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Effect of fillers on the oxidative ageing of bitumen and cohesive bond strength of mastics

By

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Abstract

The researchers in pavement materials are always in the quest for the development of new methods and techniques to investigate the time temperature dependant behaviour of binding materials. This is paving a way for the future to build durable pavements through cost effective materials and methods.

This approach by researchers to evaluate elastic, viscous and flow properties to understand complex mechanism such as ageing and moisture damage is leading to development of new methods. In this regard, the key methods for ageing includes 'Rolling Thin Film Oven (RTFO)' and 'Pressure Ageing Vessel (PAV)'. This approach to develop new methods, despite its advantages, has natural tendency to overlook the use of the good old school testing techniques such as 'Thin Film Oven (TFO)' for its potential use for long term ageing. In the first part of this research the use of TFO for long term ageing has been explored.

The research about the 'materials' aspect is focusing on the use of modifiers to enhance binder properties. The use of expensive modifiers such as polymers, anti-stripping agents, and adhesion promoters is not a cost-effective panacea to the problem. The use of fillers to enhance desirable properties and minimise undesirable effects can lead towards a more sustainable solution in this regard. It also has been argued that aggregate in asphalt mixture is a mastic coated particle than simply being bitumen coated. This means the mastics are closer to actual field binder particle interactions. The additional advantage of this approach towards use of filler can be advantageous to understand the role of aggregate in the mixture while remaining in the domain of 'binder'. This can be helpful to understand the behaviour of aggregate through cost effective techniques.

This research uses different filler to study two materials related mechanism. This include ageing of bitumen/mastics and their cohesive strength. The ageing aspect is studied through rheological testing and cohesive bond strength is studied through pull off type test techniques. The ageing part was further divided into two parts. The first part aimed at to evaluate the potential of the 'Thin Film Oven' for long term oxidative ageing as discussed earlier. The second aspect included study of the effect of the physical properties of the filler particulates on bitumen. This effect was mainly evaluated in terms of packing fraction and nature of the filler particles. The effect of fillers on the stiffening potential and long-term ageing was also evaluated using rheological testing.

The work on cohesive bond strength was carried out through pull off type tests. These tests are getting popularity in research because of their ability to address most fundamental mechanical property i.e. tensile strength. Additionally, providing more detailed information about failure mode and mechanism. The integrity of the mastics was initially studied using two techniques developed in Nottingham Transportation Engineering Centre (NTEC). The variability and procedural issues in these test methods led to development of a new test method namely 'Compression Pull Off Test Assembly'. This new test method has led to improved test procedure and helped to explain material behaviour which was not fully being captured in the previous two methods as well as in historical research methods.

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Declaration

The research described in this thesis was conducted at the University of Nottingham, Department of Civil Engineering, Nottingham Transportation Engineering Centre and University of Engineering & Technology Lahore Pakistan.

I declare that the work is my own and has not been submitted for a degree at another university.

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Lahore

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Dedicated to my parent

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CHAPTER 1 : INTRODUCTION

1.1 BACKGROUND

Binding material 'bitumen' is used in road construction all across globe because of its good adhesive, cohesive and waterproof characteristics. This binding material is relatively inexpensive and leads to durable pavements. Durability of pavement is defined as ability of the pavement to perform its intended function for a designed period of time without going through severe structural degradation. Ever increasing traffic load and its complexity along with environmental factors affect durability and integrity of asphalt.

The environmental factors including ageing and moisture damage has been widely addressed in literature as primary factors affecting its durability provided that pavement is constructed according to specifications. Ageing makes bitumen stiffer and brittle leading to its thermal cracking susceptibility while moisture degrades the structural integrity of asphalt resulting in a loss of adhesion and cohesion. The testing techniques used in this research uses adhesive/cohesive pull off bond strength which yields direct and indirect information about moisture susceptibility of bitumen.

1.2 PROBLEM STATEMENT

Poor durability and loss of integrity of the asphalt leads to the early service life failure of pavement. Furthermore, oxidative ageing and loss of cohesive strength of bitumen being two most important parameters in this regard. Earlier

deterioration of pavement costs a higher price for any highway agency due to related maintenance and road user costs. This research addresses the problem in two dimensions namely; ageing and cohesive strength studies of binder.

Ageing of binder is measured by performing tests both on binder and asphalt and the test methods are well established in the literature (Jakarni, 2012). The focus on exploring new techniques of ageing often overlook important ageing test namely Thin Film Oven Test for its potential use to evaluate oxidative ageing of bitumen. First part of this research focuses on study of two state of the art techniques namely Pressure Ageing Vessel (PAV) and Thin Film Oven Test (TFOT) of bitumen to evaluate effect of oxidative ageing. The novelty comes into account for use of TFOT for long term oxidative ageing.

The literature survey has shown that during plant mixing mastic is formed thus making aggregate as mastic coated material than simply bitumen coated (Lesueur, 2009). The physical properties of the aggregate in this binder (bitumen and mastic) affect ageing of bitumen. The effect of ageing creates need for researchers to incorporate mastics in any testing method. Rheological properties of bitumen and mastics to evaluate ageing thereby help researchers to study effect of ageing of bitumen. It is, therefore, necessary for any testing protocol to include testing on mastic. The physical and rheological properties of bitumen are affected when it is in contact with mineral aggregate.

Cohesive strength of asphalt in this research was addressed using two cost effective pull off tests techniques, which were developed at Nottingham Transportation Engineering Centre (NTEC). This is because there is no standard test method available to evaluate cohesive strength of bitumen using pull off testing technique in strain control mode of loading (Jakarni, 2012). In this regard, a new test technique was also developed as a part of this research.

1.3 SCOPE OF RESEARCH

Scope of this research involves physical and rheological testing on bitumen and mastics using different ageing techniques to evaluate the effect of filler on oxidative ageing and potential use of TFOT for long term oxidative ageing of bitumen and mastics. This study involves a literature review to understand oxidative ageing mechanism of bitumen. This research also focuses on the ageing of mastics using different fillers which were selected based upon their acidic/basic nature and other primary/secondary characteristics.

This research focuses on using pull off techniques to measure the cohesive properties of the bitumen and mastic. This testing also involves investigation of the contribution of oxidative ageing on bitumen to measure its cohesive bond strength (Taylor, 2007).

1.4 AIM AND OBJECTIVES

The aim of this research is to study the effect of long-term oxidative ageing of mastics and their cohesive bond strength. To achieve this stated aim the following objectives were achieved systematically.

- To carry out a detailed literature review on oxidative ageing of bitumen to understand its mechanism.
- Conducting rheological testing on bitumen using Dynamic Shear Rheometer to study the Thin Film Oven Test for its use in long term ageing.

- The study also involves measurement of the oxidation chemical functionalities such as carbonyl region and sulphoxide associated with oxidative ageing using Fourier Transform Infrared Spectroscopy (FTIR).
- A study of the effect of packing of fillers on the ageing properties of bitumen and mastics as Rigden voids have strong influence on the properties of mastic.
- Petrographic examination to measure mineralogical composition of fillers using X-ray Diffraction (XRD).
- Use of pull off testing to study cohesive properties of mastics using technique developed by Jakarni (2012) and Apeagyei et al. (2014) at Nottingham Transportation Engineering Centre (NTEC).
- Development of new 'compression pull off test assembly' to evaluate cohesive strength.

1.5 THESIS ORGANISATION

This thesis is organised into seven chapters. The first chapter defines aim and objectives and scope of the research. The second chapter includes literature review on ageing, ageing techniques, effect of oxidative ageing on bitumen chemistry, moisture damage. It also includes current developments and related gaps in the research area related to ageing, moisture damage and pull off bond strength. Chapter three focuses on methods and materials used in the research.

In the fourth chapter ageing techniques and use of Thin Film Oven Test for long term oxidative ageing of bitumen is discussed. Fifth chapter includes research on ageing of the mastics using acidic and basic aggregates. In chapter six, two pull off testing techniques developed at Nottingham Transportation Engineering Centre (NTEC) were used to study cohesive properties of the aged bitumen and mastics. The seventh chapter discusses the development of a new test method. It also includes relevant testing and interpretation of results. Finally, the eighth chapter summarises the research, discusses major findings and include recommendations for future research.

CHAPTER 2 : LITERATURE REVIEW

2.1 INTRODUCTION

Few of the earliest uses of bitumen as adhesive material is reported back to Hummalian period (El Kowm, Syria) around 180,000BC since then it has different uses as waterproofing and a preservative material (Boëda, 1998; Connan, 1999). Its use in construction as a waterproofing material is found to be in the civilisation of Mohenjo Daro (Pakistan), around 3000 BC. The use of bitumen as a cementing material in road construction is reported to be in Babylon, where bitumen was used to join burnt bricks and stone slabs (Abraham, 1960).

In early the 19th century, the discovery of natural sources of asphalt in Europe led to its use for various purposes. However, the use of natural asphalt started to disappear with the advent of the vacuum distillation process. Today almost 85% of the bitumen production is used in paving, which acts as binding material in asphalt mixture (The Bitumen Industry - A Global Perspective, 2011). The major use of bitumen in hot mixed asphalt for road construction has also paved its way to be used through other processes like bitumen emulsion and foamed bitumen as discussed by Thom (2008).

Three important properties of bitumen need to be assured in good balance; firstly, its fluidity at higher temperatures for proper mixing, secondly its stiffness at higher temperatures for rutting resistance, thirdly its softness at low temperatures to be crack resistant at these temperatures range. A proper combination of these quite unique properties is required for paving under

different climatic conditions. This sometime leads bitumen to be modified through polymers or filler for its use over wider ranges of temperatures.

2.2 DEFINING BITUMEN

The European specification CEN EN 12597 (2000) define bitumen as “virtually an involatile, adhesive and waterproofing material derived from crude petroleum, or present in natural asphalt, which is completely or almost soluble in toluene, and very viscous or almost solid at ambient temperatures”.

A relevant term ‘tar’ also needs to be clarified in order to avoid misinterpretation as bitumen. Tar is referred to as product from the destructive distillation of other organic matters (coal, wood etc.) in the absence of air. Customarily a prefix is used in addition to tar in order to account for the material from which it is derived, for example coal tar which is a residue in pyrolysis of coal. The developments in petroleum industry and decline in coal industry has made its use nearly disappeared. The safety concerns have further extinguished its use due to presence of high amounts of carcinogenic polycyclic aromatic hydrocarbons.

In the American paving industry bitumen is referred to as asphalt, however in UK/European terminology asphalt or natural asphalt refers to natural bitumen containing the mineral portion. The major sources of natural asphalt in the world are: Dead Sea (one of the most ancient source is also sometime referred Lake Asphaltite as called by Greeks), Seyssel (France), Val de Travers (Switzerland) typically containing 5%, 8% and 12% bitumen respectively. In America, Trinidad Lake asphalt was discovered early 20th century and has been a paving material containing bitumen (39%), emulsified water (33%) and mineral part (27%). The second source in America is Bermudez Pitch Lake (Venezuela) containing a higher

amount of bitumen 64% with 30% water and 6% insoluble matter and mineral components (Lesueur, 2009).

In year 2014, the consumption of petroleum bitumen in United Kingdom was 1505 metric tons. The split of these metric tons specifically for pavements 1,302 of normal paving grade included 78 for harder paving grade and 1,224 for softer paving grade. In addition to these 157 metric tonnes of polymer modified bitumen was being used (source: eurobitume).

2.3 MANUFACTURE OF BITUMEN

Bitumen is a by-product of vacuum distillation of crude oil. However, this 'by-product' of distillation works as a value added product for road construction which constantly needs to be economised. The properties of bitumen depend upon its crude source properties and also the manufacturing process. It is a general rule of thumb that heavier crude oil yields more bitumen. A detail of production process can be found elsewhere (Read and Whiteoak, 2003).

The product obtained from distillation process is sometimes also referred as straight run bitumen. The products from refineries are usually a soft and a hard grade of bitumen which then further are blended to produce varying grades depending upon their use. Bitumen can even further be hardened by air blowing which is mainly used for waterproofing.

2.4 EFFECT OF AGEING ON THE DURABILITY OF ASPHALT

According to Read and Whiteoak (2003) "durability can be defined as the ability to maintain satisfactory rheology, cohesion and adhesion in long term service". A more comprehensive definition is given by Scholz (1995) "Durability as it is applied to bituminous paving mixtures is defined as the ability of the material comprising the mixture to resist the effects of water, ageing and temperature variations, in the context of a given amount of traffic loading without significant deterioration for an extended period."

According to Petersen bitumen durability is affected by two major factors: a) Compatibility b) Resistance to change from oxidative ageing (Petersen, 1984). However, from an asphalt rheologist perspective two factors that majorly affect durability are age hardening and moisture damage (Airey, 2003), as discussed in section 2.8.5 and 2.9.

Bitumen ageing is a deterioration phenomenon which makes binder stiffer and brittle and is caused by three major factors: oxidation, volatile loss and steric hardening (thixotropic effect). Ageing can further be divided into two categories; short-term ageing and long term ageing. These two types of ageing occur during HMA production and in service pavements causing brittleness of bitumen, and finally resulting in cracking of the pavements. The percolation of water in these cracks, developed due to ageing further causes an early deterioration of pavement. According to Petersen (1984) three factors which could cause hardening of bitumen are:

- Loss of oily components of bitumen through volatility or absorption by aggregate
- Oxidation related change in chemical composition

- Steric hardening caused by molecular structuring

Ageing results in an increase of stiffness of bitumen and the rate of ageing depends on characteristics of bitumen and content of the asphalt mixture. The properties of aggregate i.e. nature, particle size distribution and voids in asphalt mixture makes ageing a complex process (Sengoz and Topal, 2007).

The use of antioxidant agents in polymers to resist oxidation has drawn interest of researchers to evaluate their use in bitumen. Various classes of these additives (e.g. ultraviolet absorbers, peroxide decomposer etc.) have been evaluated in terms of their effect on oxidation. An antioxidant can increase compatibility of bitumen through dispersion of the asphaltenes component of bitumen (as discussed in section 2.7.3). The dispersed particles resist changes on oxidation thus resulting in reducing the effect of oxidation on asphalt.

The growing research on asphalt has shown promising effects of antioxidants as additives on the ageing properties of bitumen, although some of these antioxidants in the field have not performed satisfactorily. This is due to problems such as degradation, volatility and loss of antioxidants. In the verification phase of a study the antioxidants showed that using certain antioxidants can reduce the hardening upon oxidative ageing and improve high and low temperature performance (Apeagyei, 2011).

2.5 SHORT AND LONG TERM AGEING

There are two ageing phenomenon namely short-term & long term ageing, the short-term ageing is caused by volatilisation of bitumen and oxidation during hot plant mix production and during very early days during the construction of

pavement. The most common type of laboratory tests to simulate this type of ageing is Rolling Thin Film Oven Test (RTFOT) and Thin Film Oven Test (TFOT).

The long term ageing is caused by oxidation and steric hardening (also known as molecular structuring) during pavement service life. Pressure Ageing Vessel (PAV) is among the most widely used tests in the laboratory simulation of the long term ageing. According to Petersen et al. (1994a) PAV successfully simulated 4 to 10 years of field ageing. It is also reported in literature that each 10 °C rise of temperature above 100 °C makes rate of oxidation double (Read and Whiteoak, 2003).

2.6 FACTORS AFFECTING AGEING

There are numerous factors that affect the ageing of the asphalt, a list of these factors is reproduced in Table 2.1. Oxygen seems to influence lesser number of these factors; however, this important parameter plays an important role in pavement deterioration alongwith water damage. This point is supported from the literature by the presence of a majority of the methods which mainly evaluate the effect of oxidative factor (Airey, 2003). In real pavement conditions these factors are not influenced in isolation rather as a complex combination of heat and time (parameters directly affecting all the factors).

Ageing through oxidation occurs through reaction of functionalities of asphalt and oxygen, this is further affected by type of bitumen and temperature at which bitumen is exposed. Volatisation, as discussed previously, occurs by evaporation of lighter components from bitumen at higher temperature. This is more significant at short term ageing. Polymerisation occurs when smaller components

combine to form larger molecules to cause a progressive hardening, however this is not a significant low temperature ageing. Thixotropy occurs by formation of structures within bitumen when it is left for extended period of time. However, these structures are broken on agitation. Syneresis or exudation of oily component occurs when these light components exude to the surface of bitumen film. Separation is also removal oily components from bitumen by absorption of these components by the porous aggregate (Mouillet et al., 2008).

Table 2.1: Factors affecting ageing (Read and Whiteoak, 2003)

Factors that influence bitumen ageing	Influenced by					Occurring	
	Time	Heat	Oxygen	Sunlight	Beta and gamma rays	At the surface	In the mixture
Oxidation (in dark)	Yes	Yes	Yes			Yes	
Photo-oxidation (direct light)	Yes	Yes	Yes	Yes		Yes	
Volatilisation	Yes	Yes				Yes	Yes
Photo-oxidation (reflected light)	Yes	Yes	Yes	Yes		Yes	
Photo-chemical (direct light)	Yes	Yes		Yes		Yes	
Photo-chemical (reflected light)	Yes	Yes		Yes		Yes	Yes
Polymerisation	Yes	Yes				Yes	Yes
Steric or physical	Yes					Yes	Yes
Exudation of oils	Yes	Yes				Yes	
Changes by nuclear energy	Yes	Yes			Yes	Yes	Yes
Action by water	Yes	Yes	Yes	Yes		Yes	
Absorption by solids	Yes	Yes				Yes	Yes
Absorption of components at solid surface	Yes	Yes				Yes	Yes
Chemical reactions	Yes	Yes				Yes	Yes
Microbiological deterioration	Yes	Yes	Yes			Yes	Yes

2.7 EFFECT OF BITUMEN CHEMISTRY ON OXIDATIVE AGEING

It is well known that asphalt durability is determined by its physical properties, which further depends on chemistry of bitumen. The understanding of the chemistry of bitumen is of vital importance even if we want to study the physical properties and its behaviour during service life. In this section a summary from the

literature related to durability of bitumen is presented with main emphasis on ageing and some of the most renowned methods of separation of bitumen into its fractions are discussed. A detailed list of methods from is reproduced below.

Table 2.2: Analytical methods used in characterising bitumen chemistry (Bagampadde et al., 2004)

Analytical tool	Reported parameter
Chemical precipitation (Rostler and Sternber ASTM D2006)	Asphaltenes, nitrogen bases, 1 st acidaffins, 2 nd acidaffins and paraffins
Adsorption/desorption chromatography (Corbett ASTM D4124)	Asphaltenes, polar-aromatics, naphthene-aromatics and saturates
Elemental Analyses	C, H, N, S, O, Trace metals (e.g. V, Ni)
Solvent precipitation (Schweyer and Traxler)	Asphaltics, Paraffinics, Cyclics
Gel Perm. Chromatography (ASTM D2007)	Molecular weight distribution
Thin Layer Chromatography	Saturates, aromatics, resins, asphaltenes
Size Exclusion Chromatography	Separates basing on molecular size
Ion Exchange Chromatography	Strong acids, strong bases, weak acids, weak bases, and neutral fraction (amphoterics)
Infrared Spectroscopy (FTIR)	Functional groups
Ultraviolet-visible Spectroscopy	Characterisation of generic fractions
Gas Chromatography	Volatile fractions
Supercritical Fluid Chromatography	Nonpolar fraction
X-ray diffraction	Crystalline fractions
Nuclear Magnetic Resonance	Saturate/aromatic carbon ratio, content of carboxylics, phenol & benzylic fractions and generic compositions
High pressure liquid chromatography	Fractions related to moving phase

The above introduction has led to the need to further explore the review to study chemistry of the oxidative ageing through elemental composition, functional analysis, and bitumen fractionation.

2.7.1 Effect of Elemental Composition on Oxidation Products

Bitumen chemistry is mainly determined by the nature of its crude oil source, this often leads to referring bitumen according to its parent oil, for example; Venezuelan bitumen referred as naphthenic due to presence of mainly naphthenic structure of the parent oil.

The typical values of elements in hydrocarbons of bitumen are carbon as 80-88% and hydrogen as 8-12%. In addition to this presences of heteroatoms include sulphur (0-9%), nitrogen (0-2%) and Oxygen (0-2%). These small quantities of heteroatoms may contribute to large change of functionality and polarity of bitumen molecules. These heteroatoms also include presence of some small traces of metals like Fe, Ni, V (etc.), among these metals nickel and vanadium being considerable in amount. Certain metal salts and vanadium content increase rate of oxygen uptake.

One of the important heteroatom Sulphur has an important effect on the oxidative ageing which is mostly found in the form of sulphides instead of its presence in elemental form. These sulphides change to sulfoxides upon oxidation. Oxygen shows its presence through carbonyl functional groups, while nitrogen has its presence in the form of pyrrolic and pyridinic structures which produce 2-quinolones during oxidation. Heteroatoms especially nitrogen and oxygen (also ring structure of bitumen) contribute towards polarity of molecules and affect bitumen physical properties. The oxidation further leads to the increase in the amount of these polar atoms (Petersen, 1984).

2.7.2 Functional Group Analysis

The Functional Group Analysis (FGA) is used to study the presence of functionalities in the bitumen. The work of Petersen shows the presence of functionalities both in oxidised and un-oxidised state namely; ketones, carboxylic acids (and their salts), anhydrides, sulfoxides, 2-quinolone, pyrrolic and phenolic types.

The structural formula of these functionalities is shown in Figure 2.1 in this picture '1' indicates naturally occurring functionalities of bitumen while '2' indicates functionalities formed on oxidation. The natural state functionalities include Phenolic, pyrrolic, carboxylic acids, and 2-quinolone-type while Ketones and sulfoxide are mainly oxidation products.

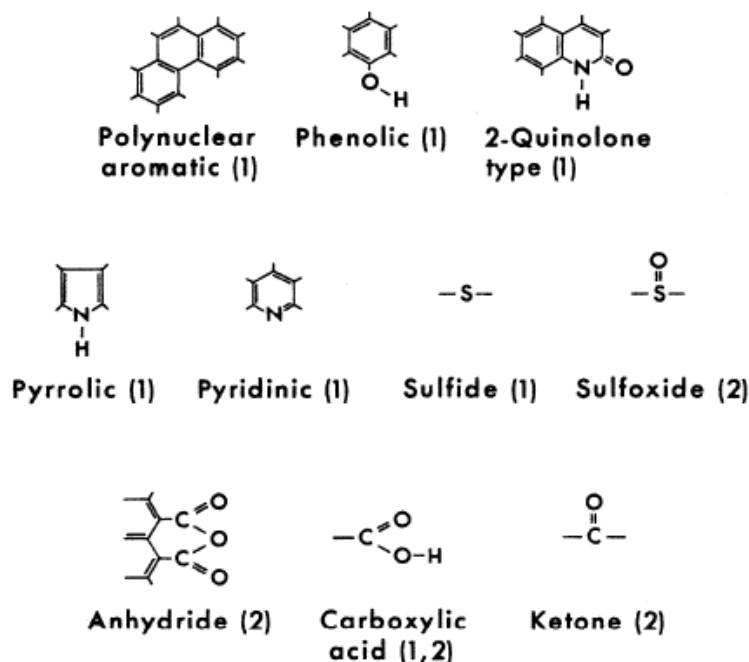


Figure 2.1: Functional groups in oxidised and unoxidised bitumen (Petersen, 1984)

The functional Group Analysis indicated that functional groups produced in bitumen during the oxidation in laboratory are similar to that of in-situ pavements ageing at ambient temperatures. The bitumen from different sources may have different rheological properties even upon similar level of oxidation and presence of similar carbonyl groups (CHO), due to the presence of heteroatoms. The infrared functional group analysis method (IR-FGA) is even more useful in analysis of aged bitumen than unaged due to more presence of the fore-mentioned functional groups.

Functionality analysis has its advantage over fractionation procedures (discussed in section 2.7.4, 2.7.5 and 2.7.6) that it can consider multiple functionalities of bitumen molecule. Effect of bitumen source (chemical composition) was shown by the Zaca-Wigmore experiment. In this test road construction variables were carefully controlled to keep constant and only varying bitumen source. The performances of these pavements were measured from the formation of cracks, which were caused by oxidative ageing.

2.7.3 Asphaltene Content of Bitumen

The asphaltene fraction content of bitumen and their heavy crudes gives a measure of compatibility of the material. It can be measured by mixing bitumen into n-heptane (40 times in volume). After separating the precipitated asphaltene (termed as HA) and further treating of maltenes fraction with iso-octane (40 times in volume) yields asphaltenes (termed as IA) (Branthaver et al., 1993). The calculation of the weight of both types of asphaltene can be used to obtain a useful parameter called Asphaltene Compatibility Index (ACI) shown as follows

$$ACI = \frac{IA}{HA + IA} \times 10$$

Both types of asphaltenes are aromatic, while aromaticity of heptane asphaltene is greater than iso-octane asphaltene. The yield of the former is usually greater than the latter. The molecular weight (M_n) values found by toluene are greater for heptane asphaltenes than iso-octane asphaltene. These values are lower when measured with pyridine instead of toluene, this shows that asphaltene molecules associate in toluene and these associations are somewhat broken in pyridine.

2.7.4 Separation of Bitumen into Fractions (SARA)

A study to understand rheology and bond strength inherently requires an understanding of the bitumen into its defined components. The detail of this is mainly taken from the extensive literature review of Lesueur (2009) and Petersen's work.

In 1836, bitumen was separated into two components by Boussingault. These components were; a solid fraction called asphaltenes 15 wt.% and a distillable fraction named 'petroleum' 85 wt.%. Later Richardson defined asphaltene as insoluble component of bitumen in naphtha from paraffinic petroleum (soluble in carbon tetrachloride CCl_4) while the soluble part of bitumen was called malthenes (which later changed to maltenes). Richardson suggested the plural forms for asphaltenes and maltenes due to presence of complex hydrocarbons although previously Boussingault used singular form for the components. Richardson also introduced the term carbenes insoluble in CCl_4 but soluble in carbon disulfide (CS_2), while the term used for compounds insoluble in CS_2 is 'carboids' though not used by the researcher. These fractions are not used in the paving industry due to their limited amounts in paving grades (Lesueur, 2009).

The difference between petrolene and maltenes, due to their interchangeable use, is given by Richardson where he refers petrolene to the compound which is a distillable fraction of bitumen while maltene can be termed as fraction of bitumen which are soluble in n-heptane (C_7H_{16}). The complex nature of maltenes created need for researchers to further separate it into fractions.

The Corbett fractions (discussed in section 2.7.5) are now known as asphaltenes, saturates, aromatics and resins. The latter two originally named by Corbett as naphthene aromatics and polar aromatics respectively (Lesueur, 2009). The basic analytical chemistry parameters of polarity, aromaticity and molar mass change in increasing order from saturates to asphaltenes.

In SARA separation as shown Figure 2.2, firstly asphaltenes are separated by n-heptane insolubility. This is achieved by blending 12g of bitumen in 1.2 L n-heptane and stirring for 1 hour close to 98 °C (boiling point of n-heptane). Secondly the residue (maltenes fraction) 10g are mixed in 50ml of n-heptane and are made to pass through chromatographic column. Saturates are separated by using n-heptane which as an eluent. Aromatics are separated by pure toluene followed by a 50/50 blend with methanol and resins are obtained by trichloroethylene. The use of different eluants affects the relative proportion of each component, so it is necessary to describe experimental conditions in order to compare different bitumen. Figure 2.3 shows the change in viscosity after mixing, compaction and during service life of pavement It also shows changes in SARA fractions over pavement life span.

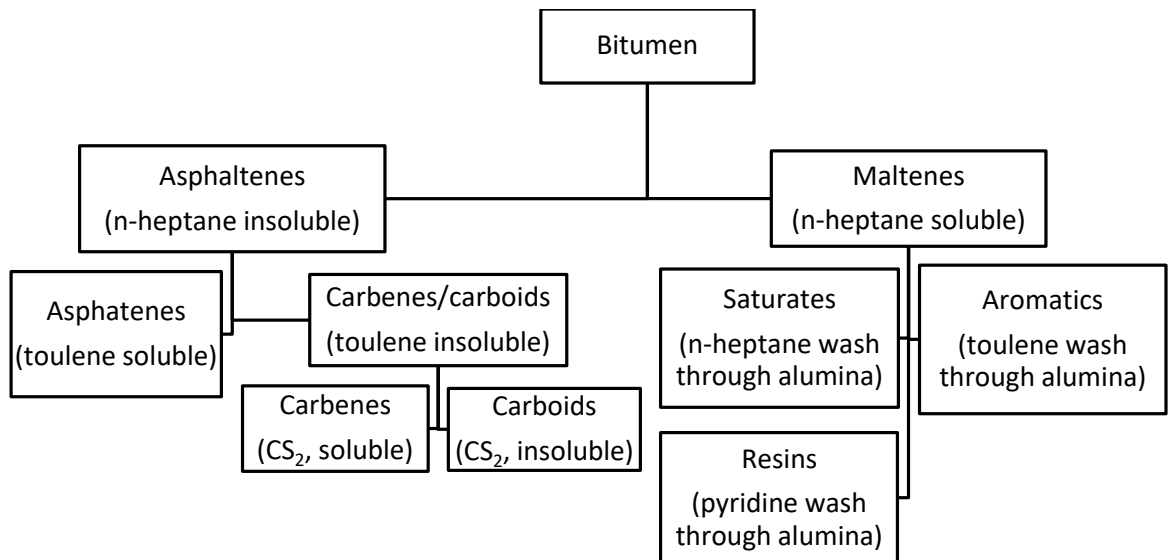


Figure 2.2: SARA fractions (Lesueur, 2009)

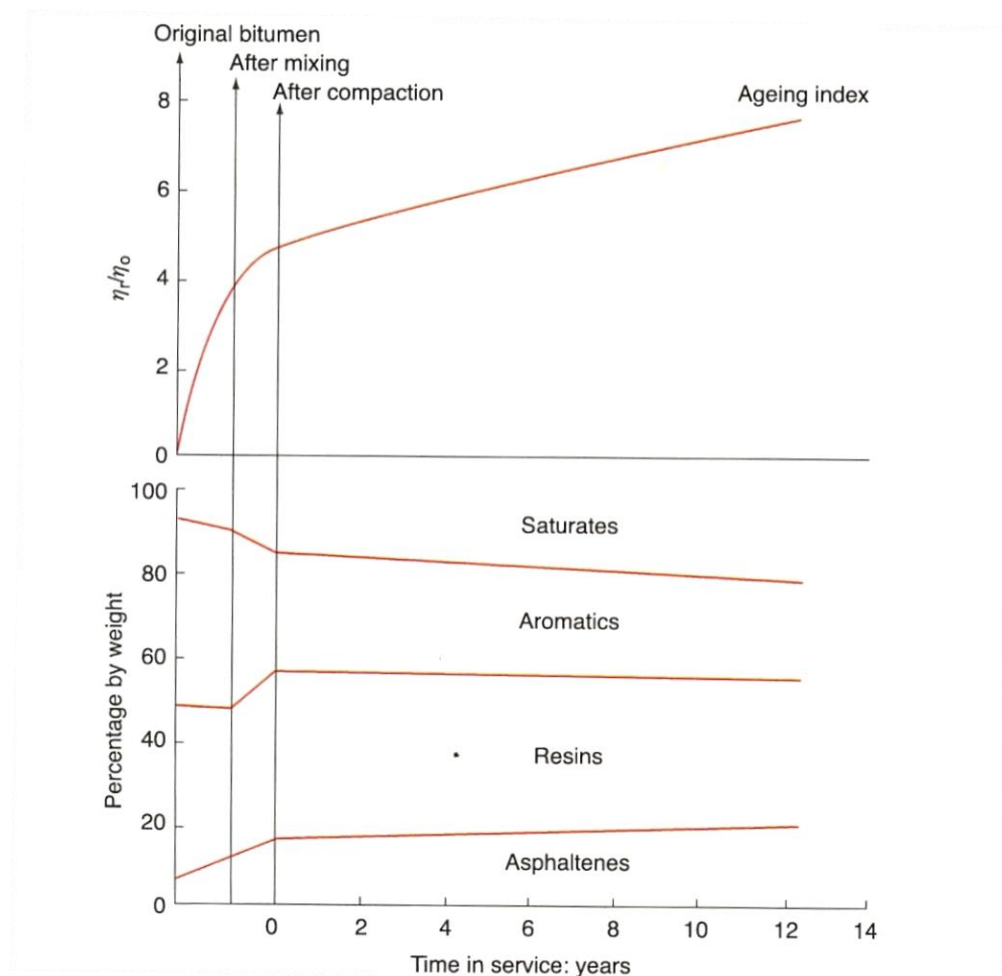


Figure 2.3: Changes in bitumen composition during life of pavemen (Read and Whiteoak, 2003)

2.7.4.1 Saturates

Saturates are light coloured liquid at room temperature with 5-15 wt % of amount in bitumen. The glass transition temperature being $-70\text{ }^{\circ}\text{C}$, density 0.9 g/cm^3 and average molecular weight around 600 g/mol . They are mainly aliphatic (which do not contain aromatic rings), as revealed by FTIR spectroscopy. Their molecular structure depends on parenting crude oil source.

2.7.4.2 Aromatics

The aromatics fraction along with resins are found abundantly in bitumen. The amount of this yellowish to red liquid at room temperature is nearly 30-45 wt %. The higher glass transition temperature $-20\text{ }^{\circ}\text{C}$ makes them more viscous than saturates. This glass temperature is close to original bitumen, average molecular weight is nearly 800 g/mol with density slightly lower than 1 g/cm^3 (at $20\text{ }^{\circ}\text{C}$). This fraction is slightly aliphatic with lightly condensed aromatic rings.

2.7.4.3 Resins

This fraction is a black solid at a room temperature with average amount 35-45 wt% which depends upon the solvent used. The original eluent used by Corbett to elute this fraction was benzene/methanol however ASTM standard uses fraction eluted by toluene/methanol. The glass transition is not clear due to their nature of being solid. The density of resins is closer to 1.07 g/mole at $20\text{ }^{\circ}\text{C}$ and act as peptising agent for asphaltenes in bitumen. In terms of chemistry, the composition of resins is closer to asphaltenes but have lower molar mass (1100 g/mole). This fraction mainly contains fused aromatic rings in its structure.

2.7.4.4 Asphaltenes

This major viscosity building fraction of bitumen is a black powder at room temperature with relative amount of 5-20 wt %. It is defined as insoluble in n-heptane but soluble in toluene, the term solubility has relative meanings because they form micelles in toluene. They are heaviest fraction of bitumen with density of 1.15 g/cm³ and its molecular weight ranging between 800-3500 g/mol.

Asphaltene structure is mainly stable from one bitumen to another. This fraction contains metal traces in bitumen like Ni, Va, and Fe. It also contains a higher amount of fused aromatic rings (4-10 rings) than resins (nearly 2-4 rings). The condensed aromatic rings in asphaltenes fraction form planer molecules which further associate with π (π) bonding. Furthermore, asphaltenes on addition to solvent will associate as depicted in Figure 2.4. This association of asphaltenes is called micelles and their size depends on the solvent, temperature and asphaltenes content. The stacking of asphaltenes (as shown in Figure 2.4) is similar to that of graphite and makes them permanently electrically charged due to higher degree of electron delocalisation. This makes these micelles to act like ions in solution.

Rostler's asphaltenes are chemically inert, this misconception may have resulted from the fact that separated asphaltenes are brittle and quite un-reactive nature at ambient temperatures. This un-reactive nature at ambient temperature make asphaltenes molecules immobile due their highly associative nature. However in molten solution, asphaltenes are chemically reactive due to their molecule mobility (Lesueur, 2009).

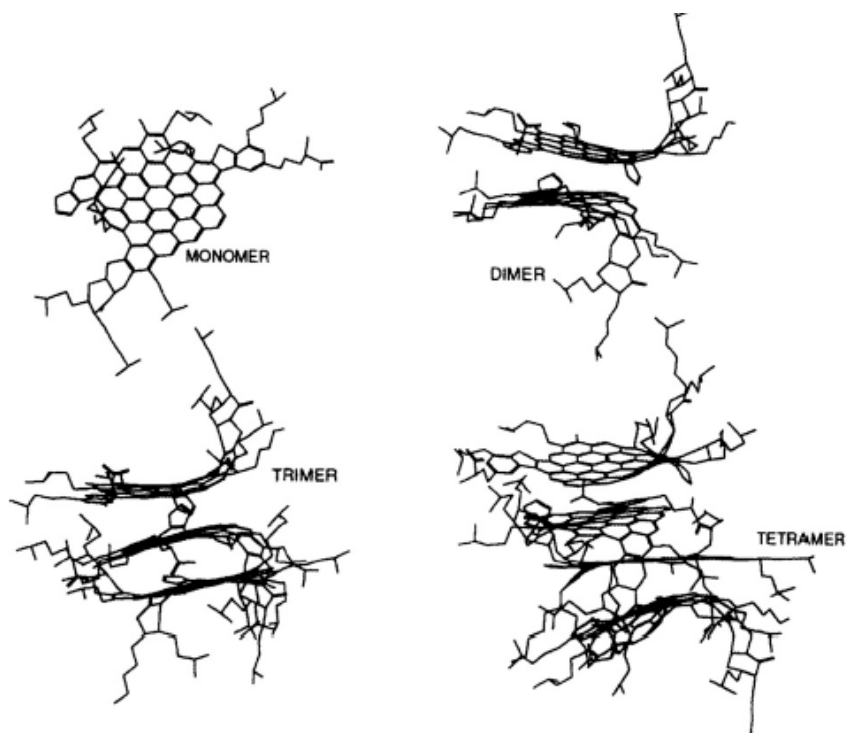


Figure 2.4: Formation of dimers, trimers and tetramers for asphaltenes

2.7.5 Corbett Fractions and their Sensitivity to Oxidation

The discussion of SARA fractions is incomplete without discussing the pioneering research performed by Corbett, because of its wide usage despite of presence of several other studies. However, chemical fractions from other sources can also be related to Corbett fractions as almost all techniques separate bitumen through increasing polarity, aromaticity and heteroatoms etc. The fractions are discussed in this section with main emphasis on the effect of oxidation.

This technique is an example of selective adsorption-desorption chromatography which is the most widely used technique for separation and has further resulted into the SARA analysis as discussed previously. This technique involves separation of asphaltenes from parent bitumen depending upon their insolubility in n-heptane (a non-polar paraffinic solvent). The dissolved maltene (petrolene) fraction is made to pass through a chromatographic column and is absorbed in

this column. Later different fractions are desorbed sequentially with different solvents based on increasing order of polarity. A schematic procedure of this technique is shown Figure 2.5.

The Saturate fraction is less polar, have low aromaticity, lower content of heteroatoms (except sulphur) and show little change on oxidation. The study by Knotneurs showed that saturate were inert on oxidation and similarly Corbett and Merz in their study on 18 years old test roads of Michigan State showed that there was no loss in saturate fractions after 18 years of service life of pavement due to oxidation. These three fractions show conversion of rest of three fractions showed conversion of nonpolar fractions towards polar fractions due to formation of oxygen containing (carbonyl) functional groups. The general trend is a loss in naphthene and polar aromatics while increasing in asphaltenes.

Corbett polar aromatics and Knotnerus's resins have shown to be highly reactive while Corbett asphaltene were intermediately reactive to oxygen uptake (Petersen, 2009). King and Corbett showed that their saturate fraction was relatively inert when comparison was made with oxygen uptake. In a study by Petersen on Wilmington (California) bitumen by ketone measurement which form on oxidation and ranked as saturates, naphthene aromatics, polar aromatics, and asphaltenes in their increasing order of oxygen reactivity (1:7:32:40 respectively) (Petersen et al., 1974b).

Corbett asphaltenes act as a thickening fraction, saturates contribute to fluidity, naphthene aromatics act as plasticiser towards polar aromatics and asphaltenes, ductility is imparted by polar aromatics and saturates and naphthene aromatics (Petersen, 2009). Saturates, naphathene aromatics and asphaltenes give bitumen complex flow properties. It was also mentioned that each bitumen has different

fractions and physical properties of bitumen are dependent on the interaction and proportion of these components.

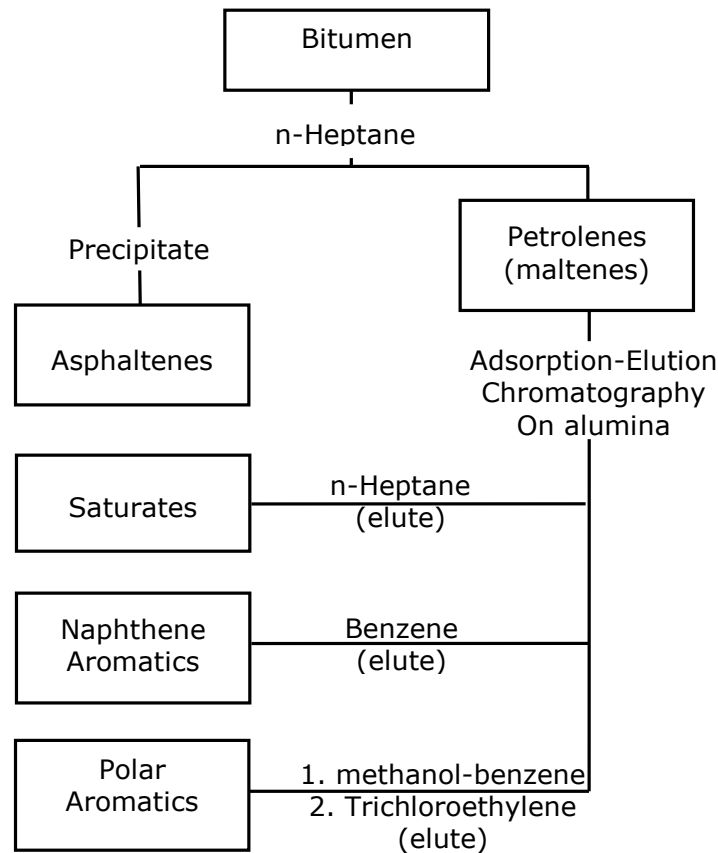


Figure 2.5: Corbett separation technique

2.7.6 Rostler's Durability Index and Heithaus Parameter

The durability of bitumen is the ability to resist damaging effects of oxidative ageing on the performance of bitumen. In the past several studies have been carried out in order to relate oxidative ageing with different bitumen fractions due to the fact of different reactivity with oxygen. A good balance of different chemical fractions is vital for durable bitumen to resist detrimental effects of oxidative ageing on physical properties. Bitumen with improperly dispersed

asphaltenes by resin will have less compatibility and will reduce bitumen durability.

According to Petersen (2009), Heithaus test has been used over the decades to measure compatibility of bitumen. It is based on the hypothesis that the polar asphaltene molecules of bitumen are dispersed (peptised) into the maltenes fraction. In this method a solution of bitumen with different (varying) amounts of toluene are titrated with n-heptane. The quantity of n-heptane which results into the flocculation is measured. The improved procedure of this method can be found elsewhere (SHRP A-370). In the SHRP programme, researchers calculated three parameters based on their experimentation; Overall compatibility of bitumen (P), asphaltenes compatibility (P_a) and solvent power of maltene (P_o).

The Heithaus parameter P (state of peptisation) correlates with the field better than Rostler durability parameters, thus are a better indicator of the hardening effect of oxidative ageing. This parameter takes into account peptisability and dispersing power of asphaltenes and maltenes respectively.

It was shown that Heithaus P and P_a value of bitumen decreases on oxidation showing that bitumen is less peptisable after ageing. On the other hand, value of P_o increases with ageing indicating that the oxidation of maltenes fraction yields more polar maltenes having more peptising power than the parent bitumen maltenes.

Rostlers durability index is defined as the ratio of the Nitrogen bases and first acidaffins to the paraffin and second acidaffins. In the past many laboratories used Rostlers durability index as a measure of the effect of oxidation. However field validation suggested it was not a good indicator of field performance and

also the omission of the important asphaltene fraction in Rostler durability index is considered as a limitation in its applicability (Petersen, 1984).

