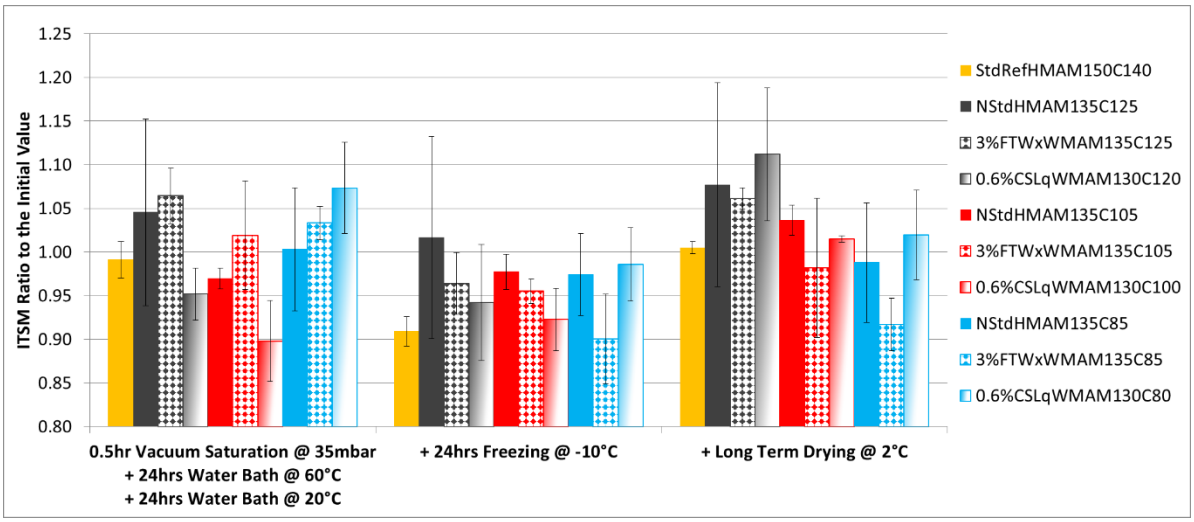


Figure 6.38 : ITSM ratio to the initial value over the test phases (cored specimens)

In order to understand and interpret the water sensitivity test results, it looks essential to analyse the behaviour of the specimens step by step through the different phases of the test. During the Vacuum Saturation phase, the water is sucked into the material by the force of suction replacing the air inside the specimens' voids.

Once the vacuum situation is removed from the material, some water may be replaced by air especially if over suction has happened. The downward trend in the saturation level of the specimens over the first two conditioning phases can confirm this issue. The specimens generally lose some pore water although they are still submerged in water.

Basically, when water replaces the air in specimen's voids, an increase in the Indirect Tensile Stiffness Modulus of the specimen should be expected if the specimen is not saturated to the point of structural damage. There is an explanation for this issue which refers to the matter of the ITSM test. Generally, in the case of dry samples, when the test load is applied vertically, the specimen experiences a small amount of deformation in the elastic region, in the form of horizontal expansion and vertical contraction. This is partly because of the changes which occur in the volume of the air voids in the sample. However, in the case of a saturated specimen (with any saturation percentage), since the ITSM test load pulse is applied in a very small fraction of time (risetime = 124ms), the absorbed water (pore water) finds no chance to escape and be drained out of the voids even if the voids are linked together. In fact, the water remains captured in the voids and due to its big volumetric coefficient of expansion, it neither complies to the volumetric changes of the surrounding void nor lets the surrounding void deform as it should. This means that the specimen does not show as much deformation as it used to in the absence of water. Thus, under the same load pulse, a smaller deformation will happen, which implies that the specimen's ITSM has increased.

It looks obvious and logical that as long as no structural damage happens through the vacuum saturation or any immediate water absorption, the higher the saturation percentage, the more the increase in the ITSM value. In fact, this extra stiffness modulus is the pressure resistance of the pore water against the volumetric change under the quick loading and unloading of the ITSM test. The increased stiffness modulus should be considered as 'virtual stiffness' since it is the materials real stiffness modulus plus a function of the pore water pressure.

However, the story may slightly change if the specimens experiences structural damage following the vacuum saturation in which case, over suction of water into the available voids

may result in expanding the voids or affecting the matrix of aggregates. In practice, it is better to avoid this phenomenon so that there is merely the effect of water in the ITSM value. However, since it is wanted to expose all of the specimens to the same situation in terms of the vacuum saturation length of time, structural damage may have happened in some cases.

In the second phase of conditioning, the specimens were placed in a 60°C water bath for 24 hours. Theoretically, this phase has been devised to simulate the issue of ageing not only at the surface of the specimen but also all through the specimen. In fact, the high temperature of water causes the bitumen to age. Since the specimen is saturated to some extent, the heat can be conducted through the specimen's voids where there is some more potential for ageing (provides more contact area to the bitumen's exposed surface). Moreover, in the presence of water, ageing can be combined with water damage. However, as will be shown later, the temperature of water may result in some healing which can increase the ITSM value. Moreover, bitumen ageing will make the bitumen stiffer which means resulting in a higher stiffness modulus. In other words, ageing increases the stiffness of bitumen but decreases its ultimate tensile capacity. This effect will decrease the ultimate tensile strength of the sample. However, in the case of the 'revised modified Lottman' test which monitors the ITSM values, obtaining higher values for stiffness modulus should be expected even after the 60°C water bath conditioning phase.

The 24-hrs 'water bath' conditioning phase at 20°C should be considered as an intermediate phase to prepare the samples for the first ITSM measurement by keeping them in water all through the period (so they do not lose any water), providing an environment to let them obtain the ITSM test temperature which is 20°C and allowing the water have its negative effect on the material in terms of debonding and stripping as long as possible.

It has to be mentioned that the negative effect of water as a stripping factor in asphalt, needs some time to appear since it should start replacing the bitumen bond through chemical reactions.

The 24-hrs 'freezing' phase at -10°C is probably the most destructive phase of the 'revised modified Lottman' test since the expansion of the pore water from 0 to -4°C will apply a significant and destroying internal pressure to the specimen's structure which can result in structural damage and a significant decrease in its post-freezing ITSM value. Looking at Figure

6.38 and Figure 6.46 can confirm this issue as they show a general declining trend or a general drop in the post-freezing ITSM value of all groups.

According to Figure 6.38 (and also Figure 6.46), this decreasing trend is followed by a generally increasing trend up to the end of the test period through the Long Term Drying phase. The 'long term drying' phase at 2°C during which the saturated samples have been kept in a 2°C dry conditioning cabinet for about 4 months, three different phenomena are expected to occur.

Due to providing enough time to the remaining water inside the specimen, one phenomenon is the stripping/debonding issue is such that a significant drop may be seen in the ITSM value. At the same time, the other phenomenon that happens is the specimen drying gradually over time. When the pore water leaves the specimen, the pore water pressure will decrease and as a result, the Virtual Stiffness Modulus will decrease. Moreover, due to the stripping phenomenon and the structural damage of the freezing phase, binder-aggregate bond and coating area should have been decreased. The other possible issue is the healing phenomenon which is expected to happen at any temperature and can neutralize the negative effect of freezing and debonding/stripping in the ITSM value.

Considering the possible behavioural reactions from the samples, the general increasing trend of the ITSM ratio bars confirms that the dominant phenomenon over the drying phase has been the healing issue.

Figure 6.46 indicates that the specimens of StdRefHMAM150C140, 3%FTWxWMAM135C125, 0.6%CSLqWMAM130C120, NStdHMAM135C105 and 0.6%CSLqWMAM130C100 mixture groups are those which have healed significantly to the point of statistically higher ITSM ratio.