This index is based on the precipitation technique using the procedure adopted by Roslter and Sternberg. In this technique, the first separated fraction is nitrogen bases which are polar and include most of the nitrogen compounds and the higher amount of oxygen containing molecules. This fraction is aromatic in nature because most of the nitrogen in bitumen is attached with condensed aromatic rings. The second fraction is called first acidaffins and this fraction is also aromatic in nature and contains a lower percentage of nitrogen. The third fraction is the second acidaffins which contains components of less reactive and aromatic nature. The fourth fraction contains most of oily components of bitumen and is composed of paraffins (alkanes).

Nitrogen bases and first acidaffins (resinous and reactive components) contribute to peptise or disperse other components, while paraffins and second acidaffin (least reactive) gives gel like properties to bitumen.

2.7.7 Bitumen Compatibility and its Fractions Interaction

Interaction among bitumen fractions is important in the sense that the behaviour of these fractions in bitumen depends upon the relative amount of other fractions too for example asphaltenes and oily fractions (saturates) may not be mutually soluble in the absence of the resinous fraction. Hence a relative proportion of all fractions is necessary to make a compatible (balanced) bitumen component system and this balanced system imparts bitumen its durability and unique viscoelastic properties. It should be recognised that greater or lesser quantities of a given fraction may be detrimental to bitumen compatibility also chemical variation within the same generic fraction may have considerable effect.

Improperly dispersed asphaltenes will result in incompatibility and ultimately will result in loss of durability. Compatibility of bitumen deals with the solubility and solvent powers of different bitumen components with each other. More polar asphaltene require maltenes with more solvent power to make a compatible system.

According to Rostler, asphaltenes are the viscosity building fraction and are peptised (dispersed) by nitrogen bases and are solvated by resinous acidaffins and gelled by paraffins. Corbett concluded that each fraction and their combination have separate function which determines physical properties of bitumen. The function of these Corbett fractions is summarised in Table 2.3 which is constructed with information taken from Petersen (1984).

Petersen also related the Rostler fractions with Corbett fractions. According to him the Polar aromatic fraction may contains many compounds found in nitrogen bases and some part of first acidaffins, naphthene aromatics may be compared with second acidaffins and some components of first acidaffins and saturate fraction can be compared with paraffins fraction.

Table 2.3: Functions of different Corbett fractions

Asphaltene	Saturate	Naphthene aromatics	Polar aromatics
Solution thickeners	Impart fluidity	Plasticiser for polar aromatics and asphaltenes	Imparts ductility to bitumen
Complex flow			

Altgelt and Harle mixed asphaltenes collected from different sources and mixed them in the same maltenes fraction and concluded that asphaltene had different

thickening power as the blend viscosities were different. Similarly maltenes from different sources had different solvency power for asphaltene (Petersen, 1984). Bitumen chemistry becomes of great importance when bitumen from different sources or different bitumen components are blended together.

2.7.8 Discussion on Structure of Bitumen

The detail in this section is mainly taken from Lesueur (2009) and Petersen's work. These two works relate to Colloidal and Microstructural models respectively.

2.7.8.1 Colloidal Model

Nellensteyn, in 1924, first emphasised the colloidal nature of asphaltenes as dispersed in the solvent phase (called maltenes) and being peptised by polar fraction resins. Pfeiffer and Saal (1940) proposed that bitumen consists of a dispersed phase made of a core of aromatic component surrounded by a less aromatic layer of molecules and dispersed in more aliphatic solvent phase. The researchers did not mention any boundary distinction between two phases but rather the continuity of low to higher aromaticity (aromaticity gradient) from solvent to dispersed phase. They also proposed that asphaltenes have a tendency to attract molecules from less aromatic maltenes, surrounding and peptising asphaltene. They also did not discuss the distribution of hetero atoms in different polar functionalities. According to researchers the properties of bitumen were a function of the strength of associations and peptisability of the dispersed phase.

The Sol and Gel model has been used to support the colloidal model. Pfeiffer and Saal (1940) proposed that bitumen having asphaltenes in highly aromatic maltenes were peptised and were not forming higher associations. The Bitumen that had less asphaltenes in lesser aromatic maltenes forming agglomerations

was labelled as sol-type. On the other hand, bitumen that had more asphaltene in less aromatic maltenes and formed agglomerations were called gel-type bitumen. The sol-gel refers to the intermediate phase. The structure of both types of bitumen is shown in Figure 2.6.

The modified colloidal model by Pfeiffer and Saal (1940) had its support from petroleum scientists; however colloidal model is difficult to be proved experimentally because of limitation due to opacity of bitumen. On the other hand, it may not be right to describe model modified by Pfeiffer and Saal (1940) as colloidal because it make no distinction between surfaces of dispersed phase (instead consider aromaticity gradient). In this molecular structuring /steric hardening was attributed to development of micelles coagulation to make a network of micelles (Lesueur, 2009).

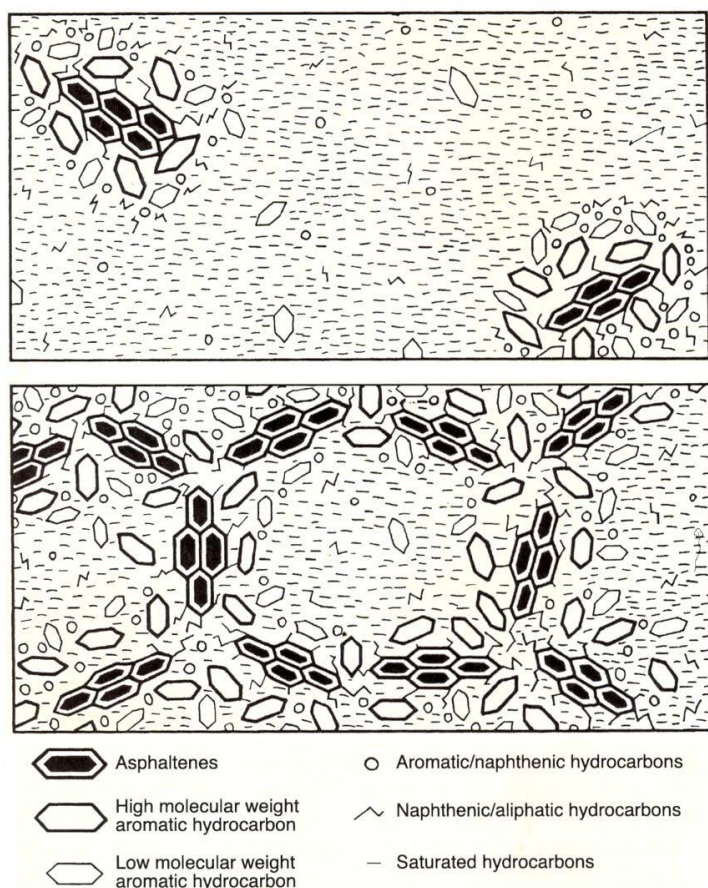


Figure 2.6: Sol type (above) and Gel type (below) bitumen (Read and Whiteoak, 2003).

In a Later study Traxler (1961) also discussed colloidal model of bitumen and emphasised on the effect of state of dispersion in physical properties of bitumen. Bitumen with well dispersed asphaltenes having high molecular weight (having high aromatic components and peptising resins) were labelled as sol-type. These sol-type bitumens showed more temperature susceptibility, ductility and less complex flow, lesser age and steric hardening. On the other hand, bitumen poorly dispersed asphaltene bitumen were labelled as gel-type bitumen and they showed lesser temperature susceptibility and ductility while more age and steric hardening and elasticity. According to Traxler (1961) steric hardening was an evidence for the development of a structure which was unstable to agitation and heat.

2.7.8.2 Microstructural model (SHRP)

SHRP researchers have questioned the validity of colloidal model while proposing a model microstructural model based on the findings of Binder Evaluation and Characterisation Programme. The microstructural model of bitumen was suggested by SHRP researchers who proposed this model based on the model suggested by Pfeiffer and Saal (1940). Bitumen was thought to consists of solvent phase (solvent moiety) and a dispersed phase (dispersed moiety). The solvent phase was suggested to be more aliphatic and nonpolar in nature with less heteroatoms. The microstructure of bitumen was composed of smaller structural units made through molecular associations were more aromatic and polar. The association forces were hydrogen bonding, dipole dipole interaction and pi-pi interaction which formed the primary structure in bitumen. According to this model microstructure in certain conditions would associate in 3D networks. Heating and shear stress would break microstructure and networks while a good solvent phase will reduce the 3D structuring but a poor solvent will promote this structuring.

The formation of polar molecules increases with oxidative ageing thus promoting more structuring although solvent power is also increased (Petersen et al., 1994a).

The bitumens having same elemental composition, density and molecular weight were considered to have different physical properties due to difference in the formation of microstructure in bitumen. According to SHRP researchers, the microstructural model has its advantage in rationalising certain phenomenon such as Newtonian rheological behaviour, viscosity dependence on temperature and steric hardening etc. However, this model is only descriptive and its details are not fully quantified. Lesueur (2009) made an important discussion on the issue and the claim of SHRP researchers he has emphasised that the colloidal model of bitumen is necessary to support peculiar features of bitumen.

2.8 ASPHALT AGEING TEST METHODS

A comprehensive discussion on ageing methods has been made by Airey (2003), Table 2.4 reproduced here suggests a summary of laboratory ageing methods for asphalt binder. The basic principle behind all these methods, including their variations, is to evaluate the durability of asphalt.

The short-term ageing methods are intended to simulate the ageing that occurs during hot plant mix, production, logistic, and pavement construction as well as during early during service life of the asphalt. The long-term test protocols mimic the ageing that occurs during the service life of the pavement.

Table 2.4: Bitumen ageing methods (Airey, 2003)

Test method	Temperature (°C)	Duration	Sample size (g)	Film thickness	Extra features
Thin film oven test (TFOT) (Lewis and Welborn, 1940)—ASTM D1754, EN 12607-2	163	5 h	50	3.2 mm	–
Modified thin film oven test (MTFOT) (Edler <i>et al.</i> , 1985)	163	24 h	–	100 µm	–
Rolling thin film oven test (RTFOT) (Hveem <i>et al.</i> , 1963)—AASHTO T240, ASTM D2872, EN12607-1	163	75 m	35	1.25 mm	Air flow—4000 ml/min
Extended rolling thin film oven test (ERTFOT) (Edler <i>et al.</i> , 1985)	163	8 h	35	1.25 mm	Air flow—4000 ml/min
Nitrogen rolling thin film oven test (NRTFOT) (Parneggiani, 2000)	163	75 m	35	1.25 mm	N ₂ flow—4000 ml/min
Rotating Flask Test (RFT)—DIN 52016, EN12607-3	165	150 m	100	–	Flask rotation—20 rpm
Shell microfilm test (Griffin <i>et al.</i> , 1955)	107	2 h	–	5 µm	–
Modified Shell microfilm test (Hveem <i>et al.</i> , 1963)	99	24 h	–	20 µm	–
Modified Shell microfilm test (Traxler, 1961; Halstead and Zenewitz, 1961)	107	2 h	–	15 µm	–
Rolling microfilm oven test (RMFOT) (Schmidt and Santucci, 1969)	99	24 h	0.5	20 µm	Benzene solvent
Modified RMFOT (Schmidt, 1973)	99	48 h	0.5	20 µm	1.04 mm ϕ opening
Tilt-oven durability test (TODT) (Kemp and Prodoehl, 1981)	113	168 h	35	1.25 mm	–
Alternative TODT (McHattie, 1983)	115	100 h	35	1.25 mm	–
Thin film accelerated ageing test (TFAAT) (Petersen, 1989)	130 or 113	24 or 72 h	4	160 µm	3 mm ϕ opening
Modified rolling thin film oven test (RTFOTM) (Bahia <i>et al.</i> , 1998)	163	75 m	35	1.25 mm	Steel rods
Iowa durability test (IDT) (Lee, 1973)	65	1000 h	TFOT residue—50	3.2 mm	2.07 MPa—pure oxygen
Pressure oxidation bomb (POB) (Edler <i>et al.</i> , 1985)	65	96 h	ERTFOT residue	30 µm	2.07 MPa—pure oxygen
Accelerated ageing test device/Rotating cylinder ageing test (RCAT) (Verhasselt and Choquet, 1991)	70–110	144 h	500	2 mm	4–5 l/h—pure oxygen
Pressure ageing vessel (PAV) (Christensen and Anderson, 1992)	90–110	20 h	RTFOT or TFOT residue—50	3.2 mm	2.07 MPa—air
High pressure ageing test (HiPAT) (Hayton <i>et al.</i> , 1999)	85	65 h	RTFOT residue—50	3.2 mm	2.07 MPa—air

2.8.1 Thin film oven test (TFOT)

This method of short term ageing was introduced by Lewis and Welborn in 1940.

In the standard test, 50g (50ml) of bitumen is put into each of four TFOT pans.

This 50g of bitumen gives 3.2mm film thickness inside the pan. The oven is then heated at 163 °C for five hours. A typical thin film oven is shown in Figure 2.7.

The amount of ageing that is produced in this method simulates ageing that occurs in plant mixing. In 1959, AASHTO this method as standard test method and later by ASTM in 1969 as (ASTM D1754, 1995a). In this method bitumen is not agitated by blowing air jet (unlike the RTFOT). In this method the change in sample weight before and after test can also be measured. According to Airey

(2003) ageing done through this method may only remain limited to the 'skin' of bitumen in TFOT pans.



Figure 2.7: Typical TFOT oven (Wu, 2009)

2.8.2 Rolling Thin Film Oven Test (RTFOT)

According to evaluation of Mallick and Brown (2004) on the RTFOT procedure suggest that its effect on the ageing of tank bitumen is similar to that in hot mix during hot mix plant production. The research by the authors then went further on to explore the closeness of the two processes. Their research suggested the 'somewhat more' ageing severity in hot mix plant asphalt; however, the same researchers argued that RTFOT was reasonably capable to simulate short-term ageing.

A table comparing the salient features of RTFOT and TFOT is presented in Figure 2.5. As the table suggests, the operation of these two methods is fundamentally quite different, but yet these two tests have been interchangeably

used in common practice for laboratory ageing purposes. In a research ageing purposes. In a research Zupanick (1994) has questioned the interchangeable use of the two methods, however this opinion is has not been widely accepted.

Table 2.5: Comparison of TFOT & RTFOT (Shalaby, 2002)

Parameter	TFOT (ASTM D1754)	RTFOT (ASTM D2872)
Sample placement	Steel pans	Glass bottle
Dimensions	140mm O.D. 9.5 mm deep	64 mm O.D., 140 mm deep
Sample size	50 g per pan	35 g per bottle
Rotation	5.5 rev/min	NA
Rolling action	Na	15 rev/min
Forced air	Na	Heated air jet
Test duration	300 min	85 min
Test temperature	163 °C	163 °C
Limitations	• Skinning, a thin crust forms on sample surface • Test duration is too long for quality control/quality assurance	• Binder may leak from bottle particularly if polymer modified • Potential for segregation in modified binders

2.8.3 Pressure Ageing Vessel (PAV) Test

In the historical development of the PAV, original ageing studies were done at 2.07 MPa (300 psi) and 60°C for 6 days. The ageing caused by original method was deemed to be insufficient and too long. In order to increase the ageing rate and to reduce test duration the ageing temperature was raised. An ageing temperature of 100°C was selected but field validation revealed that it was overly

harsh for cold climates and too mild for hot climates. This problem was solved using three elevated temperatures to simulate a different general environmental condition as 90 °C, 100 °C, and 110 °C for cold, moderate and hot climate respectively. The pressure ageing vessel is preferred for long term ageing because of its following advantages:

- Volatile loss is minimised.
- Ageing can be accomplished without high temperatures.
- Large enough sample sizes can be accommodated.
- Field climate conditions can be approximated.
- Laboratory use is practical.

The research on the evaluation of PAV by Mallick and Brown (2004) using Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR) test results suggested that PAV was capable to simulate the in-place long-term ageing of the asphalt binder.

2.8.4 Ageing Methods on Asphalt Mixture

The study on asphalt recalls a brief literature review on the basic ageing technique on asphalt mixture. The literature review indicates the presence of the two fundamental tests to simulate short and long-term ageing of asphalt mixture namely 'The short-term ageing (STOA) procedure (AASHTO PP2)' and 'The Long-term ageing (LTOA) procedure (AASHTO PP2)'. The former method simulates ageing of asphalt mixture that will occur during mixing in plant and construction. In this procedure, aggregate is heated at 180 °C for a minimum period of 6 hours before mixing with bitumen. Hot aggregate and bitumen are then mixed for 90 seconds using mechanical mixer. The loose asphalt mixture is artificially aged in a

forced draft oven either at 135 °C for four hours or 154 °C for two hours depending on stiffness of binder. However, the actual short-term ageing time in field depends upon hauling distance. Researchers have shown that STOA is more rigorous process than Rolling Thin Film Oven (RTFO) test for simulation of short-term ageing.

A study by Lee et al. (2008) with use of Gel Permeation Chromatography (GPC) indicated that the ageing effect of standard RTFOT procedure (ASTM D2872) is less than that of STOA performed on the laboratory prepared asphalt mixtures. In the study by researchers, the two methods however did show a good correlation.

The LTOA procedure simulates the ageing of compacted asphalt mixture that it will undergo during 7 to 10 years of service life. In LTOA, compacted mixture of aggregate and bitumen is aged in a forced draft oven for 5 days 85 °C. LTOA ageing period can vary between 0 to 6 days; however, the standard time is 5 days. The mixture is compacted using a small steel roller at 116 °C. PAV ageing is indicative of the long-term ageing of bitumen and is comparable with LTOA of asphalt mixture. The pressure ageing vessel test is more rigorous process than LTOA.

2.8.5 Oxidation and Composition of Bitumen

The effect of oxidation on bitumen composition has been discussed in the previous sections. This section, however, is a brief summary of the previous discussions. Oxidation has a major role towards the durability and cohesive strength of bitumen. Oxidation results into the hardening and embrittlement of bitumen thus making it more prone to cracking and loss of performance.

Oxidation further results in change of chemical functionalities in the bitumen and its fractions. Some functionalities are present in the virgin unoxidised bitumen

while some of them are formed upon as a result of oxidative ageing of bitumen. In Figure 2.8 Petersen's Model of oxidation is shown. This model shows an increase in the polar fractions upon oxidation. This explain the fact that high temperature oxidation result into more hardening due to dispersion of the molecules during the process.

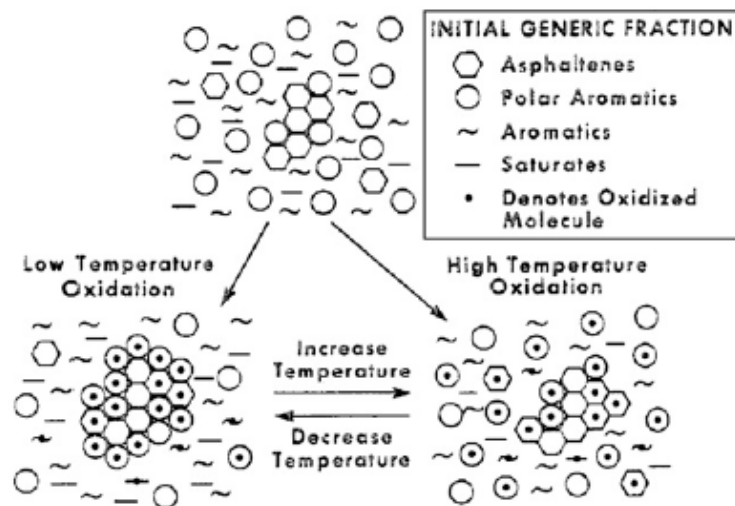


Figure 2.8: Petersen's Model of Oxidation Kinetics

2.9 MOISTURE DAMAGE

A research on cohesive or adhesive bond strength of asphalt should discuss moisture damage, its mechanism and factors affecting moisture damage etc. This also be to kept it mind that it is second important factor that affect the environmental damage to asphalt. This section aims at to discuss moisture damage in depth, so that it provides a theoretical frame work for testing in the cohesive strength of mastic.

Moisture damage is a complex interfacial phenomenon in asphalt mixture and can be defined as "Disintegration or deterioration of intrinsic property of asphalt concrete layer by entry of moisture that can be measured by asphalt concrete's

loss of mechanical properties” (Rotterdam et al., 2004). A more detailed definition of water damage is given “progressive functional deterioration of a pavement mixture by loss of the adhesive bond between the bitumen cement and aggregate surface (stripping) and/or loss of the cohesive resistance within the asphalt cement principally from the action of water” (Bagampadde et al., 2005).

Moisture damage majorly occurs during early life of pavement after construction unlike long-term ageing which occurs over extended period of time. Problems of ravelling and rutting can be observed in deteriorated pavements. Factors affecting moisture damage are shown in Table 2.6. It is important to note that aggregate properties influence moisture damage more than that of bitumen.

According to Bagampadde et al. (2005) aggregate consisting of high content of quartz and alkali feldspars show moisture sensitivity but aggregate consisting of pure quartz showed high resistance to moisture damage. Aggregates which contain alkali metallic elements (Na, K) show more moisture sensitivity, while aggregate having calcium, magnesium and iron show no moisture sensitivity. They showed that stripping was also manifested by surface characteristics of aggregate (Bagampadde et al., 2005).

Table 2.6: Factors affecting moisture damage (Sengoz and Agar, 2007)

1	Aggregate
	• Aggregate composition ○ Surface chemistry ○ Types of minerals ○ Source of aggregate • Physical characteristics ○ Angularity ○ Surface roughness ○ Surface area ○ Gradation ○ Porosity ○ Permeability • Dust and clay coating

	• Moisture content • Resistance to degradation
2	Bitumen
	• Chemical composition • Hardness • Crude source and refining process
3	Mixture design and construction
	• Air voids level and compaction • Permeability and drainage • Film thickness
4	Environment
	• Temperature • Freeze-thaw cycles • Dampness and pavement age
5	Traffic
6	Anti-stripping additives properties

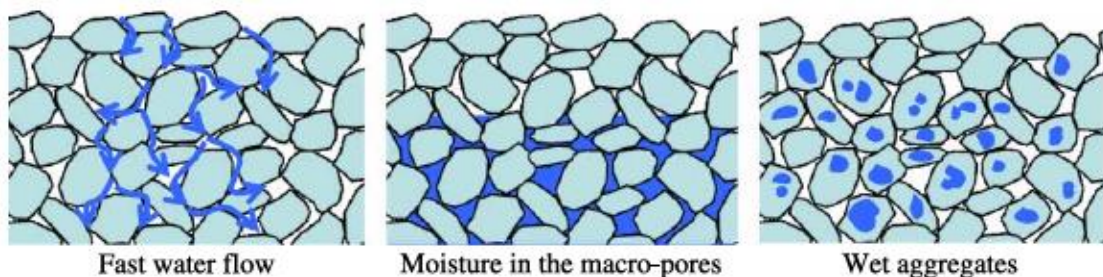
Similar to anti-oxidants, the compound to minimise the effects of stripping are called anti-stripping agents. These compounds usually consist of amino hydrogen which result in an increase of pH and improve adherence of binder to the aggregate surface (Rotterdam et al., 2004). The most common type of anti-stripping agent is hydrated lime. There are number of ways of adding hydrated lime into Hot Mixture Asphalt. Few of these methods include addition of lime to the mixer, addition to aggregate (in dry or wet condition), adding its slurry to dry aggregate before mixing, soaking or stockpiling aggregates (lime treated) before mixing (Jahromi, 2009).

Furthermore Huang et al. (2005a) showed that addition of hydrated lime (HL) to the binder before making asphalt mixture is effective in reducing moisture damage to the mixture. HL significantly increase fracture toughness at low temperatures without affecting its ability to dissipate energy through relaxation.

It also acts as a filler, improves strength and is helpful in reducing age hardening and moisture susceptibility (Jahromi, 2009).

2.9.1 Moisture Damage Mechanism

According to Kringos et al. (2008) there are three modes of moisture infiltration. The first being entry of water in connected macro-pores through rainfall (shown in Figure 2.9 a). This usually happens in open graded mixes designed for high permeability. In the second mode, stationary moisture in the form of liquid or vapour resides in the macro-pores as shown in Figure 2.9 b. This moisture may have entered through rainfall or through wet subgrade or humid environment. Third mode being the presence of water inside aggregate before laying of the wearing course and inadequate drying of aggregate (Figure 2.9 c). Water may also flow through these connected pore through 'pumping action' (when saturated wearing surface is subjected to traffic loading) as shown by Kringos et al. (2008).



**Figure 2.9: Moisture penetration into asphalt mix (a, b, c)
(Kringos et al., 2008)**

According to Tarrer and Wagh (1991) there are five mechanisms which produce moisture damage, these include; detachment, displacement, spontaneous emulsification, pore pressure, and hydraulic scouring.

In this regard, detachment means that a small layer of water separates the film of bitumen from the surface of aggregate. This is to be kept in mind that there is no breakage of the film of bitumen itself. This detachment further result in loss of adhesion. This theory can be fully explained from the theory of surface free energy, where surface tension of water is lower than bitumen.

The displacement theory relates to the bitumen film which is already broken and provide entry point for water. This entry point can be present due to improper coating or fracture in film layer system is subject to tensile stresses under repeated loading or thermal stresses. The rest of mechanism can be explained from the surface energy theory to the one similar to detachment theory.

The theory of spontaneous emulsification, pore pressure and hydraulic scouring are of least importance here. In spontaneous emulsification, bitumen (continuous phase) water (discontinuous phase) form an inverted emulsion, leading to moisture damage. This process is further increased in presence of additives and detrimental particulates which act as emulsifiers (Fromm, 1974). The pore pressure water theory relates to higher void content of asphalt mixture. The application of traffic load on water present in these interconnected voids can create a high pore water pressure and results in stripping. The hydraulic scouring is related to wheel action; therefore, it is related to surface asphalt course.

2.9.2 Moisture Damage Quantification and Role of Aggregate

In a study, Airey (2003) has summarised the moisture sensitivity evaluation methods used in the paving industry for bitumen and asphalt mixture. These methods include testing on the loose asphalt mixture and testing on compacted asphalt mixtures and with the conditioning procedures which try to simulate field conditions. These methods usually are made up of conditioning and evaluation

phase, also most of these methods use visual inspection of the aggregate surface in order to measure loss of adhesion between the bitumen and aggregate (called stripping). While some other methods which evaluate the moisture damage through mechanical tests on conditioned and unconditioned specimens. Table 2.7 outlines test methods use to evaluate moisture damage tests performed on loose mixture only.

Moisture damage in HMA pavements has extensively been documented since 1970's. The most common method used is the Lottman Method and some of its modified forms. The standard method used for moisture damage evaluation is AASHTO T283. Table 2.7 summarises the tests performed on loose aggregate coated with bitumen to measure the effect of stripping.

Table 2.7: Stripping tests for loose aggregate (Airey and Choi, 2002)

Test method	Water volume	Duration	Aggregate size	Sample size	Extra features
Static immersion test – AASHTO T182, ASTM D1664	400 ml distilled water	16 to 18 hours	Single size	100 g	-
Total water immersion test 'twit' [WHI 90]	Distilled water	48 hours	14 mm aggregate	-	25°C
Rolling bottle method – prEN 12697-11	250 ml deionised water	75 minutes	6.3 mm to 8 mm with 0.1 mm binder film	200 particles	Glass rod, flask rotated @ 40 rpm
Boiling water test [KEN 83] – ASTM D3625	500 ml distilled water	1 to 10 minutes	Single size or graded	200 to 300 g	Boiling water
Ancona stripping test (AST) [BOC 93]	200 ml distilled water	45 minutes	6 mm to 10 mm with 3 g of bitumen	60 g	Boiling water
Boiling water stripping test [CHO 93]	600 ml demineralised water	10 minutes	10 mm to 14 mm with 1.8% binder	200 g	Boiling water, Chemical attack
Ultrasound method [VUO 99]	Water	-	Test piece – 20 mm x 80 mm	2 g bitumen – 0.12 film	Ultrasound
Net adsorption test [CUR 93] - SHRP Designation M-001	2 ml of water	6 hours	Minus 4.75 mm	50 g	140 ml – bitumen-toluene sol
Modified net adsorption test [WAL 96]	2 ml of water	6 hours	Graded minus 4.75 mm	50 g	140 ml – bitumen-toluene sol
		8 hours			

The aggregate is the ingredient of asphalt mixture which contributes to more than 94% of the weight of mix and is coated with bitumen or mastic. The literature shows that surface area is the most appropriate parameter to compare the effect

of two different aggregates. The mass and volume of aggregate may give inaccurate results in this regard. The surface area of aggregate can be measured by using Dynamic Vapour Sorption (DVS) device.

Some aggregates used in pavements are hydrophilic and have affinity for water over bitumen. These aggregates are acidic and suffer from problems of stripping on exposure to the water. On the other hand, some aggregates are hydrophobic and have affinity towards bitumen as compared to water. These aggregates tend to be basic and do not suffer from stripping. Research by Scholz (1995) showed that mineral aggregate affects increase in stiffness modulus. The surfaces of aggregate having more alkaline earth metals like calcium and magnesium are less susceptible to bitumen-aggregate de-bonding (Scholz, 1995).

Aggregates having different minerals are charged in different way. This charge carried by these minerals allow researchers to classify aggregates as acidic and basic. The acidic aggregates including quartz and granite are chiefly silicates in nature. These aggregates are negatively charged when they are in contact with water while forming SiO_3^{2-} ions. The basic aggregates such as limestone, on the other hand, mainly forms carbonates when in contact with water and are remain positively charged containing Ca^{+2} . The aggregates having high silicon oxide content, e.g. quartz and granite are classified as 'hydrophilic' and are generally more difficult to coat with bitumen than basic rocks such as basalt and limestone. In addition to this aggregates having siliceous component are prone to moisture damage. The surfaces of aggregate having functional group namely 'Hydroxyl group' has affinity for carboxylic acids and moisture, thus creating a weak bond which can be broken by presence of water.

The presence of micas, chlorite and hydrated iron oxides are of particular importance. This is because they lower the overall performance of bituminous

mixture. This is why, fillers with high mica content are avoided for use in mixture as mica affects durability of mixture (Loorents and Said, 2009). Usually stripping occurs in the coarse aggregate part of the mixture and in some cases fine aggregate may be more moisture sensitive and damage may occur in the fine aggregate of mixture (Sengoz and Agar, 2007).

The testing done on asphalt mixtures does not separate the bitumen and aggregate adhesion which results in improper identification of moisture damage. This finding encourages researchers to further investigate the moisture damage assessment using dynamic shear rheometer (Wu, 2009; Scholz, 1995; Scholz, 1995; Cho and Bahia, 2010; Rotterdam, 2004).

2.9.3 AASHTO T283 (damage in asphalt mixture)

The purpose of the AASHTO T283 (Modified Lottman) test is to evaluate moisture susceptibility of asphalt mixture. The test is performed by compacting asphalt specimens to an air void level of $7 \pm 1\%$. In order to perform these tests, three specimens are selected as control and tested without any moisture conditioning while three other specimens are selected to be conditioned. These three specimens are vacuum saturated with water at saturation level of 70%–80%. These specimens are then air tightened with a plastic wrap and are then placed in plastic bag containing 10 millilitre of water and sealed again. The procedure involves a freeze cycle at $-18\text{ }^{\circ}\text{C}$ for further 16 hr. Next step involves soaking cycle in warm water bath which is constantly maintained at $60\text{ }^{\circ}\text{C}$ for 24 hr while keep in a water head of 25mm above the specimen. After this warm soaking cycle, specimens are removed and left in a water bath maintained at $25\text{ }^{\circ}\text{C}$ for 2 hours. In next step specimens are tested in UTM for their indirect tensile strength (ITS). This done by loading them at 50 mm/min at $25\text{ }^{\circ}\text{C}$. During this test force of

failure is measured (as shown in Figure 2.10). Tensile strength is calculated using following equation.

$$S_t = \frac{2,000 \times P}{\pi \times t \times D}$$

Where S_t = tensile strength (kPa), P =peak load (N), t =core thickness (mm) and D =core diameter (mm). The ratio of the ITS of wet conditioned to dry conditioned gives a parameter. This parameter/index ($TSR=S_1/S_2$) is indication of the resistance to moisture damage (Sengoz and Agar, 2007). The change in strength and modulus from dry to saturated conditions are important to evaluate the extent of moisture damage.

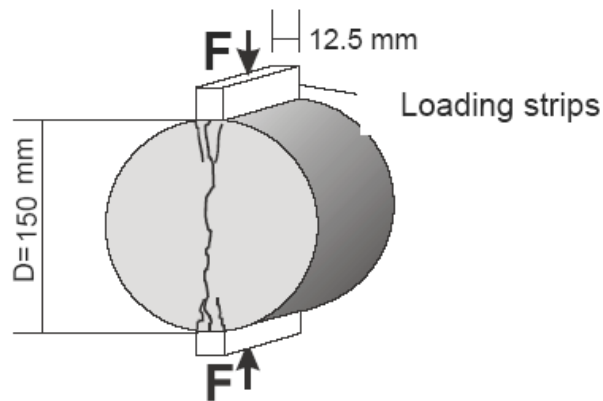


Figure 2.10: Indirect Tensile Stiffness Modulus (ITSM) test

According to Sengoz and Agar (2007) the Modified Lottman Test includes the short-term ageing of asphalt mixture (ageing during mixing, transporting and compacting) and early service life . In the pavement long-term ageing and water damage in the service life of pavement occur simultaneously. This means long-term laboratory ageing tests representing the ageing of asphalt binder during the service life of the road should be adopted in the AASHTO T283 method. The other issue with this method is that in real conditions, pavements undergo cycling of

environmental conditions, in the presence of water there is repeated hydraulic loading and pore water pressure develops. AASHTO T283 does not consider the effect of pore pressure but rather consider single loading effect on conditioned specimen.

2.9.4 SATS Test

In relation to moisture damage, Saturation Ageing Tensile Stiffness (SATS) test is quite often used in Nottingham Transportation Engineering Centre (NTEC). The test is quite unique in a sense that it combines ageing and moisture damage mechanism. These both important aspects of durability are offered in a single laboratory test. The test comprises of initial saturation before placing of samples of compacted asphalt core in environment of high temperature (85 °C) and pressure (2.1 MPa). In case of standard test, this is done in the presence of moisture during extended period of time (65 hours) (Grenfell et al., 2014). The measurements of stiffness modulus are then made before and after the test. The ratio of stiffness modulus after and before the test and the specimen saturation after the test (retained saturation) are the indication of ageing/moisture sensitivity of the compacted mixture (Collop et al., 2004). This test is particularly useful as gives similar results as AASHTO T283 when the asphalt mixtures are ranked in terms of their moisture sensitivity. The test set up is shown in Figure 2.11.

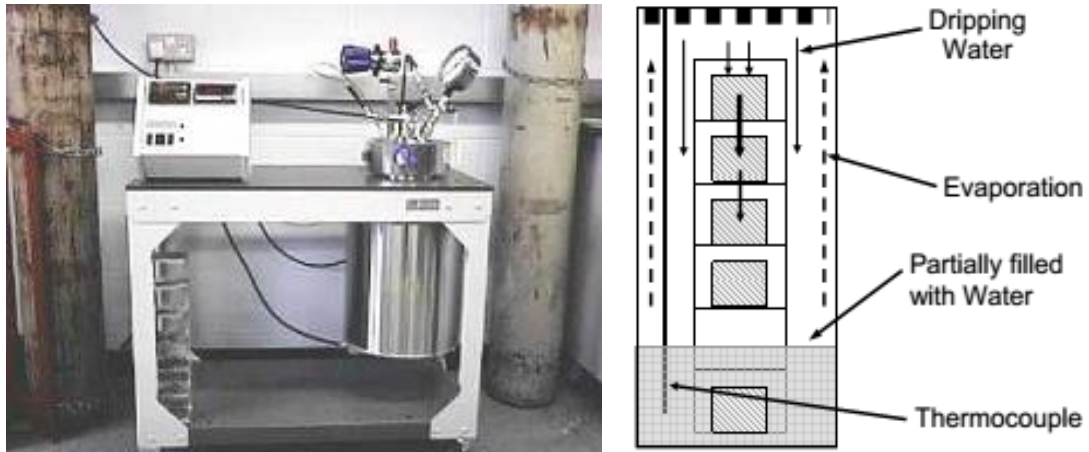


Figure 2.11: SATS test set up

In a research Grenfell et al. (2014) studied SATS and Rolling Bottle Test (RBT) to study mixture moisture susceptibility and surface energy approach to study evaluate moisture sensitivity using mixture constitutive material properties. The results illustrated a close agreement between three techniques to evaluate the moisture susceptibility. The research showed that empirical tests SATS and RBT show similar ranking of moisture susceptible binder as that to one showed by surface energy and mineralogical composition determined by MLA.

2.10 ADHESIVE AND COHESIVE FAILURE

According to Lottman et al. (1974) the measurement of adhesion with tensile-type bond is useful to identify the moisture damage potential of asphalt mixture due to stripping (as shown in Figure 2.12). This reason for this poor bond depends on the hydrophilic nature of aggregate, presence of wet aggregate in mix, higher amount of chemicals and freeze/thaw cycle. Also according to Bhasin and Little (2009) the distresses in bituminous mixtures like rutting, fatigue cracking, and water damage are related to nature and strength of the bond strength between these materials. Figure 2.12 shows the basic outline of the two failure mechanisms in asphalt.

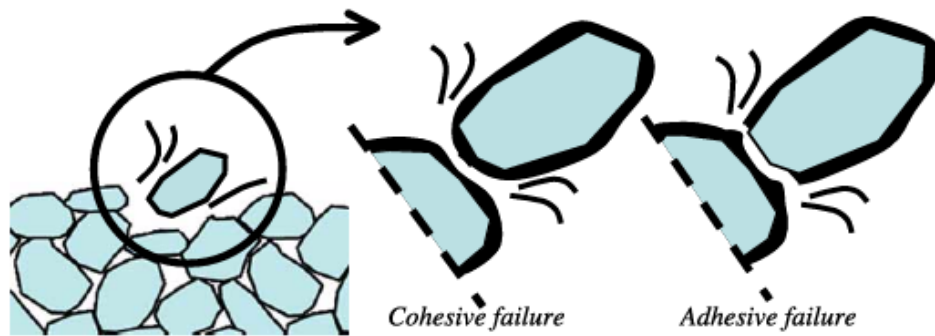


Figure 2.12: Cohesive vs. Adhesive dislodging of an aggregate (Kringos et al., 2008)

The physiochemical bond as a result of surface free energy and chemical reaction at the bitumen-aggregate interface is also a useful method to quantify the bond strength. This technique helps to establish the surface free energy of binder and aggregate which further help to compute the work done due to bond strength in dry and wet conditions.

A list of different approaches, theories and associated mechanism for adhesive/cohesive bond of bitumen on the aggregate surface are presented in Table 2.8 . The references from the table have been omitted for simplicity and can be found in the cited paper.

Table 2.8: Different bitumen aggregate adhesion theories (Bagampadde et al., 2004)

Approach	Law/Theory	Probable Mechanism
Mechanistic tenacity	Contact mechanics theory	- Hot bitumen fills the aggregate pores, cools and sets into a solid in contact with aggregate. - The interlock and key form a strong bond.

		• The bond strength depends on roughness and chemistry of the two, and bitumen cooling rate.
Molecular orientation	Electrostatic theory	• When hot, bitumen polars dissociate and diffuse towards the interface. • Induced polarisation of additional bitumen parts leads to interface build-up. • Electrostatic attraction between the oppositely charged species causes adhesion.
Chemical reaction	Valency theory	• When bitumen and aggregate are in contact, reaction between the adsorbable (bitumen) polar components and the desorbent (aggregate) reactive sites takes place leading to chemical bond formation. • In general, adhesion is specific to individual bitumen-aggregate pairs.
Energy change	2 nd Law of thermodynamics	• Equilibrium shifts such that the total of Surface Free Energies of the phases involved (bitumen, air, water and asphalt) becomes a minimum possible to ensure maximum stability. • Adhesion process is faster if bitumen has lower surface energy (when hot or with liquid additives) or when aggregate has higher energy with respect to the enveloping medium (air or water).

The cohesive strength in asphalt is the failure caused by separation of the molecules that holds the binder particles together within an asphalt film. The presence of environmental factors of moisture damage not only affect the adhesive failure but also affective the cohesive properties of the binder thus severely affecting the integrity of the pavement (Cho and Bahia, 2010). The presence of water can break this cohesive bond within the binder through the process of emulsification. The occurrence of the process of emulsification, affect the surface of the substrate/aggregate which can further lead to the increase in loss of cohesion and adhesive bond strength (Fromm, 1974). Three types of

bond failures that can occur in asphalt mixture are presented in the Figure 2.13. The failure starts by the breaking of inter-molecular bond within bitumen. The bitumen individual molecules are associated through secondary bond forces which are weaker than covalent bond. These forces are reversible and are in dynamic equilibrium which means they keep on making and breaking under the influence of external effect like temperature. These forces also dictate the physical properties of bitumen. According to Barbour and Petersen (1974) Mack's report outlines the important intermolecular forces in the bitumen namely dipole, dispersion, electron donor-acceptor, and hydrogen bond.

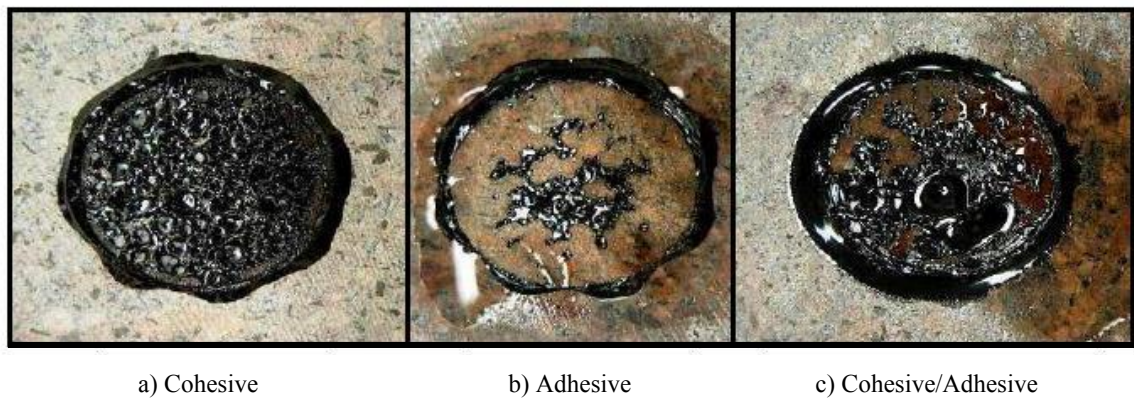


Figure 2.13: cohesive, adhesive and hybrid failure (Canestrari et al., 2010)

The Kringos et al. (2008) model explains the moisture infiltration while Bagampadde et al. (2004) summarises the theories in the literature to explain the bitumen and aggregate adhesive bond.

2.10.1 Surface Energy Theory and Bond Strength

Surface energy is defined energy that is present as excess at the surface of a material when compared its bulk mass. This free energy of material is the result

of intermolecular forces difference acting on the surface as compared to the forces acting on molecules inside the bulk material. As a result of which surface molecules get attracted to the bulk material.

In the case of liquids, the term surface free energy is replaced with surface tension. The forces responsible for surface free energy have two components; non polar (dispersive) and polar component. The dispersive forces are named as Lifshitz-van der Waal forces. The polar forces are divided into two; Lewis acid and Lewis base type of forces. The surface energy can be written as

$$\gamma^{\text{Total}} = \text{Lifshitz-van der Waal component} + \text{Acid base component}$$

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

Surface free energy dimension corresponds to that of force per unit area i.e. mJ/m² or erg/cm². In pavement materials we take into account surface energies of bitumen and aggregate, and the effect of these on bitumen-aggregate adhesion in dry and wet conditions.

Adhesion between a solid and liquid can be given by

$$W_{SL} = \gamma_{SA} + \gamma_{LA} + \gamma_{SL}$$

Where S, L and A represents solid, liquid, and air respectively.

The work of adhesion, W_{12} , can also be written as

$$W_{12} = \gamma_1 + \gamma_2 + \gamma_{12} \text{ (Dupre's equation)}$$

where; γ_1 = surface energy of material 1

γ_2 = surface energy of material 2

The moisture damage is dependent on the surface energy interactions of bitumen, mineral aggregate and moisture. The bond strength of bitumen-aggregate can be computed using surface energy concept. The bond strength (cohesive or adhesive) has to be computed both in dry and wet conditions. The strength of the adhesive bond in dry conditions can be measured using equation given as.

$$\Delta G_{BA}^a = 2\sqrt{\gamma_B^{LW} \gamma_A^{LW}} + 2\sqrt{\gamma_B^+ \gamma_A^-} + 2\sqrt{\gamma_B^- \gamma_A^+}$$

In order to measure adhesion in wet conditions following equation can be used.

$$\begin{aligned} \Delta G_{BWA}^a = & \left\{ \left(\left(\sqrt{\gamma_A^{LW}} - 4.67 \right)^2 \right) + \left(2 \times \left(\sqrt{\gamma_A^+} - 5.05 \right) \times \left(\sqrt{\gamma_A^-} - 5.05 \right) \right) \right\} \\ & + \left\{ \left(\left(\sqrt{\gamma_B^{LW}} - 4.67 \right)^2 \right) + \left(2 \times \left(\sqrt{\gamma_B^+} - 5.05 \right) \times \left(\sqrt{\gamma_B^-} - 5.05 \right) \right) \right\} \\ & - \left\{ \left(\left(\sqrt{\gamma_B^{LW}} - \sqrt{\gamma_A^{LW}} \right)^2 \right) + \left(2 \times \left(\sqrt{\gamma_B^+} - \sqrt{\gamma_A^+} \right) \times \left(\sqrt{\gamma_B^-} - \sqrt{\gamma_A^-} \right) \right) \right\} \end{aligned}$$

γ_B^{LW} , γ_B^+ and γ_B^- are surface free energy components of bitumen.

A Goniometer help to measure static contact angle of the probe liquids on binder surface under static conditions as shown in Figure 2.14. In order to measure contact angle under dynamic conditions the Dynamic Contact Angle analyser (DCA) as well as Wilhelmy Plate. The latter is used to measure this contact angle under dynamic conditions as shown Figure 2.15. The contact angle can then used to compute surface free energy components of bitumen. The surface free energy of aggregate is computed using Dynamic Vapour Sorption (DVS). The surface energy components calculated with the help of these instruments are then used to compute the work of adhesion with and without presence of water. This work of adhesion or bond energy is then used to calculate moisture sensitivity of asphalt mixture.

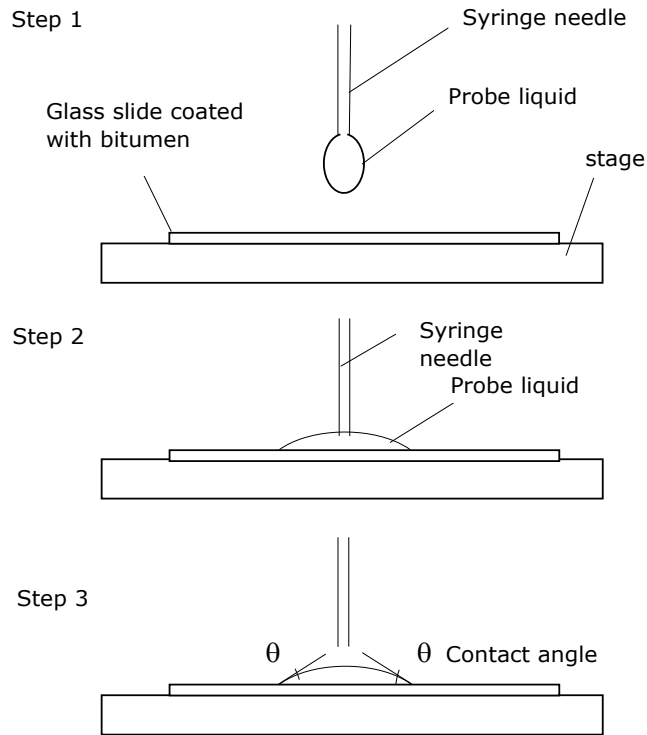


Figure 2.14: Static Contact Angle measurement –Schematic diagram

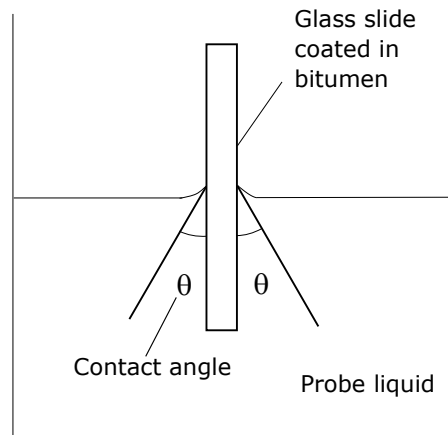


Figure 2.15: Contact Angle Measurement; Wilhelmy Plate Technique

The ratio of adhesive bond energy in dry condition (ΔG_{BA}^a) to bond energy in presence of water (ΔG_{BWA}^a) maybe used predicts moisture sensitivity of bituminous mixtures. The ratio of the two parameter is called R_1 . A higher value of R_1 shows better moisture damage resistance (Bhasin, 2006). In a study on different mixtures, it was inferred that asphalt mixture with ratio ' R_1 ' more than 1.5 were more resistant to moisture than the one with a ratio lower than 0.8.

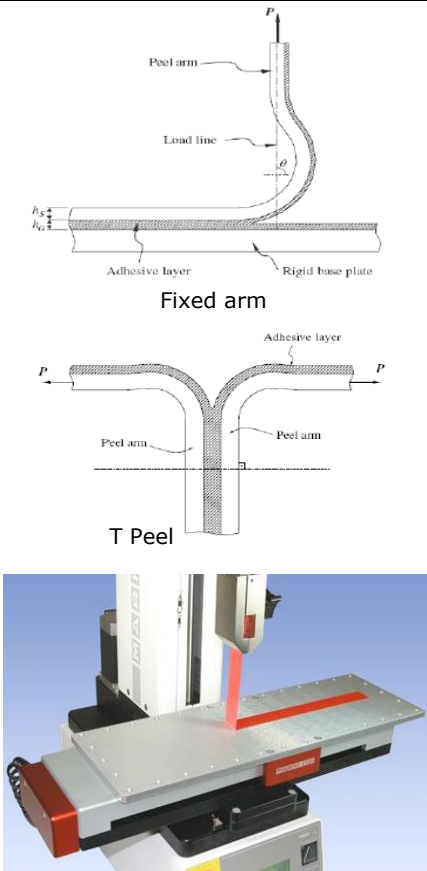
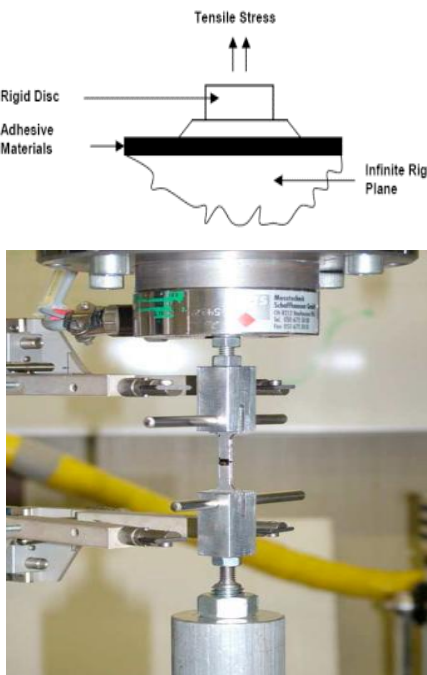
Bhasin (2006) further multiplied R_1 ratio with specific surface area (SSA) of aggregate to incorporate surface roughness and surface area effects.

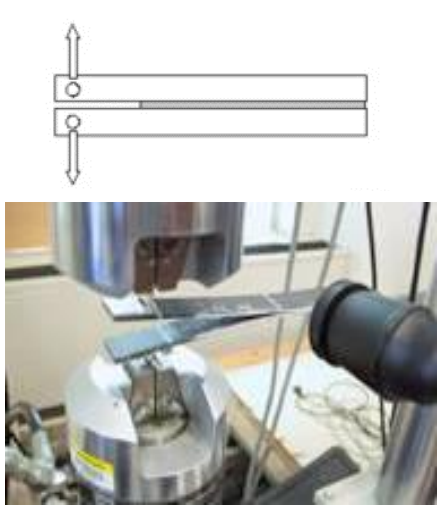
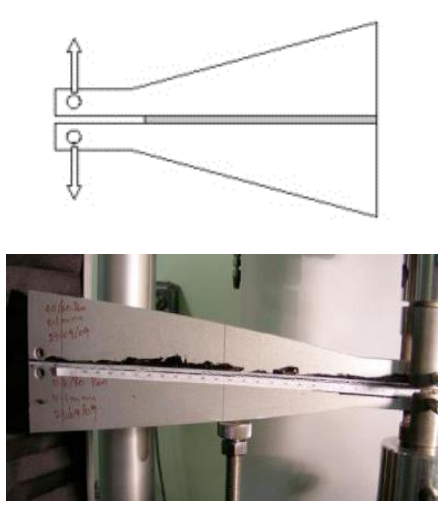
2.11 PULL OFF TESTING AND COHESIVE STRENGTH

The second fundamental factor affecting durability and bond strength of asphalt has been briefly discussed in section 2.9. This section focus on the direct pull off test with main emphasis on the cohesive strength of bitumen. This is mainly due to the advantage of this test using the test techniques which are based on the most fundamental principle but at the same time are advanced ones to measure the bond strength. These tests methods have the capability to address the cohesive strength of bitumen.

Jakarni (2012) summarised the pull off tests which helped to formulate his testing technique using a new method for pull off testing to evaluate the bond strength. The methods discussed included Peel test, pull off test, double cantilever beam (DCB) test, and tapered double cantilever (TDCB) test as shown in Table 2.9.

Table 2.9: Different types of Adhesion tests (Jakarni, 2012)

Adhesion test Methods	Brief Descriptions	Figures
Peel Test	- Simple adhesion test method conducted by peeling a thin flexible adhesively bonded peel arm at a specified angle and deformation rate. - Typically used to measure the adhesive bond strength of bonded joints and laminates of composite materials in aerospace and automotive industries. - Based upon Elastic-Plastic-Fracture-Mechanics (EPFM) approach. Various standards have been developed (differ in the way that the load is applied but remain the same in the basic principles). - Useful for predicting the initial capability of adhesive materials. - Resulted in complex deformation behaviour of the tested specimens (i.e. cannot measure the fundamental aspect of adhesion between adhesive layer and substrates, and cannot directly assess the cohesive strength of adhesive materials). - Results are dependent on various factors such as peel angle, thickness and mechanical properties of peel arm, deformation rate and test temperature. - Results usually reflect the stress and strain of specimens failing under conditions of extensive yielding. - Include a large degree of plastic deformation of peel arm.	 The figure illustrates the Peel Test through two diagrams and a photograph. The top diagram, labeled 'Fixed arm', shows a peel arm being lifted at an angle θ from a rigid base plate, with labels for 'Peel arm', 'Load line', 'Adhesive layer', and 'Rigid base plate'. The bottom diagram, labeled 'T Peel', shows a T-junction configuration with two peel arms being pulled in opposite directions, labeled 'Peel arm' and 'Adhesive layer'. The photograph shows a mechanical testing machine performing a peel test on a red adhesive specimen.
Pull Off Test	- Conducted by measuring the tensile stress required to detach or fracture the coatings of adhesive materials in direction perpendicular to substrates. - Typically used to measure the mechanical tensile strength of paint films, varnishes, mortars and concretes. - Various testing techniques and procedures have been developed. - Useful in comparing properties and providing relative ratings of different types of adhesive materials. - Can be applied using wide ranges of substrates (i.e. metals, plastics, woods and aggregates). - Results are influenced by the procedures for specimen preparation, deformation rate and test temperature. - Possible problems are due to unevenly distributed tensile stress throughout the coated surfaces.	 The figure illustrates the Pull Off Test through a diagram and a photograph. The diagram shows a 'Rigid Disc' applying 'Tensile Stress' to 'Adhesive Materials' bonded to an 'Infinite Rigid Plane'. The photograph shows a mechanical testing machine with a pull-off head attached to a specimen, performing the test.

Double Cantilever Beam (DCB) Test	• Conducted by pulling apart two beams of identical substrates with layer of adhesive materials in between, at certain deformation rate. • A crack is initiated first by inserting a wedge into the adhesive materials (i.e. presence of flaws). • Typically used to measure the fracture resistance of adhesive and bonded joints of a thin adhesively bonded fibre composite materials under mode I tensile loading conditions. • Based upon Linear-Elastic-Fracture-Mechanics (LEFM) approach. • Results need to be analysed using several different approaches such as Corrected Beam Theory (CBT), Experimental Compliance Method (ECM) and ASTM Method.	
Tapered Double Cantilever Beam (TDCB) Test	• TDCB test is similar to the DCB test in terms of basic principles and procedures for specimen preparation, except the two beams of identical substrates are tapered away from the point where the load is applied. • Results are independent of crack length values. • Useful for measuring tough adhesive materials without the occurrence of plastic deformation of the arms. • Can be used to determine the rate of crack growth under various cyclic loading and environmental conditions. • Based upon Linear-Elastic-Fracture-Mechanics (LEFM) approach. • Relatively complex and expensive in term of specimen preparation.	

In their research, Poulidakos and Partl (2011) discussed four stages of pull off bond failure, this failure mode is quite peculiar to tensile type pull off tests especially when cohesive failure is more likely to occur as shown in Figure 2.16. In this figure four stages of failure are shown. This also contains the sample (extreme right) tested at low temperature for a proper brittle failure to occur. The decrease in temperature has changed the failure mode. In case of the ductile failure the phenomena happening is called cavitation. This structure is due to nucleation of the micro-voids either present at the substrate surface or within the binder. This dendritic type formation is called fibrillar structure. This type of phenomena is more visible ductile type failure. In next Figure 2.17, an attempt by the researchers was made to relate these four stages of failure with the material response under the application of load.

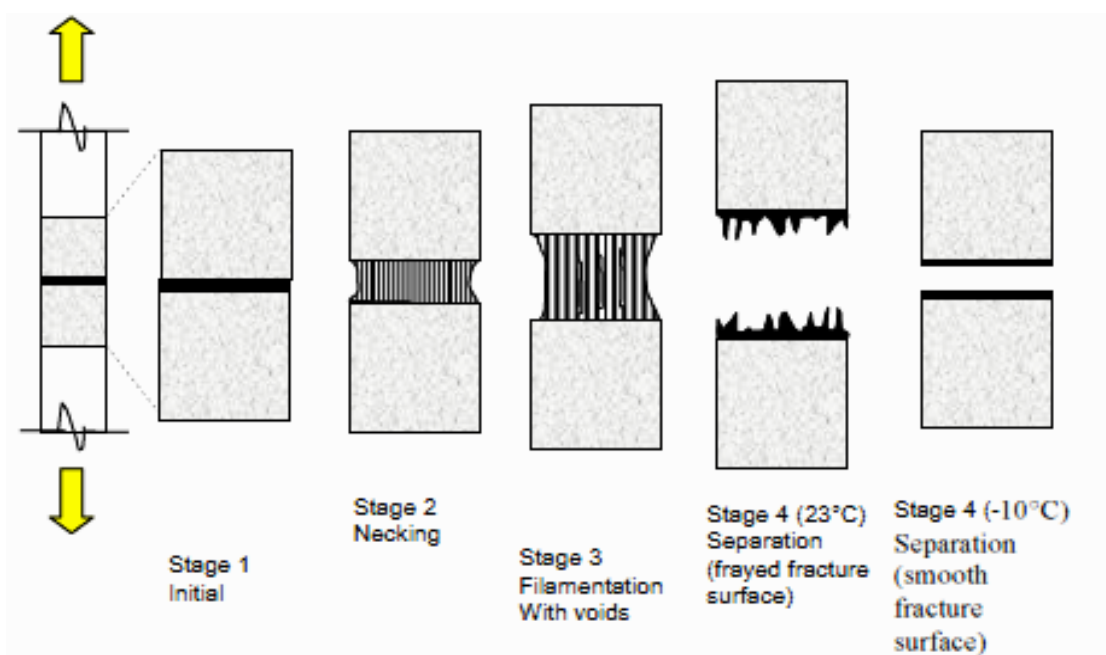


Figure 2.16: Four stages of bond failure (Poulikakos and Partl, 2011)

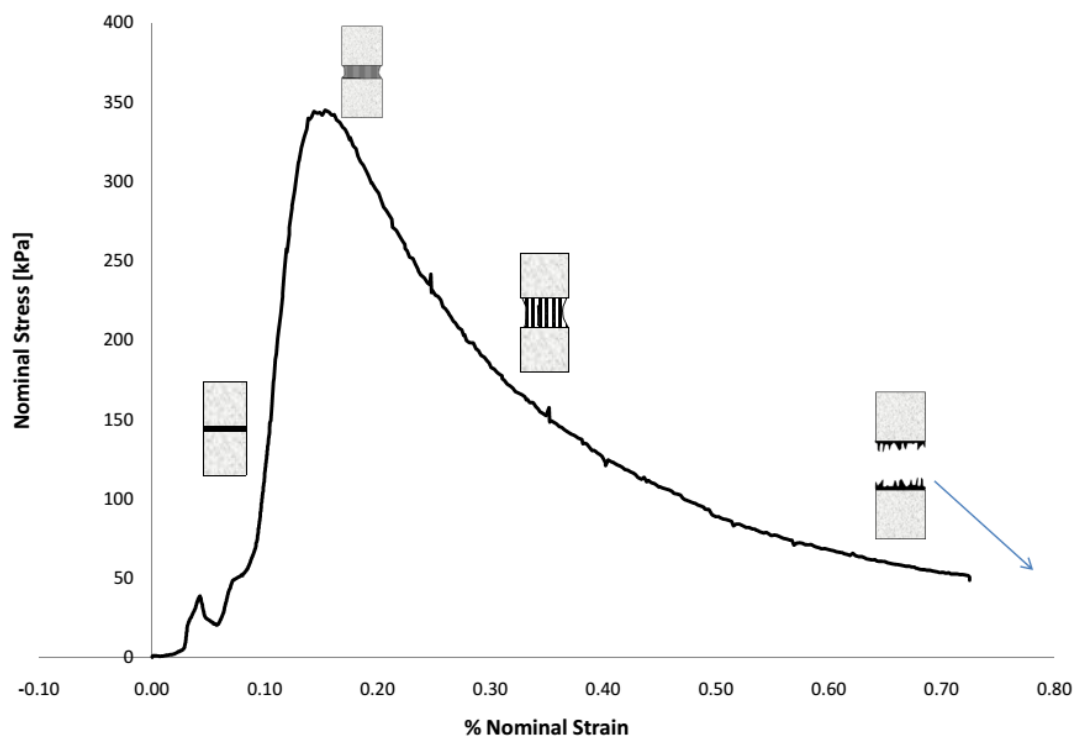


Figure 2.17: Stress strain curve for ductile type failure (Poulikakos and Partl, 2011)

2.12 BITUMEN RHEOLOGY EVALUATION

The definition of rheology is rooted in the Greek words “ρεω” and “λογος”. The former has its meaning “to flow” and later as “word, science” leading to definition “the study of the flow” as described by Ferguson and Kembrowski see Airey (2002). The behaviour of bitumen is time and temperature dependant, so its flow properties (in stiffer or viscous phase) leads bitumen to be classified as rheological material. This means its behaviour can be studied using the methods in the domain of rheology.

Rheological studies on bitumen are mainly studied using the Dynamic Shear Rheometer, which is a complex and powerful instrument for characterising the flow properties of bitumen. This testing system forms the essential part of the United States performance based binder specifications contained in their Superpave test protocols. In the United Kingdom, ‘Design Manual for roads and Bridges, Volume 7: Pavement Design and Maintenance’ and the Highway Agency’s Specification for Highway Works require rheological studies of binder to be performed by means of DSR testing (Airey and Hunter, 2003).

In DSR testing viscoelastic moduli of bitumen are measured in oscillatory (sinusoidal) loading mode. The data measurements are made at different temperatures, frequencies, strain and stress levels. Essential basic parameters measured in DSR are complex modulus and phase angle at intermediate to upper testing temperatures (5-85 °C). This device uses time-temperature superposition to construct thermo-rheologically simple linear viscoelastic master curves.

2.12.1 Principle and System

DSR can be used in controlled strain and controlled stress mode. In the former, the machine applies sinusoidally shear load applying a constant strain to bitumen film thickness and measures the resulting stress. In stress controlled mode sinusoidally shear load with constant stress and measures corresponding strain.

The DSR test is performed by through oscillation of the spindle about its axis of rotation. In this rotation, the plate first moves from point to B. After this the plate changes its direction and moves point C while making its way from point A. In next step it moves back to original point A from point C. This completes one loading cycle. During this cycle, upper plate is made to rotate around its axis by application of the torque while the base spindle is kept fixed during the operation as shown in Figure 2.18.

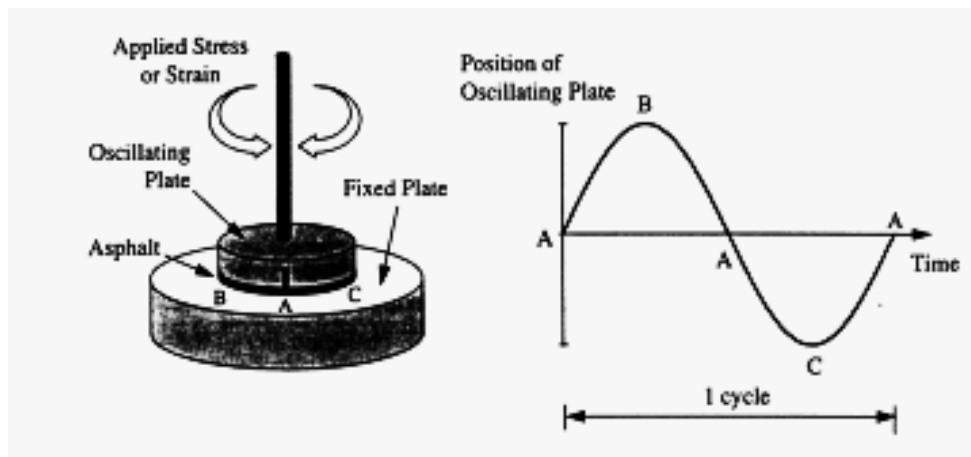


Figure 2.18: Schematic outline DSR Test

DSR consists of three major parts: 1) rheometer, 2) controller, and 3) the computer. The rheometer has a housing, motor for applying torque, transducer to measure response and a temperature control and measurement system. The controller acts as an interface between the rheometer and computer and contains

data acquisition and signal system. The rheometer is operated by an inbuilt software which performs various types of tests and analysing of the resulting data. A schematic diagram of DSR is shown in Figure 2.19.

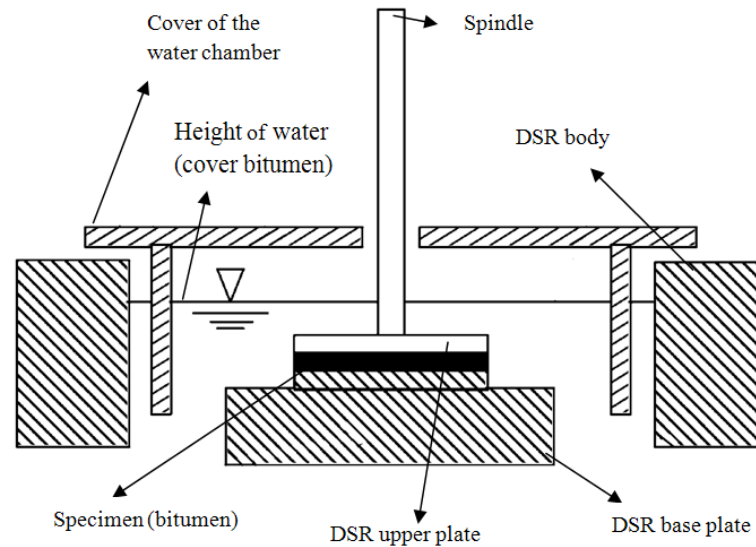


Figure 2.19: DSR Schematic diagram (Airey and Hunter, 2003)

2.12.2 Viscoelastic Parameters

The basic rheological parameters measured in rheological testing are complex modulus (G^*) and phase angle (δ). Complex modulus (G^*) is the material resistance to shear deformation under cyclic loading, whereas phase angle refers to the lag between applied stress and strain (as shown in Figure 2.20). The in-phase ($\delta = 0^\circ$) refers to pure elastic behaviour while out-of-phase indicates the pure viscous response. The ageing of bitumen and mastics results in an increase of complex modulus (G^*), storage modulus (G') and loss modulus (G'') while phase angle (δ) decreases. The decrease in the gap of the DSR plates results in the reduction of complex modulus while impacting the other parameters accordingly (Rotterdam et al., 2004). In rheological testing, the shear stress and strain are calculated as:

$$\sigma = 2T/\pi r^3$$

$$\gamma = \theta r/h$$

here γ = shear strain (%), θ = deflection angle, σ = shear stress (Pa), T = torque (Nm), and r = radius (m)

The viscoelastic parameters are as follows:

$$G^* = \sigma^* / \gamma^*$$

G^* = Shear modulus

σ^* = Peak stress

γ^* = Peak strain

$$G^{*2} = G'^2 + G''^2$$

$G' = G^* \cos \delta$ = storage modulus = elastic component

$G'' = G^* \sin \delta$ = loss modulus = viscous component

These rheological parameters can be calculated as described by Airey and Hunter (2003). The sinusoidally varying shear stress and resulting strain (Figure 2.20) can be expressed as:

$$\sigma(t) = \sigma_0 \sin \omega t \text{ and } \gamma(t) = \gamma_0 \sin (\omega t + \delta)$$

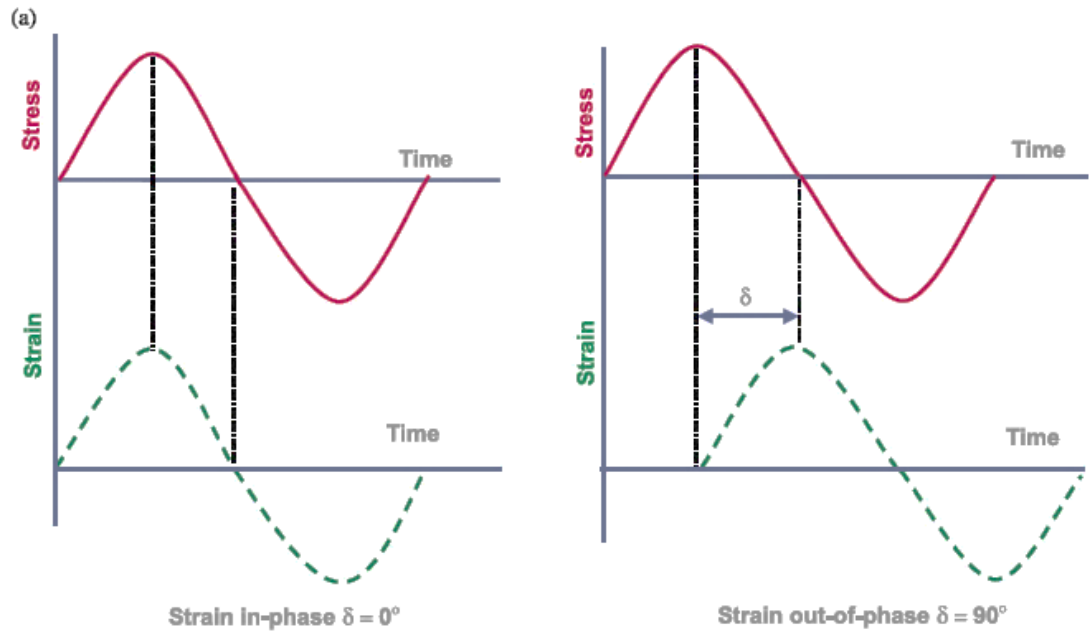


Figure 2.20: The phase difference (Shalaby, 2002)

The sinusoidally varying stress and strain can also be represented by another complex number notation as

$$\sigma^* = \sigma_0 e^{i\omega t} \text{ and } \gamma^* = \gamma_0 e^{i(\omega t + \delta)}$$

The complex shear modulus (G^*) is then defined as

$$G^* = \sigma^* / \gamma^* = (\sigma_0 / \gamma_0) e^{i\delta}$$

So

$$G^* = (\sigma_0 / \gamma_0) \cos \delta + i (\sigma_0 / \gamma_0) \sin \delta$$

$$G^* = G' + iG''$$

It is more useful to characterise bitumen in the linear viscoelastic range because characterisations of bitumen in the non-linear range make mathematical modelling of bitumen complex and difficult to characterise in laboratory (Airey, 2002).

2.12.3 Parallel Plate Geometry

In DSR testing protocols various test geometries are used, including parallel plate (Figure 2.21) and cone and plate geometries. The researchers in paving industry mostly use the parallel plate assembly and its modifications. The 8mm plate is used for intermediate design temperature (5 to 40 °C) and at high temperature (40 to 85 °C) 25mm geometry is used. The gap size used for 8mm plate is 2mm while for 25mm plate, the gap is maintained at 1mm. The use of these plates is as follows

- 8-mm parallel plates with a 2-mm gap when $0.1 \text{ MPa} < G^* < 30 \text{ MPa}$.
- 25-mm parallel plates with a 1-mm gap when $1.0 \text{ kPa} < G^* < 100 \text{ kPa}$.

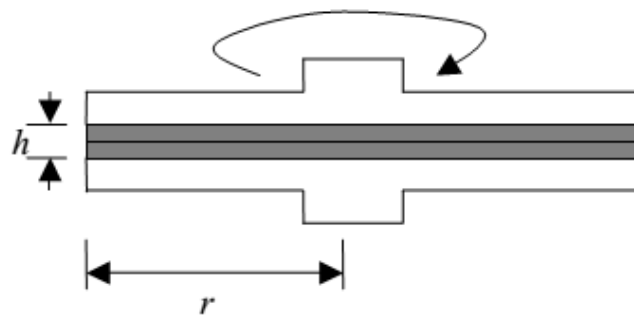


Figure 2.21: Testing geometry of DSR (Rahman, 2004)

In order to measure rheological properties, two types of tests are performed namely; strain (amplitude) sweep and frequency sweep either in controlled-stress or strain controlled mode. The strain sweep test is used to define the region of linear behaviour. The limit of linear viscoelasticity is defined as the point beyond which the value of complex modulus decrease to value that is corresponding to 95% of its G^* at zero strain. In a particular test, the temperature and strain/strain level used depend on the stiffness of binder which depends on the penetration and ageing history of binder being tested.

Few other plate geometries also serve their specific purpose in asphalt rheology area e.g. cup and bob geometry and cone and plate geometry. The cup and bob geometry is used for low viscosity material response while cone and plate geometry is used to measure the response in non-linear region. However, if temperature sweep test is performed then parallel plate geometry is preferred over cone and plate due to variation of gap with thermal expansion.

2.12.4 Time-Temperature Superposition & Master Curves

In rheological testing measurements obtained at different temperatures in the DSR can be fitted on a master curve at a specific reduced frequency by the use of shift factors calculated through the Arrhenius and Williams–Landel–Ferry (WLF) equation. The shifting is done by use of time-temperature superposition principle (TTSP).

The master curve is constructed at a reference temperature (arbitrarily selected). This means that rheological parameters obtained at higher and lower temperatures can be transposed graphically into lower and high frequencies respectively. This process of shifting, manually or through optimisation, helps to make a continuous master curve. The two fundamental rheological material responses can be plotted for master curves through the use of shift factors.

2.13 FILLERS AND ASPHALT DURABILITY

Filler can be defined as “solid material capable of changing the physical and chemical properties of materials by surface interaction or its lack thereof and by research on the filler effect on bitumen was conducted by Richardson. The effect

of bitumen, in his own words in a later publication is “the writer called attention... to the fact that the more or less satisfactory or unsatisfactory nature of a sheet asphalt pavement depends on the surface area of the particles composing the mineral aggregate of sand and filler entering into its construction, the amount of bitumen which may be used in such a mixture, without being present in excess, being dependent on the extent of the sub- division of the aggregate and its available surface area to which bitumen may adhere” (Richardson, 1915).

Another widely reported work in literature is by Einstein in 1911 who discussed the effect of ‘suspended particles’ in a liquid. These filler particles linearly increased the stiffness of the suspension system by magnitude of Einstein coefficient.

In an important study in domain of filler was by Rigden (1947), who divided the filler properties into primary (intrinsic) and secondary characteristics (derived). The primary characteristics included particle density, particle shape, particle surface texture, particle size distribution and its surface area. the secondary characteristics included bulk density, fractional voids, void diameter and permeability of fillers.

He also devised a test method which “sum up the fineness of the whole material, i.e. it measure a secondary characteristics of a filler which is dependent on a number of the primary characteristics” (Rigden, 1947). The detailed discussion of Rigden voids can be found in section 2.13.1.

In a study Grabowski and Wilanowicz (2008) summarised properties of filler from early 20th century research.

- The interstices in the fillers are filled with bitumen. The filler particles provide the contact points between the particles of aggregate and bitumen.
- It acts as cementing material for the aggregate particles while forming a high-consistency binder/mastic.
- Acts as an extender of the bitumen and may stiffen the binder depending upon the nature of the filler.
- The fineness of the filler determines the stiffening effect.
- Literature lacks the availability of the test to accurately predict the performance of the different fillers.
- When added to bitumen, bulk volume of filler can be related to its stiffening effects.

2.13.1 Ridgen Voids

The underlying assumption is that the densest packing (maximum bulk density) of filler can be obtained by compacting dry filler in a mould. Ridgen Voids in asphalt technology is a fundamental test to assess filler for potential stiffening of bitumen. Ridgen voids is a result of a complex set of factors including particle size, particle size distribution, particle shape, surface area, etc.

The concept typically used to describe the filler effect in bitumen was established during the 1940's. Ridgen proposed that the amount (volume) of bitumen that filler can hold in its void structure is related to the observed stiffening in the mastic. The term $\emptyset/\emptyset_{\max}$ (solid volume fraction/ maximum packing fraction) has been used to model the behaviour of suspensions and predict exponential increase in stiffness as $\emptyset$ approaches $\emptyset_{\max}$.

The calculation of the Rigden voids also can help to calculate the 'effective filler concentration' (the volumetric concentration yielding the same stiffness of different fillers in bitumen-filler system) as demonstrated by Lerfald and Horvli (2003) and Jiménez et al. (2008).

Some researchers have suggested the maximum Rigden Void value to avoid undesired stiffening effect of filler in bitumen and the value is typically around 50%, i.e. 50% of the compacted volume of the filler can be air voids. Rigden proposed that fillers can accommodate a fixed volume of bitumen within their void structure. Bitumen in excess of the "fixed voids" is termed free bitumen as shown in Figure 2.22 (after Rigden (1947)). Therefore, for a fixed volume of bitumen, the stiffening is a function of the quantity of free bitumen, which is a result of the level of voids within the filler structure. Essentially, Rigden described the point at which the filler concentration causes changes in the viscous nature of mastic.

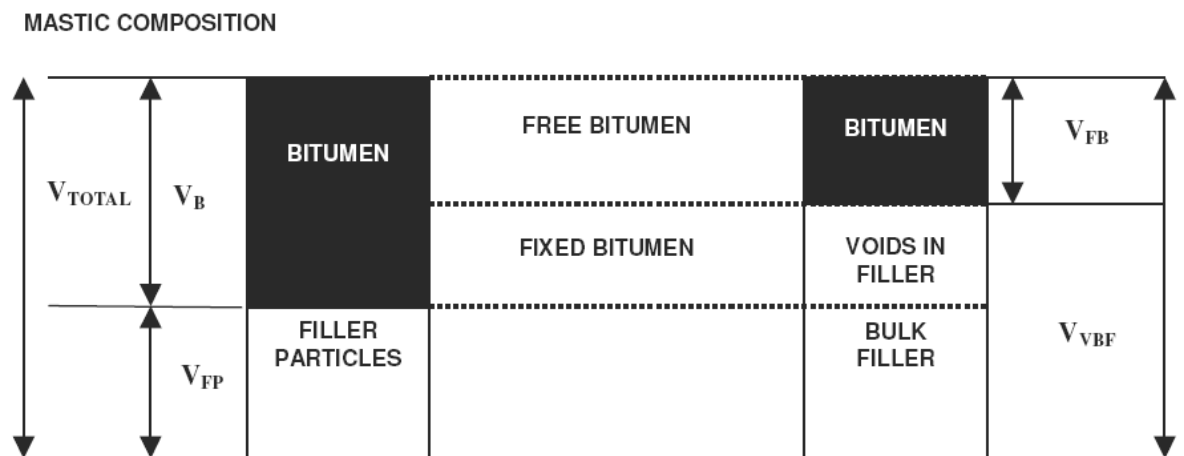


Figure 2.22: Illustration of the concept of "free bitumen"

Where:

V_{TOTAL} = total volume of the mastic

V_{FP} = volume of filler particles

V_B = volume of bitumen

V_{FB} = volume of free bitumen

V_{BF} = bulk volume of filler.

2.13.2 X-ray Diffraction (XRD)

X-ray diffraction method is one of the state of the art tool in material sciences used to characterise the crystalline solids. The method found its way from the discovery of X-rays which enabled the researchers to look at the crystalline structure at micro level for two key areas:

- Characterisation of materials with crystalline structure
- Crystalline structure itself

The basic principle in x-ray diffraction is that each crystal solid has its own structural properties serving as a of fingerprint for quantification of its structure measuring atomic packing, inter-atomic distances and bond angle (etc.) in a crystalline structure.

X-rays are generated by bombarding a metal target like Copper (Cu) with a beam of electrons. These electrons are previously emitted from a hot tungsten filament. The striking electron beam ionises electrons of the K-shell of the target atom. This generates X-rays from the target material as a result of electron transfer from higher L (2P) or M (3p) levels to lower energy levels.

The crystal shape is determined through the axis length and angle using basic geometrical principles to classify it as cubic, tetragonal, orthorhombic, hexagonal etc. A large database exists that helps to identify the crystals through its x-ray

diffraction finger print. The Bragg's equation is used to calculate the angles of diffraction through using $n\lambda = 2d \sin \theta$. Where n being an integer, λ wavelength of x-ray, d the distance between the parallel planes and θ angle of incidence.

2.13.3 Effect of Oxidative Ageing on Mastics

Bitumen and mineral filler joined together form mastic, which include mineral filler as aggregate particle passing sieve 200 (less than $63\mu\text{m}$). In the pavement industry, different materials like hydrated lime, cement, volcanic limestone and granite dust are referred to as fillers. The earliest use of mastic can be referred back to the study of Richardson (1915).

The use of asphalt mixtures can be considered as a composite of mastic coated aggregate and bitumen, instead of plain classification of mixture as bitumen coated aggregate system. In a study to evaluate thixotropy in bitumen, Traxler (1937a) showed that relative viscosity (mixture viscosity/zero solid concentration binder viscosity) was independent of the nature of suspension particulates. However according to Wu (2009) and Mettas (2009) it was affected by the nature of the suspending particulates. The reinforcement in bitumen is divided into three categories as) a volume filler b) a physico-chemical reinforcement c) a particle interaction reinforcement. The SHRP researchers simplified the criteria related to mineral filler in Superpave mix design, which govern bitumen-filler interaction with use of dust/bitumen ratio ranging between 0.6 and 1.2. However this idea further need to be validated (Huang et al., 2007).

The fillers are often characterised based on the optimum bitumen content, which decrease as filler content increase because less bitumen is needed to coat and lubricate aggregate. This is the main reason for the behaviour of filler as an extender in the bituminous mixture (Huang, 2007; Kandhal, 1998). Mineral filler

may hold some of the polar functional groups of bitumen thus delaying the increase in viscosity of binder on ageing. Limestone has more ability to absorb polar components through bitumen as compared to acidic minerals like granite and gritstone (Mettas, 2009; Wu, 2009)

The research by Huang and Zeng (2007) has shown that increasing the filler content in HMA increases its strength. The strength of filler is greater than that of binder hence increasing content of the filler would decrease the content of bitumen and hence increase strength of mastic. According to researchers although the strength of HMA increase with filler content, the increase of brittleness will affect fatigue resistance.

One of the main advantage of using research on mastic is that it provides an insight into the interaction of binder and filler, which is not captured by testing on binder alone (Abbas et al., 2005). One of the problem in mastic testing reported is the settlement of filler after ageing, this problem in a study by Mettas (2009) was solved through remixing prior to DSR testing.

The use of filler results into increased strength of tensile strain at low temperature thus retarding crack propagation. These particulates also increase fatigue life of mineral fillers (Abbas et al., 2005). The presence of certain impurities like micas, chlorite and secondary mineral like clay and hydrate iron oxide can significantly lower the performance of bitumen mixture (Loorents and Said, 2009).

In asphalt mixture, a major contribution of filler is expected towards ageing because of substantial part of total surface area contributed by mineral filler. A large amount of research has been published on mineral fillers in the past but little research is reported regarding the effect of different fillers on the long-term

ageing characteristics of bitumen. Ageing of mastic increase complex modulus and decrease phase angle. This indicate that bitumen has become harder and brittle. The mastic improves the adhesion properties and provides thick film of coating layer and thus minimise ageing process. Mastic also improves moisture resistance and oxidative ageing of asphalt mixture by reducing porosity of the asphalt mixture. This make the access of water and air in mixture more difficult. The chemical nature of fillers might make them to have greater affinity with bitumen, which improve resistance of bitumen to be displaced by environmental effects.

Gubler et al. (1999) while using PAV mastic ageing in Swiss Federal Laboratories understood the mechanism of addition of filler delaying the ageing o of filler can delay ageing of the binder particles which in turn hurdle the diffusion of oxygen to bitumen.

2.13.4 Bitumen Aggregate Bonding and Film Thickness

The polar functionalities at the bitumen aggregate interface help to make bond between these materials through use of electrostatic force, hydrogen bonding and Van der Waal interactions. If the aggregate surface is covered with a coating which is non-polar the adsorbing ability of aggregate changes (Read and Whiteoak, 2003). Studies have shown that carboxylic acids, ketones, and sulphoxides increase as the oxidation increases. This is true both at the interface and also at a distance of 25-100 μm from the aggregate surface (Jahromi, 2009). Bitumen adsorption on aggregate surface and sensitivity of being displaced by water has been discussed by Petersen et al. (1974a) and Huang et al. (2005b).

In asphalt, the presence of moisture may decelerate the adsorption of oily components in bitumen-aggregate interaction and this is affected by several

factors such as temperature and time for which it is submerged in water. In a study in Wyoming various samples, which have been subjected to freeze/thaw cycle, were tested using infrared spectrometer. The results revealed that presence of water did not affect sulphoxides and ketones but displaced carboxylic acids. This shows that by ageing bitumen one can minimise moisture damage compared to unaged binder upon freeze/thaw conditioning (Huang et al., 2005a).

According to Read and Whiteoak (2003) bitumen film thickness has an effect on the durability of asphalt mixture and can range from 5 to 15 μm . A more precise range of film thickness is reported by Sengoz and Agar (2007). The literature review shows that film thickness of binder has an effect on the ageing of the asphalt mix even when mix production details of two different mixtures is the same. In order to calculate binder film thickness for ageing, the Heitzman's method is considered to be more reliable by Mettas (2009). According to him this is because it is considering specific gravity and absorption of these materials.