However, the specimens of NStdHMAM135C125, 3%FTWxWMAM135C105, NStdHMAM135C85, 3%FTWxWMAM135C85 and 0.6%CSLqWMAM130C80 have not healed significantly. Looking from the view point of statistical analysis, considering the error bars, it can be extracted that the ITSM ratio of these mixture groups probably has not changed at all.

It looks logical to state that the higher AV content results in less healing and the higher the binder-aggregate work of adhesion or the binder work of cohesion the more the healing.

Therefore, it can be mentioned that the higher tendency of the first group to heal relates to their lower AV content and higher 'work of adhesion/cohesion' whereas the lower tendency of the second group to heal is due to the lower 'work of adhesion/cohesion' (in the case of 3%FTWxWMAM135C105 and %FTWxWMAM135C85) and higher AV content (in the case of 0.6%CSLqWMAM130C80, NStdHMAM135C85 and 3%FTWxWMAM135C85).

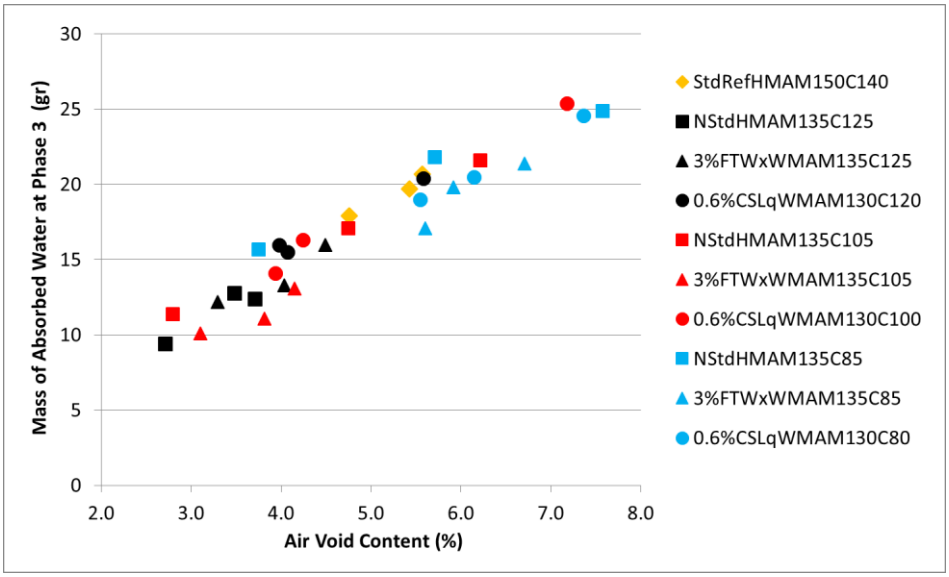


Figure 6.39 : Mass of absorbed water vs AV content (cored specimens)

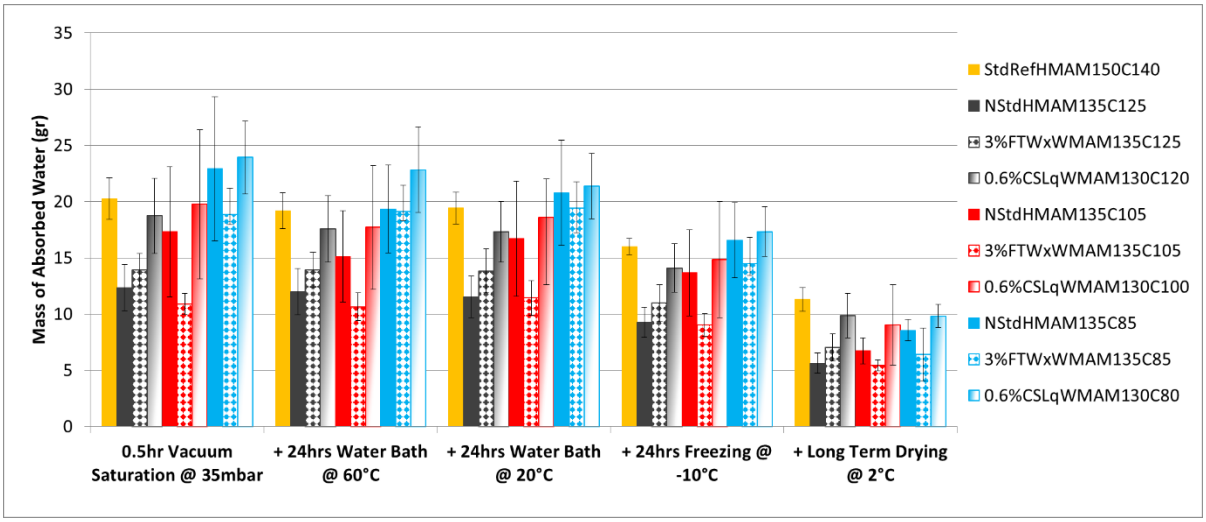


Figure 6.40 : Mass of absorbed water over the test period (cored samples)

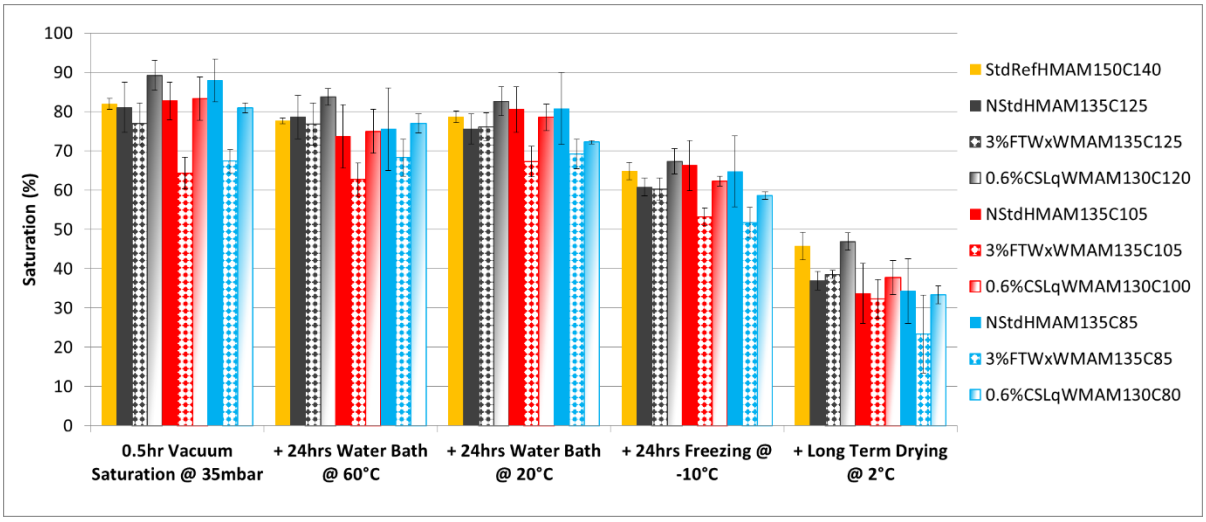


Figure 6.41 : Saturation percentage over the test period (cored samples)

Samples of 3%FTWxWMAM135C85 have relatively higher AV content (Figure 6.3) and lower saturation percentage by the end of phase 1 (vacuum saturation phase) as shown in Figure 6.36. This shows that the air voids are not linked together as much as the other sample groups. In other words, they are relatively less permeable. This issue decreases the extra pore water pressure and as mentioned before, the virtual ITSM will be closer to the real value. That is why the ITSM ratio is just over 1.0 by the end of phase 3. However, the bar chart in Figure 6.46 reveals that their post-freezing ITSM significantly reduces. It can be said that they have relatively weaker binder-aggregate bond strength or binder cohesive strength which cannot resist the water expansion pressure. This conforms to the results of Figure 5.5 and Figure 5.6 illustrating the values of binder-aggregate 'dry bond strength' calculated in the current research using the results of SE measurements through DCA for the binders and DVS for the aggregates. The ITSM ratio remains nearly constant by the end of the drying phase. It means that the positive effect of healing over the drying phase should have neutralized the negative influence of stripping or binder cohesive failure. This shows that this material is relatively more sensitive to water which can be confirmed through the SE calculations for measuring the 'work of debonding in presence of water' (Figure 5.4).

Samples of 0.6%CSLqWMAM130C80 have relatively the highest AV content (Figure 6.3) and a high saturation percentage, as well by the end of phase 1 as shown in Figure 6.38. This shows that the air voids are mostly linked together. In other words, the samples are relatively permeable. This issue increases the extra pore water pressure and the virtual ITSM will be much bigger than the real value. It can be seen that the ITSM ratio is the highest between the

mixture groups by the end of phase 3. This should be directly due to the highest AV content and high permeability. Moreover, the bar chart in Figure 6.38 reveals that their post-freezing ITSM significantly drops. It can be said that this is due to their relatively weaker binder cohesive strength which decreases the resistance to water expansion pressure and in the presence of a high AV content significantly damages the specimen. It was shown and argued in the previous chapters that CatSurfLq reduces the binder's cohesion strength due to reducing its surface tension slightly. The ITSM ratio remains nearly constant by the end of the drying phase. It means that the positive effect of healing over the drying phase should have neutralized the negative influence of cohesive failures over the drying phase. Since the ITSM ratio remains higher than 3%FTWxWMAM135C85, it can be concluded that this mixture is less sensitive to water compared to the FTWax-WMA which has been compacted at 85°C.

In the case of NStdHMAM135C85 samples, at the end of phase 3, the ITSM ratio remains about the value of 1.0. Although during the rest of the test, the same story as 3%FTWxWMAM135C85 and 0.6%CSLqWMAM130C80 can be observed, from the view point of the statistical analysis, it can be interpreted that the variations of the ITSM ratio has not been significant over the test phases. This shows that the material shows very limited sensitivity to water.

Samples of StdRefHMAM150C140 have relatively high AV content (Figure 6.3) and also high saturation percentage by the end of phase 1 (vacuum saturation phase) as shown in Figure 6.36. This shows that the air voids are about 80% linked together. In other words, the samples are relatively permeable. However, the ITSM ratio at the end of phase 3 is at a value of 1.0 with a relatively small scatter. This means that the pore water does not produce any resistant internal pressure to be appeared as virtual stiffness for the specimens. Referring to the statements of Shell Bitumen Test Data Chart, and according to what was mentioned in Section 6.1, regarding the reason why the Reference HMA has such a high AV content, it is expected that due to the high mixing temperature, the viscosity of bitumen is at such a low level that causes it to drain in the mould and results in a relatively porous and permeable material.

It seems logical that bitumen film thickness has an influence on the moisture susceptibility characteristics of HMA because it affects durability of the mixture. Mixtures with thick asphalt films are less susceptible to water damage than the mixtures with thin asphalt films since very small amounts of water can move through the mixture that contains thick asphalt films.

In fact, in the case of StdRefHMAM150C140 the voids shape and configuration might be different from the ones that are formed through the cool-compaction process of a high viscosity binder. Probably due to the drainage of bitumen, the film thickness is thin and consequently the voids are so big or linked together in such a way that the pore water pressure is not developed under the load pulses since it can be drained to lower the pressure or to bigger voids. That can be the reason why the ITSM ratio stays on the value of 1.0 despite there being much absorbed water, high AV content and high saturation. However, the bar chart in Figure 6.38 reveals that their post-freezing ITSM significantly drops. This is expected referring to what was mentioned regarding the Freezing phase and also due to the issue of thin bitumen film thickness. Then the ITSM ratio increases sharply by the end of the drying phase. It means that the positive effect of healing has been so significant that have totally recovered the negative influence of stripping over the drying phase as well as the destructive performance of freezing from the Freezing phase. In fact, according to the bar chart of 'work of debonding in presence of water' (Figure 5.4), the bitumen-aggregate bond in the case of this mixture group is relatively less sensitive to moisture. Thus, it is rational to believe that water has not caused any serious damage (stripping/debonding or cohesive failure in bitumen).

Figure 6.38 shows that the samples of 0.6%CSLqWMAM130C120, NStdHMAM136C105 and especially 0.6%CSLqWMAM130C100 have ITSM ratios below 1.0 at the end of Phase 3 of conditioning. Since a loss of cohesion can lead to a weakened pavement which is susceptible to pore-pressure damage (Majidzadeh & Brovold; Kandhal; Birgission et al., cited in Williams & Breakah 2010), the drops of the ITSM ratios can indicate that the samples have experienced some structural damage following the vacuum saturation process. In fact, the cohesive strength of the mastic of the three mixtures has weakened due to the presence of water through increased saturation and void swelling or expansion. Cheng et al. (2003) showed that the cohesive strength can be damaged in various mixtures by the diffusion of water into asphalt mastics. It can be seen that this has not happened in the mixtures of 3%FTWxWMAM135C105 which is of a lower AV content (nearly the same as 3%FTWxWMAM135C125).

The ITSM ratio of 0.6%CSLqWMAM130C120, NStdHMAM135C105 and 0.6%CSLqWMAM130C100 remains nearly constant until the end of the 'freezing' phase. It means that the materials have not been affected or damaged through the freezing process. In fact, it can be expected as they have already been damaged through the vacuum saturation phase. Thus, voids expansion through the vacuum process should have produced enough

degrees of freedom for the inside material so no more damage occurs due to the water freezing expansion. The specimens then generally experience a healing phenomenon over the 'drying' phase and this is why their ITSM ratios have increased until the end of the 'drying' phase.

3%FTWxWMAM135C105 follows nearly the similar trend to StdRefHMAM150C140 with a smaller drop in its 'post-freezing' ITSM ratio. This can be due to the higher stiffness of the FTWax-modified binder of 3%FTWxWMAM135C105. Moreover, the slightly bigger (just over 1.0) ITSM ratio at the end of phase 3 should be related to the virtual stiffness which is produced by the resistance of pore water pressure against the deformation under the ITSM test load pulses (as described previously).

Since the manufactured specimens, except the ones of StdRefHMAM150C140, have been mixed at such a range of suitable temperatures for mixing (according to the Shell BTDC) that have resulted in adequate coating of the aggregates. Thus, it seems that the bitumen film thickness should be so thick that the majority of permeability of the specimens can be considered to be because of the voids (micro pores) which exist inside the bitumen (mastic).

For the specimens of those mixture groups which have low AV content, such as NStdHMAM135C125, 3%FTWxWMAM135C125 and 3%FTWxWMAM135C105, it does not seem to be logical to relate the increase of ITSM ratio at the end of phase 3 to the produced pore water pressure. In fact, the amount of inserted water is too small to affect the ITSM value. In the case of these samples, it can be said that bitumen ageing during the 60°C water bath should have strengthened the specimen via stiffening the binder. Moreover, healing may have happened over the process due to the quite high temperature of the bath.