2.14 SUMMARY

The summary of literature review is discussed with respect to main subject matter. Firstly, bitumen chemistry needs to be more discussed more often by bitumen rheologists. This because mechanical response of material cannot be fully understood while ignoring the binding material chemistry. Techniques in analytical chemistry can be applied to bitumen chemistry to better understand its behaviour. Discussion on bitumen chemistry is no complete without discussing the structure of bitumen, in this regard two models exist namely colloidal and microstructural. In terms of ageing, oxidation changes the bitumen chemistry by increasing polar components and functionalities in bitumen. It is to ensure that different components in bitumen are in relatively good proportion and relative

presence of one component is supported by other component (i.e. compatibility is ensured). A detailed literature review of bitumen makes it necessary to analyse oxidised bitumen to study either their fractions or functional groups. It has been discussed that identifying functionalities is simpler method to understand effect of oxidation. In order to analyse oxidation functionality test such as FTIR can be useful in this regard.

Different factor which s affect ageing namely oxidation, volatilisation, polymerisation, thixtropy, synerisis and separation. There are two main types of ageing one that occur during hot mix asphalt plant, laying and very early service life of pavement. The second type of ageing which occurs during the service life of pavement is long term oxidative ageing. Both of these ageing types are simulated various test methods and their variations reported by Airey (2003). The most commonly used short term ageing equipment namely TFO was identified to be useful for long term oxidative ageing. The use of TFO has its advantage due to simplicity of design.

Fillers have effect on the durability of asphalt and this effect can be quantified through physical and chemical properties of the filler. Physical properties which mainly affect is the packing of filler measured through Rigden void. This parameter is quite complex number to measure the primary properties. The filler's packing is measured through Rigden voids apparatus. While the chemical properties of fillers are measured through test such as XRD. Fillers properties thereby affect the ageing characteristics of the mastics as well as the bond strength at bitumen and aggregate interface.

Rheological properties of bitumen are measured through Dynamic Shear Rheometer (DSR). The principle, system, parameters of this apparatus has been discussed in depth. This method uses time-temperature superposition principle,

a brief introduction to time-temperature superposition has been discussed in this chapter. Furthermore, Dynamic Shear Rheometer is a powerful tool to evaluate rheological properties of various binder and its modifications (such as aged binder).

Shear modulus is not enough to describe the material phase angle measure the. Two materials having same complex modulus but different phase angle will behave differently. The material having more phase angle will have viscous behaviour. DSR measure this behaviour of material at different temperature and loading times. Later time temperature superposition principle is used to construct master curve. These master curves show complete material response at a single temperature reference temperature and wide frequency range, which make it easier to compare two different materials.

There are three modes of moisture infiltration to aggregate in hot mix asphalt. These include water flow through aggregate voids, presence of moisture in macro pores of aggregate, presence of water in aggregate. The moisture damage tests on hot mix asphalt include tests on loose aggregate and compacted mixtures. The tests on loose moisture include tests such as Rolling Bottle test and compacted mixtures include AASHTO T283 and SATS. It has also been discussed that acidic rocks have higher silicate content and are prone to moisture damage. The basic rocks on the other hand are expected to have lesser moisture susceptibility. Furthermore, presence of impurities such as mica, chlorite reduce the performance of aggregate in asphalt mixture. There is an increasing interest among researchers to quantify moisture susceptibility tests by performing tests on bitumen and mastics through more simple tests such as pull off testing. These tensile type testing techniques provide direct measure of adhesive and cohesive bond strength of binder when it is coated on substrate. There is need to further improve and assess these testing techniques.

CHAPTER 3 : RESEARCH METHODOLOGY

3.1 INTRODUCTION

The damage to durability of bitumen affects its properties in two ways, namely oxidative ageing and cohesive/adhesive bond failure in asphalt. The literature review indicated that durability is also related to a factor from bitumen chemistry namely 'compatibility of bitumen' (Petersen, 1984). A discussion of this factor has been made in the literature review. The scope of this research is limited to physical aspect of durability to evaluate the cohesive strength through pull off testing.

3.2 EXPERIMENTAL DESIGN

A basic methodological flow chart to achieve stated objectives is presented in Figure 3.1. Detailed discussions on materials and methods have been made in sections 3.3 and 3.5 respectively. This research is further divided in two themes namely durability (in terms of ageing) and Integrity of asphalt (in terms of cohesive bond failure). It is to be said that the term Integrity in this research refers to cohesive bond strength of mastics. These terms have been used interchangeably.

A less detailed and simplified version of the flow chart is presented in Figure 3.2. This figure divides study in two parts; first part is about ageing techniques and second part involves testing on the effect of filler properties on mastics. It has been shown that how cohesive strength part is related to the mastics and ageing.

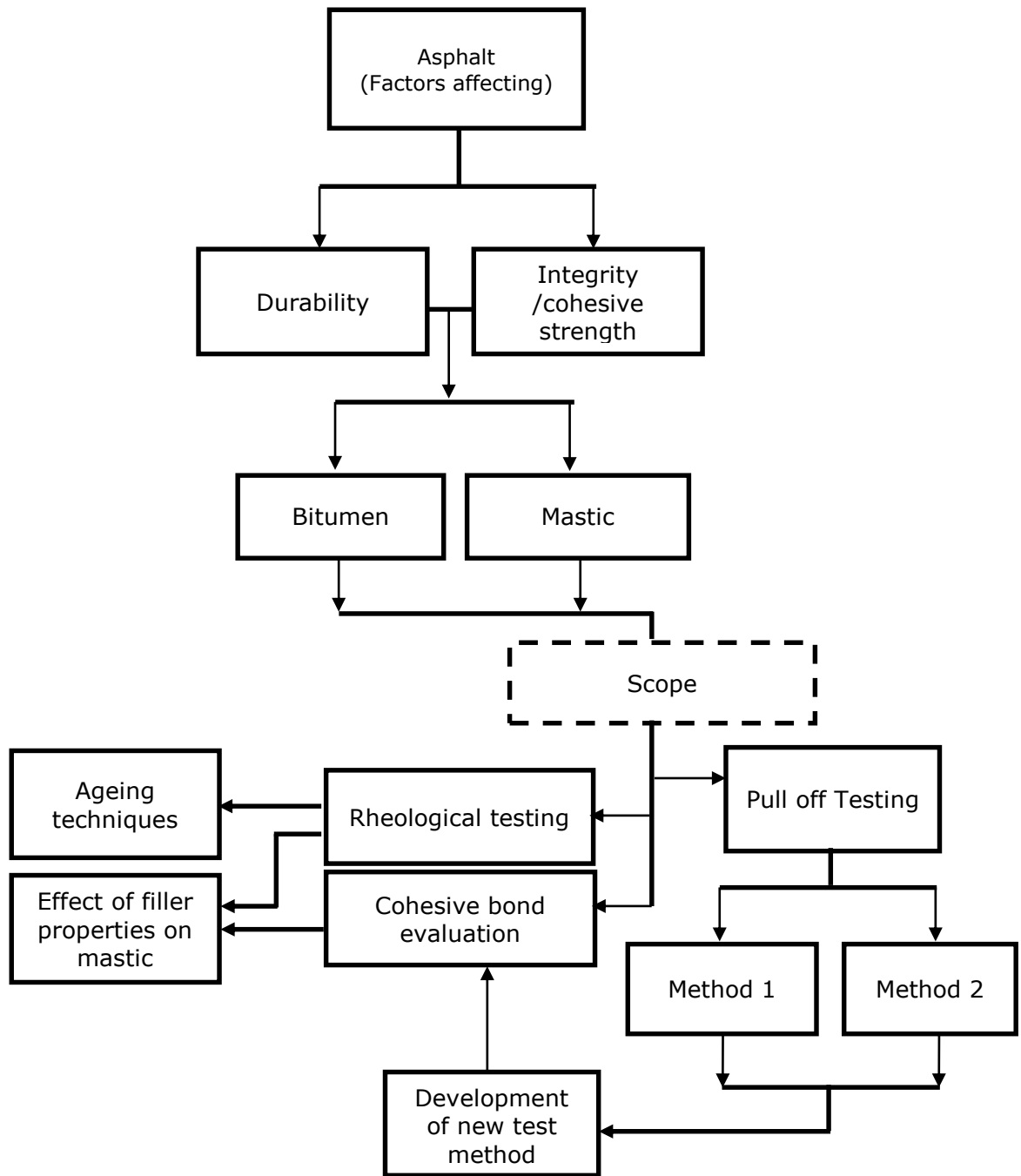


Figure 3.1: Experimental flow chart

These two areas are discussed in four different chapters of the thesis. The chapter 5 discusses the ageing part while chapter 6 discusses the effect of filler properties, mainly packing, on mastics. The scope of both of these chapters mainly involved rheological testing on the binder. The rheological testing for this purpose was done on bitumen and mastics with 40% and 20% filler as a percentage of the volume of the bitumen.

The research on cohesive bond strength is discussed in a great length in chapter 6 and 7. Cohesive strength of the mastics further divides this chapter into three main areas. Firstly, study of the cohesive bond strength through method 1 and method 2. The method 1 used a complex testing geometry to study cohesive bond properties, while method 2 used a quite simplified approach to study bond strength of the mastics.

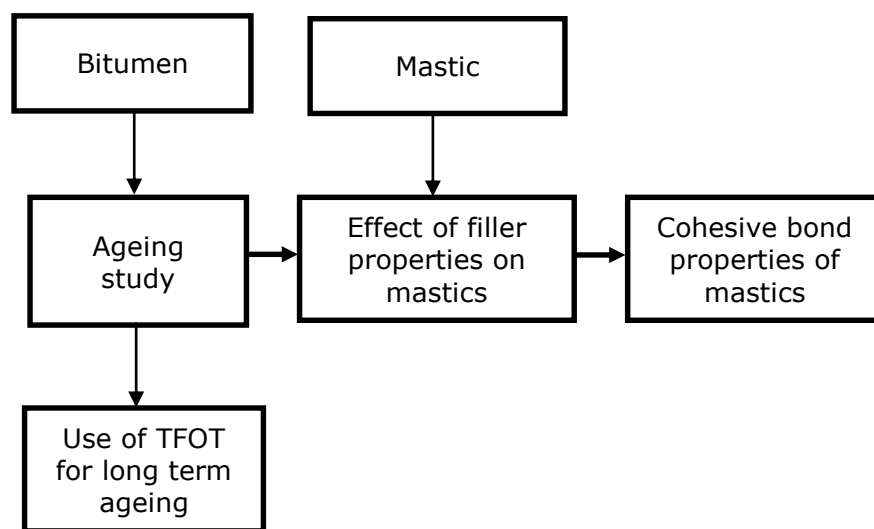


Figure 3.2: summary of experimental programme

In addition to the pull off testing using two existing methods, a new method has been developed in this research to evaluate the bond strength. The experimental design and materials of this new method are kept separate to avoid any confusion between two different phases of research.

In general sense, the purpose of these both type of studies 'ageing' and 'pull off bond strength' is to study durability and integrity of asphalt. The later explicitly being stated is an inherent part of the durability

3.3 MATERIALS

The materials for this research consisted of bitumen, filler and mastics. The following discussion summarises the materials and basis on which particular materials were selected. After discussion of individual materials, a concise summary of these materials is presented Table 3.2 which included their testing conditions and relevant material abbreviations used in the analysis.

3.3.1 Bitumen

A laboratory penetration grade 40/60 was selected for this research (Chapter 4, Chapter 5, Chapter 6). The selection of this medium grade bitumen has its advantage in two ways; firstly, availability of research on same grade and secondly for its wider use in UK pavements. In chapter 7, different bitumen were used from two different sources in Pakistan.

The bitumen (excluding that of Chapter 7) was penetration grade 40/60. It was prepared by blending 23.8% of Pen 160/220 (soft grade) and 76.2% of Pen 30/45 (hard grade), which were procured from Shell Bitumen by Nottingham Transportation Engineering Centre (NTEC). Blending of these grades was achieved by mechanical mixing to yield 12 kg blend of Pen 53 (40/60) with basic properties listed in Table 3.1. A brief description of these methods is presented in section 3.5.1.

Table 3.1: Basic bitumen parameters

Bitumen type	Penetration (dmm)	Softening Point (°C)	Density (g/cm ₃)
40/60	53	50.4	1.030

3.3.2 Aggregate Filler

The aggregate fillers used in this research were selected based upon their generic properties acid and basic nature.

- Basic nature fillers: Limestone and Ordinary Portland Cement (OPC)
- Acidic nature fillers: Granite and Gritstone

The source of limestone and granite was from Torr quarry and Bardon Hill respectively. In this research gritstone was obtained by sieving gritstone dust over 63µm sieve. A quantity 40 Kg of gritstone was sieved in laboratory to yield 2.3 Kg of filler. From morphological studies point of view these fillers are derivate of an igneous rock (granite) and sedimentary rocks (Gritstone and Limestone). The OPC is a widely used construction material made through a very controlled process.

3.3.3 Mastics

The mastics were prepared by volume method, despite the common practice in paving industry to use filler in mixes by weight method. This mastic preparation by mass mainly exists due to ease of process and its cost effectiveness. The problem in this method, despite its popularity, lies in ignoring the important factors e.g. Rigden voids (a complex material property already discussed in literature review). Therefore, in this research volume method was adopted. The second purpose of using filler percentage by volume was to make comparison with existing studies such as Wu (2009) and Liao (2007). This was to compare the stiffening potential of different fillers. The mastics used in this research were 40% and 20% filler by volume. Section 3.5.4 discusses the detailed procedure for mastic preparation.

Table 3.2: Materials description

Category	Material	Condition	Abbreviation
Fillers	Limestone filler	fines	Limestone
	Granite filler	fines	Granite
	Ordinary Portland cement	fines	OPC
	Gritstone	fines	Gs
Unmodified Bitumen	Pen 40/60 (12kg blend of 76.2% 10-3549 + 23.8% 10-2639) 57 pen	unaged	40/60
	5 hours TFOT aged 40/60	aged	5 hr TFOT 40/60
	Standard (20hr) PAV aged 40/60	aged	20 hr PAV
	1 day TFOT aged 40/60	aged	1 day TFOT 40/60
	2 day TFOT aged 40/60	aged	2 day TFOT 40/60
	3 day TFOT aged 40/60	aged	3 day TFOT 40/60
unaged mastic (40% by volume)	Limestone mastic	unaged	Ls
	Granite mastic	unaged	Gr
	OPC mastic	unaged	OPC
	Gritstone	unaged	Gs
1 day TFOT aged	Limestone mastic	aged	1 day TFOT Ls
	Granite mastic	aged	1 day TFOT Gr
	OPC mastic	aged	1 day TFOT OPC
	Gritstone mastic	aged	1 day TFOT Gs
unaged mastic (20% by volume)	Limestone mastic	unaged	Ls(17)
	Granite mastic	unaged	Gr(17)
TFOT aged mastic (20% by volume)	5 hr Limestone	aged	Ls(20)5hr
	21 hr Limestone	aged	Ls(20)20hr
	5 hr Granite	aged	Gr(20)5hr
	21 hr Granite	aged	Gr(20)20hr

3.4 EQUIPMENT

A list of equipment used in this research is as follows. The detailed testing techniques are discussed further in section 3.5. In order to carry out experimental design for the research, four different types of equipment were used.

- **Conventional bitumen tests** were used to capture the basic material properties. These included penetration test, softening point test and specific gravity of the bitumen.
 - Penetration testing was a necessary part of British Specification and served as a basis to identify the bitumen consistency in a single empirical value.
 - Softening point to measure the point at which material behaviour change from more elastic to viscous component. However, this method was also based on empirical value as in reality for complex material like bitumen there is no single sharp softening point.
 - Specific gravity of bitumen was measured using BS standard 2000-549:2007. The specific gravity of bitumen was measured at 25 °C using pycnometers by filling it to the mark and weighing it on balance.
- **Filler tests** mainly required ASTM sieves, Pycnometers, Ridgen voids apparatus and test liquids (water, methylated spirit)
- **Ageing**

The desired asphalt ageing levels were achieved using Thin Film Oven (TFO) and Pressure Ageing Vessel (PAV). The thin film oven (TFO) served two folded purpose namely; short-term ageing and long-term ageing. In this research TFOT refer to use of Thin Film Oven for short-term and long-term ageing, in order to not confuse it being for being a new test method. In this research, the testing regime involved testing using PAV which was used in attempt to bench mark severity of TFO for long-term ageing.

- **Evaluation of rheological properties**

The conventional tests were empirical to capture the time-temperature dependant response of the material so a detailed rheological testing was needed, which was performed by use of Dynamic Shear Rheometer (DSR) as shown in Figure 3.3. The frequency sweep tests at different temperatures under controlled strain mode were used to obtain rheological data to construct master curves to compare. These master curves were used to compared different asphalts.

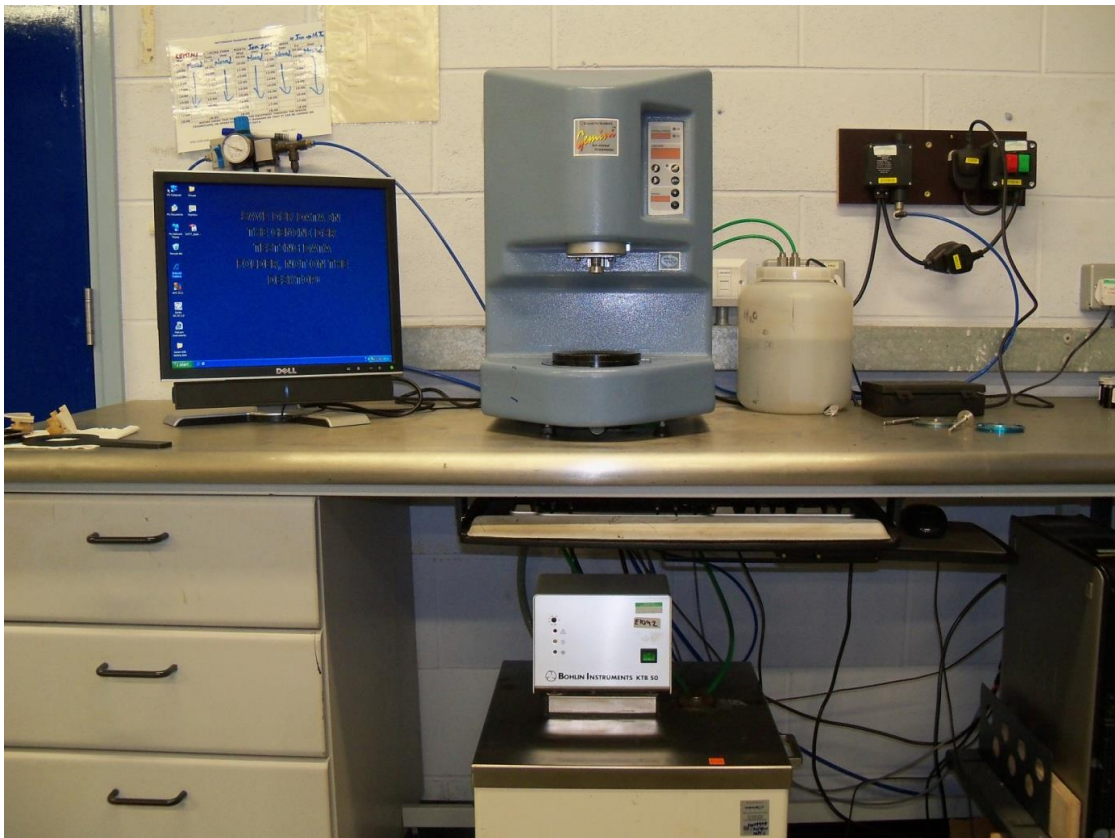


Figure 3.3: Dynamic Shear Rheometer (DSR)

- **Pull off testing**

For carrying out pull off testing, two Servo-hydraulic dynamic testing machines were used. This testing was done in two different testing phases (as shown in Figure 3.4A & B) to measure adhesive/cohesive strength upon

application of tensile type load. In the first phase of testing Instron in Figure 3.4A was used while for the second phase of testing Instron shown in Figure 3.4B was used.



A: Instron testing machine (Phase 1)



B: Specimen in testing rig Instron (Phase 2)

Figure 3.4: Instron for pull off testing

3.5 METHODS

This section discusses the brief testing methods for bitumen and fillers. A detail of mastic preparation is also included. The specific discussions on ageing, rheological and pull off testing have been made in sections 3.6 3.7 and 3.8.

3.5.1 Conventional Tests

This section includes discussion on the conventional binder testing which were empirical in nature and provides the most fundamental material properties. It included penetration and softening point test. The density of the bitumen was 1.03 (g/cm³).

3.5.1.1 Penetration test

The penetration is used to measure the consistency of bitumen, higher the penetration grade of the bitumen higher the consistency of the bitumen which means softer the bitumen. In road construction, generally soft penetration grades are preferred for cold climate and hard penetration grades are used for hot climate. The schematic diagram of this method is presented in Figure 3.5.

The standard test method used in this research was "BS 2000: Part 49 Penetration of bitumen and bituminous materials." The other standards in practice were AASHTO T 49 and ASTM D 5: Penetration of Bituminous Materials. A step by step procedure for penetration test is given below.

- Bitumen was heated at 163 °C and then poured into a container to a depth such that its depth in the container was greater than 10mm more than the expected penetration. After pouring the bitumen was allowed to cool down at atmospheric temperature. The container was then placed in water bath to maintain the temperature of the bitumen.
- In testing, a needle was mounted on bitumen so that it just touched the surface of bitumen. The needle was then allowed to penetrate freely in the

container for 5 seconds and the penetration was used to measure the depth of fall of the needle and three readings were taken.

- The measurement was measured in units of 0.1 mm and reported in penetration units. A reading of 5.3mm meant a penetration number of 53.

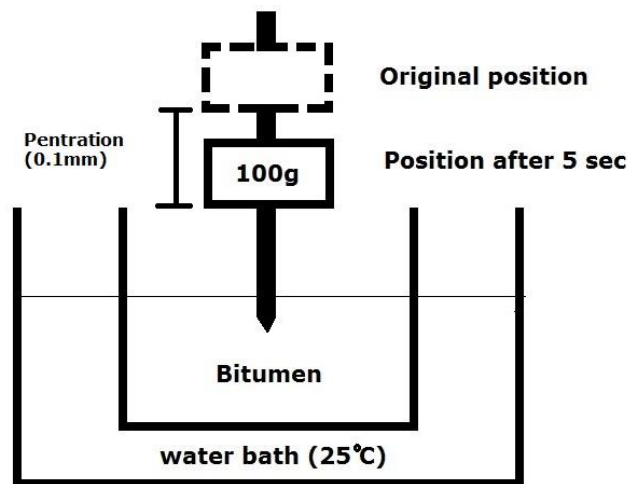


Figure 3.5: Schematic diagram of penetration test

3.5.1.2 Softening point test

Bitumen did not have had a well-defined melting point unlike water. This binding material (bitumen) changes its consistency slowly with rise of temperature; therefore, it was necessary to establish a melting point through standard test method to measure the softening point. The standard in practice to measure softening point of the bitumen was "BS 2000: British Standard Methods of test for Petroleum and its products. Part 58: Softening point of bitumen".

In this method, two horizontal disks of bitumen were placed in two brass rings. The assembly was then heated at a controlled rate in a liquid bath while each supporting a steel ball. Heat was increased at the rate of 5 ± 0.5 °C per minute. The softening point was reported as the temperatures (average of two) at which

the two disks were softened enough to allow balls to fall a distance of 25 mm while enveloped with bitumen. The temperature was recorded to nearest of 0.2 °C. The detailed schematic diagram of this test is shown in Figure 3.6.

The average temperature of two specimens was taken as softening point and it was standard requirement that two methods did not differed by more than 1°C. The softening point used in conjunction with the penetration to calculate the Penetration Index (PI) was 0 for Pen 40/60.

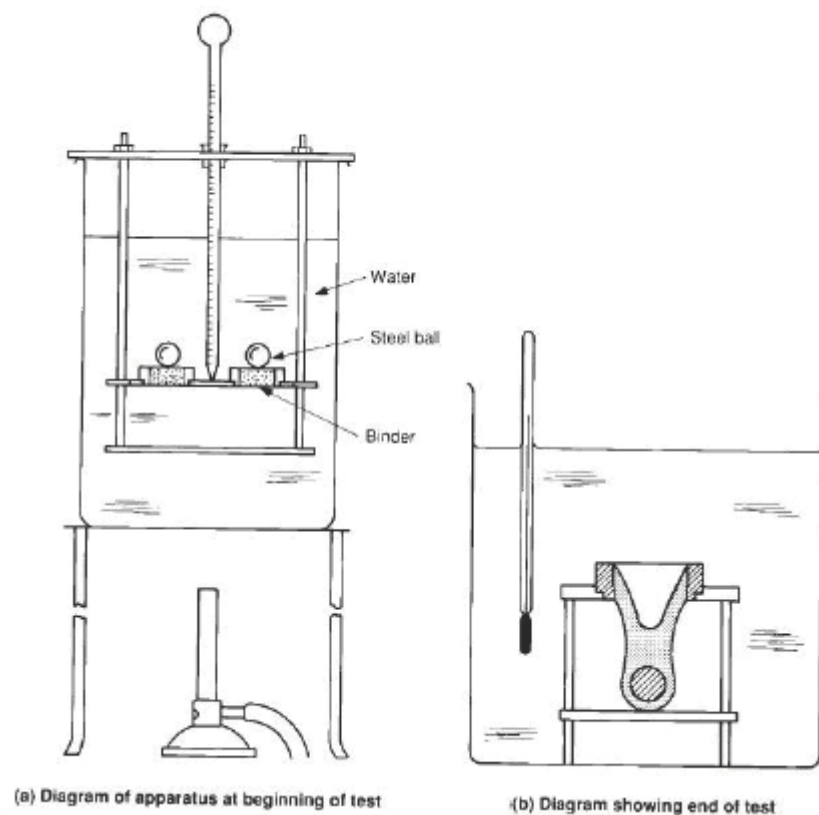


Figure 3.6: Schematic diagram of softening point test (Millard, 1993)

3.5.2 Filler Tests

In this research fillers refers to aggregate particles passing sieve 200 (63 µm).

The fundamental to involved particle density, Rigden voids, particle size distribution (PSD) advanced test (X-ray diffraction) were performed on the filler.

3.5.2.1 Particle density (Specific gravity)

This Test method is based on the replacement of test liquid (of known density) with filler. The difference between particle density and bulk volume density is shown in Figure 3.7. The bulk density does not incorporate the presence of voids present as an explicit measurement in the filler so measurement of the particle density (specific gravity) of the filler become of importance. In this test Pycnometers (known volume) containing filler was filled with the liquid of known density. The volume of liquid was calculated by dividing the mass of added liquid by its density. The volume of filler was calculated by subtracting this volume from pycnometer volume. "BS EN 1097-7:2008 Determination of the particle density of filler-Pycnometer method." was used to measure the particle density.

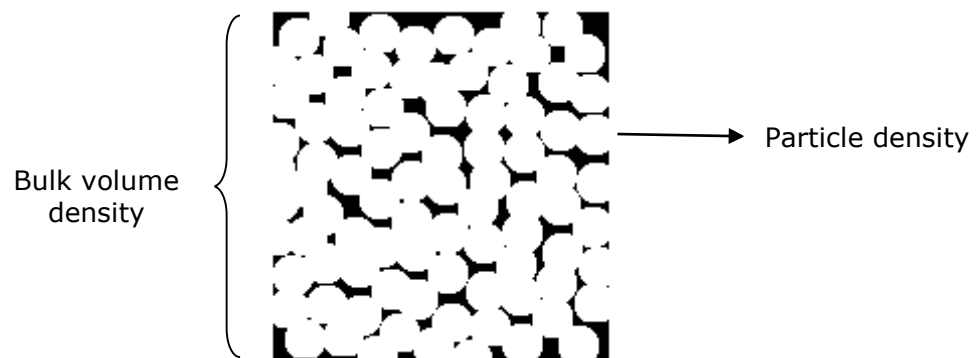


Figure 3.7: Bulk volume density and particle density

The test apparatus included Pycnometer, water bath, balance, drying oven, vacuum desiccators with desiccant, vacuum pump, spatula, test sieve (0.125mm) and material (suitable liquid, demineralised water, acetone).

Procedure

In this research test portion was dried in oven at a temperature of 105 °C in an overnight. The purpose of this was to dry any moisture present in the test portion

and to achieve constant mass. This test portion was then left in desiccators for at least 90min. It was often checked for presence of lumps, in case of lumps presence, they were pulverised with spatula and mixed again. The filler was dry sieved using 0.125 mm sieve and passing filler particles were retained.

In this research density determination was carried out using three test specimens with a calibrated pycnometers and suitable liquid of known density. Firstly, clean and dry pycnometers were weighed with stopper as m_0 then pycnometers were filled with 10 ± 1 g of filler and weigh was taken as m_1 . In next step sufficient quantity of liquid was added to completely submerge the filler Figure 3.8 (a, b) while taking precaution that liquid should percolate through the filler in the pycnometers. Later, stopper was inserted in the pycnometers and it was placed in vacuum desiccators and evacuated with vacuum pump in approximately 5min to a pressure less than 3.0 kPa. The whole assembly was then left in vacuum desiccators for at least at a pressure less than 3.0 kPa.

After 30min air pressure was restored in the desiccators, the pycnometers were then taken out to fill with liquid. The pycnometers without stopper were placed in water bath at 25 ± 0.1 °C so that top was 2 to 3mm above water level; it was then left in water bath for 60min as shown in Figure 3.9. After this time, stopper was replaced in pycnometers causing an amount of liquid to come out of the capillary. After this time, pycnometers were removed from water bath and quickly cooled under cold (running water) to prevent expansion of liquid due to warm handling. The outside of pycnometers was dried and weighed as m_2 as shown in Figure 3.8 (c).

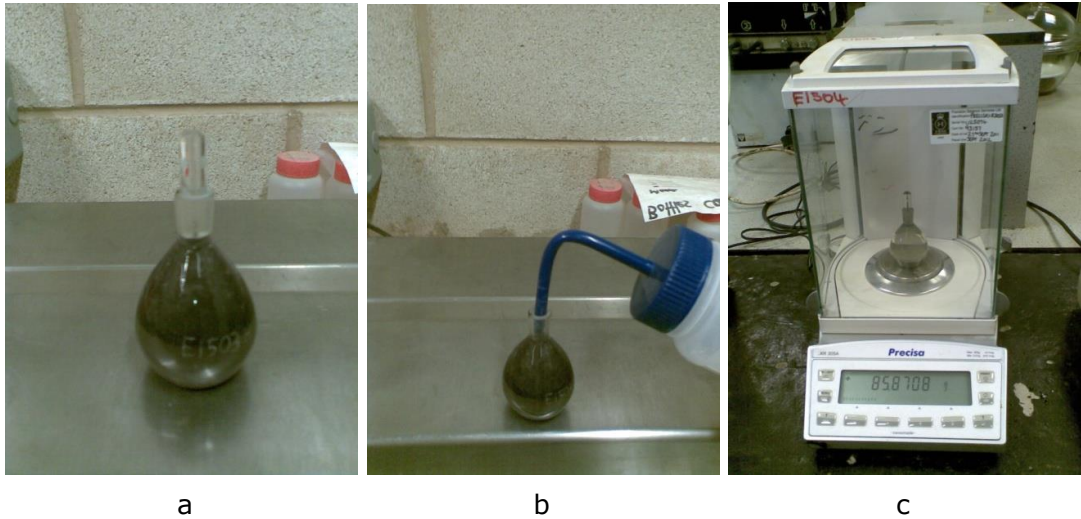


Figure 3.8: Weight of pycnometer after fully submerging filler in water



Figure 3.9: Pycnometer left in water bath

The particle density of filler was calculated in mega grams per cubic meter ($\text{mg}/\text{m}^3 = \text{g}/\text{cm}^3$) by using following equation.

$$\rho_f = (m_1 - m_0) / (V - (m_2 - m_1) / \rho_l)$$

Where

m_0 = mass of empty pycnometer with stopper (in grams)

m_1 = mass of the pycnometer with filler test portion (in grams)

m_2 = mass of pycnometer with filler, topped up with liquid (in grams)

V = volume of the pycnometer (in mm)

ρ_l = density of liquid at 25 °C (in mega grams per cubic meter)

ρ_f = particle density of filler at 25 °C (in mega grams per cubic meter)

The particle density was calculated as mean of three determinations to nearest 0.01 Mg/m³, where 1 mega gram per (cubic meter) = 1000 kg / m³.

- The volume of pycnometer was calculated using Annex A of BS EN 1097-7:2008 and liquid density was calculated using Annex B of BS EN 1097-7:2008.
- The volume of pycnometers was determined was as 50.76, 50.66, 50.8 for bottles marked as D, G, H respectively.
- The density of liquid was already known, for water it was taken as 1 g/cm³ and for methylated spirit mineralised as 0.815 at 25 °C.

The results of particle density of different fillers are shown in Table 3.3 and summarised in Table 3.4. It is important to note that specific gravity of ordinary Portland cement (OPC) was measured in methylated spirit mineralised instead of water. This was because OPC react with water, this would give inaccurate measurement of particle density.

Table 3.3: Specific gravity calculations

Filler	OPC			Gritstone						Granite					
Type of solvent	Methylated spirit mineralised			Water			Methylated spirit mineralised			Water				Methylated spirit mineralised	
Pycnometer number	D	G	H	D	G	H	D	G	H	D	G	H	H'	D	G
Pulverise any lumps with a spatula and mix the lumps	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
dry sieve using a 125-micron sieve retain passing filler	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Mass of clean and dry 50ml density bottle +stopper, m_0	30.815	28.417	29.255	30.815	28.418	29.254	30.815	28.416	29.23	30.823	28.417	29.232	29.231	30.816	28.417
weight of pycnometer + filler (10 ± 1g) m_1	40.051	38.382	39.685	40.256	38.094	39.239	40.679	39.035	39.79	40.878	39.042	38.885	39.7	41.369	38.905
Add suitable liquid to completely submerge specimen	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Replace stopper and put into a vacuum desiccator	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Apply a vacuum of 30mbar	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Time for which vacuum applied (min)	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Fill pycnometer with suitable liquid	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Place pycnometer without stopper in water bath at 25±0.1 °C	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Top of bottle protruding 2-3mm above water surface	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
After 60mins replace stopper & dry the top	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Quickly cool the samples under running water	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dry and weigh the pycnometer, m_2	78.937	76.976	78.266	87.481	85.132	86.295	79.195	77.24	78.116	87.317	85.477	85.875	86.087	79.558	77.036
Volume of pycnometer (ml), V	50.76	50.66	50.8	50.76	50.66	50.8	50.76	50.66	50.8	50.76	50.66	50.8	50.8	50.76	50.66
Density at 25 °C (mg/m ³), P_i	0.815	0.815	0.815	1	1	1	0.815	0.815	0.815	1	1	1	1	0.815	0.815
Particle density of filler (mg/m ³) $P_f = (m_1 - m_0) / (V - ((m_2 - m_1) / P_i))$	3.031	3.015	3.014	2.671	2.672	2.667	2.818	2.808	2.797	2.327	2.515	2.534	2.372	2.704	2.708
Mean particle density (0.01 mg/m ³)	3.020			2.670			2.808			2.437				2.705	

Table 3.4: Summary of specific gravity of fillers

Filler		Sp. Gravity
Name	Sample No.	
Limestone	06-3820	2.623*
OPC	11-1292	3.020
Gritstone	11-1293	2.808
Granite	07-1247	2.705

Note: Limestone sample numbers 06-3820 were taken from 02-2709 having density which was previously determined.

Comment on Particle density determination of granite

When the specific gravity test was performed for granite, during the procedure filler leaked out of the pycnometer while replacing the stopper. The specific gravity determination for granite with water was carried out twice. This problem was unavoidable as it was observed in all bottles even when extreme caution was taken into account. The same filler was then tested using another liquid 'methylated spirit mineralised' and the problem did not occur. The observation was also made that air bubble did not escape properly in case of water. The presence of air voids inside the filler was could also be another cause for inaccurate specific gravity. It was anticipated that some components from granite had reaction with water, also when specific gravity of gritstone measured with methylated spirit mineralised. It was 5% higher than the one measured with water.

3.5.2.2 Rigden voids

The procedure described as per EN 1097-4:2008 was used to determine the volume in dry-compacted filler (Rigden voids). The volume of compacted filler is measured after application of blows with dropping block on column height of

compacted filler. The particle density of compacted filler was then used to calculate percentage air voids in the compacted filler column.

The test apparatus included ventilated drying oven, desiccators, spatula, Rigden voids compaction apparatus (dropping block, plunger, base plate), balance, filter paper, test sieve.

Procedure

The test portion was dried at 105 °C to a constant mass and was left to cool in desiccators for 90min. It was made sure that portion before drying had minimum mass of 150g as per test specifications. The specimen was checked for presence of lumps. In case of presence of lumps, they were pulverised with spatula and lumps were mixed with test portion. The test portion was dry sieved with 0.125 mm sieve and passing material was retained.

The plunger and filter paper was inserted into empty cylinder of dropping block and the height of plunger was measured on a scale and recorded as h_0 . Empty dropping block without plunger with filter paper was weighed as m_0 . Filter paper was removed and 10 ± 1 g filler was added into the cylinder. In order to make surface of filler even dropping block was tapped on table. In next step filter paper and plunger was inserted taking care that filler did not stick on the side of the cylinder. Plunger then was gently pressed to compact filter.

Dropping block with filler and plunger was positioned between pilot bars on the base plate. Dropping block was raised to upper stop and made to fall freely on base plate as shown in Figure 3.10 (left). It was repeated for 100 times at intervals of approximately 1s. After 100 impacts, the height (h) of compacted filler was measured and weight of dropping block noted as m_1 after removal of

plunger as shown in Figure 3.10 (right). Air voids determination was carried out using three separate test specimens. Calculations were made using height of compacted filler, particle density and other parameters.

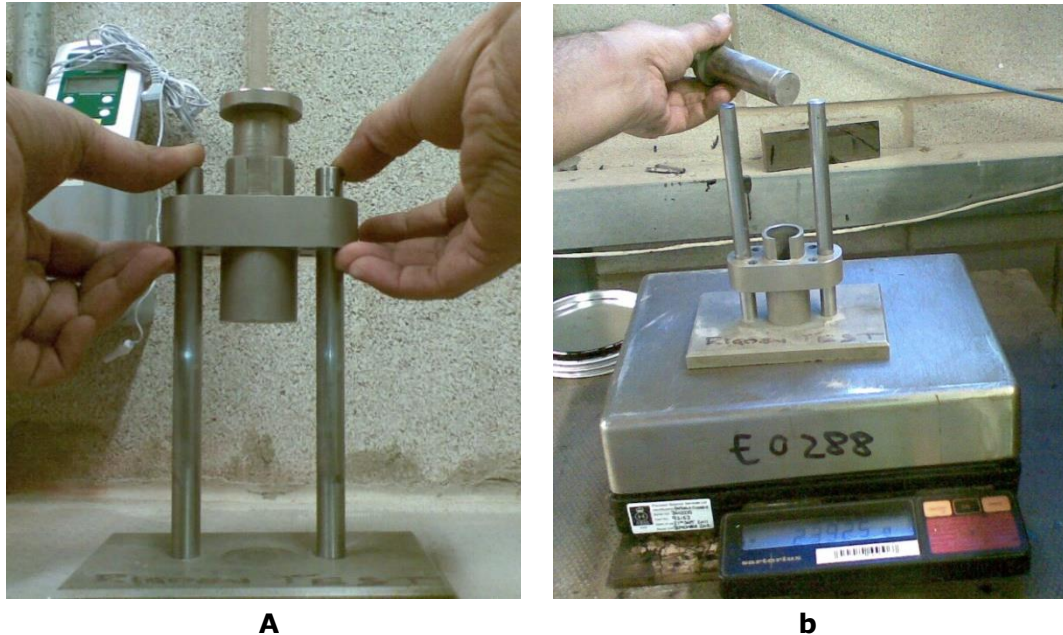


Figure 3.10: Rigden voids apparatus a) application of blows b) compacted filler

The following equation was used to measure the voids in percent.

$$v = (1 - (4000 \times m_2) / (\pi \times a_2 \times \rho_f \times h)) \times 100$$

where

v = voids in percent

m_2 = mass of compacted filler (gm)

a = inner diameter of dropping block cylinder (mm)

ρ_f = particle density (mg/m^3)

h = height of compacted filler

Results for percent voids in different filler are shown in the following table.

Table 3.5: Rigden voids calculation

Material	Inner dia of dropping block cylinder	Wt. Of dropping block and filter paper (without plunger)	Filler to be added 10±1 g and blows	height of compressed filler	wt. of dropping block with compacted filler+ filter paper	wt. of compacted filler	Particle density (specific gravity)	Voids in percent (Rigden voids)	Rigden voids (mean)
	α	m_0	Yes	h	m_1	$m_2 = m_1 - m_0$	ρ_f	v	v
	mm	g	g	mm	g	g	mg/m ³	%	%
Ls	25.4	2382.7	✓	11.3	2392.6	9.9	2.623	34.09	33
	25.4	2382.7	✓	12.1	2393.3	10.6	2.623	34.10	
	25.4	2382.7	✓	11.1	2392.7	10	2.623	32.23	
OPC	25.4	2382.7	✓	11.8	2392.4	9.7	3.02	46.29	45
	25.4	2382.7	✓	11.6	2392.5	9.8	3.02	44.80	
	25.4	2382.7	✓	11.5	2392.4	9.7	3.02	44.89	
Gs	25.4	2382.7	✓	12	2392.9	10.2	2.808	40.27	40
	25.4	2382.7	✓	11.8	2392.8	10.1	2.808	39.85	
	25.4	2382.7	✓	11.8	2393	10.3	2.808	38.66	
Gr	25.4	2382.7	✓	11.6	2392.6	9.9	2.706	37.76	38
	25.4	2382.7	✓	11.5	2392.5	9.8	2.706	37.86	
	25.4	2382.7	✓	11.4	2392.5	9.8	2.706	37.31	

3.5.2.3 Particle size distribution (PSD)

The standard method for determination of particle size distribution of mineral filler is "BS EN 933-10: 1997 Determination of fines- grading of fillers (air jet sieving)". Based on the availability of equipment alternative test method BS 933-1:1997: Determination of particle size distribution-sieving method" was used in the research, which originally is used for determining particle size distribution of natural or artificial lightweight aggregate up to 90mm nominal size.

In this test procedure material is divided and separated by means of series of sieves into different particle size, when sieves are placed in descending order. The method calls for dry and wet sieving. The mass of the particles retained on different sieves is measure and cumulative/passing percent for each sieve is calculated. The test apparatus included test sieves with lid and pan, ventilated oven, washing equipment, balance, trays, and sieve shaker.

Procedure

The test portion was dried at 105 °C to a constant mass. The specimen was checked for presence of lumps. In case of presence, lumps were pulverised with spatula and mixed with remaining test portion. After this step specimen was allowed to cool, and its mass was recorded as m_1 .

A small quantity of filler was then placed on 63 μ m sieve and washed thoroughly as shown in Figure 3.11. Filler was then added in small quantities to avoid overloading and damaging of the sieve. The sample was agitated with sufficient vigour to wash the particles smaller than 63 μ m. Its washing was continued until the water coming out of sieve was clear in colour. This washed filler was carefully collected in a tray. The tray was then left in oven overnight at 105 °C to a constant mass as shown in Figure 3.12. After drying it was allowed to cool and weighed as m_2 as shown in Figure 3.12. The filler was then poured into sieves which were arranged in order of their decreasing size (from top to bottom) with pan attached underneath. The lid was then placed over top sieve and sieving was carried out on the sieve shaker for 5min.

After sieving, filler was retained on a larger sieve which was carefully collected, weighed and recorded on data sheet. This step was repeated for all sieves including the filler which was also weighed on pan. The calculations to compute

particle size distribution were made on a data sheet for filler retained/passing on each sieve.