The remarkable drop in the post-freezing ITSM ratio of both NStdHMAM135C125 and 3%FTWxWMAM135C125 indicates that both groups of the specimens have experienced a significant damage due to the frozen pore water expansion. This damage has been recovered and healed over the drying period in a way that the initial ITSM ratios have been revived by the end of the drying phase. As a fact, moisture can damage asphalt through two ways:

1) Loss of bond between asphalt cement or mastic and fine and coarse aggregate, or
2) Weakening of mastic due to the presence of moisture.

Figure 6.40 shows the mass of absorbed water through the test phases. It can be seen that the general trend of the bar charts at each phase of the test, except the last phase, to a great extent

conforms to the trend of the bar charts of Figure 6 which shows the AV content of the different groups. This issue could also be expected referring to Figure 6.39 which indicates that the more AV content, the more absorbed water.

It should be mentioned that although the moisture sensitivity evaluation test was performed on both types of the manufactured samples (i.e. gyro and cored samples), investigating the effect of compaction temperature on the moisture susceptibility of the samples and extracting conclusions on this matter were inevitably done only based on studying the test results of the cored specimens as so far presented. The reason was the problem with saturating and water conditioning the gyro samples through the various phases of the test. In fact, the gyro samples were so dense and impermeable that they could hardly be saturated to a level beyond 20% at the end of the vacuum saturation phase. The significantly low AV content of the gyro samples in addition to the sealed greasy coating of the samples' circumference, which was because of easing the demoulding process after finishing the gyratory compaction, have made such sealed specimens that needed much stronger vacuum saturation pomp and much longer time to be saturated to the point that some influence of water could be observed on the mechanical properties of the samples.

However, attempts to perform the 'revised modified Lottman' moisture sensitivity evaluation test on the gyro samples resulted in the following charts, which do not deliver any useful conclusion except to the fact that the gyratory compactor has made the samples significantly impermeable and therefore insensitive to moisture damage. In other words, it can be stated that gyratory compaction has made the samples' moisture sensitivity insensitive to their material and manufacture temperature.

Figure 6.42 shows that after about 4 month of conditioning, the level of saturation increased to a significant value. The ratio of the samples' ITSM at this stage (4th Conditioning Round) to their initial ITSM value has been worked out and presented as 'pre-freezing' ITSM ratios (Figure 6.43).

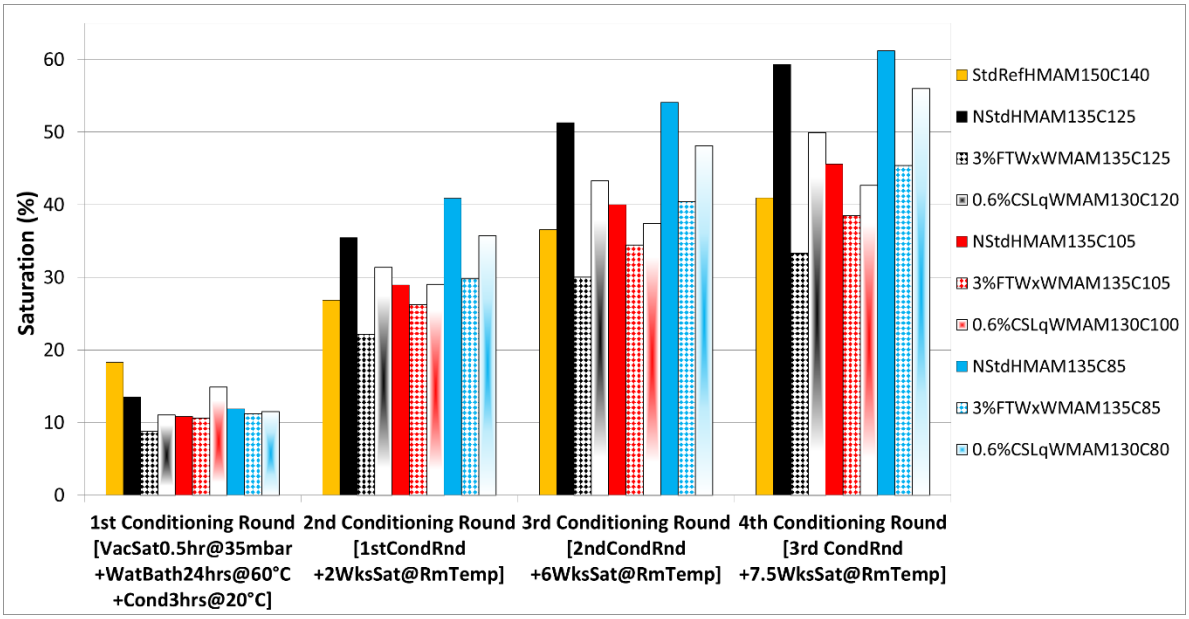


Figure 6.42 : Saturation percentage over the test phases (gyro samples)

According to Figure 6.43, it seems that the amount of healing over the 4 months of leaving/conditioning samples in lab/room temperature water has neutralised/offset all damages of the primary conditioning phases, as well as any moisture/water damage which should have happened over this 4-month period itself in such a way that the pre-freezing ITSM ratios to the initial value are about 1.0 (except for NStHMAM135C125). Comparing the pre-freezing ITSM ratios of Figure 6.43 with the 1st post-freezing ITSM ratios (Figure 6.44), which have been calculated using the immediately measured ITSM values of the samples after the freezing phase, shows how the materials have been damaged following the freezing action due to the similar reason mentioned for the cored samples. However, between various sample groups, no significant difference is distinguishable.

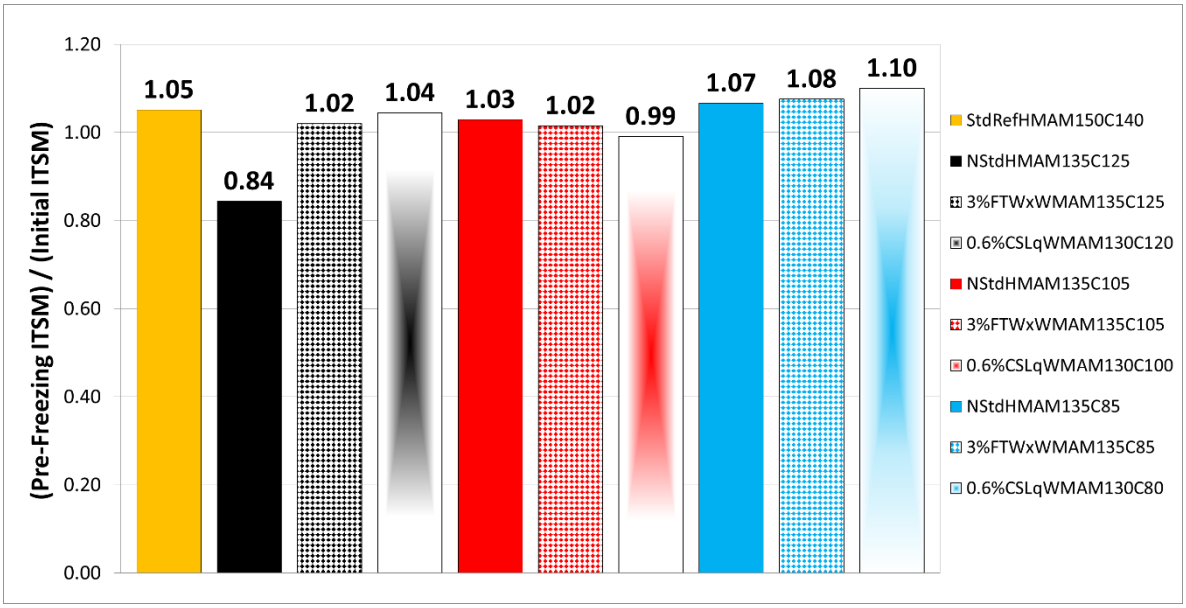


Figure 6.43 : Ratio of pre-freezing ITSM value to the initial ITSM value (gyro samples)

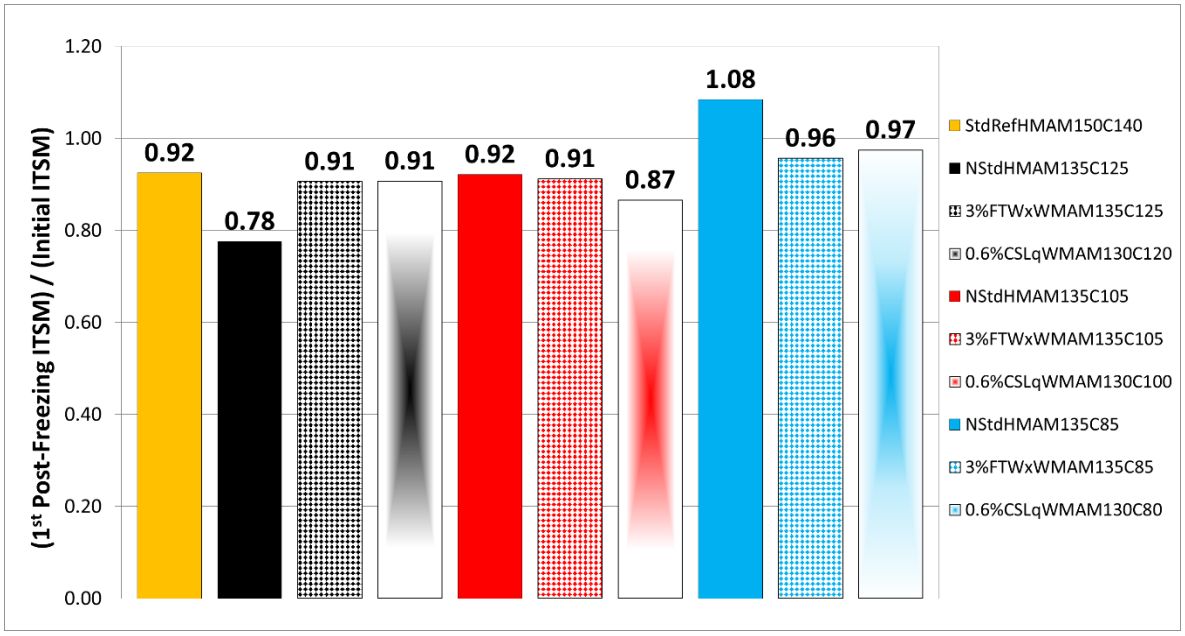


Figure 6.44 : Ratio of the 1st post-freezing ITSM value to the initial ITSM value (gyro samples)

Following the freezing phase, the gyro samples were left in lab/room temperature water bath for another 7 months to monitor the water damage/healing over this period. The 2nd post-freezing ITSM ratios (Figure 6.45) represent the ratio of samples' ITSM values after this 7-month period of conditioning in lab/room temperature water bath to their initial ITSM. The results illustrate that another period of significant healing has happened in the samples. The high rate and tendency of the gyro samples, which have been made by Dene limestone, to heal

over the time when they are placed in water, shows their low water sensitivity. In fact, compared to the cored samples, made by Tunstead limestone, it seems that the gyro samples are of higher tendency to self-heal which shows their relatively lower moisture sensitivity. This can prove the results of SE calculations for work of debonding in the presence of water (Figure 5.4) in terms of the higher water sensitivity of the samples made by Tunstead limestone compared to those manufactured using Dene limestone. As mentioned in the previous chapter, this can be referred to the higher absolute value of the basic polar surface energy component of Tunstead limestone compared to the absolute value of the acidic polar surface energy component of Dene limestone.

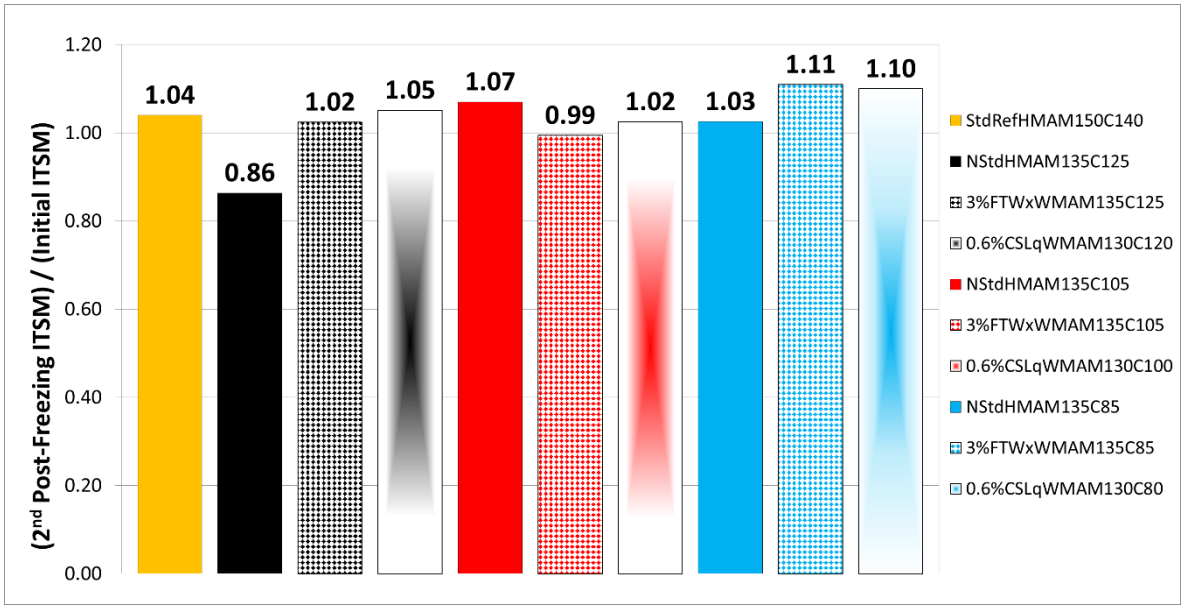


Figure 6.45 : Ratio of the 2nd post-freezing ITSM value to the initial ITSM value (gyro samples)

Basically, since the AV contents of the gyro samples have not been influenced by the compaction temperature, also the samples are suspected to be damaged by the gyratory compactor (as mentioned in the ITSM test results), they may not be reliable cases for studying the relation between the compaction temperature and durability or moisture sensitivity.

6.6.2. CONCLUSION

Putting everything together, it seems that for the asphalt materials which have been mixed at a proper temperature (the temperature at which adequate coating can happen), regardless of using

any of the additives, the ITSM ratio (the ratio of materials ITSM at the end of each conditioning phase to the initial ITSM value) remains over 80% with a safe boundary.

Comparing the mixtures of each 'compaction temperature group' shows that CatSurfLq-WMA's self-healing generally occurs with highest rates. In other words, over the 'drying' phase, CatSurfLq-WMA mixtures have healed more than FTWax-WMA, Non-Standard HMA and the Standard Reference HMA mixtures. Since over this phase of conditioning, the pore water should have tried to replace bitumen and develop the debonding/stripping/cohesive failure phenomenon. Referring to the results, this damage has happened at the lowest level in the case of the CatSurfLq-WMA mixtures compared to the other mixtures. However, in the case of the specimens of the mixture groups with the lowest compaction temperature, the same level of healing occurs over the 'drying' phase. According to Figure 6.46, in the case of each of the 'material groups', the level of self-healing decreases by decreasing the compaction temperature.