Figure 3.11: Washing of filler on 63 μ m sieve



Figure 3.12: Drying and weighing of fillers after washing on 63 μ m sieve

Table 3.6: Particle size distribution (PSD) calculation

Particle size distribution (wet) with EN sieve.								
Filler	Mass of sample	Mass retained on 63μ after washing	Sieve (EN size)	Mass retained		Corrected mass	% retained on Sieve	Total % passing
				Cum.	Individual			
	m ₁ (g)	m ₂ (g)	mm	g	g	g	%	%
Granite	122.1	22.1	2.8	0	-	-	-	-
			2	0	-	-	-	-
			1	0	-	-	0	100
			0.5	0.6	0.6	-	0.49	99.51
			0.25	2	1.4	-	1.15	98.36
			0.125	6.7	4.7	-	3.85	94.51
			0.063	18.6	11.9	-	9.75	84.77
			Pan	21.9	3.3	3.3+122.1-22.1	84.60	0.16
	Total mass (g)			21.9	21.3	103.3		
Gritstone	155.10	1.90	2.8	0	-	-	-	-
			2	0	-	-	-	-
			1	0	-	-	-	-
			0.5	0	-	-	-	-
			0.25	0	-	-	-	-
			0.125	0	-	-	0.00	100.00
			0.063	0.70	0.70	-	0.45	99.55
			Pan	1.90	1.20	1.2+155.10-1.9	99.55	0.00
	Total mass (g)				1.90	154.40		
Limestone	127.40	4.20	2.8	0	-	-	-	-
			2	0	-	-	-	-
			1	0	-	-	-	-
			0.5	0	-	-	-	-
			0.25	0	-	-	0	100
			0.125	0.1	0.1	-	0.08	99.92
			0.063	3.5	3.4	-	2.67	97.25
			Pan	4.1	0.6	0.6+127.4-4.2	97.17	0.08
	Total mass (g)			4.1	4.1	123.8		

Table 3.7: PSD summary of different fillers

Comparison of particle size distribution			
Sieve (EN size)	Granite	Gritstone	Limestone
(mm)	% passing	% passing	% passing
2.8	-	-	-
2	-	-	-
1	100	-	-
0.5	99.51	-	-
0.25	98.36	-	100
0.125	94.51	100.00	99.92
0.063	84.77	99.55	97.25
Pan	0.16	0.00	0.08

More than 95% of gritstone and limestone particles were passed through sieve 200 while granite particles were 84.77% passing sieve 200. The granite has 85% passing 200 and 95% passing sieve 100 so it was considered to be acceptable.

3.5.3 X-ray Diffraction (XRD)

X-ray diffraction was used to characterise fillers with different mineral composition. The method uses the basic principle that each crystal solid has its own structural properties serving as that of fingerprint for quantification of its structure measuring atomic packing, inter-atomic distances and bond angle etc. in a crystalline structure.

Methodology

In X-ray diffraction analysis samples were taken from fillers representative sample. These samples were pulverised to remove lumps, and then about 0.5 gram of each filler was placed on a glass slide separately. The filler specimen uniformly spreaded as shown in Figure 3.13. The specimen in glass was then

placed in the diffractometer and relevant software adjustments were made. The diffractometer (Figure 3.14) was left overnight to carry out the test.

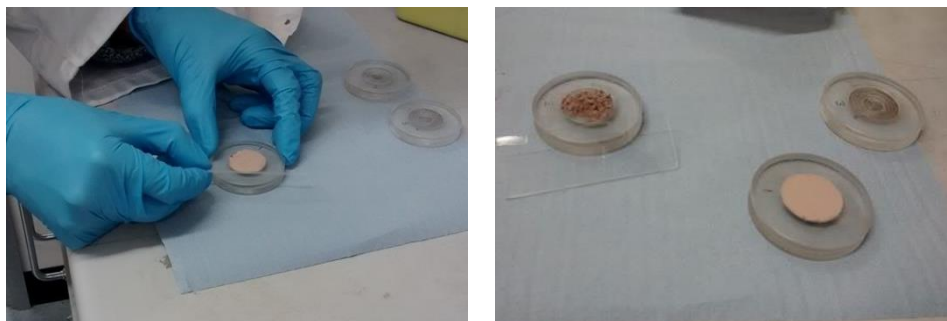


Figure 3.13: Sample preparation for XRD

The specimens were then analysed by X-ray diffraction using Siemens D500 X-ray diffractometric. The diffractometer had following specifications:

- Cu K-alpha radiation source, 1-40kV range
- Theta-2 Theta goniometer
- Slit widths of different range
- Nickel filter and diffracted beam crystal monochromator
- Computerised control of diffractometer and Diffrac-AT peak identification software



Figure 3.14: X-ray diffractometer

3.5.4 Mastic Preparation

There were two options for mixing of bitumen and filler to make mastics namely methods: 1) mixing by paddle stirrer, 2) mixing with hand around 160 °C. The smaller quantities of mastics are prepared with hand mixing and for larger quantities for bitumen paddle stirrer is used. In this research mixing by hand was considered to serve the purpose due to smaller quantities of mastic (less than 500 g). The detailed procedure used for mastic preparation is discussed below:

- Mineral fillers were put into an oven at 105 °C oven for 24 hours to ensure that filler particles were moisture free.

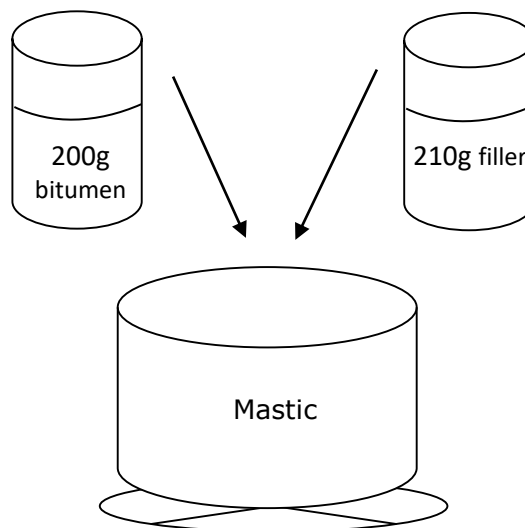


Figure 3.15: Mastic preparation schematic diagram

- The mass of bitumen was measured and filler needed to yield required proportions of mastics were calculated based upon volume and mixed together as shown in schematic Figure 3.15. Filler contents for preparing mastics were calculated based on 29% and 17% by compositional volume of mastics.

- The bitumen stored in an appropriate tin was preheated in a 160 °C oven for sufficient period of time to make sure that bitumen was liquid enough and ready to pour.
- Accurate quantities of bitumen were poured into a smaller tin. This tin was then placed on a hot plate used for mastic preparation, bitumen was stirred for 30 seconds by hand.
- After this, accurate volume of filler was added slowly and stirring was continued for 4.5 minutes.
- In mixing process mastic was stirred continuously as it cooled down until temperature become low (75 °C) to prevent settling of filler at high temperature.

The brief material description, testing conditions and respective abbreviation are listed in Table 3.2. The calculations have been made in Table 3.8 regarding computation of compositional and effective volume of fillers in bitumen-filler suspension (Liao et al., 2015).

Table 3.8: volume calculations for mastics

Filler	Mass of filler	Specific gravity	Mass of bitumen	Compositional volume	Rigden voids	Effective volume
	M _f (g)	S _f	M _b (g)	V _f (g)	ε	V _e
Limestone	209.84	2.623	200	29	33	44
OPC	241.6	3.02	200	29	45	53
Gritstone	224.64	2.808	200	29	40	49
granite	216.48	2.706	200	29	38	47
Limestone	78.69	2.623	150	17	33	25
OPC	90.6	3.02	150	17	45	31
Gritstone	84.24	2.808	150	17	40	28
granite	81.18	2.706	150	17	38	28

Where: Compositional volume = $V_f / (V_f + V_b) \times 100 = M_f / S_f / (M_f / S_f + M_b / S_b) \times 100$

Effective volume (Heukelom, 1965) = $[100 / V_{fR}] \times 100 = [100 / (1 - \epsilon)] \times 100$

3.6 AGEING METHODS

The standard ageing testing techniques were used to age binder both in standard and non-standard ways. The 'standard tests' referred to ageing time and temperature which were part of British Standards, whereas term 'non-standard' referred to testing where any of these test parameters was altered for TFOT testing. In this section first discussion on selection on ageing time and temperature has been made and then detailed test methods are discussed in further sections.

3.6.1 Ageing Time and Temperature Selection

For two phases of testing 24 hours and 20 hours were selected as long-term ageing periods respectively. For mastics A (containing 40% filler by volume of bitumen) 24 hour was selected as ageing time while for mastics B (containing 20% by volume of bitumen) the ageing time was reduced to 20 hours.

In order to test binder at extreme conditions, initially bitumen was then aged for 3 days but this ageing also proved to be quite harsh for the binder. The ageing time for bitumen was then reduced to 2 days.

In the same way mastics were aged for different days, the maximum ageing time for limestone was 2 days but binder was very stiff and very difficult to pour. It was anticipated that if mastic was heated at elevated temperature and long period of time, it might alter the ageing history of mastic. Finally, 24 hours was selected as the highest ageing time for the first phase, even these mastics required heating at 200 °C and had difficulty in pouring. In the 2nd phase the

ageing time was further lowered to 20 hours to have lesser stiffer bitumen as compared to that of 24 hours and secondly to allow removal of aged samples (after 20 hours) of one completed tests and placing of new samples within a one-day time window.

The standard mixing temperature for RTFOT and TFOT ageing was 163 °C while for PAV ageing temperature was 100 °C which was corresponding to moderate climate.

3.6.2 Thin Film Oven Test (TFOT)

TFOT oven was used for short and long-term ageing in this study. The effect of heat and air were determined from changes incurred in physical properties measured before and after ageing with this test.

3.6.2.1 TFOT pan bitumen thickness calculation

In a standard TFO test 50g of bitumen produces 3.2mm thick film. However, in this research 3mm thick film was selected. In order to achieve this film thickness following calculation was made.

Pan diameter= 140 mm

Volume of 3mm thick bitumen in pan (of 140mm dia) = $\pi r^2 h$

Where r = radius of pan

h = film thickness

Bitumen volume in TFOT pan (3mm film thickness)

$$= (3.14 \times 7^2 \times 0.3) = 46.18 \text{ cm}^3$$

Density of bitumen = 1.03 g/cm³

Weight of bitumen required for 3mm film thickness = 47.6 gm

3.6.2.2 TFOT ageing parameters

- Standard test procedure

ASTM standard: D 1754-97 (2002)

Ageing temperature: 163 °C

Ageing duration: 3 hrs

Film thickness: 3.2mm

- Modified Test parameters for research

Ageing temperature: 163 °C

Max temp which can be achieved: 163 °C

Ageing time tried: 0, 1, 2 days

Ageing time suitable for virgin binder: 2 days

Ageing time suitable for mastics: 1 day

Film thickness: 3mm

Volume of bitumen: $\pi \times \text{pan radius}^2 \times \text{film thickness}$

Procedure

- The oven was preheated to a test temperature for 2 hours after. It was ensured that oven was levelled as per BS Standard requirement (having not more than 3° tilt during rotation).
- Empty pan weight of TFOT were labelled and weighted as w_1 .
- 46.18 ±0.5 g of bitumen was placed into pans.
- The pans were allowed to cool down at room temperature for 30min and weight was recorded as w_2 .
- The samples were then allowed to be aged in the oven for 5 hours (or desired time in case of longer duration of ageing) and time for the ageing keeping the test temperature not more than 15 min. In case of 20 and 24 hours ageing sample were left for ageing overnight.

- After test the samples were weighed to the nearest 1mg as w_2 and the change in the mass of the binder calculated.
- The bitumen was collected in the container for further testing.

3.6.3 Rolling Thin Film Oven Test (RTFOT)

The standard RTFOT was carried out as part of research to serve as a bench mark for the short-term ageing. This equipment is shown in Figure 3.16 and its brief testing procedure is as following:

- Oven is the preheated to the test temperature (163 ± 1) °C after ensuring that oven was levelled.
- Binder was heated until fluid enough to pour while stirring in between to remove air bubble and to ensure homogeneity.
- After heating bitumen, it was poured into RTOT bottles as 35 ± 0.5 g. These bottles were then allowed to cool down.
- The bottles were then arranged in the carriage, after closing the oven carriage was allowed to rotated at 15 ± 0.2 rev/min with airflow at the rate of (4.0 ± 0.2) l/min for 75 ± 1 min at 163 ± 1 °C.
- After ageing period bitumen was collect for further testing.



Figure 3.16: Rolling Thin Film Oven (RTFO)

3.6.4 Pressure Ageing Vessel (PAV) Test

PAV test is a standard method to simulate long-term ageing of bitumen. In this research, standard PAV was performed to establish bench mark for TFOT ageing. The standards used for PAV were BS 2000-535: 2005 and AASHTO R 28-02: Accelerated Ageing of Asphalt Binder Using a Pressurised Ageing Vessel (PAV). The test set up for Pressure Ageing Vessel is shown in Figure 3.17.

The original ageing studies on PAV were done at 2.07 MPa (300 psi) and 60°C for 6 days, but in later studies the ageing time was reduced by increasing ageing time to 90 - 110 °C depending on climate. In this research 100 °C was selected as ageing temperature for PAV test, which corresponded to moderate climate conditions. This temperature fairly represents temperature for UK weather conditions.



Figure 3.17: Pressure Ageing Vessel system

Procedure

- Forced draft oven was preheated to the ageing temperature.
- The RTFO aged binder was heated until it was sufficiently fluid to pour. The sample was stirred in between to remove any trapped air bubble.
- The sample, after stirring, was then poured into required number of PAV pans. The amount of binder (bitumen/mastic) poured into pan was $50\text{g} \pm 5$ which gave a binder film thickness of 3.2mm. It was ensured that binder was evenly distributed over the entire base of the pan by tilting the pan.
- The pans were then placed into a pan holder and then placed in preheated Pressure Ageing Vessel. PAV was then sealed ensuring all clamps and bolts were secure and tightened.
- After closing the lid of the pressure ageing vessel, it was allowed to return to the ageing temperature.
- After PAV achieved its desired ageing temperature, it was pressurised to 2.07MPa for 20 hours for ageing to occur within the specimen.

- Once ageing period was over, the pressure was released and the pans were removed from PAV.
- The binder from the pans was collected in a container after heating in an oven at 163 °C.

3.7 RHEOLOGICAL TESTING USING DSR

Rheological properties of the bitumen and mastics were measured using Malvern Gemini 200 Dynamic Shear Rheometer (DSR). Evaluation of viscoelastic properties binder made DSR an essential part of the test scheme as the conventional penetration and softening point tests were empirical testing techniques. The detailed DSR test set up including is shown in Figure 3.18, it is shown exclusive of temperature control unit.

Throughout rheological testing (both for amplitude and frequency sweep) following points were taken into consideration.

- The gap between the testing plates
- Trimming of the specimen
- Temperature of the specimen
- Cleanness of the plates



Figure 3.18: Dynamic Shear Rheometer

3.7.1 DSR Sample Preparation

Before mounting the binder between the plates, the zero gap was established. The bitumen was then heated until it was sufficiently fluid to pour. The required pouring temperature varied according to ageing history of bitumen and mastics. This heating was anticipated to remove any existing structuring due to steric hardening (molecular associations) that could significantly increase the measured modulus. Researchers have shown that steric hardening can increase the complex modulus by as much as 40 percent.

Plates are warmed sufficiently so that good adhesion between bitumen and plates is achieved. Specimens can be formed by following different procedures: In a study Airey and Hunter (2003) evaluated three methods of sample preparation evaluated namely; hot pour, silicone mould and weighing. The results showed that pouring the hot bitumen sample directly on the plates of DSR and then trimming the edges was most effective way of sample preparation. (Airey and

Hunter, 2003). However, in this research, in this research silicon mould method of sample preparation method was used to avoid excessive heating for bitumen. The other available options were;

- Pouring hot bitumen on the lower plate.
- Pouring bitumen on upper plate (removable).

The bitumen was heated and stirring occasionally to make sure it was homogeneously mixed and air bubbles were removed during the heating process, until it became fluid enough for pouring. Before pouring bitumen into silicon mould it was made sure that moulds were cleaned with acetone and from oily residues of methylated spirit. The plates were also cleaned in the same way; the plates in the water chamber were sufficiently heated to a temperature between 40 °C to 70 °C depending upon the stiffness of binder to achieve good adhesion between plates and binder.

For adding the sample to the plate, firstly the plates fastened in the DSR and the gap was zeroed. The plates were then lowered to heat at ambient temperature so that good bond between the plates and bitumen could be achieved. For 8mm plate, the heating temperature was 40 °C and for 25mm plate 70 °C was used. After the plates were sufficient warm, the bitumen from silicon mould was placed onto the plates. The upper plate was lowered to squeeze the bitumen, which then was trimmed along the edges as in Figure 3.19 (left). After trimming the plates were lowered for 50 µm and exact gap was achieved (2 mm for the 8mm plate, and 1 mm for the 25mm plate). This procedure resulted into bulging along edges as shown in Figure 3.19 (right).

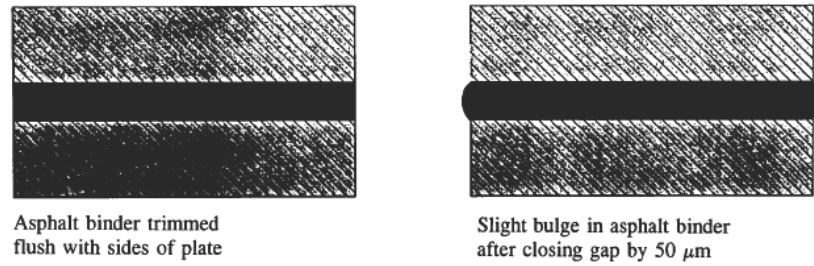


Figure 3.19: Trimming of specimen

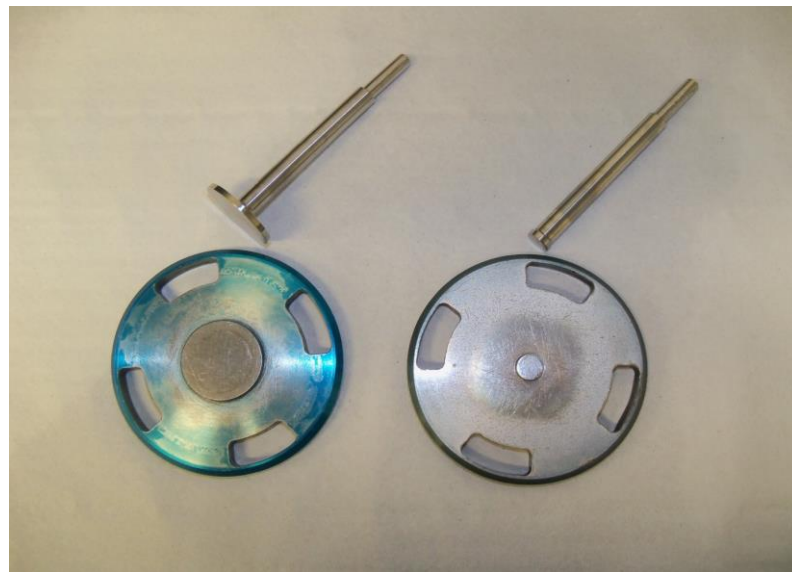


Figure 3.20: Standard DSR plates: 25mm and 8mm

3.7.2 Procedure

After sample preparation, the test parameters were established for oscillation and temperature. At each test temperature a suitable thermal equilibrium time was used to avoid thermal gradient in specimen. Thermal equilibrium temperature is of great importance. The British standard required a minimum of 600 seconds thermal equilibrium; however, for some binders this time was be insufficient. In this research it was used ranging from 600 to 900 seconds.

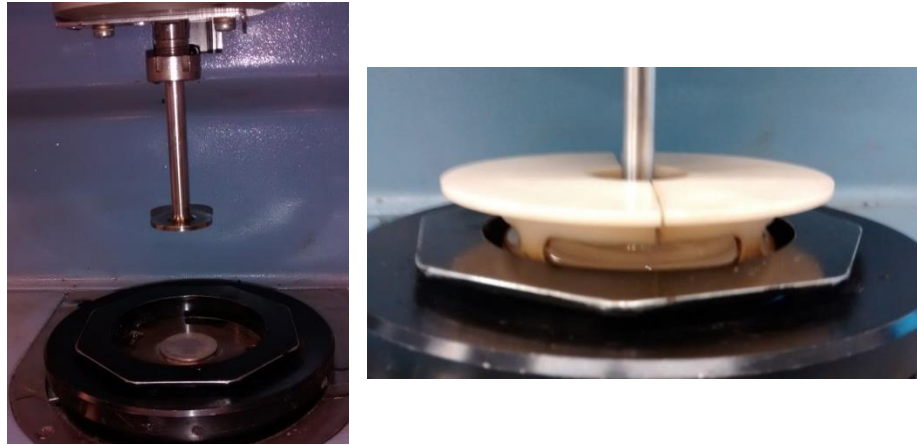


Figure 3.21: DSR testing plates

For stiffer and aged binders test was carried from high to low temperatures, this was adopted to avoid shearing of specimen at lower temperatures and then using at higher temperatures. For mastics low to high temperatures were used in order to avoid settling of filler at high temperatures. However, for aged mastics the chances of settling filler were less so a trade-off has to be made in selection of low to high or high to low temperature range.

3.7.3 Amplitude Sweep Tests

It was necessary to establish the limit of linear visco-elasticity to measure the rheological properties. This was to make sure that material response was measured within its linear region in frequency sweep test. Limit of linear visco-elasticity was measured through amplitude sweep test. The strain was then gradually applied to the thin bitumen film until nonlinearity appeared in response. The limit of linear viscoelastic behaviour was defined as point beyond which measured value of G^* decreased to 95% of its zero strain value as shown in Figure 3.22 taken from (Petersen et al., 1994b).

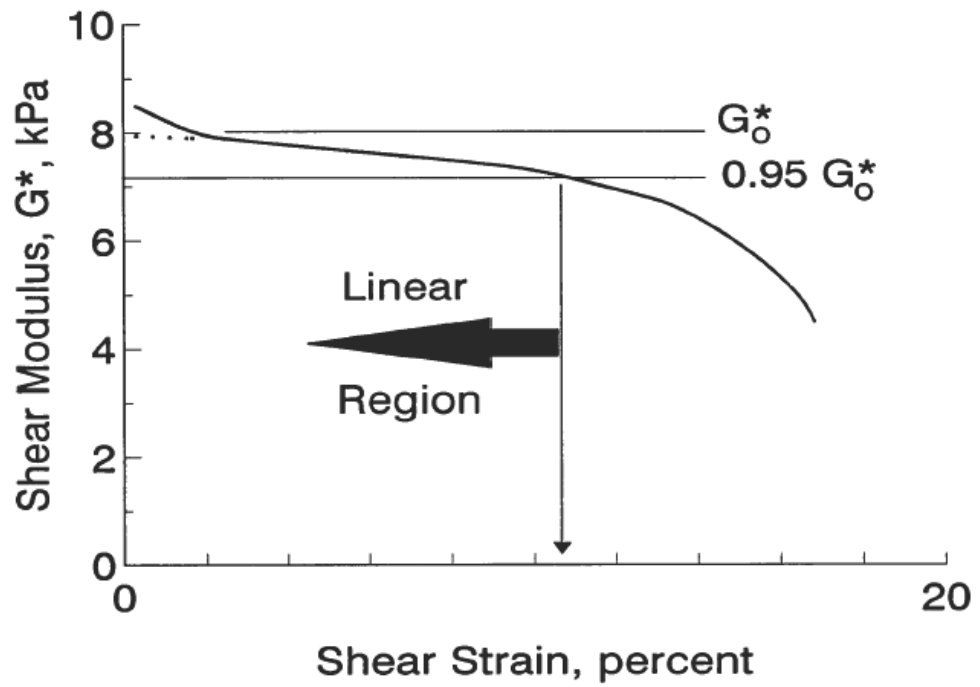


Figure 3.22: Strain Sweep to Determine Linear Region

From amplitude sweep test, the strain level was measured for frequency sweep to be conducted at the selected strain. Following test parameters were used for rheological testing.

Amplitude sweep test parameters

- Mode of loading used was strain control and min strain and maximum strain was selected as per standard test method. The test frequency of 1 Hz was used.
- Plate geometries consisted of 8mm and 25mm diameter Gap between the plates used were 2mm for 8mm and 1mm for 25mm, with excess of 50 μm before trimming the specimens.

- For measuring the lower limit of linear viscos-elasticity temperatures used were 10 °C for 8mm and 40 °C for 25mm, which were lowest temperature of each plate geometries and also the temperatures where shear failure was expected to happen if material response exceeded linear viscos-elastic limit.
- Thermal equilibrium time was 900 seconds; this time was vital part of the test to avoid thermal gradient within the binder. The minimum of 600 seconds is established as the lower limit for rheological testing. It was necessary that after each temperature interval the specimen achieved 900 sec thermal equilibrium time. In some cases, the temperature was lowered to 600 to fit the testing within one-day testing window.

3.7.4 Frequency Sweep Tests

The rheological response of bitumen and mastics were measured by frequency sweep test performed from temperature range of 0 °C to 80°C. Test temperature and strain levels used were mainly dependant on the stiffness and ageing history of binder being tested. The DSR test result report consisted of complex modulus, phase angle and other rheological parameters. For unaged binder and mastics strain level of 0.5 and 1% were used for 8mm and 25mm plate geometry. However, for aged binder and it was considerably lower.

Frequency sweep test parameters

- For frequency sweep the mode of test consisted of strain control.
- Frequency range used was 0.1Hz to 10Hz. (for some tests it was 0.01 to 10 Hz).
- The target strain was calculated from amplitude sweep test.

- Plate geometries used were 8mm and 25mm. The temperature range for 8mm plate was 10 °C to 40 °C and for 25mm was 40 °C to 80 °C. The temperature intervals varied from 5 and 10 °C.
- Test temperature range was between 10 to 80 °C and
- The thermal equilibrium time was selected as 900sec (in some cases min 600sec was used).

3.8 TESTING REGIME FOR RHEOLOGICAL TESTING

The experimental design consisting of rheological testing for ageing studies has been re-defined here. This will be further used in chapter 4 and chapter 5. The testing is divided mainly into two parts; ageing techniques and effect of filler packing on mastics. The first part ageing is shown in Figure 3.23. In this research three ageing conditions namely unaged, short and long-term ageing were used both for bitumen and mastics. The research with these conditions were also used in chapters on cohesive strength of asphalt.

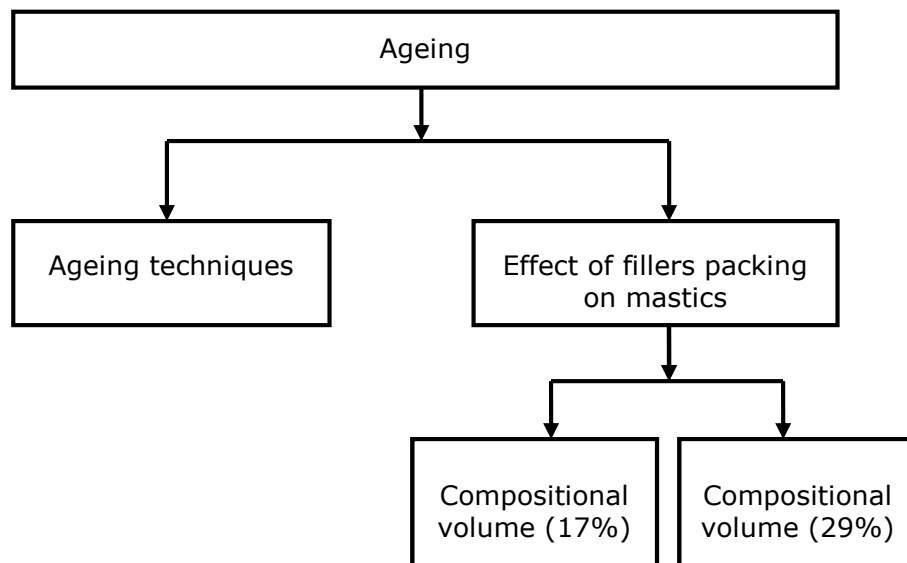


Figure 3.23: Testing scheme on ageing

In chapter 4, Initially binder was aged in laboratory from 1 day to 3 days to select optimal ageing period at extreme ageing levels. The ageing trials shown that three and two days ageing very severe for the binder. In this research one-day ageing was selected to be appropriate.

3.9 PULL OFF TESTING

The durability evaluation of binder leads to the need to measure the adhesive/cohesive strength of the binder-aggregate system. Adhesion being the inter-molecular force that binds two unlike materials together (binder and substrate) while cohesion being an inter-molecular force holding two similar particles together. In this mainly work related to chapter 6 has been discussed. The pull off testing of chapter 7 has been dealt in respective chapter. In that few cross-references have been made to this section.

3.9.1 Test Method Selection

The bonding evaluation of binding phenomenon required a more fundamental and direct method to measure adhesive/cohesive bond strength. The first step in the research was to use the existing method to evaluate bond strength. The test methods for this research were selected on following basis.

- Method where rate of strain can be controlled
- Method addressing the direct bond strength through tensile type testing
- Simplicity, practicality and cost effectiveness.

Although existing testing techniques of pull off testing like Pneumatic Adhesion Tensile Testing Instrument (PATTI) had their advantages of being repeatable and

providing simplistic means to evaluate the bond strength; however, this method has its limited capability of only providing maximum bond strength.

3.9.2 Modification to Gap Plate Assembly

The gap assembly design by Jakarni (2012) in his work "Adhesion of Asphalt Mixtures" was used to establish bitumen film thickness within the sandwiched substrate plates. The design of un-modified assembly is shown in Figure 3.24. However, during testing phase there was problem in establishing the correct film thickness. This was mainly due to the fact that the aluminium plate gauge used to make the U shape geometry was thin, when little compression was applied it bent under the force. This was due to large moment arm from the joint to the point of application of force. Various modifications were considered to make it more rigid. Attaching two aluminium collars served the purpose preventing the bent of the outward bent of the plates as shown in Figure 3.24.



Figure 3.24: modified gap assembly

A starret 263 ML micrometer screw gauge head was procured for the gap assembly. The micrometer had least count of 0.1mm and range between 0 to 25mm. It was mounted over the plate assembly and fixed through a screw. This micrometer served as a small compression device to establish the required gap.

3.9.3 Selection of Substrate

Aluminium was used as substrate throughout the study and a conditioning time of 24 hours was used. The main testing was carried off with aluminium substrate due the fact that study was mainly intended to be cohesive failure where type of substrate plays a lesser role. The selection of the aluminium substrate was again based on available research that as control material. In addition to this, the use of aluminium was also based on its higher thermal conductivity 205 – 250 Watts per meter Kelvin (W/mK). In comparison thermal conductivity of stainless steel is 16 (W/mK) and of air at 20 °C is 0.0257 (W/mK). This meant that the binder and aluminium substrate system cooled down faster as compared to steel. This made the only gap assembly available to prepare multiple specimen at the same time This also helped avoiding excessive heating of the binder.

3.9.4 Identification of Failure Mode

The failure mode was identified through visual observation, if plates were predominately covered with bitumen/mastic it was labelled as cohesive failure. In case of visibility of the major substrate surface, it was labelled as adhesive failure. A mix of coated and uncoated surface was labelled as mixed adhesive/cohesive failure. Figure 3.25 shows a cohesive type failure of one of the binder, the plates are arranged horizontally in order of top and bottom plates.

The rest of the results can be found in the appendix with exception of unaged granite for which the mode of failure was cohesive as shown in Figure 3.25.



Figure 3.25: Failure mode identification

3.9.5 Pull Off Test (method 1)

The testing, in this part was carried out with the method developed by Jakarni (2012). The complete testing set up used by the researcher is shown in Figure 3.26. This pull off method for of adhesive/cohesive bond strength had its advantage of being the most fundamental testing technique available for further research in the area. In this method Instron servo-hydraulic frame was used. This was capable of conducting testing under varying deformation rates and temperatures. In this research a 10 and 20 mm/min loading rate and a test temperature of 25 °C was used.



Figure 3.26: Test setup

3.9.5.1 Specimen Preparation

The binder was heated until fluid enough to pour. In the meanwhile, the substrates were fixed within the grooves of the steel plates as shown in Figure 3.27. The binder was then poured onto the substrate fixed in these plates. The two parallel plates containing substrates were then put into gap assembly as shown in Figure 3.28.

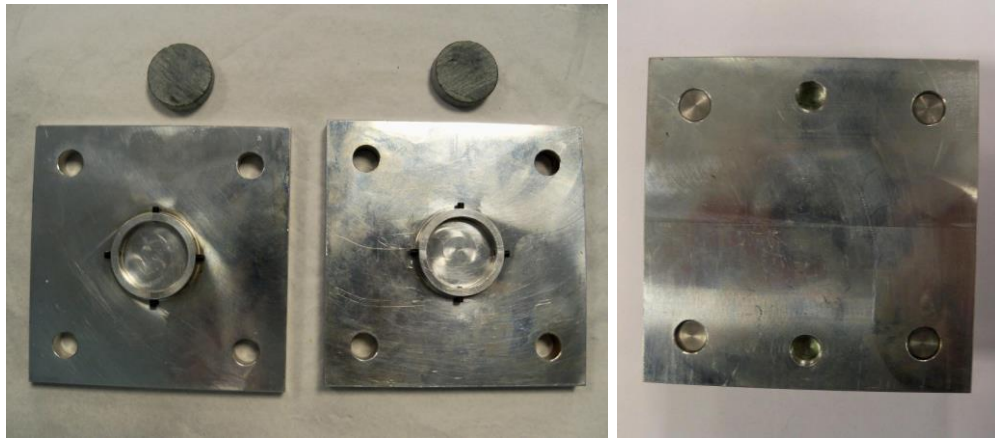


Figure 3.27: Parallel plate geometry with aggregate substrate

The two plates were squeezed together with little hand pressure, a micrometer compression device used to further compress the binder film to required thickness. Spacer bars were also introduced in four holes to prevent the lateral movement of the plates as shown in Figure 3.28. The pressure was applied gently not to overload micrometer and if needed whole assembly was heated at ambient temperature for 1 or 2 minutes to help in establishing the bitumen thickness. The micrometer was used to apply further pressure on to the plate to establish the desire gap.

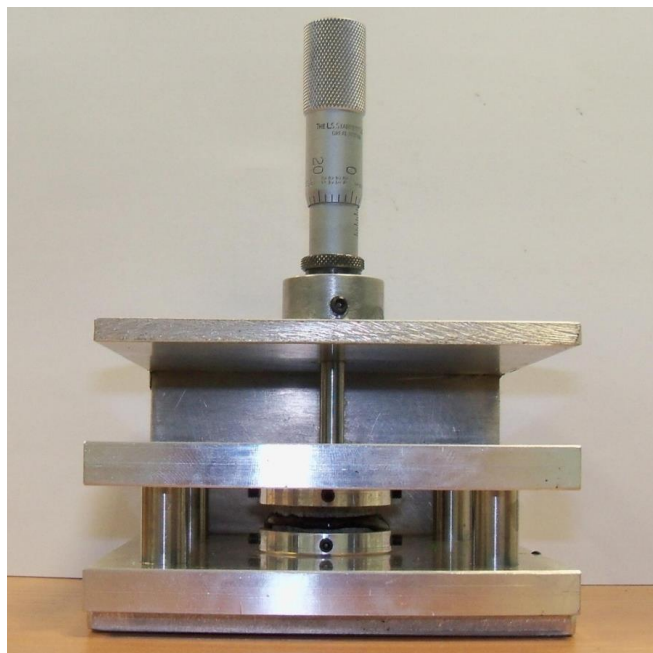


Figure 3.28: Sample preparation in gap assembly

After establishing the required gap, the specimen was cured at room temperature to allow sufficient adhesive bond development. A time of 15 minutes was used as curing time, sufficient enough, to allow bond development so that the plates could be removed from the plate assembly and second specimen could be prepared. The specimen was then left at room temperature at 24 hours to allow full development of cohesive and adhesive bond.

3.9.5.2 Test Procedure

After curing time, the complete plate assembly was attached to the testing rig. This was achieved with the help of screws attached to the bottom of plate as shown in Figure 3.27 (left). Both upper and lower plates were fixed in the similar manner with the help Allen/hex keys. Allen keys of various sizes were used to fasten the screws throughout pull off testing.

A universal joint was procured to attach the testing rig to the loading arm of the servo-hydraulic machine Instron. The advantage of universal joint was to provide four ways movement for specimen to be adjusted while uniaxial tensile load was applied. This universal joint served the purpose of application of uniaxial tensile load.

The two vertical rods in the testing rig served two folded purpose, creating a single integrated system for plate attachments and also guiding mechanism for the movement of plates. Two craver clamps were used to fasten the testing rig to the Instron servo-hydraulic frame. The base plate of Instron with the help of craver clamps was attached to testing rig. The testing rigid testing rig consisted of two parts. The upper plate had two vertical hollow cylindrical rods and a base plate having two vertical solid rods. The solid rods can slide into the hollow

cylindrical. This testing rig was capable to distribute axial tensile load on the plates containing bitumen. This testing rig is shown in Figure 3.29.



Figure 3.29: Testing rig (method 1)

The whole test assembly was then cured at 25 °C room temperature for 15 minute in controlled environment. This assembly was left to further condition at room temperature for 24 hours. After 24 hours the specimen was installed in UTM and was test after making relevant software adjustments. A constant cross head speed of 20 mm/min was applied in tensile mode. The detailed test procedure has been presented in Appendix D. This procedure has been taken from the work of its originator Jakarni (2012).

3.9.6 Pull Off Test (method 2)

The excessive handling and lengthy procedure in the method 1 lead to lot of test variables which were anticipated to be contributing to the poor repeatability of the method. This lead to search for alternative method which was as fundamental

as the above method yet was simpler in its sample preparation. The existing test technique developed by Apeagyei et al. (2014) in Nottingham Transportation Engineering Centre was deemed to be more suitable to carry out further testing.

3.9.6.1 Sample preparation

In this phase of testing silicon mould method of sample preparation was used film was used for binder film thickness control as shown in Figure 3.30. It was chosen to avoid excessive heating of the binder of the specimen from the same binder. Most of testing was carried out using 25 mm silicon mould (25mm) with 1mm bitumen/mastic film thickness. When 25mm silicon mould was used the binder film was pressed in compression device to achieve 500 mm gap (Figure 3.31). The aluminium plates used in the research had diameter of 25.4.

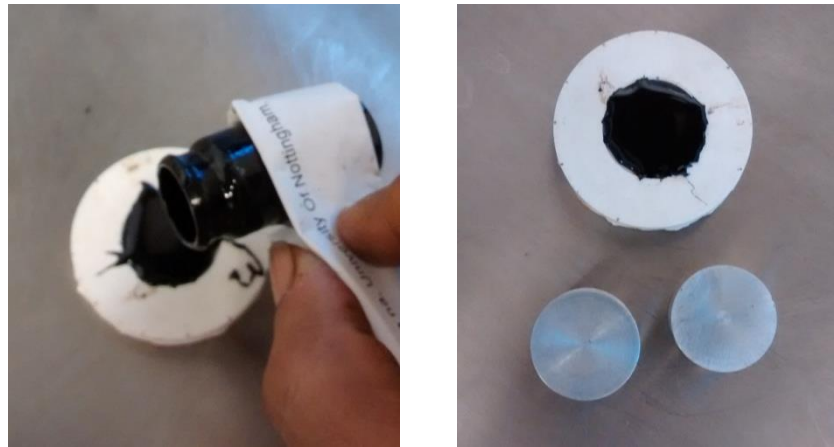


Figure 3.30: Silicon pouring method

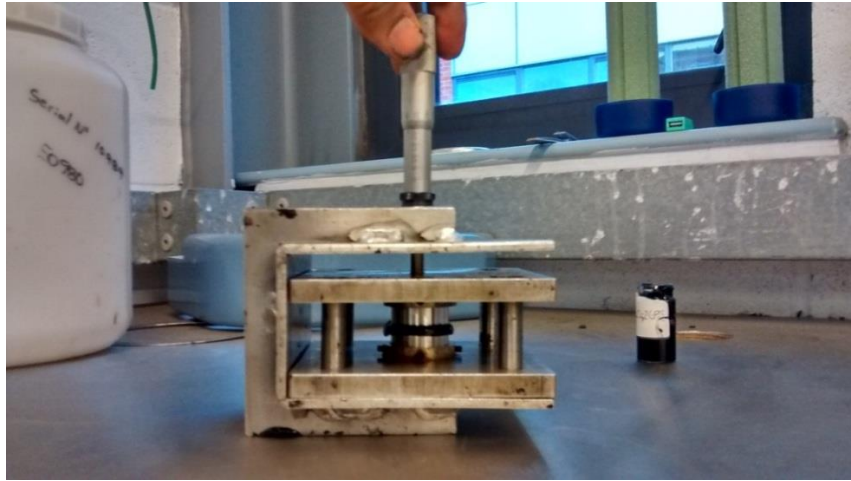


Figure 3.31: Establishing the film thickness using gap assembly

3.9.6.2 Test Procedure

The binder-substrate specimen (Figure 3.32 a) was added into test mould (shown in Figure 3.32 b) and fastened by means of three screws apart at an angle of 120°. The bitumen plate system was then mounted with bespoke tensile testing rig (Figure 3.33) in the servo-hydraulic test machine Instron with a 5kN tensile rig. Three replicates were used for 2nd phase of testing on average. After mounting the binder-substrate system in the testing rig, necessary software adjustments were made to perform test. A uniform cross head speed of 20mm/min was used to test specimen at a temperature of 20 °C. This cross head speed and test temperature was used in all the testing with this method. For every new test, parameters were loaded from present 'test method' file and displacement transducer was zeroed. The pull off load was then applied in strain control mode. The detailed test procedure is omitted here as there were no special software considerations. The test settings were similar to that of any normal tension test. This included test rate, safe operating and plot limits etc.



a: binder-substrate specimen



b: Specimen in mould

Figure 3.32: Test plate system for pull off testing (method 2) .



a: Specimen in during testing



b: Specimen after testing

Figure 3.33: Pull off testing (method 2)

The peak failure load was divided by the cross-sectional area of the plates to compute the bond strength, Figure 3.33 b shows a specimen after pull off testing. The results from testing were plotted in terms of force-displacement graphs and area under the curve before fracture was calculated to capture the effect of different fillers on the adhesive/cohesive properties.

3.10 SUMMARY

This chapter discusses experimental design, materials and relevant methods in detail. The emphasis has been made on the rationale behind the selection of material variables, test parameters and test methods. In this some of the associated problems and limitations during testing phase has also been discussed. The procedure has been discussed in detail. A special emphasis has been made on the ageing methods, evaluation of filler properties, rheological testing, and pull off testing. This chapter provides the experimental basis for the evaluation of the effects, mechanism and methods discussed in chapter 4, 5, 6 and 7.

CHAPTER 4 : STUDY ON AGEING TECHNIQUES

4.1 INTRODUCTION

The study of the most important environmental factor namely ageing of bitumen in asphalt pavements and its adverse effect on durability has been a matter of concern for highway agencies and researchers. This focus has led researchers in the paving industry to search for new methods and techniques to understand and evaluate this important process of pavement deterioration which results in its embrittlement.

In standard test practice the PAV is used as a yard stick to measure the effect of the long-term ageing of the bitumen. The ageing by this method has its advantages such as limited loss of volatiles, acceleration of oxidative process without resorting to high temperatures, reasonable amount of binder which can be aged and practicality (Mouillet et al., 2008). The PAV was developed to simulate 5-10 years in service. The literature review also indicated the presence of several other test methods and their variations to evaluate short and long-term effects of ageing. The use of TFO for short-term oxidative ageing indicated the possibility of its use for long-term ageing.

4.2 AMPLITUDE SWEEP & LINEAR VISCOELASTICITY

The first part of the research focuses on evaluating limits of linear viscoelasticity to evaluate the rheological response of the binder. Amplitude sweeps were performed as a part of the testing to define the limit of linear viscoelastic behaviour of the binder. This testing was performed using 8mm and 25mm

spindle geometries. A typical amplitude sweep test performed on the binder is shown in Figure 4.1. The limit of linear viscoelasticity was defined by the response of material falling below 0.95 times the maximum complex modulus. The Figure 4.2 shows a comparative graph of amplitude sweep tests performed on the 8mm spindle geometry using different ageing regimes for Pen 40/60.