It can also be seen that FTWax-WMA mixtures nearly experience the same level of healing as the Non-Standard HMA mixtures. In fact, it can be said that while FTWax either resists against the healing phenomenon (via stiffening the binder) or has no effect on this matter or has less resistance to water damage (debonding), CatSurfLq works in a reverse way. This issue conforms to the results of the SE calculations (Figure 5.4) for 'work of debonding in presence of water'. However, the effectiveness of CatSurfLq decreases through lowering the compaction temperature through which the permeability of the material increases.

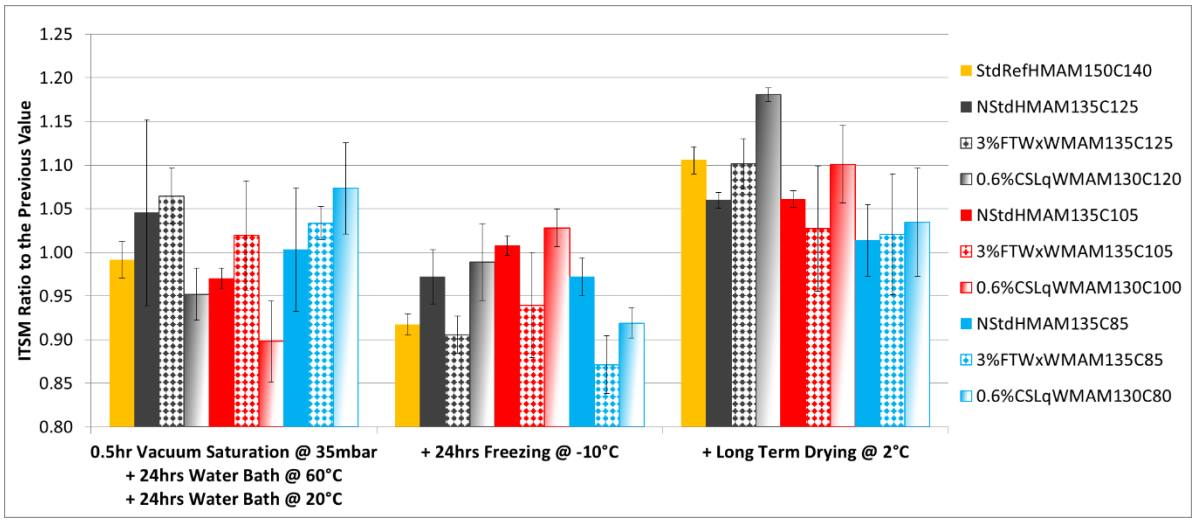


Figure 6.46 : ITSM ratio to the previous value over the test phases

The post-freezing ITSM value/ratio of all mixture groups generally drops, regardless of using WMA additives. This shows that using FTWax and CatSurfLq in asphalt cannot make the mixture withstand the expansion damage of the freezing.

However, looking at Figure 6.46 illustrates that FTWax-WMA mixtures, generally have experienced more damage through the 'freezing' phase.

Moreover, in general, regardless of the materials (additives) the damage occurs with lower levels for the mixtures which have been compacted at about 100°C and with higher levels for the materials which have been compacted at about 85°C.

CatSurfLq-WMA mixtures generally (except to 0.6%CSLqWMAM130C80) show more resistant to the freezing failure compared to the rest of the materials especially the FTWax-WMA. Since the freezing damage includes debonding, this conforms to the results of 'work of adhesion' calculations. However, reducing the compaction temperature decreased the effectiveness of CatSurfLq in such a way that the resulted specimens experience more damage compared to the Non-Standard HMA mixtures but still significantly less damage than the FTWax-WMA specimens. The closer level of post-freezing ITSM ratio between the CatSurfLq-WMA mixtures and the Non-Standard mixtures when they are compacted at about 125°C and 100°C conforms to the SE calculations results in terms of their level of bond strength. Thus, it can be concluded that the less the compaction temperature the lower the potential of self-healing and the higher the moisture damage.

In addition, it can be concluded that the lower the compaction temperature, the more the freezing damage especially when additives are used as CatSurfLq reduces the surface tension of the binder and binder's ultimate tensile strength and FTWax reduces the binder-aggregate bond strength as well as the binder's cohesive strength.

When CatSurfLq-WMA is compacted at about 100°C, it experiences less freezing damage. The same story happens when no additive is being used. In general, it seems that using additives such as FTWax and CatSurfLq, not only does not help the mixture resist freezing damage, but also in the case of FTWax and generally, regardless of the additive used, when compacted at about 85°C, they worsen the behaviour of the materials in terms of resisting against freezing damage.

Putting Figure 6.41 and Figure 6.46 together says that although FTWax-WMA mixtures are generally less permeable but more sensitive to water damage. Thus, it can be concluded that they are more water/moisture sensitive compared to the CatSurfLq-WMA mixtures and even the Non-Standard HMA which has no additive.

7. CONCLUSIONS

7.1. MAJOR STATEMENTS

- Compaction at lower temperatures does not have a considerable effect on the performance (permeability and mechanical properties i.e. durability and strength) of asphalt mixtures, whether they contain additives or not (i.e. HMA, wax-WMA or chemical-WMA) unless it occurs below 100°C (i.e. 80 and 85°C), in which case, in spite of some limited negative influences on asphalt performance, overall behaviour still remains in acceptable ranges.

- It was found that FTWax could be used as an additive to compact WMA at temperatures down to 85°C, although the reduction in viscosity of the binder it produced suggested it might only produce a 15°C temperature reduction. However, the overall better performance of the warm-produced HMA mixtures than the WMA mixtures illustrates that the waxy additive may have just eased the production of asphalt and made it energy-saving but have not necessarily resulted in producing a better material.

- It was found to be possible to compact CatSurfLq-WMA mixtures down to 100°C with reasonable mechanical properties. However it did not seem to enhance the properties of the WMA significantly over that of cool compacted HMA.

- It was found that HMA could be produced warm and compacted at lower temperatures down to 85°C (in laboratory situation) and its mechanical properties were not found to be significantly affected.

- It was realised that WMA additives make the mixture more sensitive to production temperature (i.e. mixing and compaction temperatures).

- Compaction of FTWax-WMA mixtures at the reduced temperature of 105°C can result in minimising the mixture's AV content and permeability as well as maximising the indirect tensile stiffness modulus and fatigue resistance.

- Gyratory compactors compact the asphalt mixtures to a certain density regardless of the temperature (and probably material/additive) because they are, in effect, strain-

controlled. Thus, the compaction process in a gyratory compactor is widely insensitive to temperature. Therefore gyratory compaction is not a suitable method for investigating the performance of compaction plant that imposes a fixed, or set vibratory stress.

7.2. DETAILED/SECONDARY STATEMENTS

7.2.1. BINDER TEST RESULTS

- FTWax, as a waxy additive of WMA, is a rheology and surface energy modifier of bitumen, whereas CatSurfLq, as a chemical additive of WMA, is just a surface energy modifier of bitumen (and, as expected, aggregate modifier), which has no significant influence on the rheological behaviour of bitumen.

- Adding FTWax significantly increases the softening point and decreases the penetration grade and these changes increase by increasing FTWax dosage.

- Adding CatSurfLq has nearly no influence on the penetration grade and softening point of bitumen.

- Just after FTWax's melting temperature (transition point), the viscosity of the modified binder drops and the viscosity curve shifts down afterwards. However, it seems that at temperatures lower than the transition point the crystallisation phenomenon in the wax structure results in a considerably increased binder viscosity.

- The results of the BS EN-based Brookfield viscometry testing do not confirm as much reduction in viscosity as promised by some of the previous researchers, whereas the ASTM-based test nearly confirms the issue, to some extent illustrating that FTWax is able to reduce the production temperature of asphalt up to 15°C.

- FTWax significantly increases the complex shear stiffness of the binder and reduces the phase angle and the higher the dose of FTWax the bigger the changes.

- CatSurfLq does not have any influence on the complex shear stiffness of the binder, nor upon the phase angle.

- FTWax decreases the surface tension of bitumen significantly (about 40%) by decreasing the non-polar and basic polar components. This means that this additive decreases the ultimate tensile strength of bitumen. FTWax, also increases the acidic polar component of the surface energy of bitumen

- CatSurfLq reduces the surface energy of bitumen via decreasing the polar components. It is expected that this additive increases the surface energy of aggregate so it can work as promised in the sense that it can increase the dry bond strength of the binder-aggregate interface in asphalt mixture.

- It is thought that the dosage of CatSurfLq or the density of surfactants in the 0.6%CatSurfLq-modified binders is higher at the binder-aggregate or binder-air interface. This phenomenon takes place during preparing and in the bitumen coating of the Wilhelmy plate DCA measurement test samples.

- The high dosage modified binder (with 5% CatSurfLq) does not represent the behaviour of the 0.6%CatSurfLq-modified binder at interfaces as it shows a significant increase in the SE of the modified binder which is not expected.

- Although bitumen is expected to show some acidic properties, the bitumen in this research shows basic tendencies. Therefore, it is expected to develop stronger bonds with acidic aggregates.

7.2.2. BINDER-AGGREGATE INTERACTION TEST RESULTS

- It looks logical that in order to calculate the 'work of adhesion' for the 0.6%CatSurfLq-WMA mixtures, the SE values of the 0.6%CatSurfLq-modified bitumen should be combined with those of the 5%CatSurfLq-modified aggregates (as explained in Section 5.1).

- FTWax decreases the binder-aggregate dry bond strength and increasing its dosage has an even stronger decreasing effect.

- Dene limestone makes stronger bonds with either of the bitumen types compared to Tunstead limestone. As mentioned before, it refers to the fact that Dene limestone and the used bitumen were from different polarities or acid-base tendencies (means compatible with each other as here: acidic aggregate mixed with basic bitumen),

whereas Tunstead had the same polarity as the bitumen (incompatible as both had basic tendencies). This means that before selecting the asphalt materials for fabrication, special attention should be paid to the issue of their polar (acid-base) compatibility.

- The dry bond strength of the 0.6%CatSurfLq-WMA mixtures can be slightly higher than that of the HMA mixture.

- It is thought that the chemical additive may not be able to significantly increase the adhesion unless it influences the non-polar SE component of the aggregates significantly while decreasing the polar and non-polar SE components of the bitumen at the same time.

- The moisture susceptibility of HMA and the 3%FTWax-WMA (3%FTWxWMA) is expected to be the same when Tunstead limestone is used in the mixture, whereas when Dene limestone is used, the moisture sensitivity of 3%FTWxWMA is somewhat worse than that of HMA.

- Generally, the moisture susceptibility of the mixtures with Dene limestone (gyro samples) is expected to be less than that of the cored specimens which have been manufactures using Tunstead limestone.

- Tunstead limestone shows higher tendency to have bitumen replaced by water. In fact the higher absolute value of the basic polar component of Tunstead limestone compared to the acidic polar component of the Dene limestone is responsible for this.

- It seems that a lower dosage of FTWax develops slightly lower moisture susceptibility than the mixture with higher dosage.

- Increasing the binder-to–aggregate introduction temperature from 135°C to 150°C, influences the properties of bitumen in such a way that its cohesive strength significantly decreases. Weakening the cohesive strength of a cooled coating due to increasing the temperature of binder-to-aggregate introduction phase could be a theory commonly known as ‘The Theory of Weak Boundary Layers’. However, this study suggests an alternative understanding involving some kind of bitumen flow on the surface of aggregate substrate when bitumen is introduced to the substrate. This can have a negative influence on the quality and adequacy of coating in terms of bitumen

film thickness and adhesion strength. In fact, bitumen's low viscosity and its tendency to flow on the substrate, does not let it stay in a static manner to be stable enough while cooling down and develop the adhesion. By this means, the chance of forming a proper coating under the metal stub is lowered.

- FTWax-modified coatings are the only ones which have experienced some adhesive failure. Adding 3% of FTWax to pure 70/100 pen bitumen reduces the surface energy of the binder due to which the cohesive tensile strength of the modified bitumen reduces. FTWax, also, reduces the binder-aggregate adhesive tensile strength to a lower level than the cohesive tensile strength of pure bitumen 70/100 pen. In fact, it seems that 3% FTWax is able to reduce the adhesive tensile strength of the pure base binder to such a low level that some adhesive failure has occurred in parallel with cohesive failure.

- The 'work of cohesion', and consequently the cohesive strength of the 3%FTWax-modified binder, is less than the 0.6%CatSurfLq-modified binder due to the lower surface energy of the former compared to the latter. However, the stiffness of the FTWax-modified binder is significantly higher than that of the CatSurfLq-modified binder. Therefore, the failure of the FTWax-modified coating under PATTI is mostly stress-controlled as the material is more brittle and fails suddenly with an ultimate tensile rupture when. Whereas, the CatSurfLq-modified coating under PATTI is strain-controlled as the sample deforms much more due to its flexibility and fails in the form of yielding. In fact, the significantly higher deformation of the CatSurfLq-modified coating samples under PATTI makes the test sample fail at lower tensile stresses compared to FTWax-modified coatings as well as the other samples.

- FTWax reduces the ultimate tensile strength of bitumen and as it increases the stiffness of the binder, the overall behaviour becomes a stiff but brittle material at asphalt operating temperatures. Therefore, it is expected that FTWax-WMA mixtures will have higher stiffness modulus and their failure under fatigue will be mostly in a brittle form, but at high number of cycles.

- CatSurfLq reduces the surface energy of bitumen but it does not influence the stiffness. Therefore, having the PATTI test results as a background, it is expected that the resulting CatSurfLq-WMA mixtures are of lower stiffness modulus than FTWax-WMA

and their failure under fatigue resistance is mostly controlled by the vertical deformation instead of brittle failures. Moreover, they are expected to have higher rutting potential.

7.2.3. MIXTURE TEST RESULTS

- The findings of this research can be justified through and confirm the criteria and recommendations of the Shell Bitumen Test Data Chart (BTDC) for 'ideal bitumen viscosities to have optimal mixing and compaction'. Therefore, mixing and compaction temperature of asphalt mixtures (i.e. HMA, wax-WMA or chemical-WMA) should be picked according to/ considering those criteria.

- The mixing temperatures proposed by BSEN 12697-35 for producing HMA mixtures with penetration grade bitumen does not seem to necessarily conform to the empirical criteria of the Shell BTDC.

- In general, the lower the compaction temperature of bituminous mixture (whether HMA, wax-WMA or chemical WMA), the higher the air void content of the resulting asphalt concrete. However, in this respect, FTWax-WMA should be considered as an exception in the sense that its minimum AV content is achieved at 105°C not at the higher compaction temperatures (i.e. 125°C).