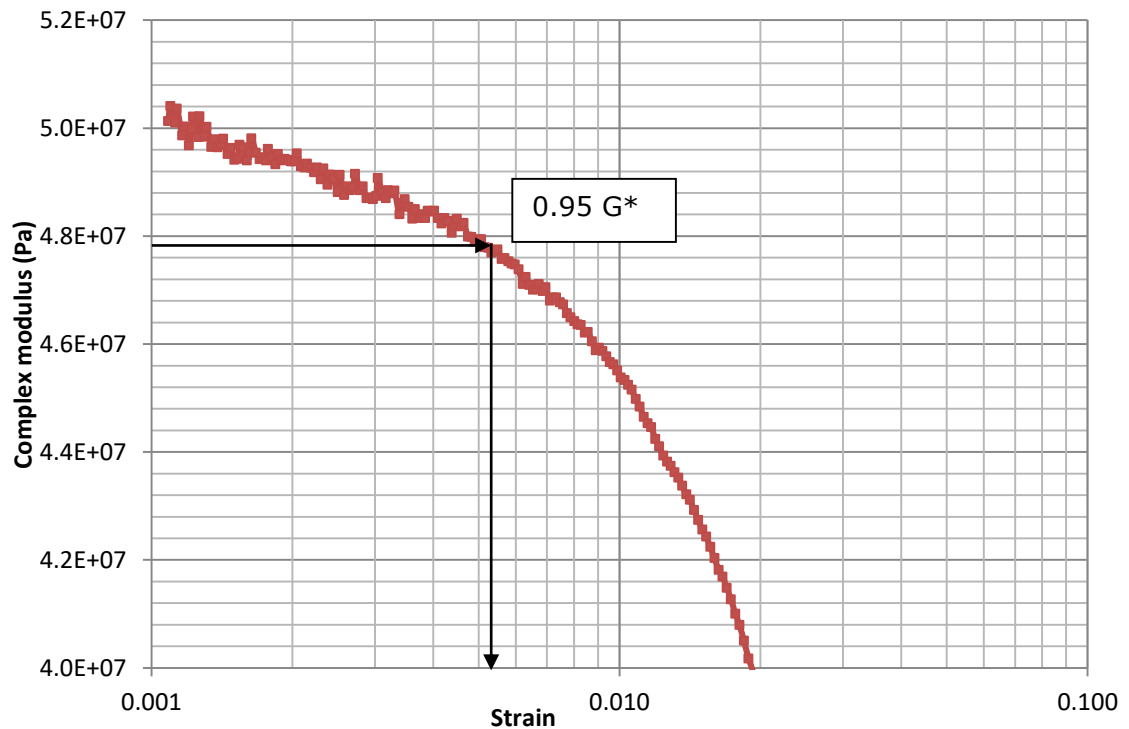


Figure 4.1: Amplitude sweep test for 8mm spindle

Figure 4.2 shows that a DSR amplitude sweep successfully established the limits to identify the lowest strain limit for the non-linear rheological behaviour of binder. The same graph shows a kink in the data which is mainly due to the behaviour of material in the region of non-linearity which occurs after the material passes this limit. This apparent anomaly is therefore of no concern in further discussion on evaluation of rheological properties. The result showed that the pressure ageing vessel aged binder and thin film oven test (TFOT) aged binder have limits of linear viscoelasticity of a similar order. It is important to

note that testing was done at the lowest test temperature for both the spindles. This was done to avoid likelihood of shear failure at relatively lower strain levels.

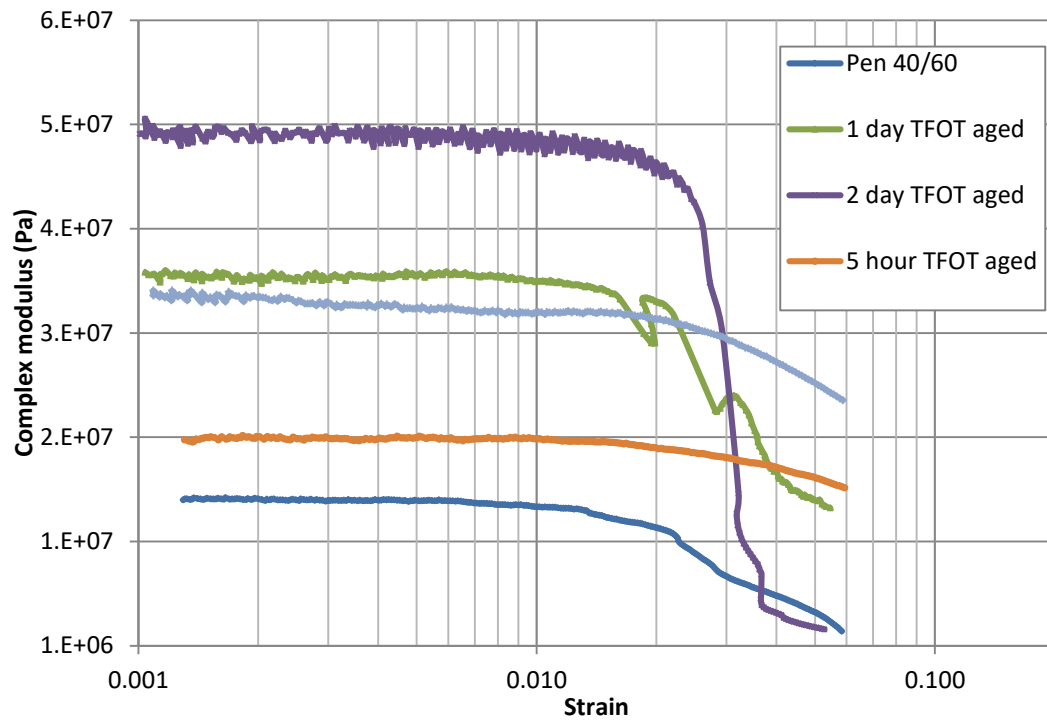


Figure 4.2: Amplitude sweep 8mm (Pen 40/60)

4.3 MASTER CURVE DEVELOPMENT USING GENERALISED SIGMOIDAL FUNCTION

In the second part of testing, the rheological tests was performed using both 8mm and 25mm DSR spindles for a temperature range from 10 to 80 °C. The data obtained was then linearly transposed using shift factors (shown in Figure 4.6) which led to the construction of master curves.

The shifting was done by use of the time-temperature superposition principle (TTSP). An optimisation technique was used for the complex modulus and phase angle isothermal plots to construct mater curves.

The initial shift factors served as a base value for optimisation and were calculated using the Williams–Landel–Ferry equation (WLF) through DSR software. The shifting factors, in a real sense, were calculated using the method termed 'numerical, non-linear least square shift' (Yusoff et al., 2011). In this method the shape factors of the sigmoidal function and shift factors (for various complex modulus isothermal plots) were solved simultaneously using non-linear least squares fitting. This was achieved using the Solver function in MS Excel. This has the advantage of not assuming any functional form of relationship of shift factor vs temperature.

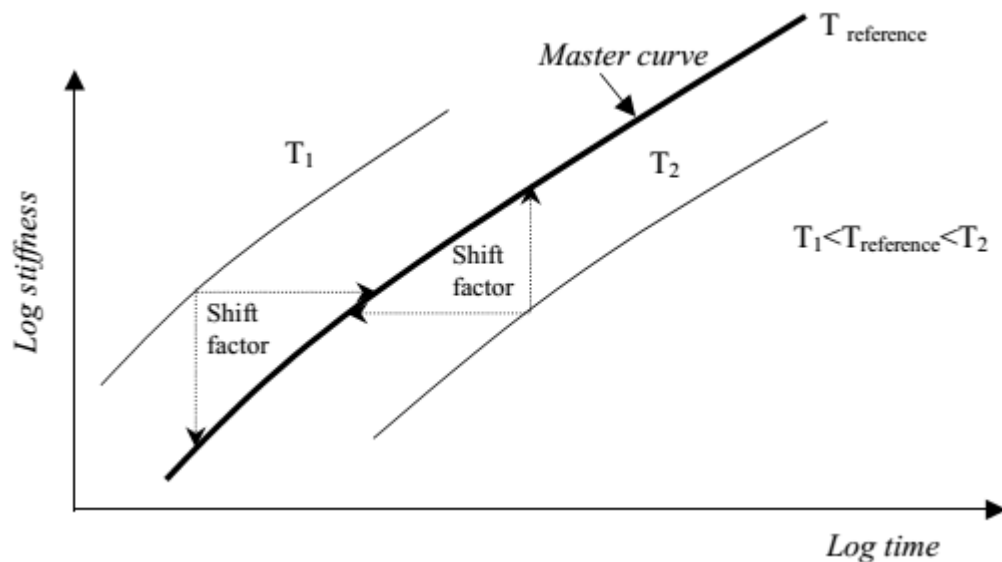


Figure 4.3: Typical Isothermal plot and master curve Rahman (2004)

The master curves for the data were constructed at a reference temperature of 30 °C from the isothermal plots of the higher and lower test temperatures. Figure 4.4A shows the master curves for complex modulus (G^*) for the Pen 40/60 which also shows the raw data for these temperature ranges. Figure 4.4B shows a typical master curve for phase angle. In this research the same shift factors were used for the complex modulus and the phase angle for bitumen (see section 4.4 for a discussion on this subject)

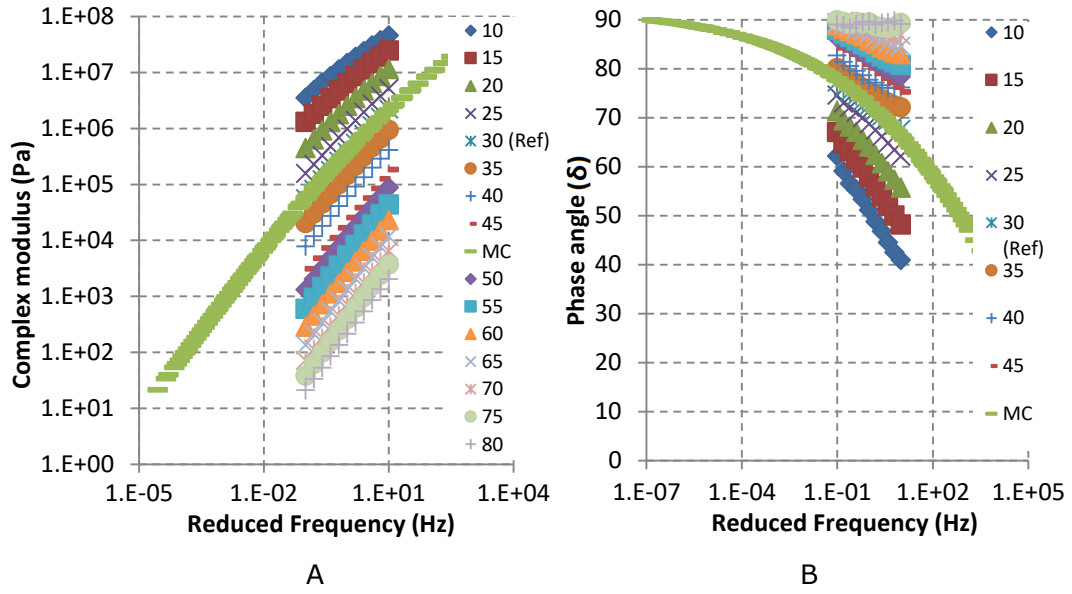


Figure 4.4: Master curves for G* and phase angle

The popular Witczak Sigmoidal model was used to fit the data to master curves generated through the optimisation technique. This model has been used in MEPDG. This model yielded a good fit for complex modulus and phase angle data obtained from the LVE frequency sweep tests undertaken (Rowe et al., 2009). The generalised sigmoidal model has been used in MEPDG and has been supported in a study by Yusoff et al. (2011). The model is given as

$$\log |G^*(f, T)| = \delta + \frac{\alpha}{1 + e^{\beta + \gamma (\log f_r)}}$$

The model parameters are defined as

α = Difference between upper and lower asymptote

β = Shape coefficient

δ = Lower asymptote

γ = Shape coefficient

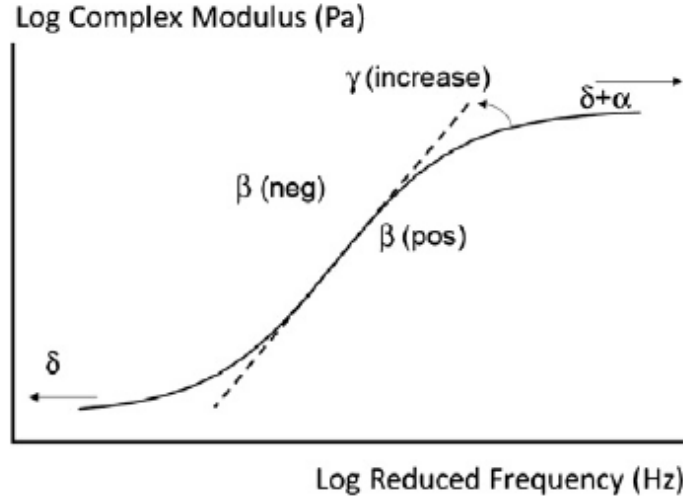


Figure 4.5: Generalised sigmoidal function parameters

An alternative sigmoid, Richards' equation, had its advantage over the standard logistic function. This generalised logistic curve or Generalised Logistic Sigmoidal Model has the ability to give a better fit for non-symmetric master curve data. This model is given as follows.

$$\log |G^*(F, T)| = \delta + \frac{\alpha}{\left(1 + \lambda \cdot e^{(\beta + \gamma(\log f_r))}\right)^{\frac{1}{\lambda}}}$$

The logistic model has been preferred in this research. The models described require calculation of different shape factors namely α , β , γ and δ . These shape factors define the shape of the curve. The non-symmetrical shape is taken into account through the λ coefficient. The model parameters of generalised sigmoidal functions were calculated through simultaneous optimisation. These parameters determined the curvature characteristics. A description of shape factors of the Generalised Logistic Modified Sigmoidal is given in Figure 4.5. These shape factors for this first part of the research are listed in Appendix A.

4.4 G* SHIFT FACTOR PLOTS

The first step in comparison of the PAV and TFOT requires the use of the shift factors to comment on the validity of the model for complex modulus and phase angle master curve plots. The shift factor plots in Figure 4.6 yielded a fit of the data which indicates that the shift factors successfully transposed the data. The PAV and one day TFOT shift factors were almost identical but differed from the 5h TFOT and unaged virgin binder. The difference between them is more pronounced for higher temperature and the 25 mm spindle. This indicates material behaviour is apparently more easy to understand at higher testing temperatures.

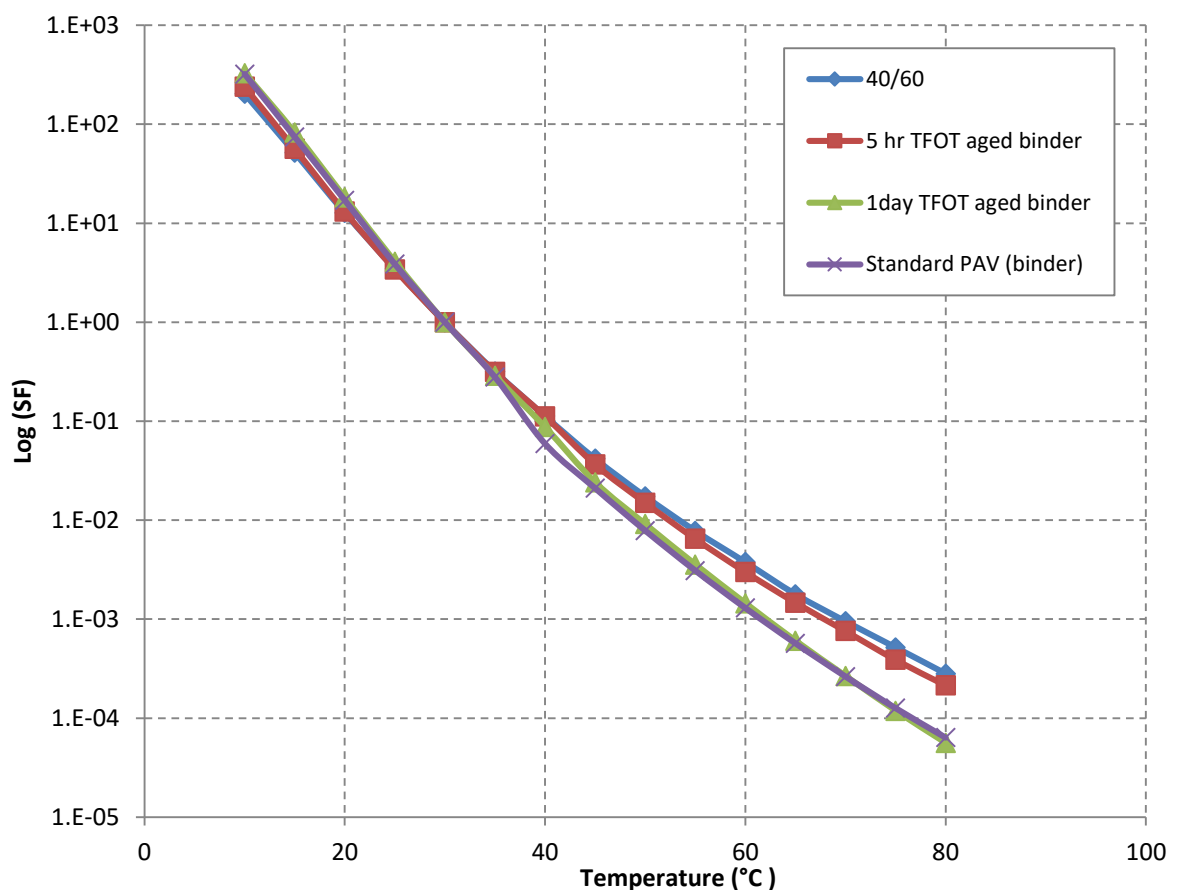


Figure 4.6: G* SF comparison for 40/60 ageing conditions

The data analysis also included computation of the shift factors for the phase angle, optimised just as for the complex modulus master curves. This was done on the unaged mastics to check shifting and application of the Generalised Modified Logistic Sigmoidal function to the data of mastics. The first step involved shift factor calculation from complex modulus data exactly as computed for the unmodified binder (represented in Figure 4.7). The analysis shows that complex modulus shift factors warranted the use of the model for analysis of aged and unaged mastics too. The shift factors from complex modulus master curves were dependant on the ageing history and filler type. It can be seen from the shift factor plot that the numerical shifting approach used in the construction of the master curve gives a good fit. This is due to the shifting flexibility of this method.

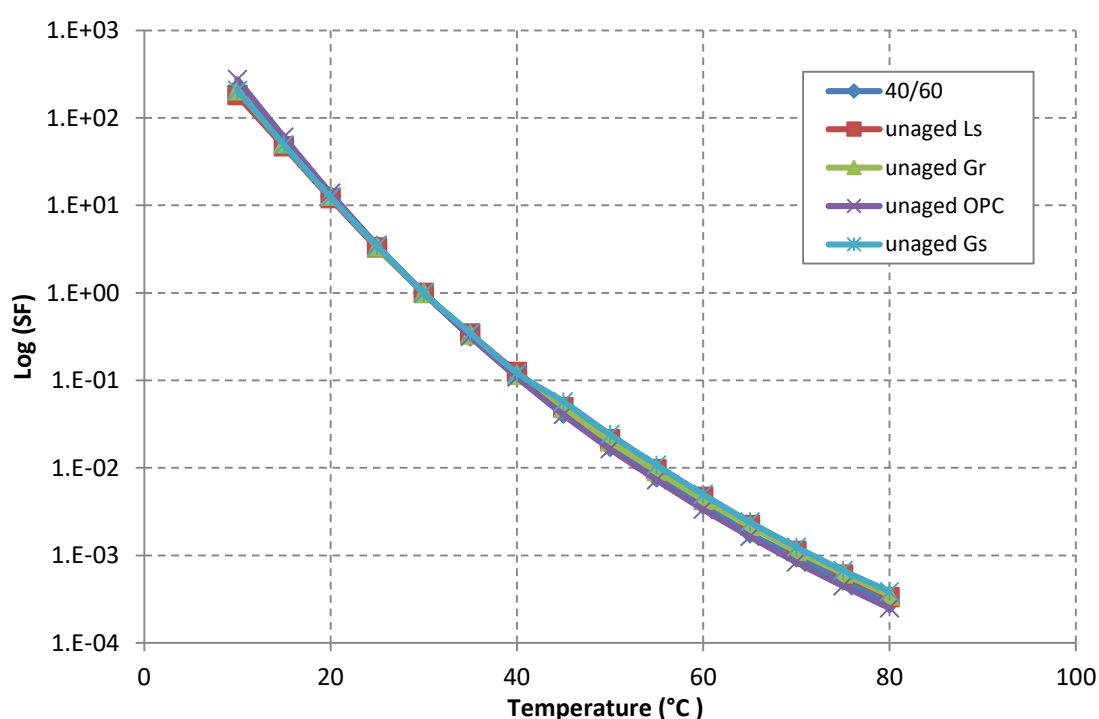


Figure 4.7: The use of shift factors in generalised sigmoidal function

4.5 COMPARATIVE AGEING PAV AND TFOT

A comparative study of ageing history of the binder shows that the binder ageing effect is more apparent at higher pavement temperatures where material behaviour is more viscous. The material response at lower temperature becomes less apparent due to the dominant stiffer behaviour. This is in-line with what has been seen from the shift factor plots. The PAV and TFOT master curves show that TFOT ageing is of a similar order. A closer look at the results indicates that the 1 day TFO complex modulus is higher than that of PAV ageing. This is equal to the magnitude that has happened during short term ageing.

In simple words, the effect of 1 day TFO ageing is of similar increase as that of short term ageing. The graph represents a fairly uniform optimised master curve. It is worth noting that at high frequencies the master curve approaches a limiting value. This limiting value for bitumen and PMBs is known as the glassy modulus (G_g) at 1×10^9 . This limit varies for aged and unaged mastics depending upon the percentage and type of mineral fillers. This phenomenon occurs due to physical interaction in the mixture. This happens, because the addition of filler increases the elastic response of the material (Yusoff et al., 2013).

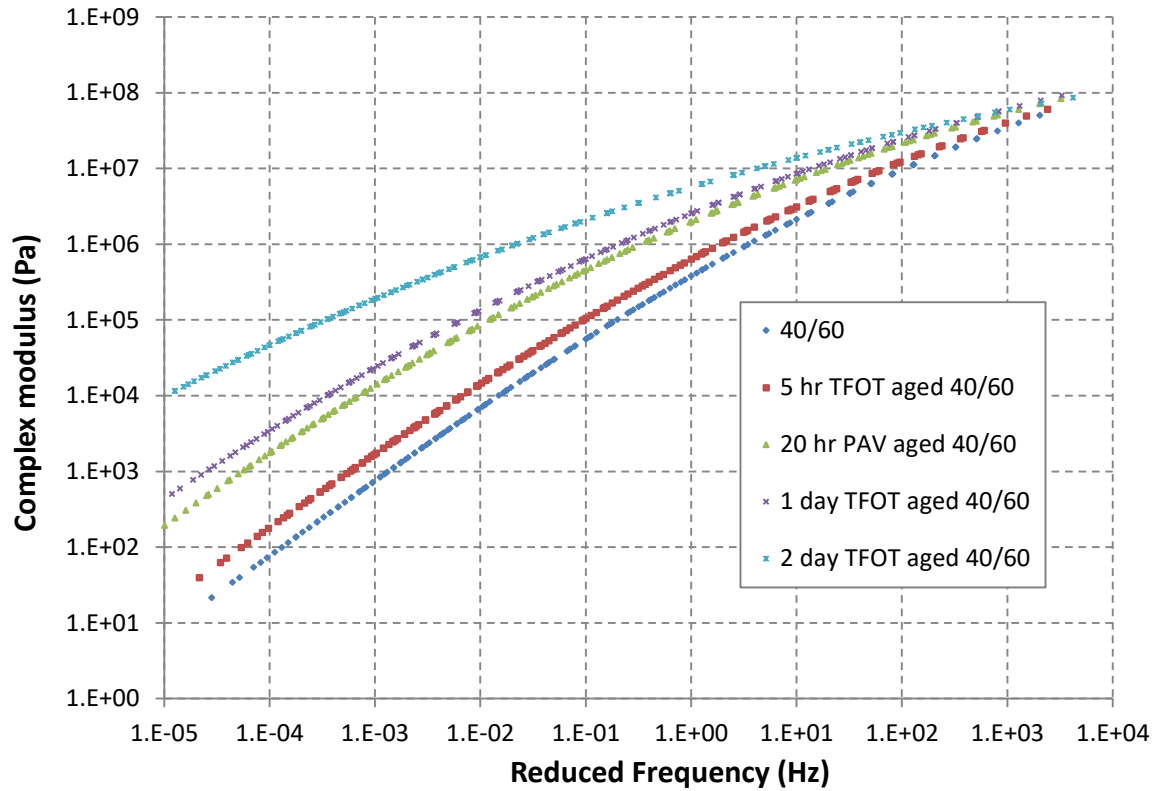


Figure 4.8: Ageing conditions comparison of Pen 40/60

The results are consistent with phase angle master curves, where TFOT and PAV show identical binder behaviour both at higher and lower reduced frequencies. In Figure 4.9 phase angle seems to be more sensitive to material response. The same graph shows that 2 days ageing was rather severe for the binder, and this ageing regime may not be appropriate for studying the material viscoelastic response. This led, in subsequent research, to limiting the ageing time to 1 day only.

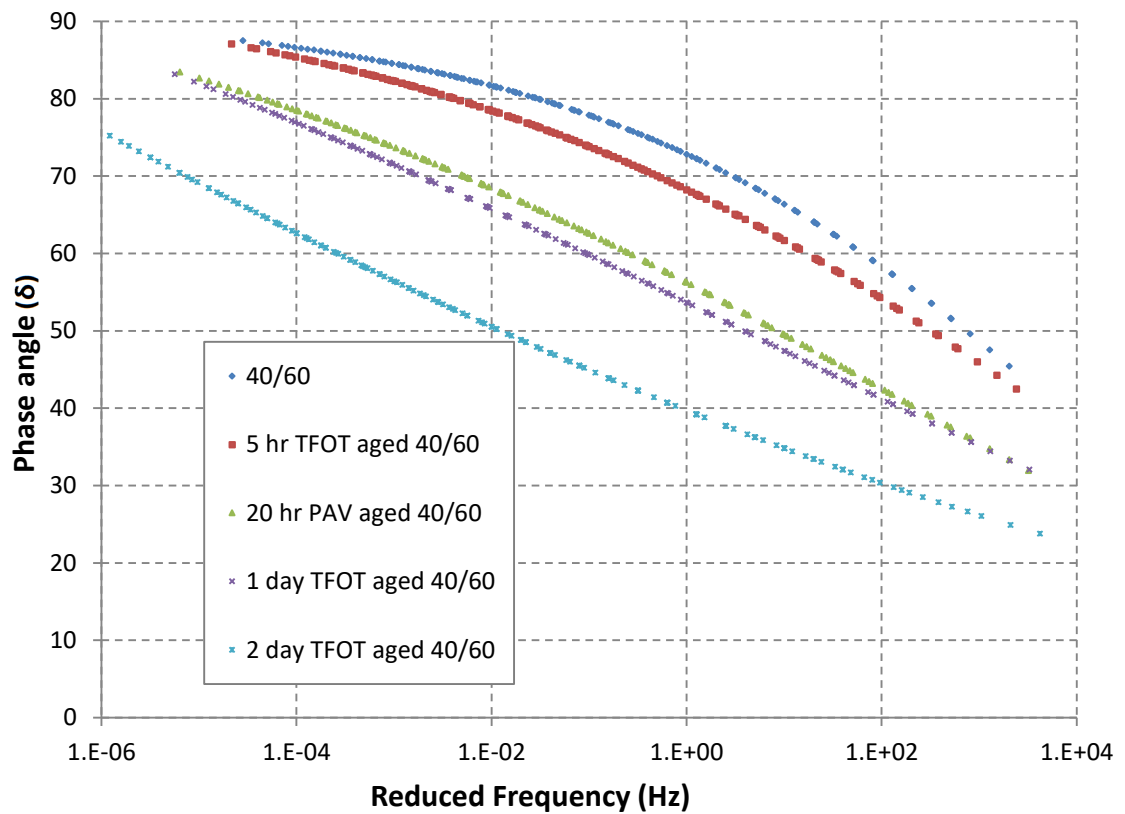


Figure 4.9: Phase angle for ageing conditions comparison

4.6 BLACK SPACE DIAGRAM

The material response was studied in terms of a black space diagram. In this diagram inconsistencies in data are identified (as discussed in the literature review). The black space diagrams or black diagrams were constructed to study material behaviour without the use of the Time Temperature Superposition Principle. This diagram had its advantage in identifying anomalies in data without the use of any shift factors and time temperature superposition principle i.e. temperature and frequency.

The complex modulus master curves of all binders fall within a narrow band and do not differentiate the differences of modification clearly. Black diagrams bring out the modification differences as seen through the differences in the shapes of the curves.

The black space diagram accurately predicts the behaviour just the way it is demonstrated from the complex modulus (G^*) and phase angle (δ) master curves. The black diagram supported the argument that the 1 day TFOT ageing was able to accurately show the rheological response of the material in a similar way to the PAV. The differences reveal that 1 day and PAV ageing had little difference in terms of their black space diagram analysis. The 2 days ageing response was different compared to one day, suggesting limiting the ageing to one day in further study.

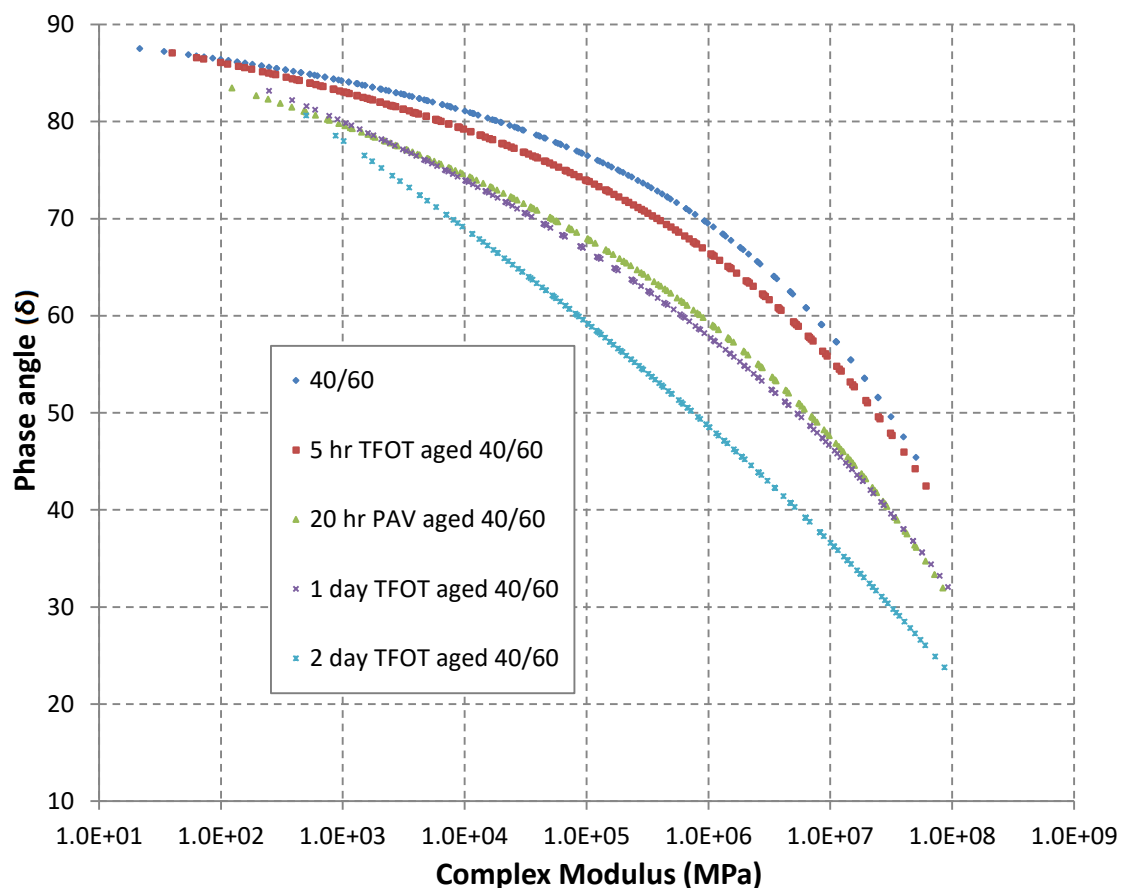


Figure 4.10: Black diagram for ageing conditions comparison

The ageing index was calculated to check the severity of ageing at a single temperature and frequency. Ageing index can be defined as the ratio of a physical property of aged bitumen to the physical property of the original bitumen. These indices were computed at temperatures of 25 °C and 60 °C at a frequency of 2.5 radian (4 Hz). The ageing indices of aged asphalts were computed relative to Pen 40/60. The calculation of ageing index based on penetration or softening point was deemed unnecessary due to the empirical nature of the tests. Instead these values were extracted from complete the rheological response from 0 to 80 °C. These values are show in the following table and figure.

Table 4.1: Calculation of ageing indices

Ageing condition	Values at @60 C @.4 Hz			Values at @25 C @.4 Hz		
	G*	phase angle	Ageing index	G*	phase angle	Ageing index
Unaged	6503.8	84.37	1.00	1.95E+06	66.19	1.000
5 hr TFOT	11059	81	1.70	2.88E+06	61.33	1.474
Standard PAV	35776	73.11	5.50	7.17E+06	49.03	3.666
1 day TFOT	62610	67.51	9.63	8.83E+06	46.86	4.519
2 day TFOT	288770	52.08	44.40	1.41E+07	33.06	7.194

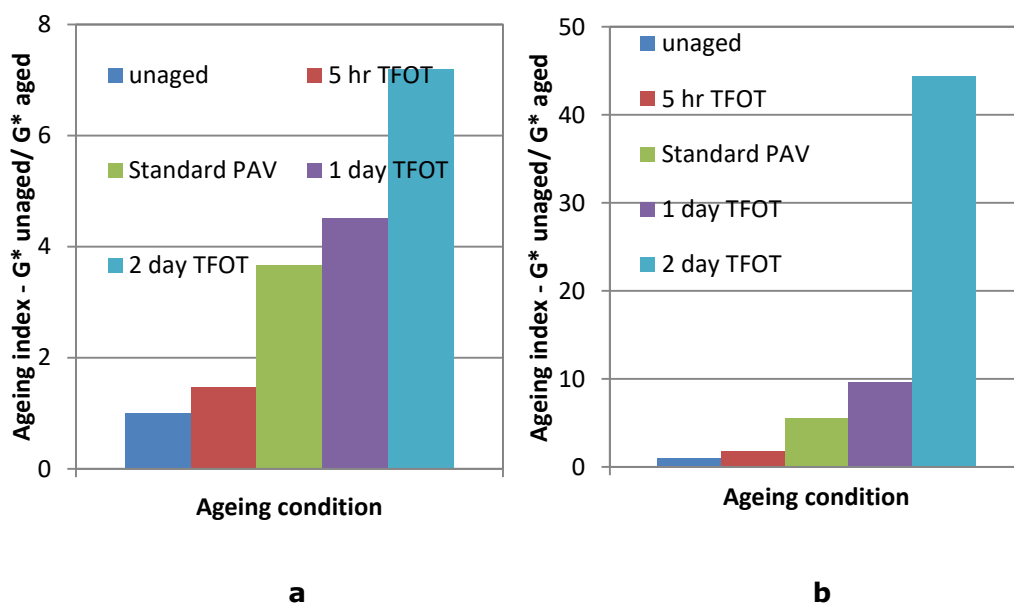


Figure 4.11: Ageing indices at 2.5 rad a) 25 °C b) 60 °C

The existing data cannot provide a complete picture; however, an attempt has been made to draw conclusions as follows.

- 2 days ageing resulted in massive hardening as depicted by ageing indices and associated errors (depicted by complex modulus master curves) making it unsuitable for further rheological testing.
- Thin Film Oven can be used to study long term oxidative ageing of binder. It is appropriate to limit ageing to 1 day. This is to avoid excessive hardening of the binder.
- One-day ageing Thin Film Oven (TFO) represents ageing which is more than what is expected to occur during 5 to 10 years' service life of a pavement.
- There is concern that there may be reduced bond strength between aggregate and bitumen as compared with that in the PAV. This is because the added pressure, in the case of PAV, might limit the loss of oily components. The loss of these components in the case of TFOT might result in more hardening than ageing. For this reason, there is a need to study the chemical functionality changes after TFOT oxidative ageing.

4.7 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR or infrared absorption spectroscopy is a test method which is used to detect and identify chemical functionalities in a compound. This compound can be in gas, liquid or solid phase. This spectroscopy can be performed on both organic and inorganic compounds. FTIR provides reliable and quick information related to

aliphaticity, aromaticity and oxygen rate. In the case of bitumen, this technique helps identify functional groups within the binder. This method is being widely used to study chemical functionalities especially that formed on oxidation; thus this method is useful in identifying oxidation products. A typical FTIR is shown in Figure 4.12.



Figure 4.12: FTIR spectrometer (Wu, 2009)

The principle of infrared is that different bonds vibrate at different frequencies when activated by external energy sources. For example, in the case of carbonyl ($\text{C}=\text{O}$), carbon and oxygen have a strong dipole charge difference. Upon excitation with infrared the molecule resonant at higher frequency thus gives a strong peak in the IR spectrum. A given bond type can only reach a higher energy activation level by absorbing a quantum corresponding exactly to a specific infrared (IR) frequency. In the case of bitumen this molecular bond is covalent. Every bond type has a specific frequency at which it vibrates under vibrational energy from an infrared light source. The absorbance or transmittance corresponding to each bond under vibrational energy is measured in terms of wavelength (μm) or wavenumber (cm^{-1}). The peaks along the wavenumber axis are peculiar to specific chemical bonds. Thus FTIR is a powerful method providing a tool to track formation of both sulfoxide and carbonyl bonds. These main

oxidation products of bitumen have the following wave numbers as per Anderson and Goetz (1973).

- C=O in carbonyl ($1,700\text{ cm}^{-1}$)
- S=O from oxidation ($1,030\text{ cm}^{-1}$)

Various indices can be calculated from this information corresponding to different peaks. The FTIR indices are measured by calculating the areas from valley to valley. The area calculation as compared to the height of the band is more useful as it simultaneously takes into account vibrations of the same type (Marsac et al., 2014) . Different indices are given by the following expressions (Mouillet et al., 2008).

- Aromatic structures (aromaticity index $-A_{1600}/\Sigma A$)
- Aliphatic structures
- aliphatic index $(A_{1460}+A_{1376}) / \Sigma A$
- branched $A_{1376}/(A_{1460} + A_{1376})$
- long chains $A_{724} / (A_{1460} + A_{1376})$
- Oxygenated functions
- Carbonyl index – $A_{1700} / \Sigma A$
- Sulphoxide – $A_{1030} / \Sigma A$

The carbonyl content of FTIR testing is represented by carbonyl area (CA) which is defined as the peak area in the carbonyl region. This content is the integration of the area from 1660 to 1753 cm^{-1} . Here carbonyl compounds are further composed of ketones, dicarboxylic anhydrides, carboxylic acids and 2-quinolone types. All of these compounds are oxidation products, which is why they are all studied under the umbrella of carbonyl. Their relative proportions in bitumen are of increasing order from ketones to 2-quinolone. Among these Ketone is the

major oxidation product (Petersen, 1975). An infrared spectrogram showing different chemical functionalities and their corresponding areas is represented in Figure 4.13. The left graph is plotted on a different scale to accommodate the larger peaks in the FTIR spectrum. However, the region of interest in this research is carbonyl and sulphoxide region.

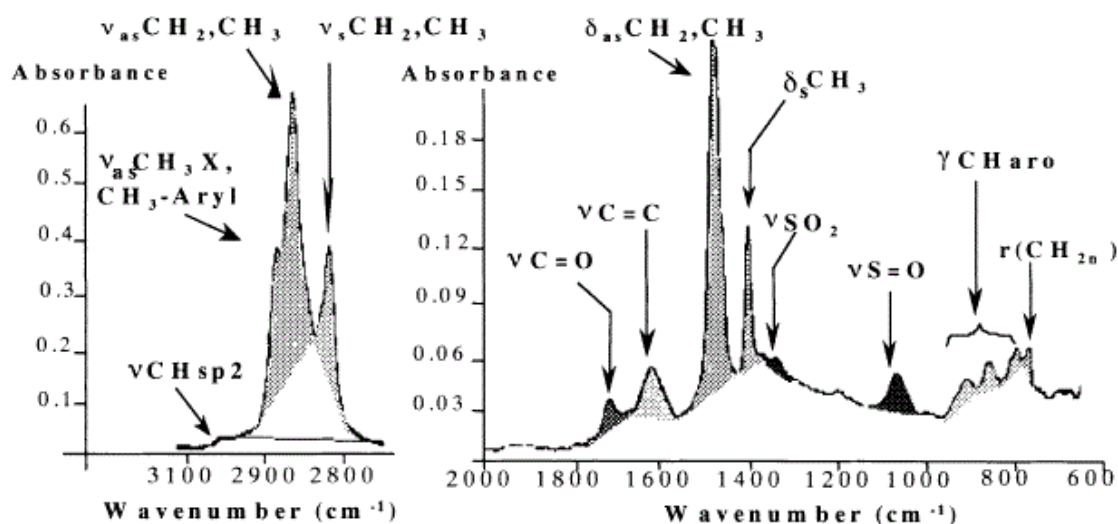


Figure 4.13: Functional groups identification on typical FTIR spectrum

There are several methods of sample preparation to obtain an FTIR spectrum. Many of these methods involve studying the spectra of bitumen when it is dissolved in a solution. This solution is then analysed in the FTIR. The most commonly used solvents are CCl_4 and CS_2 . A common method of sample preparation is to use a potassium bromide (KBr) or sodium chloride (NaCl) plate to hold the bitumen. In this research a dry method of sample preparation was used. This method involved placing the dry specimen of bitumen on the spectrometer in the FTIR.

4.8 COMPARISON OF OXIDATION PRODUCTS THROUGH FTIR

In this research the RILEM (I_{CO}) method was used to calculate the oxidation products. In this method, the baselines are drawn between the values at certain limiting points as per Marsac et al. (2014). The fixed areas under the curve are used both for the carbonyl region and aliphatic hydrocarbons in the bitumen as shown in Figure 4.14. In this method the wave numbers of aliphatic hydrocarbon including methyl (CH_3) and ethylene groups (CH_2) are selected as references. This was because these groups are not significantly affected by oxidation. In analysis, the fixed carbonyl area (A_{1700}) limit ranged between wave number 1,660 and 1,753 cm^{-1} . The fixed reference area (A_{ref}) was between 1,350 and 1,525 cm^{-1} . The area of sulfoxide was calculated as the area between 1000 and 1,105 cm^{-1} . It is to be noted that the original RILEM method does not take into account the sulfoxide content. Thus, the limiting values for the sulfoxide content were taken from Belgian Road Research Centre (BRRC) method namely 'Bitumen analysis by FTIR spectrometry testing and analysis protocol'. The RILEM method was a modification of the method adopted at l'Institut français des sciences et technologies des transports (IFSTTAR).