- At viscosities less than 0.2 Pa.s, during the mixing process and moulding, bitumen drainage takes place in the mixture which increases the compacted materials porosity and permeability.

- Applying the WMA additives (i.e. FT wax and CatSurfLq chemical additive), generally, increases the AV content and permeability of the resulted asphalt mixture compared to a comparable reference mixture which is manufactured without using any additives. (Non-Standard HMA).

- FTWax significantly reduces the surface energy of bitumen and binder-aggregate bond strength, following which mixture has less internal friction during mixing and compaction. In fact, by this means it increases the lubricity of the mixture, increasing the workability and compactability. This influence is in addition to the rheological

influence which is expected from FTWax, as a waxy additive of WMA, in the sense that it reduces the viscosity significantly at temperatures over the transition point.

- CatSurfLq increases the binder-aggregate bond strength due to which the associated mixture's internal friction during the mixing and compaction increases which means this additive reduces the lubricity, workability and compactability.

- While FTWax increases the indirect tensile stiffness modulus (ITSM) of the asphalt mixtures by increasing the stiffness of the binder, CatSurfLq has no effect on asphalt mixture's ITSM since it does not modify the binder's stiffness.

- Reducing the compaction temperature of HMA to as low as 85°C does not negatively influence its indirect tensile stiffness modulus. This can be contrasted to the response of FTWax or CatSurfLq when compaction temperature is reduced to below 100°C (i.e. 80 to 85°C). Then the asphalt mixture's stiffness (ITSM) is, to some extent, sensitive to temperature and the ITSM value reduces to some extent.

- FTWax significantly increases the mixture's resistance to fatigue failure in such a way that even samples compacted at as low as 85°C last as long as standard HMA under the fatigue resistance evaluation test (ITFT).

- CatSurfLq does not have any effect on the fatigue resistance of the derivative mixtures since they perform very similarly to their counterpart HMA (as long as the compaction temperature is not reduced to as low as 80°C in which case the CatSurfLq-WMA behaves worse than the counterpart HMA).

- The fatigue resistance of the studied asphalt mixtures, at least in the laboratory scale, is not significantly sensitive to the compaction temperature when it is around and above 100°C. However, it decreases when the compaction temperature is as low as 80°C and increases at any of the studied compaction temperatures if FTWax has been added to the mixture.

- The fatigue resistance of the asphalt mixtures are highly controlled by the stiffness of the binder/mixture and the air void content of the mixture. The former can be controlled by the use of additives and the latter through the compaction temperature.

- The resistance of the FTWax-WMA mixtures to permanent deformation, in general, is as much as or much more than the standard reference HMA or the Non-Standard HMA mixtures considering that this resistance is not influenced negatively by decreasing the compaction temperature.

- The resistance of the CatSurfLq-WMA mixtures to permanent deformation is quite remarkably less than their counterpart non-standard HMA and FTWax-WMA mixtures as well as the standard HMA. Moreover, this resistance is significantly decreased by reducing the compaction temperature. Also the mechanism of cohesive failure is seen only in CatSurfLq-WMA mixtures. CatSurfLq chemical additive reduces the cohesive tensile strength of the binder because the additive reduces the binder's surface tension and 'work of cohesion'.

- The complex stiffness modulus of the asphalt specimens is highly influenced by the air void content of the samples as a result of the fact that the volumetric properties and permeability of the materials are influenced by the compaction temperature.

- Reducing the compaction temperature, does not change the E^* and viscoelastic behaviour of the FTWax-WMA mixtures.

- The indirect tensile stiffness modulus of asphalt mixtures mixed at a proper temperature (the temperature at which adequate coating can occur), regardless of using any of the WMA additives (i.e. FTWax or CatSurfLq), does not reduce more than 20%.

- CatSurfLq-WMA, regardless of compaction temperature, has generally higher tendency for self-heal after moisture damage through a 'drying' process compared to FTWax-WMA or HMA.

- It can also be seen that FTWax-WMA mixtures nearly experience the same level of healing as HMA mixtures over the drying process after moisture damage.

- The effectiveness of CatSurfLq on self-healing decreases when lowering the compaction temperature because the permeability of the material increases.

- FTWax and CatSurfLq in asphalt cannot make the mixture withstand the expansion damage of freezing. In general, regardless of the additive used, the damage occurs with

lower levels for the mixtures which have been compacted at about 100°C and at higher levels for the materials which have been compacted at about 85°C.

- The lower the compaction temperature the lower the potential for self-healing and the higher the moisture damage.

- The lower the compaction temperature, the more the damage of freezing on asphalt mixtures especially when additives are used as CatSurfLq reduces the surface tension of the binder and the binder's ultimate tensile strength while FTWax reduces the binder-aggregate bond strength as well as the binder's cohesive strength.

- Using WMA additives such as FTWax and CatSurfLq, not only does not help the mixture resist freezing damage, but also in the case of FTWax and generally, regardless of the additive used, when compacted at about 85°C, they worsen the behaviour of the materials in terms of resisting against freezing damage.

- Although FTWax-WMA mixtures are generally less permeable, they are more sensitive to water damage. In fact, they are more water/moisture sensitive compared to the CatSurfLq-WMA mixtures and their counterpart HMA mixtures.

8. PROPOSALS FOR FUTURE WORK

This research and its findings suggest the following avenues for future study:

- The current study was performed on two additives of WMA (i.e. FTWax and CatSurfLq). However, there are several other additives to produce WMA through the main 3 technologies (i.e. wax, chemical additives and foaming technologies). Therefore, the study is worth extending to a wider range of WMA additives since different additives have different properties. Especially it is recommended that such a study includes foaming technology which was removed from this research in the first year of study due to the high volume of tasks.

- In this study asphalt mixtures were manufactured using gyratory and slab roller compaction methods. It may be worth investigating the influence of cool compaction on asphalt properties when they are compacted by other method(s) of compaction. (e.g. Marshal compaction method).

- Asphalt specimens in this research were fabricated in laboratory. It may be worth studying the influence of cool compaction on field-produced asphalt samples (field trial cores).

- The research can be extended to other types of aggregate such as granite, with different physical, chemical and mechanical properties from limestone. Also, considering alternative binder source which should have a more acidic nature can develop particular and quite different situation which is worth studying.

- It is also worth studying the effect of using binders with significantly less pen grade or polymer-modified binders on the behaviour of cool-compacted asphalt mixtures (with or without presence of WMA additives).

- The effect of RAP (Reclaimed Asphalt) can be investigated on the properties of cool compacted WMA or HMA mixtures. Firstly, it is expected that the layer of stiff and aged bitumen, which coats the aggregates of RAP material, does not let the chemical additives interact with the aggregate surface easily. Therefore, the application and performance of chemical additives of WMA in the presence of RAP may decrease. It

seems that this issue has a worthwhile potential of being studied as a research program. Secondly, Adding RAP materials to asphalt mixture decreases the mixture's lubricity, workability and compactability due to the amount of hard and stiff bitumen, which is added with RAP to the virgin mixture. In this situation, performance of WMA waxy additives is worth being investigated. These situations, are expected to be even more complicated at reduced compaction temperatures.

- Micromechanical modelling of the WMA and HMA mixtures which are compacted at different reduced temperatures should be worth studying. This issue was included in the initial programs of the current research but later in year 2 was removed due to time limitations.

- This study has not undertaken the microstructural visual investigations such as X-Ray CT or Scanning Electron Microscopy (SEM), which definitely can deliver more clear and realistic visual picture of the post-failure structure of the tested samples under the destructive performance tests.

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