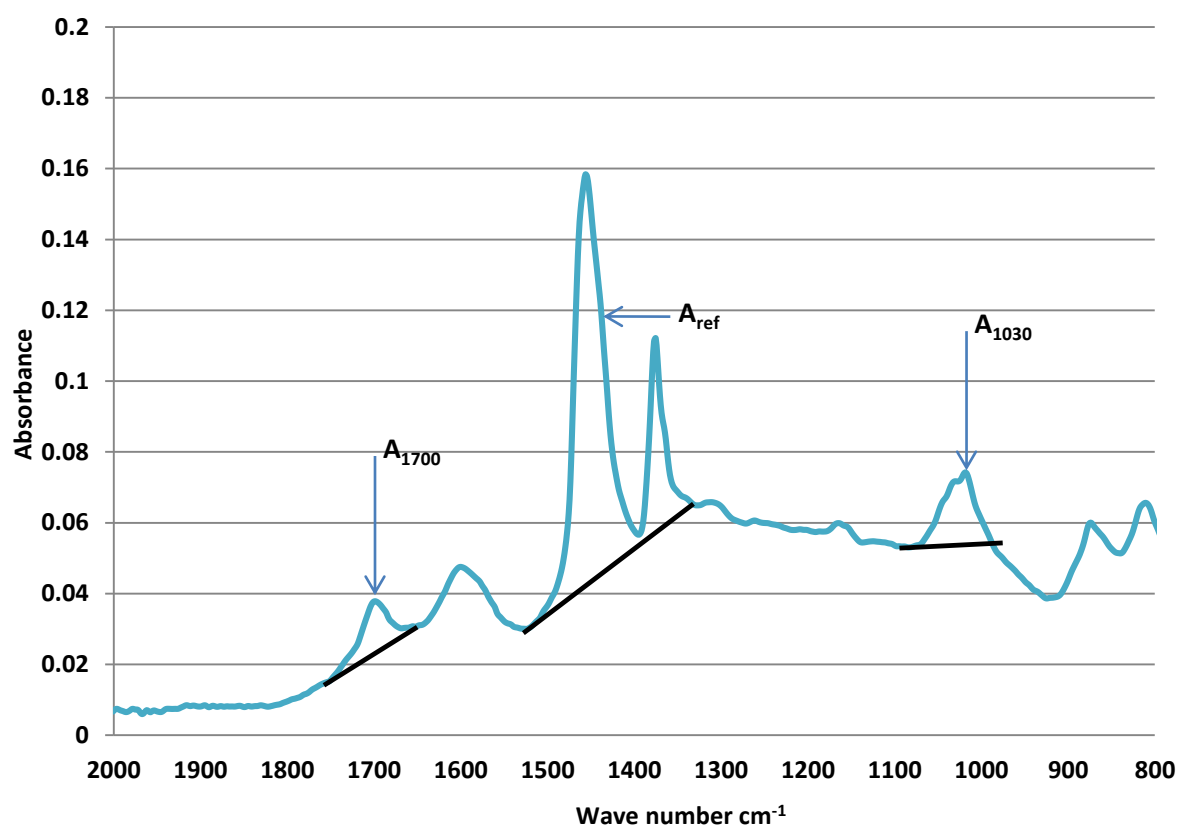


Figure 4.14: Determination of the areas for the RILEM I_{co} index

From FTIR Index calculation using the RILEM method (I_{co}) it can be seen that the oxidation pattern follows the same trend as that seen from changes of physical properties on ageing.

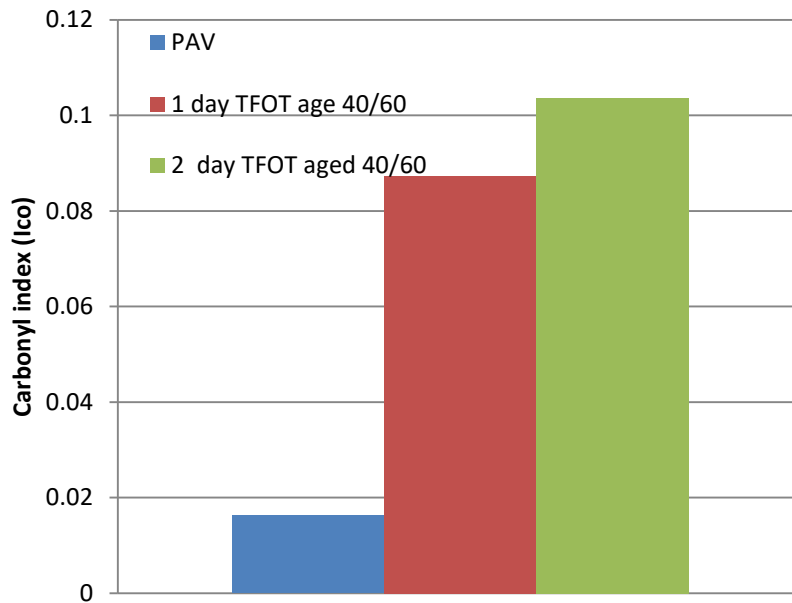


Figure 4.15: Carbonyl index comparison

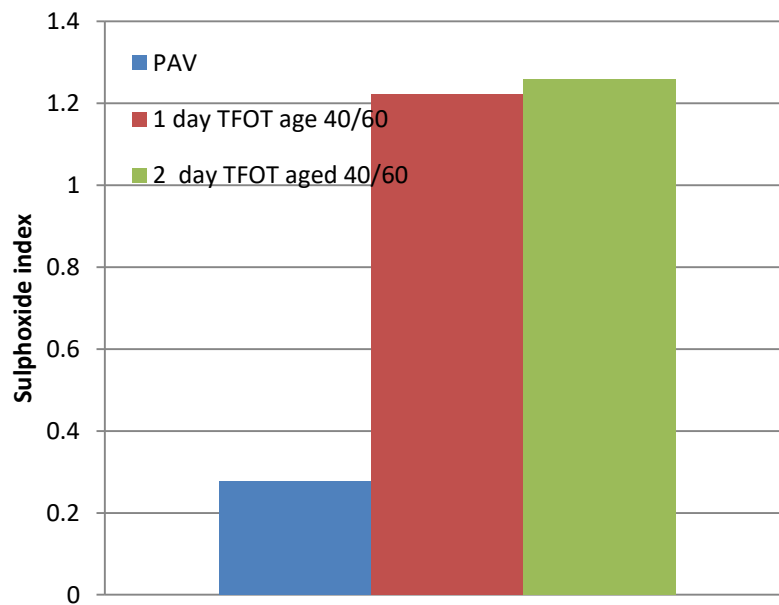


Figure 4.16: Sulphoxide index comparison

The graphs in Figure 4.15 shows that the carbonyl index increases upon different levels of ageing using PAV and TFOT. The large index difference between 1 day TFOT aged bitumen and PAV aged shows presence of more carbonyl region oxidation products in the former. The lower difference between 1 day TFO and 2

days TFO ageing reveals major oxidation has happened during the one day. The increase of oxidation products becomes somewhat steady with increase of time. Especially in case of sulphoxide as shown in Figure 4.16, there is little difference between one day and two days ageing. It can be observed that the increase of sulphoxide is not as sensitive to oxidative ageing as carbonyl after one day. This lower increase of oxidation products reveals that more physical hardening has happened rather than oxidation.

The discussion can be supported from Petersen's work studying Boscan bitumen ageing using a 15 μ m film binder thickness at 130 °C, coated on an inert fluorocarbon column packed in a gas chromatograph column and analysed thorough differential spectroscopy, which showed the presence of ketones and sulphoxides as the main oxidation products. The additional products at the later stages of oxidation included smaller amounts of carboxylic acids and dicarboxylic anhydride. It can be clearly seen from Figure 4.17 that ketones and sulphoxides are the main oxidation products with an initial abrupt increase upon oxidation and later showing a slower increase on further oxidation. The sulphoxide molecules are more easily formed on oxidation and the inflection point in sulphoxide formation is clearly noticeable; however, the inflection point for ketones formation is not noticeable. The proposed explanation given was that this inflection point is not shown due to high temperature for oxidation and associations of polar molecules upon oxidation. It was claimed that this hyperbolic trend for ketone and sulphoxides formation was typical for all bitumens.

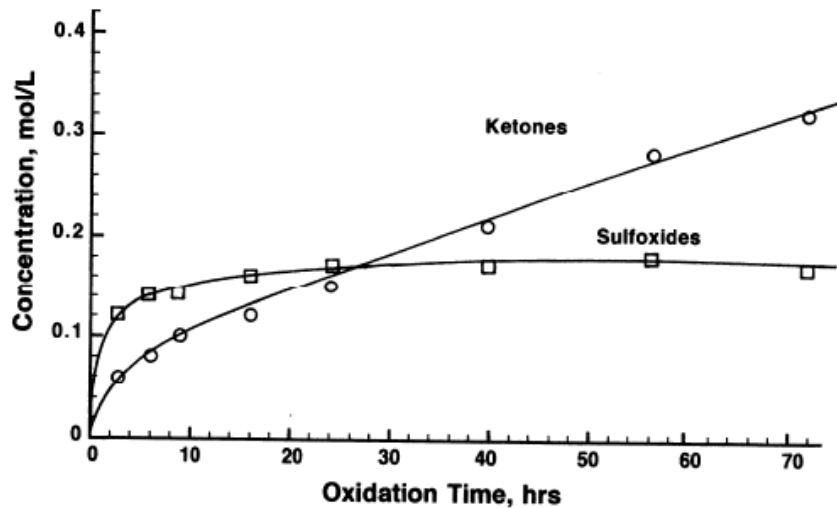


Figure 4.17: Kinetic oxidation of SHRP AAG-1 core bitumen at 113°C

The initial spurt of sulphoxide becomes somewhat steady with time during oxidation at high temperature and this trend was reported to depend upon environmental parameters affecting bitumen. This steady state is also the result of depletion of sulphides for low sulphur concentration bitumen, and for high sulphur content bitumen this effect is associated with formation and thermal decomposition of sulphoxides with oxidation.

When compared to the PAV, the TFOT carbonyl index reveals that actually oxidation has happened in 24 hours. This indicate that more oxidation has happened in case of TFOT. This effect is not truly captured in terms of ageing index computed from complex modulus. Even the master curves do not fully capture the effect. There is concern of a greater loss of oily components in TFOT ageing over an extended period of ageing.

4.9 SUMMARY

In summary, this part of the research has focused on the use of the TFO for oxidative ageing for longer ageing durations. This ageing regime is more severe than the one used in the standard testing procedure. A discussion has been made to assess the severity of TFOT ageing when compared to PAV ageing of the binder. The result has also been studied through a useful analytical chemistry tool. The tool used was FTIR spectroscopy, which was used to identify the functional groups on oxidation. In the case of bitumen, the functional groups identified were the well-known carbonyl group and sulphoxides. The carbonyl content is more sensitive to oxidation products as compared to sulphoxide. The amount of these oxidation products has been computed in terms of carbonyl and sulphoxide index. These components were computed as areas under the curve from valley to valley. The analysis has indicated a relatively large amount of oxidation products. The analysis has indicated the unsuitability of 2 days ageing for any further rheological testing. The results of these FTIR analyses are in accordance with what has been studied through rheological tests. The results and discussion indicate the promising use of the TFOT for long-term oxidative ageing of the binder. It is further recommended to limit the TFO ageing period to 20 hours.

CHAPTER 5 : EFFECT OF FILLER PROPERTIES ON MASTICS

5.1 INTRODUCTION

The addition of mineral filler to asphalt mixture improves its properties such as rutting resistance (Chen, 1997). Some of these fillers such as hydrated lime are competitive with polymer additives (Lesueur and Little, 1999). In relation to mastics, Anderson (1987) showed that mineral filler affects the bitumen in different ways such as by increasing its stiffness and moisture resistance. It also acts as an extender, increase workability and improve ageing characteristics. Its role in the asphalt mixture can be discussed in terms of its mechanical and chemical aspects (Liao, 2007). The increase in stiffness is quite a complex phenomenon which has not been fully understood yet. Researchers in this area have been trying to simplify this complex problem while attempting to reduce it to a few parameters. In this regard, in the widely cited work of Shashidhar and Romero (1998), they reduced problem to two factors only namely; maximum packing fraction (ϕ_m) and generalised Einstein coefficient (K_E). This research focus on the use of traditional as well as non-traditional approaches toward the stiffening potential.

In this research, the effects of filler's primary and secondary characteristics were studied. The primary properties were directly studied through filler tests. The primary characteristics studied in this research involved density, specific gravity and particle size distribution. The relevant laboratory tests were performed. Traxler and Miller (1936) further classified the primary characteristics into two aspects as important primary characteristic and less important primary

characteristics. The important primary characteristics included PSD and shape of particles while less important primary characteristics were texture, hardness, strength, specific gravity etc. According to them secondary characteristics were void content, surface area, average void diameter etc. In this research, the Rigden void apparatus was used to calculate the packing of the fillers which was a measure of the primary (indirectly) and secondary characteristics (directly) of the filler. According to Traxler et al. (1933) and Rigden (1947) the void content of filler is the most important parameter to influence the properties of a bitumen mastic. According to Rigden (1947) the mechanism of interaction in mastics between binder and filler is best explained by the theory of packing of particles. This research explores the effect of the nature of filler on the ageing of bitumen. Ageing (as measured through viscosity) according to Rigden is independent of the nature of bitumen and filler. This was, however, found to be dependent on fractional voids in mastics. The fractional voids is the void content when the filler mass is removed from the bulk volume of the compacted dust. The quantity of bitumen to this point is referred as fixed bitumen. Any excess of bitumen to above this amount is referred to as free bitumen.

One of the earliest references to work on bitumen-filler suspension is the work of Richardson (1915). According to him, the role of the filler was not only void filling but it also included some sort of physico-chemical interaction between filler and bitumen. According to him limestone and Portland cement are considered to be better fillers as they adsorb a thicker layer of bitumen. This means they reduce the effect of ageing on bitumen.

In a study by Traxler (1937b), the relative viscosity was independent of the type of rigid particle in suspension. However according to him packing of filler played a very important role in the properties of mastics. According to Anderson and Goetz

(1973) the Rigden work on fillers provides a baseline for any further research on fillers.

5.2 ADSORPTION AND CATALYTIC EFFECT

It is important to note that the concept of Rigden's fractional voids does not account for the agglomeration of filler in mastic, its degree of dispersion and most importantly the interaction at the bitumen-filler interface. In this section, an attempt has been made to provide a theoretical background for one of the important interfacial phenomena which is not accounted by the afore-mentioned parameter. The detail of this phenomenon is discussed in section 5.9 at greater length. In order to achieve this objective, an amplitude sweep test was performed on the mastic to calculate the region of linear visco-elasticity both for 8mm and 25 mm spindles. In the second part of the testing, frequency sweep tests were performed on the mastics to study their viscoelastic behaviour at low and high pavement temperatures.

The total surface area of filler is much larger than that of the same volume of coarse aggregates which will result in the adsorption of the heavier polar fractions and a catalytic effect from the aggregate. The catalytic ability of filler here refers to its ability to accelerate the ageing process. This point led to the view that studying mastic ageing is more advantageous to research these effects as compared to studying mixtures.

In this part of the research, the effects of filler primary and secondary characteristics were studied. The primary characteristics were directly studied through filler tests. The characteristics studied in this research were density, specific gravity and particle size distribution. The relevant laboratory tests were

performed. The Rigden void apparatus was used to calculate the packing of filler which was a measure of its primary and secondary characteristics.

In the first part of the study an amplitude sweep test was performed on the mastic to calculate the region of linear visco-elasticity both for 8mm and 25 mm spindles. In the second part, frequency sweep tests were performed on mastics to study their viscoelastic behaviour at low and high pavement temperatures.

According to a study by Gubler et al. (1999), filler can delay the ageing of the binder by being an obstacle to diffusion of oxygen to the heart of the bitumen. This can be further elaborated by reference to Tunnicliff (1962) stiffening gradient as shown in Figure 5.1. According to him there are adsorbed and non-adsorbed layers surrounding the filler particle as shown in Figure 5.1.

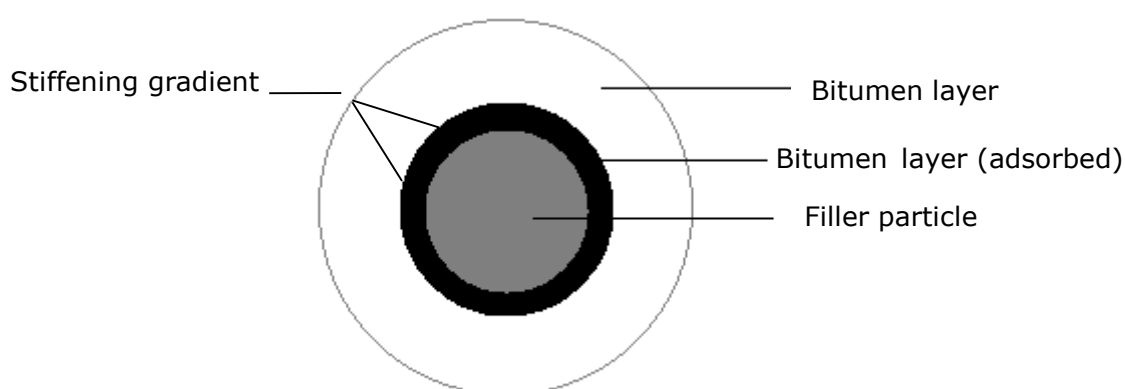


Figure 5.1: Bitumen layer on filler particle

The stiffening effect of the filler is more at the surface of the particle but then decreases with increase of distance from the adsorbed layer. This explains the phenomenon where aggregate fillers with similar primary properties, even the same packing fraction, result in different stiffening effects. Figure 5.2 explains the different stiffening effect of fillers based on the surface activity. The filler on the

left has low surface activity as compared to that on the right with high surface activity. This figure is taken from Buttlar et al. (1999) to illustrate the surface activity of fillers. The surface free energy and acidic and basic character play important roles in this regard.

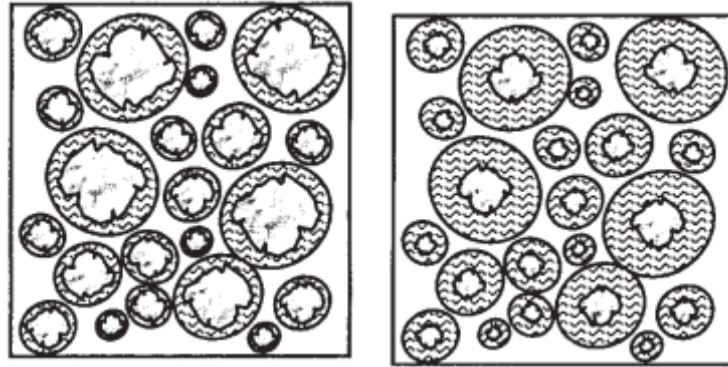


Figure 5.2: Low surface activity vs high surface activity

5.3 COMPOSITIONAL AND EFFECTIVE VOLUME

In this part of the research mastics were prepared by mixing fillers into a volume of bitumen. The particle densities of the fillers were calculated using pycnometers and water/methylated spirit as test liquids. The volume fractions however are expressed as compositional volumes of filler as a suspension in the bitumen. This notation of 'compositional volume' is used throughout this chapter. Another notation is used in this chapter, where the effective volume of bitumen takes the effect of the packing into account using Rigden voids. The compositional volume and effective volume are expressed through the following expressions taken from Heukelom (1965). The calculation of these volumes is presented in Table 5.1.

$$V_f = \frac{\frac{M_f}{S_f}}{\frac{M_f}{S_f} + \frac{M_b}{S_b}}$$

$$V_e = \frac{100}{V_{fR}} V_f = \frac{100}{(1 - \epsilon)} V_f$$

where

M_f refers to mass of filler

S_f is the specific gravity of filler

M_b equals to mass of bitumen

S_b is the specific gravity of bitumen

ϵ refers to Rigden voids of mineral filler.

Table 5.1: Compositional and effective volume calculation

Filler	Mass of filler (g)	Specific gravity	Mass of bitumen (g)	Compositional volume (%)	Rigden voids (%)	Effective volume (%)	Free bitumen volume content
	M_f	S_f	M_b	V_f	ϵ	V_e	V_{FB}
Limestone	209.84	2.623	200	29	33	44	56
OPC	241.6	3.02	200	29	45	53	47
Gritstone	224.64	2.808	200	29	40	49	51
Granite	216.48	2.706	200	29	38	47	53
Limestone	78.69	2.623	150	17	33	25	75
OPC	90.6	3.02	150	17	45	31	69
Gritstone	84.24	2.808	150	17	40	28	72
Granite	81.18	2.706	150	17	38	28	72

The Rigden voids is an important parameter to incorporate the effect of the secondary properties of the filler as a suspension in the bitumen (referred to as mastic throughout this chapter). The advantage of this test is that it is very simple to carry out and describes the secondary properties of filler which in turn are dependent on its primary characteristics. Historically researchers have demonstrated that it is difficult to relate stiffening potential of filler in bitumen using any single parameter. Examples of such parameters can be surface area, specific gravity, particle size distribution. Many researchers have affirmed the

usefulness of the parameter called 'Rigden voids' such as Heukelom Wijga (1971), Anderson et al. (1992) and Kandhal et al. (1998).

Two mastics concentrations were used in this research, 40% by volume of bitumen (29% compositional volume) and 20% (17% compositional volume) to account for high volume concentration and low volume concentrations respectively. This was based on studies such as Gubler et al. (1999) that suggest that binder should be added on a volumetric basis instead weight basis.

These filler concentrations were divided into two groups as 17% compositional volume concentration and 29% compositional volume concentration. This notation will be referred to from now on instead of plain volume concentration. The discussion on effect of packing of filler is made for both volume concentrations. The effect of filler on ageing is discussed taking into account the both volume concentrations.

5.4 EFFECT OF PACKING ON STIFFENING POTENTIAL OF FILLERS

The rheological testing performed on the unaged bitumen and mastics. In order to explain these results, the effect of packing on ageing of the bitumen was studied in terms of master curves. These curves were plotted for all the mastics as shown in Figure 5.3 and Figure 5.4. In addition to this black diagrams have also been plotted as shown in Figure 5.5.

The results indicated that filler added to an unaged bitumen acts as a stiffening agent to increase the stiffening effect of the composite. The penetration grade 40/60 has considerably lower stiffness as compared to all bitumen-filler mastics.

This effect is apparent at both higher and lower temperature ranges of the testing as shown in Figure 5.3. Further, from the figure it can also be seen that dynamic shear modulus of mastic is dependent on the moduli of both bitumen and filler. This means a harder penetration grade bitumen will have a higher complex modulus.

In these relatively high percentage filler volume concentration mastics, the effective volume concentrations were 44%, 54%, 49% and 47% for limestone, OPC, gritstone, and granite respectively. These values corresponded to 33%, 45%, 40% and 38% Rigden voids respectively. These amounts yielded 29% compositional volume of the fillers in the suspension. It is important to note that packing and volume concentration are not the same. This is because the volume occupied by particles is represented by its concentration while packing is concerned with inter-particle space. The packing is incorporated through Rigden voids.

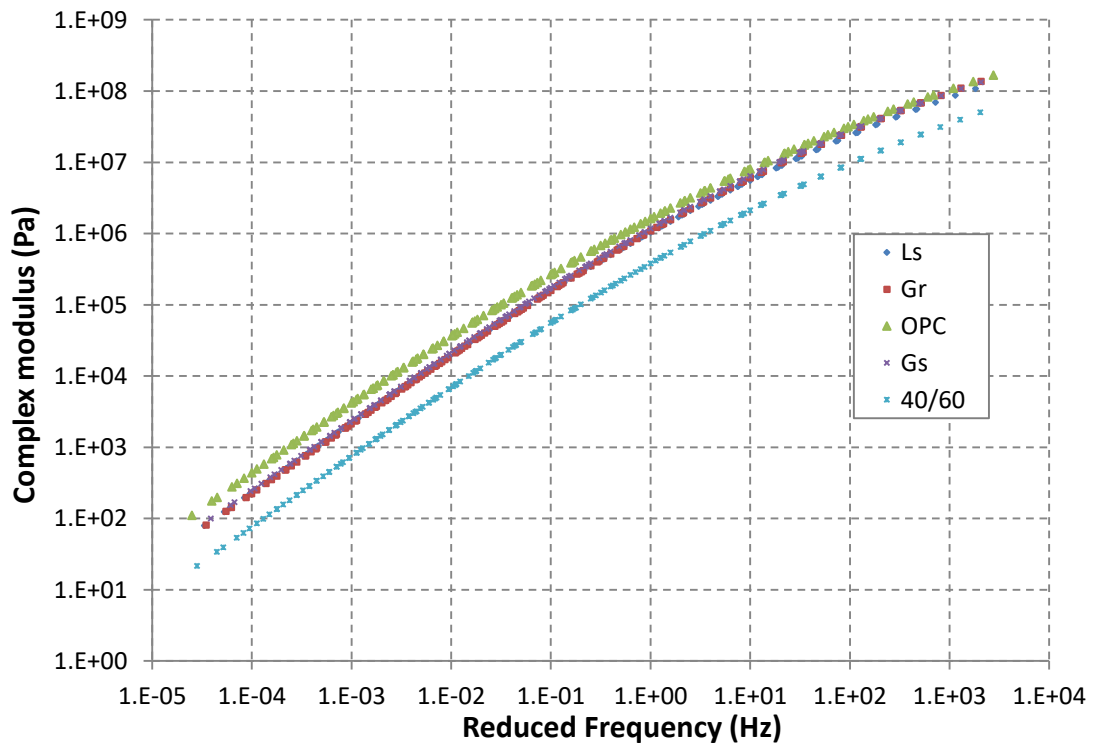


Figure 5.3: G^* of unaged mastics (29% compositional volume)

The granite and gritstone fillers have nearly identical packing so their identical behaviour is as anticipated. This is reflected in their similar effective volumes. The addition of Ordinary Portland Cement has a considerable effect on the mastic stiffening potential of mastics which is more pronounced in the lower frequency range. A similar behaviour is observed from phase angle master curves (Figure 5.4).

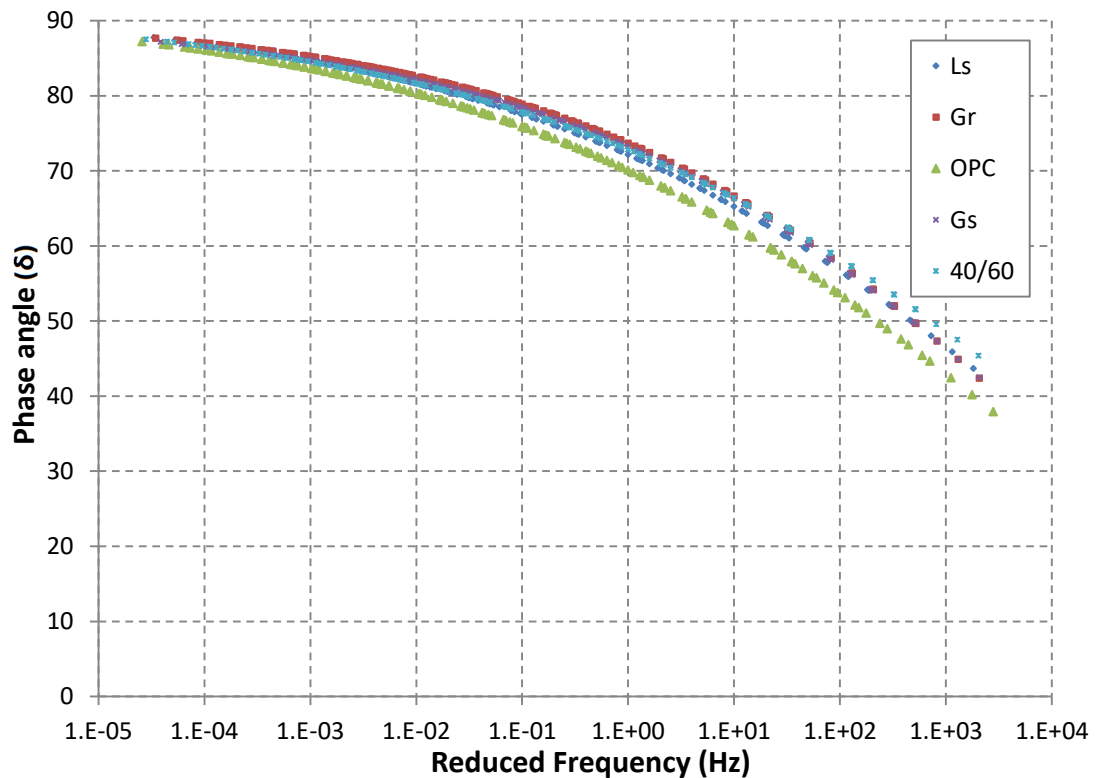


Figure 5.4: Phase angle of unaged mastics (29% volume)

From the above discussion it is clear that the additional information provided by the phase angle was very useful in identifying material behaviour which was not reflected in its complex modulus. However, it is important to note that phase angle is also sensitive to compliance of the machine so it might not be able to provide a reliable picture for very stiff binders (Airey, 2002). For this reason, shift factor plots were made.

The shift factors indicate the overall fit of the isothermal temperature plots to master curves using the time temperature shifting principle. This is shown in Figure 5.6. The differences described in the previous discussion are somewhat more apparent in the black diagram. This has its advantage in that it provides a comparison of materials without any manipulation of the data. On a side note, from the complex modulus, phase angle, and black diagram curves it is also clear that filler influence at lower temperatures cannot be quantified in terms of their type. This is consistent with a study by Anderson et al. (1992).

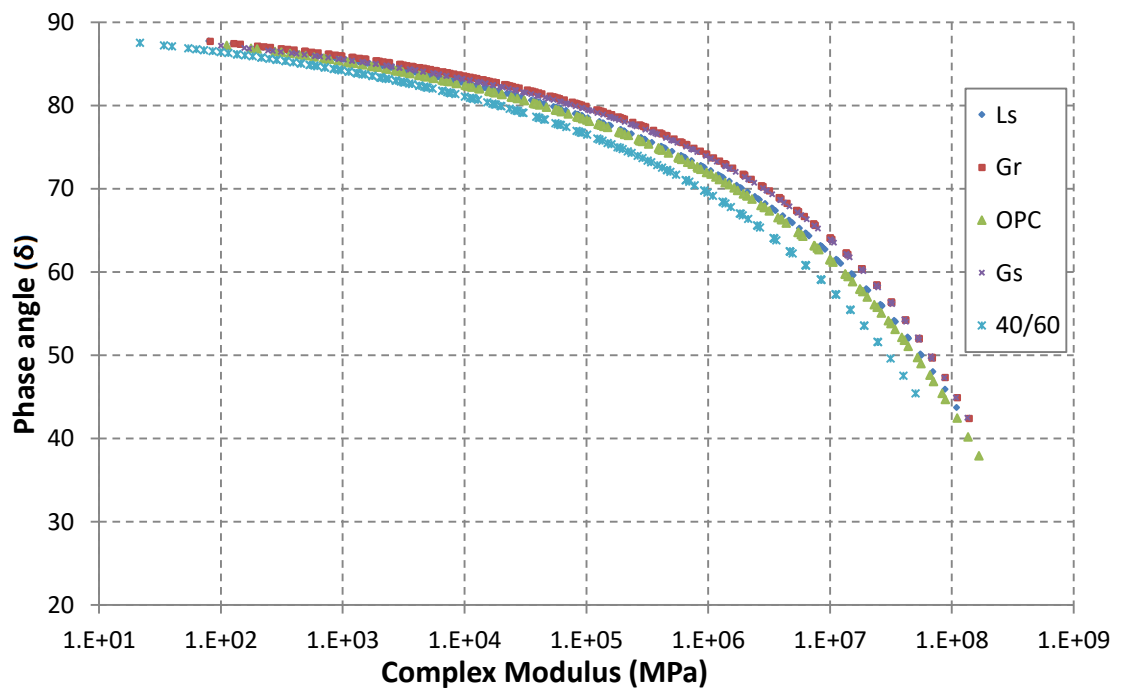


Figure 5.5: Black diagram of unaged mastics (29% volume)

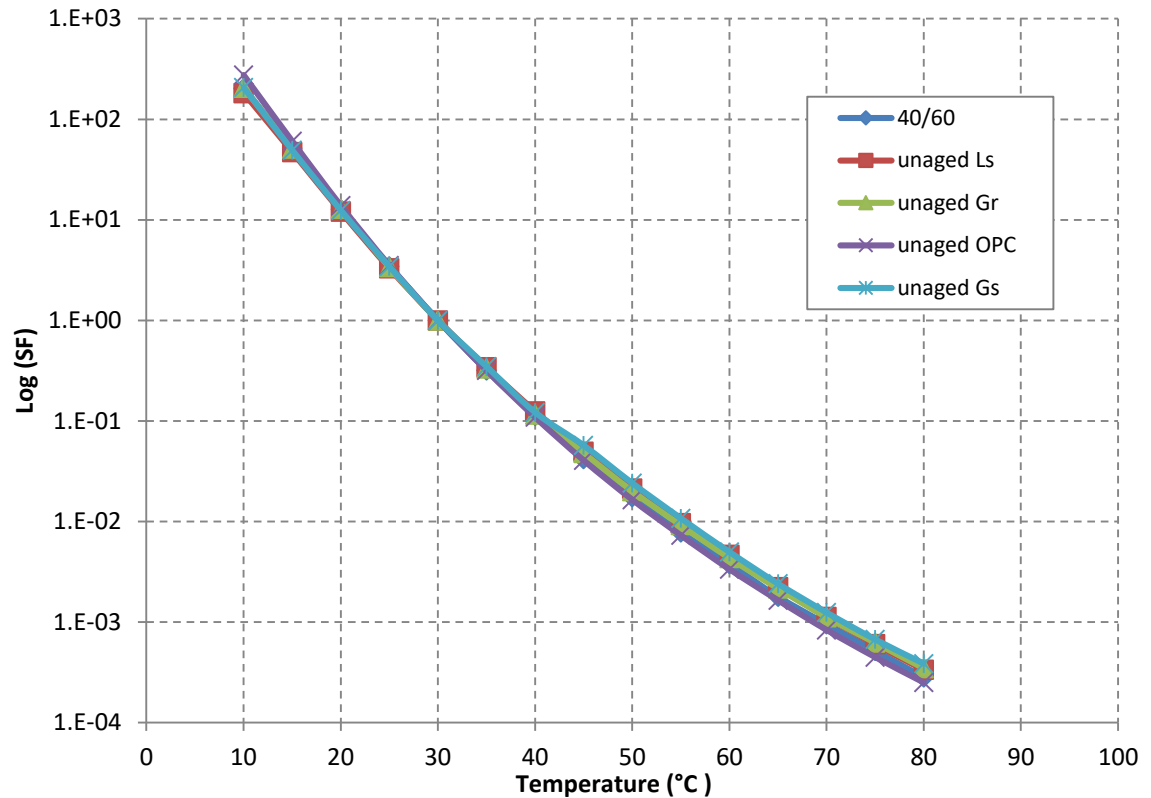


Figure 5.6: G* Shift factors comparison of unaged mastics

In addition to the above discussion it can be seen that OPC has the highest stiffening potential which is attributed to its effective volume in this mastic. This is clear from its master curve plot. This means OPC mastics have more mass in the same volume and subsequently more fine particles. These provide more stiffening effect in the suspension. As far as limestone is concerned, it has lower effective volume (as compared to gritstone and granite) so it should have less stiffening effect in comparison with these two fillers. This should also be seen from its coarser particle size distribution. However, it seems this does not happen in this bitumen filler interaction. A possible explanation is that limestone is a basic filler. Limestone, thus, is expected to increase the stiffening as per Winniford (1961) when compared to gritstone and granite (both being acidic fillers). According to these researchers, acidic fillers result in lower viscosity, while basic filler results in higher viscosity in bitumen with high asphaltene content. The

theory that basic fillers have more stiffening potential explains the behaviour seen in the phase angle master curves.

Although the acid/basic theory has explained these differences to some extent, this theory still needs further explanation. It was anticipated that long-term oxidative ageing of the mastic would further explain the behaviour of OPC and could provide a possible explanation for the high stiffening potential of the limestone despite its relatively lower effective volume concentration. It is also to be concluded from this discussion that the fractional void theory of Rigden does not provide a full picture of bitumen-filler interaction. There are several studies which support this fundamental observation such as Ishai and Craus (1996), Anderson and Goetz (1973) and Hashin (1962). According to research by Anderson and Goetz (1973) different fillers have different reinforcement in the mastic depending on their nature as well as the type of bitumen. According to them "the presence of some sort of physico-chemical interaction" was the cause of one kind of reinforcement in mastic.

It was also anticipated that the role of granite and gritstone in respective mastics could be further elaborated in the aged mastics. This is because the role of filler type still remains a little unclear in unaged mastics when discussion is made about their effect on oxidation. The discussion supports the claim of various studies that different fillers have different stiffening potential (Taylor, 2007). The effect of packing of fillers further needed explanation in terms of its role in oxidative ageing. This is explored in section 5.9. The next section first explores this idea to further build this theory of bitumen-aggregate interaction. A comparison will be made with an existing study to check the validity of the previous discussion.

5.5 COMPARISON WITH RESEARCH FINDINGS FROM LITERATURE

A detailed literature survey was carried out to identify the research data from different studies to make a comparison with the findings of the current study. Most of the available data served the purpose of comparing different models from the study of composites. However, the work of Liao (2007) provided some suitable data for a direct comparison between the two research studies as shown Table 5.2. A comparison of basic research parameters is presented in the following table. The bitumen properties such as its source, penetration, softening point, and specific gravity were all similar. The fillers in the two studies were slightly different in terms of their physical properties.

Table 5.2: Comparison of parameters of this research with Liao (2007)

Material	Material Property	Present research	Liao (2007)
Bitumen	Bitumen Grade	40/60	40/60
	Source	Venezuelan	Venezuelan
	Penetration (dmm)	53	50
	Softening Point (°C)	50.4	50.2
	Density (g/cm ³)	1.03	1.02
Limestone Filler	Source	Torr Quarry	Longcliffe
	Specific gravity	2.623	2.74
	Rigden voids	33	24
Cement Filler	Source	Ordinary	Ordinary
	Specific gravity	3.02	3.18
	Rigden voids	45	28
Gritstone Filler	Source	Bardon Hill	Bayston Hill
	Specific gravity	2.808	2.65
	Rigden voids	40	32

The role of filler in occupying volume is clear from the increased mastic stiffnesses as compared to the base bitumen, if we consider the data of Liao (2007). Analysis of 35% intermediate concentration by weight in Figure 5.7 reveals that the stiffening effect of OPC is identical to that of limestone. This is due to the identical effective volumes of the two fillers. The relatively higher stiffness of gritstone as compared to cement and limestone is attributed to its higher effective volume in the respective mastic. It is worth noting that the effective volume of 35% gritstone is 25.6% followed by limestone (22.2%) and cement (20.6%). This is because it has less free bitumen and subsequently results in a stiffer mastic. It is important to note that in this study the effect of the nature of the filler is not clear from this data. The observed differences are mainly due to their respective effective volumes. The filler content of these mastics is quite low as compared to this research data. In Liao (2007) the filler's role is mainly volume filling rather than any physico-chemical or inter-particle interaction role.

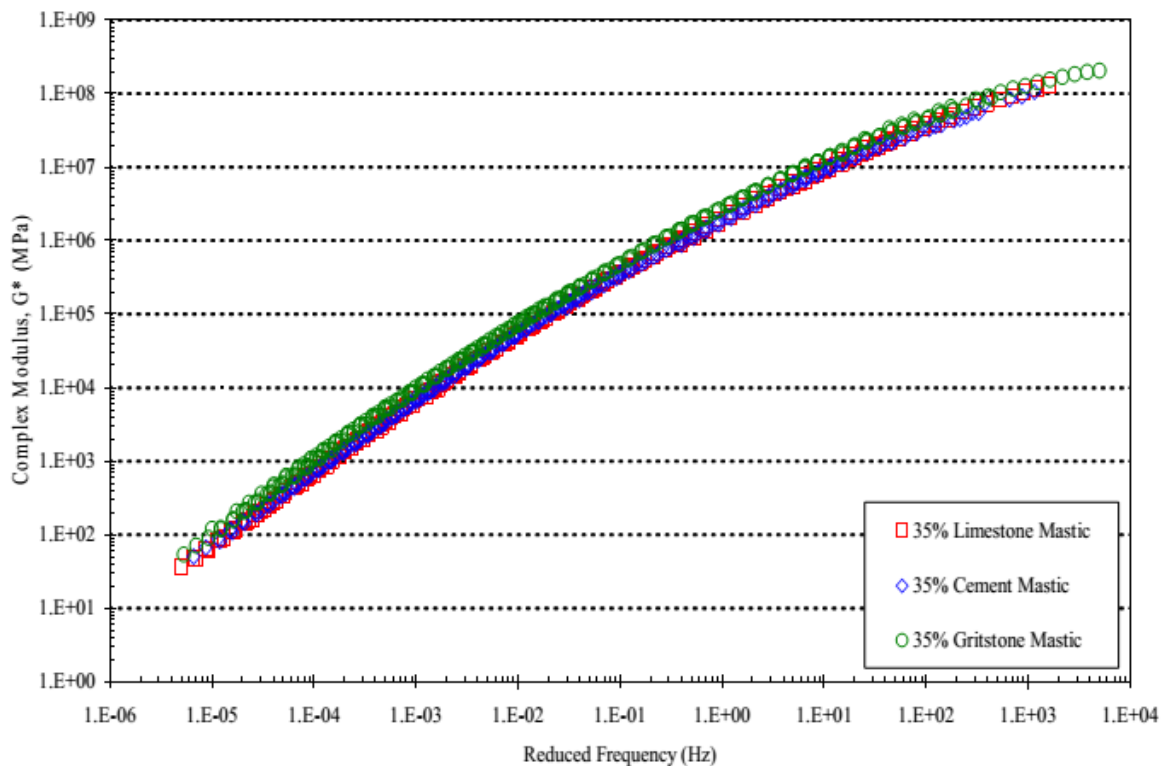


Figure 5.7: G^* master curve comparison for mastics containing 35% filler

In order to make the difference clearer, data at increased filler content was selected (see Figure 5.7). At 65% filler content the limestone has the lowest complex modulus at high temperatures. The OPC then has slightly increased stiffness as compared to limestone. The theory of volume filling effect of mastic would suggest it should be otherwise. It is important to note that both OPC and limestone are basic. The only reason for a difference between the two mastics given by Liao (2007), is that the increased stiffness of OPC is due to the fact that the mastic properties were measured when submerged in the water bath of the DSR. The presence of cement in the water leads to hydration and gives more stiffness to the mastic. It is clear from the role of cement in mastic when comparison is made of its intermediate concentration and high concentration. In contrast to the explanation given by Liao (2007), this research suggest that this difference is due to the slightly more basic nature of OPC. The basic character according to Winniford (1961) should have resulted in a greater stiffening effect. The more basic effect at little higher percentage is of volume filling. The stiffness increased at 65% compared to 35% as expected. The gritstone has higher stiffness as compared to the two other fillers. This can be attributed to its high effective volume and more inter-particle contact which is clear from its coarse particle size distribution too.

In Figure 5.9 the stiffness is in increasing order for 15, 35, and 65% limestone mastic. Its rate of increase from 15% to 35% is relatively less compared to the increase from 35% to 65%. This might be due to the fact that an increase in filler at this percentage incorporates its two additional roles. These two roles include the role of filler as physico-chemical reinforcement and also inter-particle interaction. These two roles, especially inter-particle interaction, are more pronounced beyond 35% filler content. The inter-particle interaction is due to the filler skeleton present in the mastics. The surface activity is more pronounced in the case of OPC filler.

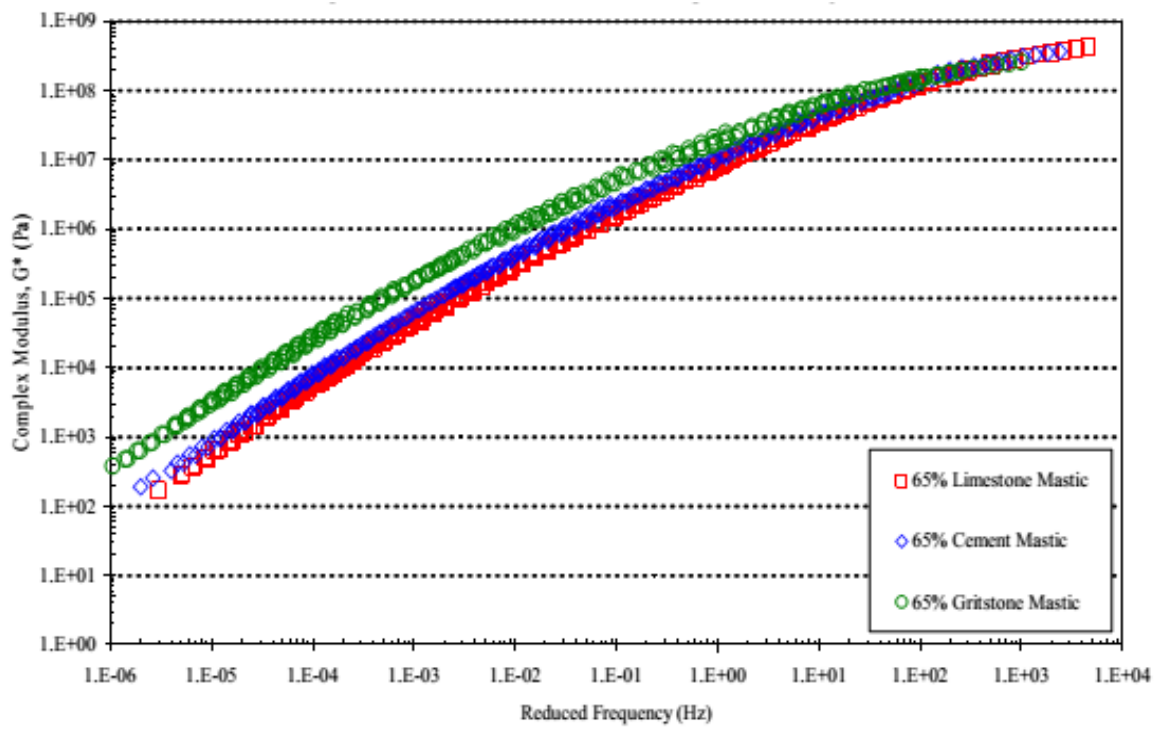


Figure 5.8: G^* MC for bitumen filler mastics containing 65% filler

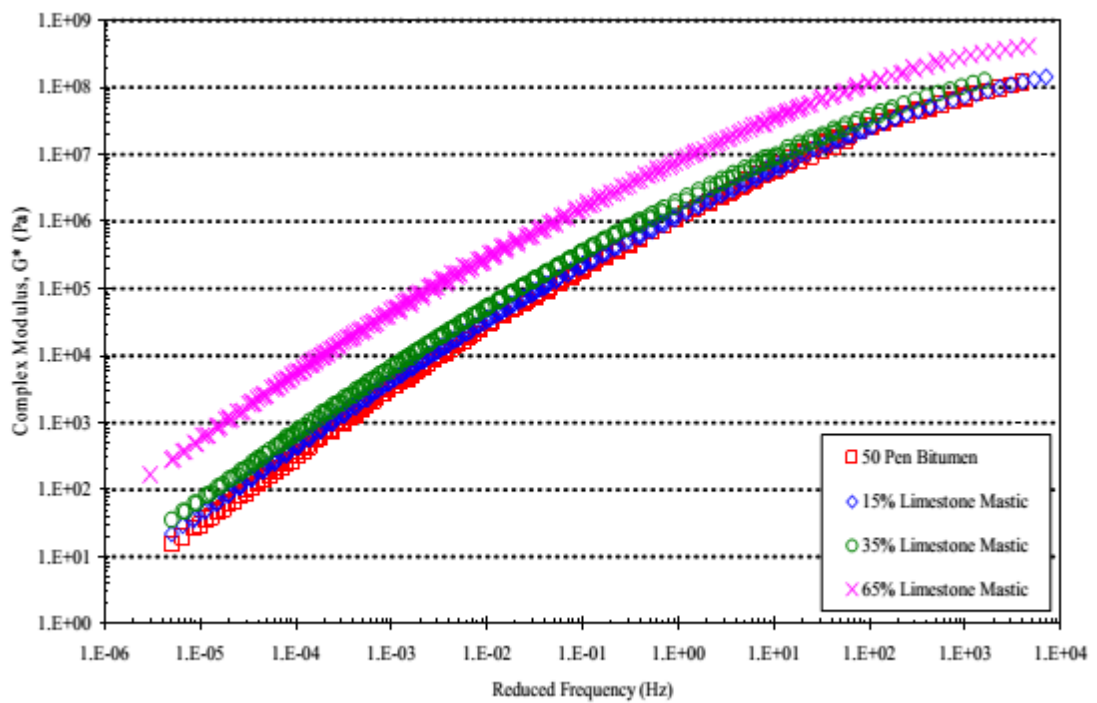


Figure 5.9: G^* MC for binders at different filler volume content

The above discussion supports the research finding in terms of the role of filler in volume filling. It also supports the additional role of the filler as physico-chemical reinforcement and the role of the filler skeleton to further enhance its stiffening effect in mastics.

5.6 EFFECT OF MINERAL MORPHOLOGY ON STIFFENING

According to Chen (1997) mineral type (as discussed previously) as well as micro-interfacial morphology play an important part in determining the role of filler properties in mastics. In continuation of the previous discussion, the role of mineral morphology is found to affect the stiffening potential of fillers. The discussion is made on both the basic fillers of used in this research to understand and differentiate between their similar stiffening potentials.

The study of filler particle shape is vital as its shape directly affects the maximum packing. According to mineral morphology, a smooth surface results in low stiffness. The particle shape and surface texture are determined through microscopy. Scanning Electron Microscopy (SEM) has been used to examine the shape of the particle. The effect of particle shape on stiffness of mastics can be summarised as in Figure 5.10. In a fixed solid phase volume mastic, the viscosity of the suspension decreases from rods type particles to spherical particles.

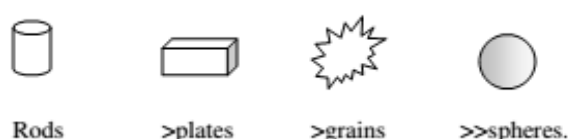
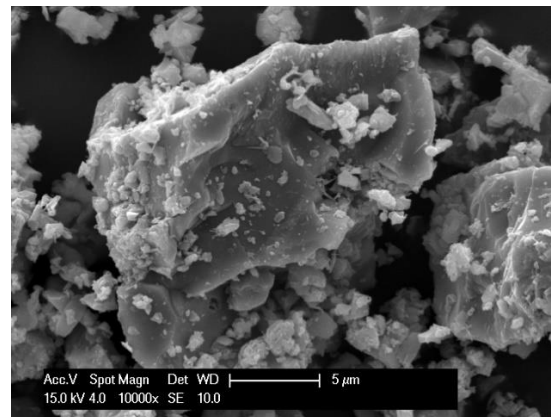
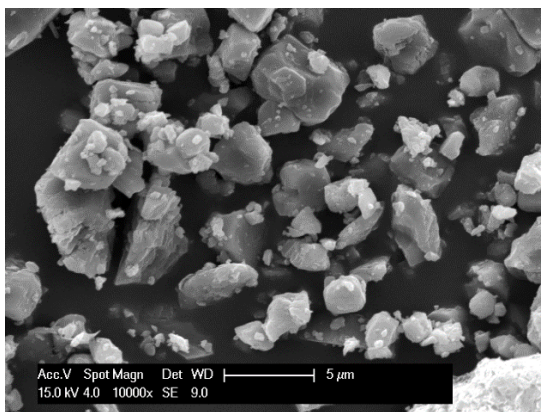
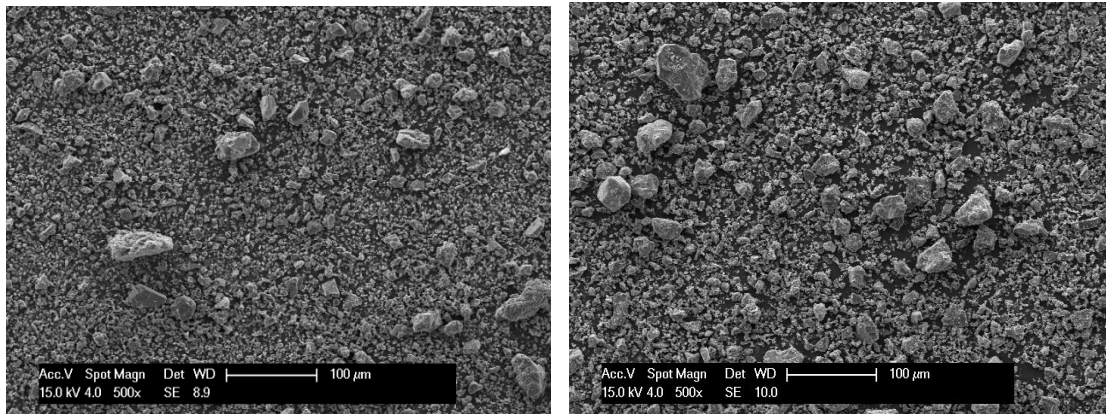


Figure 5.10: Effect of particle shape on intrinsic viscosity of suspension

Figure 5.11 shows micrographs of the fillers at resolutions of 100 μ m and 5 μ m. The SEM results indicate that both particles are medium grain spherical and have rough superficial textured surfaces. The angular particles are believed to result in

more stiffness than spherical particles. The non-smooth surface of these fillers is expect to give their respective mastics a high pull off strength due to mechanical interlocking. As both fillers have similar shape so no difference due to shape was anticipated. The filler surface activity can be divided into two parts namely physical hardening and chemical adhesion. The adhesive/pull strength of these materials is evaluated in chapter 6. The physical hardening aspect is discussed here. The limestone filler has finer particles as compared to OPC. The OPC filler particle has a number of crystalline materials on its surface. Here the fineness of the filler does not seem to be a significant contributing factor as compared to surface texture. This fineness is in the context of comparison between limestone and granite. The rougher texture and presence of this crystalline material gives OPC more stiffening potential as compared to limestone filler. In this research the effect of the fine/coarse nature of OPC cannot be separated due to two further factors (in addition to texture and presence of crystalline materials) helping OPC to give increased stiffness. These factors are its high effective volume and basic character.





a) Limestone

b) OPC

Figure 5.11: Scanning Electron Microscopy (SEM))

As discussed in section 5.10 the limestone has increased stiffness as compared to acidic filler. This can be attributed to the presence of finer particles. The fine particle size can be seen through the particle size distribution (PSD). These finer particles might have resulted in more surface free energy. According to Shashidhar and Romero (1998) the increased surface energy may give rise to interaction between particles, giving rise to inter-particle chains and agglomeration. This will prevent efficient particle packing and would give rise to more stiffening potential. Through this discussion it can clearly be seen that the role of filler is not as simple as volume filling and having physio-chemical interaction but it is also strongly dependant on acidic/basic characteristics too.

5.7 FTIR TEST ON MASTICS

In this section, discussion is made based on FTIR tests on mastics in an attempt to investigate chemical functionalities in aged as well as unaged mastics. The FTIR tests were directly carried out on aged and unaged mastics. The spectrogram shown in Figure 5.12 covers the carbonyl region $C=O$ ($1,700\text{ cm}^{-1}$) and sulphoxide $S=O$ ($1,030\text{ cm}^{-1}$). The figure shows little or no peak for the

carbonyl region. In addition to this there was no clear difference in terms of the carbonyl region due to ageing of mastics when compared to the FTIR results discussed in the previous chapter (presented in Appendix A). This might be due to interference of functionalities present in particulates with FTIR spectra. This interference is indicated by a shift of the C–H bond spectrum (bending) of alkanes. This is reflected in spectra of unmodified aged and unaged bitumen which shifted the peak from wave number 1470 cm^{-1} to 1420 cm^{-1} . According to Marsac et al. (2014) the methyl (CH_3) and ethylene groups (CH_2) are normally considered to be constant and not affected by oxidation. The vertical change in relation to horizontal shift on mastic ageing render the FTIR test performed directly on mastics to be not feasible especially when perform directly on mastics. Due to this reason no further FTIR tests were directly performed on mastics.

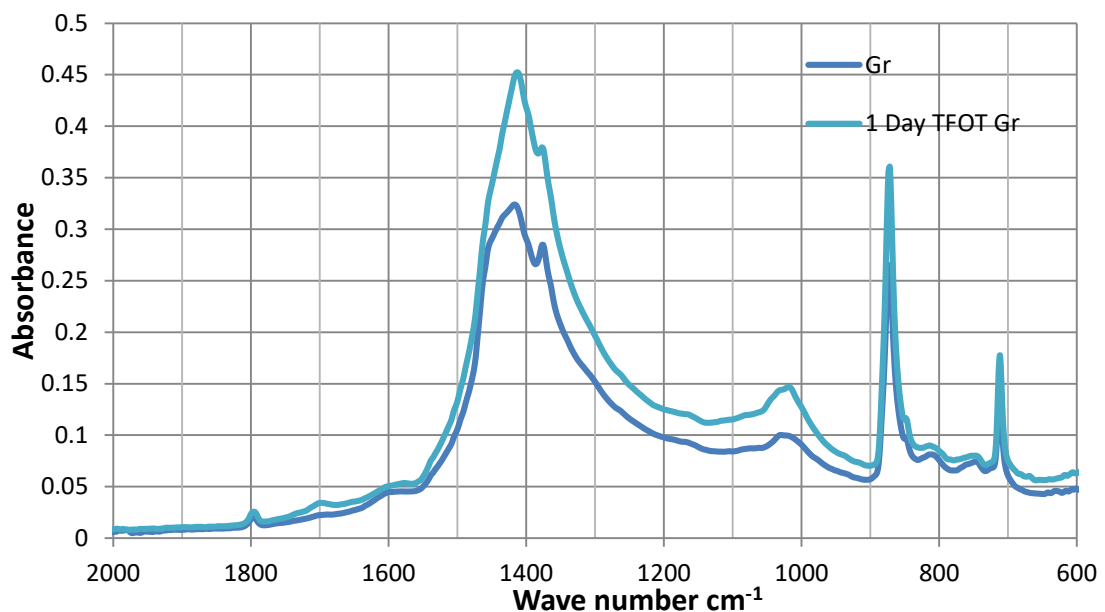


Figure 5.12: FTIR spectrum of unaged and aged mastic

In addition to the previous discussion, the validity of FTIR results from recovered binder from mastics can also be questioned based on knowledge of bitumen chemistry. The addition of bitumen forms several new bonds at the bitumen aggregate interface. The presence and amount of these functional groups not

only depends on the active nature of surface but also other physical properties of filler such as surface area, porosity etc. The recovery of bitumen from mastics was deemed not to provide solid information in this regard. The FTIR is a useful tool to provide information to identify oxidation products from one ageing stage to another on the same material. But in terms of differentiating between the ageing effects of different fillers, the FTIR was thought not to serve the purpose well. This point is in discussion after a series of experiments performed on a similar study of mastics by Rami Alfaqawi at Nottingham Transportation Engineering Centre, at University of Nottingham.

Instead of using FTIR due to this problem, effort was shifted towards application of a micromechanics model from colloid science and suspension rheology. The next section gives a brief introduction to these models and checks their validity based on the research data.

5.8 MODELS TO PREDICT OF STIFFENING EFFECT OF MASTICS

Several analytical micromechanics models have been proposed in the field of particulate composite rheology. These micromechanical models are used to predict the fundamental stiffening properties of a composite based on the properties of individual constituents. These models compute the basic mechanical reinforcing effects e.g. volume filling effect, rather than other complicated material dependant stiffening mechanisms such as surface activity etc. The maximum solid packing can be found out experimentally using rheological testing. It is defined as the point on the filler content axis at which the viscosity of the suspension becomes infinite. It is actually the value of solid filler fraction at the asymptote of the viscosity curve. In this research several micromechanics models are discussed and applied to the data. These models include Maron-Pierce,

Krieger and Dougherty, Lewis and Nielsen, Mooney model, Hashin, Christensen and Lo.

In Figure 5.13, constructed using this research's data, it can be seen that mastic stiffness modulus increases with increase of filler volume fraction. The volume fraction is defined as $\phi_2 = \frac{V_1}{V_1 + V_2}$. Here V_2 is the filler volume while V_1 is the bitumen volume.

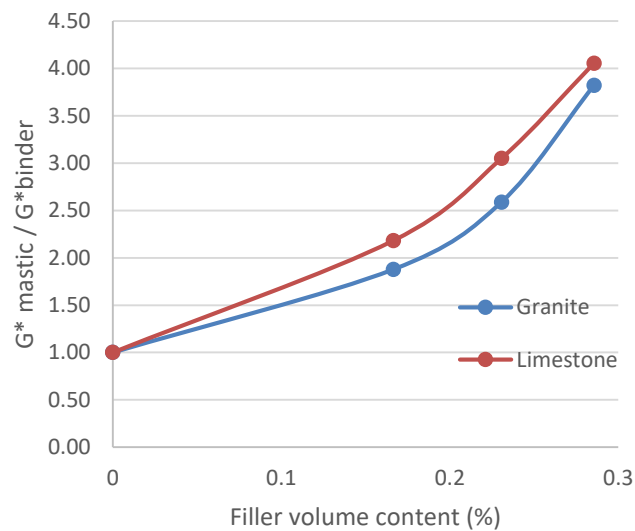


Figure 5.13: Stiffening ratios for limestone and granite

The data for the lower filler content is taken from data analysis on low concentration volume mastics in Section 5.11. There are several mathematical models in the literature which help to quantify the trends in the curve. The presence of several models is due to adoption of different models from the science of colloids for different types of suspension. Most of these models are either a) direct or indirect modifications of Einstein's equation of suspension of a particulate suspension system or b) can be computed from an elastic analysis of these two component systems. Examples of these models include Maron-Pierce and Nielsen's etc. Some of the models are applied and explained in this research;

the details can be found elsewhere Huang et al. (2007). The fore-mentioned approaches relate viscosity and stiffness through the following expression and can be compared with each other on this basis too as per Shashidhar and Romero (1998).

$$\left(\frac{\eta}{\eta_1} - 1\right) = \frac{4 - 5V_1}{3 \times (1 - V_1)} \cdot \left(\frac{G}{G_1} - 1\right)$$

Where G and G_1 refer to shear modulus of mastic and bitumen and η and η_1 mean viscosity of mastic and bitumen respectively. V_1 is Poisson's ratio of bitumen, which is 0.5. Thus the above equation can be reduced to

$$\frac{\eta}{\eta_1} = \frac{G}{G_1}$$

This shows that the stiffening effect can be measured in terms of shear modulus values instead of viscosity measurement for these particle suspension system. Shashidhar and Romero (1998) used the Nielsen-modified Kerner's equation (discussed later), a detailed discussion of which can be found in Shashidhar and Romero (1998) and Nielsen (1970). The functional form of this model expressing the increase of modulus upon filler addition to bitumen is a function of filler packing and Einstein's coefficient as follows.

$$\frac{M}{M_1} = f(\phi_1, K_E)$$

Bitumen-filler mastic is a particulate-filled composite as per colloid science. In this composite bitumen is a matrix while the suspended material 'filler' is the particulate phase. Several researchers have used different micromechanics based models to predict the properties of such composites like Einstein, Mooney, Kerner and Nielsen (Chen, 1997). In this research some of these models have been used to predict the stiffness modulus of the mastic by taking into account the

packing of the filler. Abbas et al. (2005) studied some of the micromechanics-based models and according to them these models are not sensitive to DSR results of the binder and they underestimate the stiffening of mineral fillers.

5.8.1 Einstein Model for diluted composites

In this research the Einstein model was not chosen because of its applicability being limited to filler volume fractions less than 10 percent only. The Einstein Model to calculate viscosity assumes a suspension which is very dilute such that there is almost no inter-particle interaction (Mooney, 1951). The model given by Einstein yields a linear relationship when plotted with respect to solid volume fraction. This is because it does not include the effect of maximum packing fraction. As per Einstein the viscosity of the system keeps on increasing indefinitely as long as the suspension remains in a dilute phase. The model is represented by the following expression:

$$\eta_r = 1 + K_E$$

where η_r = viscosity of composite

K_E = Einstein constant, 2.5 for a suspension of rigid spherical particulates in a matrix such as bitumen with Poisson's ratio of 0.50 (Nielsen, 1970). This coefficient has, however, been generalised to take into account the non-ideal nature of a real system (Shashidhar and Romero, 1998). The problem with the Einstein model is that his particulates are inert and monodisperse (i.e. containing particles of uniform size).

The models given below, have been developed since Einstein's basic analysis of rigid particulates in a dilute suspension of viscous liquid. These models extend the work of Einstein on composite suspensions (Mooney, 1951).

5.8.2 Maron-Pierce Model

Maron and Pierce (1956) theoretically derived a relation for relative viscosity. This relation was later used by Heukelom and Wijga (1971) to compute the stiffening effect through following expression.

$$G_m = G_b \left(1 - \frac{\phi}{\phi_m}\right)^{-2}$$

Where ϕ is the volume fraction of filler in mastic, it is defined as the volume fraction of filler that is added to bitumen.

ϕ_m refers to maximum packing fraction.

As defined earlier, maximum packing is a vertical asymptote to the curve in the graph of stiffening ratio against filler volume content. This parameter represents the maximum quantity of filler that can be added to bitumen without emergence of air voids. These air voids occur when the value of ϕ_m is less than the value of ϕ_2 .

As is known Rigden showed that filler volume fraction ϕ controls the stiffening of the bitumen mastic suspension. It is important to note that the stiffening effect is complicated by the presence of an adsorption layer. These increase effects result in increased effective volume of filler. This will eventually reduce the maximum packing ϕ_m in suspension calculated through viscosity measurement.

5.8.3 Nielsen Model

Nielsen (1970) modified Kerner's equation to compute the stiffening potential of fillers in mastics. The original Kerner's equation ignored the effect of packing on fillers. Nielsen realised this problem and introduced a factor ψ . This factor included the effect of filler packing. The Nielsen model is given as

$$\frac{M}{M_1} = \frac{1 + AB \phi_2}{1 - B \psi \phi_2}$$

where

M =Any modulus (shear, elastic, etc.)

Φ_2 = volume fraction filler

A , B , C , ψ are constants, if ψ is removed from the famous Lewis and Nielsen model it becomes Kerner's equation.

Φ_m , in general, is the maximum volume fraction, some studies have taken it as constant at 0.63 for mastics, for example Zhang et al. (2011), Lesueur and Little (1999) and Heukelom and Wijga (1971) Lesueur and Little (1999).

The constant 'A' takes into account parameters such as Poisson's ratio and geometry of the filler phase.

The constant 'B' takes into account the relative moduli of the filler and matrix phase and is defined as

$$B = \frac{\frac{M_2-1}{M_1}}{\frac{M_2+A}{M_1}} = \frac{\frac{G_2-1}{G_1}}{\frac{G_2-A}{G_1}}$$

It is important to note that the shear modulus of the fillers, 24GPa, is much higher than that of asphalt, so $B \approx 1$. This constant takes into account Φ_m (the packing fraction). The constant ' ψ ' can be computed from the following expression of filler fraction volume and maximum volume fraction.

$$\psi = 1 + \left(\frac{1 - \Phi_m}{\Phi_m^2} \right) \Phi_2$$

When the above three equations are combined the following expression is obtained; here $B = 1$ because filler modulus is very large as compared to bitumen.

$$\frac{M}{M_1} = \frac{1 + A \phi_2}{1 - (1 + C \phi_2) \phi_2}$$

where C is a constant which depends on ϕ_m and is given by the following expression

$$C = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right)$$

5.8.4 Mooney's Equation

A model to calculate the stiffening effect of spherical particulates in suspension was given by Mooney (1951). He made use of a self-crowding factor 'k'. This factor was the inverse of maximum packing fraction. In the following expression it is given as $1/\phi_m$. The 2.5 factor in the equation refers to Einstein's coefficient K_E .

$$G_m = G_b e^{\left(\frac{2.5 \phi_2}{1 - \frac{\phi_2}{\phi_m}} \right)}$$

5.8.5 Krieger-Dougherty Model

Krieger and Dougherty (1959) presented their model to calculate the stiffening effect of a matrix-particulate system. This model also makes use of Einstein's coefficient for a monodisperse phase. The monodisperse phase refers to a matrix containing unimodal uniform size particles. This model is represented by the following expression.

$$G_m = G_b \left(1 - \frac{\phi_2}{\phi_m} \right)^{-K_E \phi_m}$$

Here K_E is Einstein's coefficient

Φ_2 as described earlier is the volume packing fraction

ϕ_m refers to the maximum packing fraction

5.8.6 Chong Model

This model is used to predict the stiffening potential of fillers in mastics. This model makes use of maximum packing and Einstein's coefficient along with a varying amount of filler volume fraction.

$$G_m = G_b \left(1 + \frac{K_E \Phi_2}{2} \cdot \frac{\frac{\Phi_2}{\phi_m}}{1 - \frac{\Phi_2}{\phi_m}} \right)^2$$

Where K_E refers to Einstein's coefficient

Φ_2 as described earlier is the volume packing fraction

ϕ_m refers to the maximum packing fraction

5.8.7 Robinson Model

Robinson (1949) proposed a model to predict the stiffening potential of fillers in mastics. This model makes use of the maximum packing fraction (ϕ_m) and Einstein's coefficient (K_E) to compute the stiffening ratio.

$$G_m = G_b \left(1 + K_E \cdot \frac{\Phi_2}{1 - \frac{\Phi_2}{\phi_m}} \right)$$

These parameters are as defined earlier.

5.8.8 Hashin Model

Hashin (1962) proposed a model for an approximate isotropic heterogeneous material containing spherical particulates. This model, just like the Nielsen model, is similar to Kerner's model. The ratio of stiffness modulus of these two-phase linear elastic composites can be computed by following expression.

$$G_c = G_m \left(1 + \frac{15(1 - \nu_m) \left(\frac{G_p}{G_m} - 1 \right) \nu_p}{7 - 5 \nu_m + 2(4 - 5 \nu_m) \left(\frac{G_p}{G_m} - \left(\frac{G_p}{G_m} - 1 \right) \nu_p \right)} \right)$$

where G_c is the complex modulus of the composite

G_m is the shear modulus of the matrix (bitumen)

G_p refers to the shear modulus of the particle, taken as 24 GPa

ν_m is the Poisson's ratio of the matrix phase, taken as 0.5 (Kim and Little, 2004)

ν_p is the filler volume fraction

This micromechanics model is purely theoretical without any adjustable parameters. This model under predicted the stiffening potential of filler so it has been omitted from analysis here.

5.8.9 Christensen and Lo Model

This micromechanics model was proposed by Christensen and Lo (1979) to account for the stiffening due to spherical particulates in a matrix phase. This is also a purely mathematical model and has no adjustable parameter. This model is also excluded here, due to underestimation of the stiffening ratio. The closed form of this model is presented as follows.

$$\left(\frac{\mu}{\mu_m}\right)^2 A + \left(\frac{\mu}{\mu_m}\right) B + D = 0$$

where μ corresponds to stiffness modulus of composite; it is referred as G_c in previous models. μ_m is the stiffness modulus of the matrix phase, commonly referred as G_b . Here A, B and C are constants and can be computed through the following expressions.

$$\begin{aligned} A = & 8 \left[\frac{\mu_i}{\mu_m} - 1 \right] (4 - 5v_m) \eta_1 c^{\frac{10}{3}} - 2 \left[63 \left(\frac{\mu_i}{\mu_m} - 1 \right) \eta_2 + 2 \eta_1 \eta_3 \right] c^{\frac{7}{3}} \\ & + 252 \left[\frac{\mu_i}{\mu_m} - 1 \right] \eta_2 c^{\frac{5}{3}} - 25 \left[\frac{\mu_i}{\mu_m} - 1 \right] (7 - 12v_m + 8v_m^2) \eta_2 c \\ & + 4(7 - 10v_m) \eta_2 \eta_3 \end{aligned}$$

$$\begin{aligned} B = & -4 \left[\frac{\mu_i}{\mu_m} - 1 \right] (1 - 5v_m) \eta_1 c^{\frac{10}{3}} + 4 \left[63 \left(\frac{\mu_i}{\mu_m} - 1 \right) \eta_2 + 2 \eta_1 \eta_3 \right] c^{\frac{7}{3}} \\ & - 504 \left[\frac{\mu_i}{\mu_m} - 1 \right] \eta_2 c^{\frac{5}{3}} - 150 \left[\frac{\mu_i}{\mu_m} - 1 \right] (3 - v_m) v_m \eta_2 c \\ & + 3(15 v_m - 7) \eta_2 \eta_3 \end{aligned}$$

$$\begin{aligned} D = & 4 \left[\frac{\mu_i}{\mu_m} - 1 \right] (5v_m - 7) \eta_1 c^{\frac{10}{3}} - 2 \left[63 \left(\frac{\mu_i}{\mu_m} - 1 \right) \eta_2 + 2 \eta_1 \eta_3 \right] c^{\frac{7}{3}} \\ & - 252 \left[\frac{\mu_i}{\mu_m} - 1 \right] \eta_2 c^{\frac{5}{3}} - 25 \left[\frac{\mu_i}{\mu_m} - 1 \right] (v_m^2 - 7) \eta_2 c \\ & - (7 + 5 v_m) \eta_2 \eta_3 \end{aligned}$$

where μ_i is the stiffness modulus of filler and is same as G_p in the Hashin (1961) model. v_i and v_m are Poisson's ratios of particle and matrix phase respectively. The value of C is volumetric concentration. These values can be taken as 0.12 for

filler as per Zhang et al. (2011) and 0.5 for bitumen as per Anderson and Goetz (1973).

$$\eta_1 = \left[\frac{\mu_i}{\mu_m} - 1 \right] (49 - 50v_i v_m) + 35 \left[\frac{\mu_i}{\mu_m} \right] (v_i - 2v_m) + 35(2v_i - v_m)$$

$$\eta_2 = 5v_i \left[\frac{\mu_i}{\mu_m} - 8 \right] + 7 \left[\frac{\mu_i}{\mu_m} + 4 \right]$$

$$\eta_3 = \left[\frac{\mu_i}{\mu_m} \right] (8 - 1v_m) + (7 - 5v_m)$$

5.8.10 Discussion of models

A general discussion on the effect of variables on stiffening potential in these models can be summarised from Shashidhar and Romero (1998). According to them the factors which affect the stiffening potential are mainly dispersion, mixing, agglomeration, average particle size, gradation, particle shape, interface properties. The main factors which affect maximum packing fraction are mainly dispersion of the particulate in the matrix phase, their mixing, agglomeration, shape, average particle size and gradation as per particle size distribution. The second important parameter, Einstein's coefficient, is dependent on agglomeration, average particle size, particle shape and interfacial interaction of particle and bitumen. These factors altogether affect the stiffening potential of fillers.

In this research, the morphological analysis indicated that the particles are roughly spherical so no adjustment is needed in terms of particle shape in the previously discussed models related to prediction of stiffening potential of fillers. In the case of non-spherical particles, the aspect ratio, which is the ratio between the longest and shortest dimensions, has a significant effect on rheology of the

suspension. An increase in particle aspect ratio lowers maximum packing fraction ϕ_m and increases generalised Einstein's coefficient K_E as per Shashidhar and Romero (1998). As stated earlier, in this research no such adjustment is needed.

In order to fit the models to the measured data, non-linear regression was used. Maximum packing and Einstein's coefficient were calculated accordingly. For example, values of maximum packing as per the Nielsen model were 0.48 and 0.4 for limestone and granite respectively. The fitted models are compared in Figure 5.14 and Figure 5.15. The analysis shows that these models reasonably predict the stiffening potential of fillers. Most models accurately predict the stiffening effect at lower concentrations with exception of the Chong model. This model underestimates the stiffening at lower concentrations and overestimates the stiffening effect at higher concentrations. The Maron-Pierce model underestimates the stiffening potential for granite mastic at higher concentrations. These deviations are noticeably more apparent beyond 24% volume fraction. An advantage of these models is the reasonable prediction of maximum packing as well as stiffening potential of fillers over limited available data.

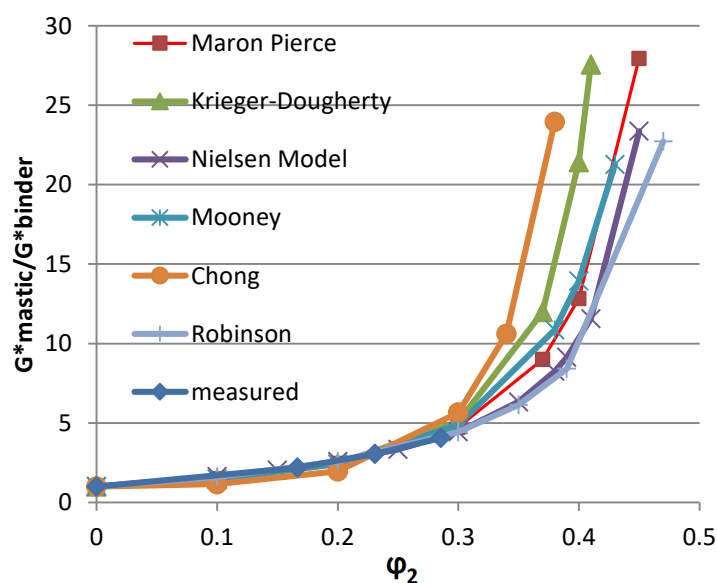


Figure 5.14: Micromechanics models for limestone mastics

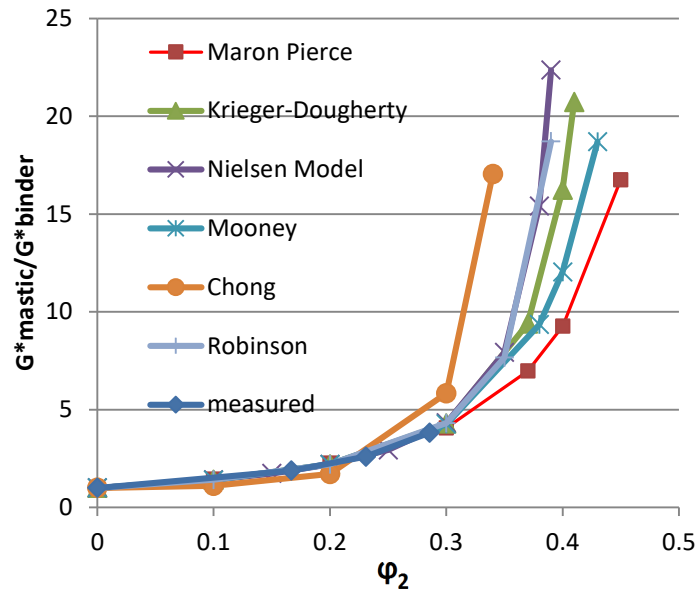


Figure 5.15: Micromechanics models for granite mastics

The stiffening potential differences between these micromechanics models are made more evident when values are plotted on a line of equality graph. These graphs were plotted for fillers when they are added in volume fraction up to 28.6%. The figure shows good agreement between measured and predicted stiffness except for the Chong model. The overall value of K_E ranged from 1.43 to 5.66, whereas the value of ϕ_m varied from 0.40 to 0.82. The value of maximum packing fraction varied quite significantly when measured through different models shown in Table 5.3.

Table 5.3: Micromechanics models parameters

Model	Limestone mastic		Granite mastic	
	ϕ_m	K_E	ϕ_m	K_E
Maron Pierce	0.77	-	0.82	-
Krieger-Dougherty	0.47	3.394	0.462	3.01
Mooney	0.79	2.02	0.49	1.43
Nielsen	0.49	5.24	0.41	3.27
Chong	0.48	5.66	0.40	3.01
Robinson	0.53	4.91	0.42	3.13

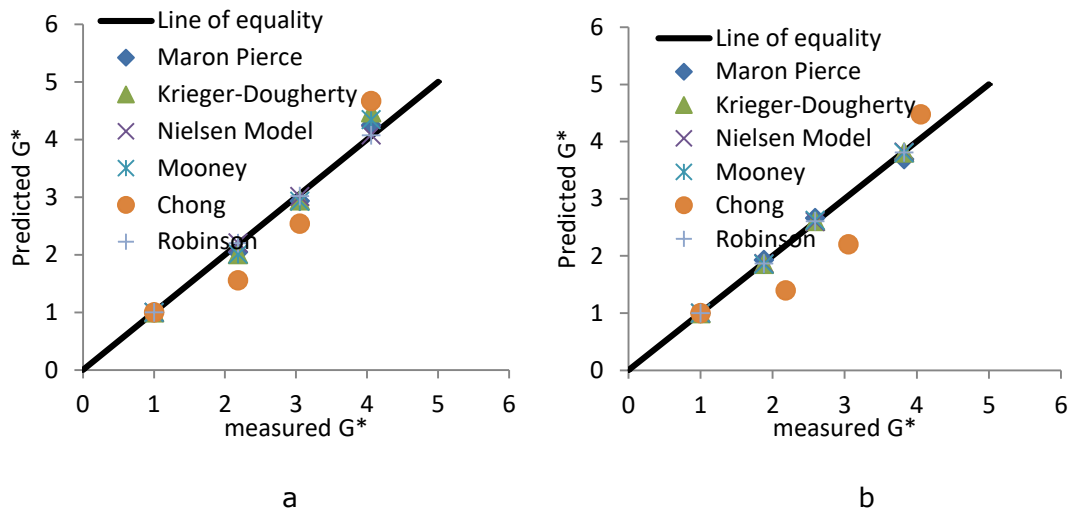


Figure 5.16: Line of equality graph a) limestone b) granite

The primary objective of this section was to evaluate micromechanics-based methods for predicting the stiffening potential of fillers in a bitumen matrix phase. In this research six models were fitted to the measured data to predict the stiffening potential of fillers. These models included Maron-Pierce Model, Nielsen Model, Mooney's Equation, Krieger-Dougherty, Chong et al. Model and Robinson. The discussion on the models can be summed up in the following points.

- Micromechanics based models have the ability to predict stiffening potential from the properties of the individual ingredient properties.
- It is difficult to precisely model the mastic data with any single model, due to the presence of complex stiffening effects beyond volume filling. This is line with Buttlar et al. (1999). This aspect is further discussed in the next section.
- Although these models somewhat accurately predicted the stiffening potential of fillers, yet these models have their limitation,

only accounting for volume filling, they do not account for any physico-chemical interaction.

5.9 EFFECT OF FILLER PACKING ON AGEING

In continuation of the discussion in the sections 5.4 and 5.5, this stage of research addressed two interlinked issues namely; a) stiffening effect of packing of fillers in terms of their role in oxidative ageing b) effect of the surface activity (acidic/basic nature) of the aggregate on ageing.

Data analysis on the aged mastics indicates less difference between fillers at lower temperatures. The difference in properties is visible at lower reduced frequencies where OPC had lowest stiffening effect followed by limestone as shown in Figure 5.17. The gritstone behaviour at higher temperature may be attributed to slightly higher catalytic activity towards ageing. Gritstone is then followed by granite. This seems to reflect the effect of mastic ageing by the acidic nature of the aggregate at higher temperatures. This difference of stiffness of aged gritstone and granite is further evidenced in terms of its phase angle plot in Figure 5.18. The behaviour of OPC is best explained by its generic and high basic character which seems to contribute least towards the effect of filler on ageing. So far from the knowledge gained in this research, basic filler increases the stiffening of the bitumen in unaged mastic. On the other hand, in aged bitumen, the stiffening is increased due to acidic nature. This is because the acidic character during ageing acts as a catalysing agent.

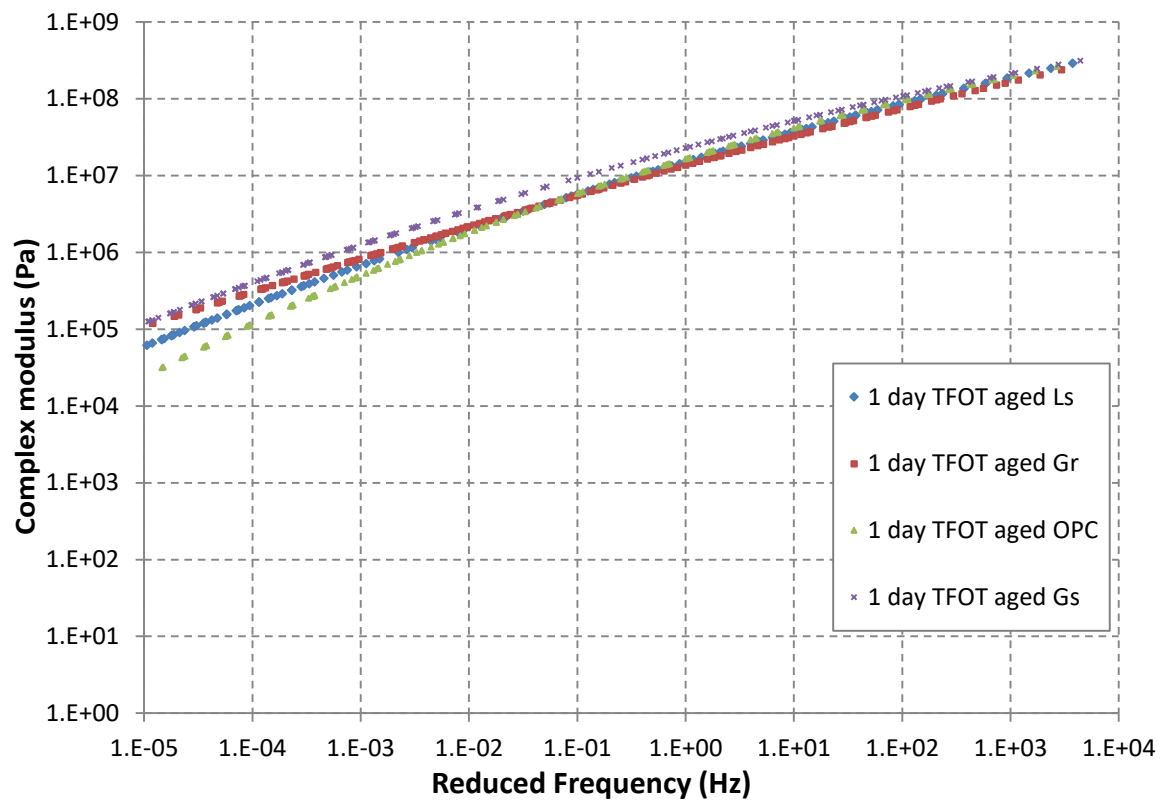


Figure 5.17: G* one day ageing comparisons (29%)

The phase angle master curves for the mastics indicate more viscous behaviour of the basic aggregates OPC and limestone at intermediate to high temperatures as compared to the acidic aggregates. The acidic aggregates granite and gritstone have less viscous effect which reflects on the catalytic ability of these fillers. The results are consistent with the discussion made about complex modulus master curves. The catalytic effect of mineral surface (quartzite and granite) is supported by a study by Petersen et al. (1974b). In their study they compared oxidation forming functionalities of quartzite and inert fluorocarbon 80 aggregate. It was also discussed that certain polar functional groups are strongly adsorbed onto the surface of the aggregate, this reduced ability to promote oxidation. This phenomenon, functional group adsorption, deactivates the ability of the surface either physically or chemically. However, their study did not give any clear

difference between acidic and basic aggregates. This is discussed in greater depth in a recent study by Wu (2009).

In this research, this phenomenon of functional group adsorption is mainly demonstrated by cement filler. Ordinary Portland Cement (OPC) has higher effective volume in the bitumen as compared to the other three fillers, which logically should have exhibited stiffer behaviour in the bitumen-filler suspension. This stiffness increase on ageing is retarded by adsorption of polar fractions on the filler, thus reducing the effect of ageing. However, on the other hand limestone has the least effective volume as compared to the three other fillers, and is expected to exhibit the least stiff behaviour. This means this filler has only a volume filling role in the bitumen or the role of an extender. The results of OPC in aged and unaged mastics have indicated that the role of filler in the bitumen is far more complex than can be explained by packing of the filler alone. A possible explanation of this behaviour is the combined effect of the physical, chemical and physico-chemical interactions of these particles with bitumen. This effect of physico-chemical interaction was demonstrated by Ishai and Craus (1996), the details can be found elsewhere.

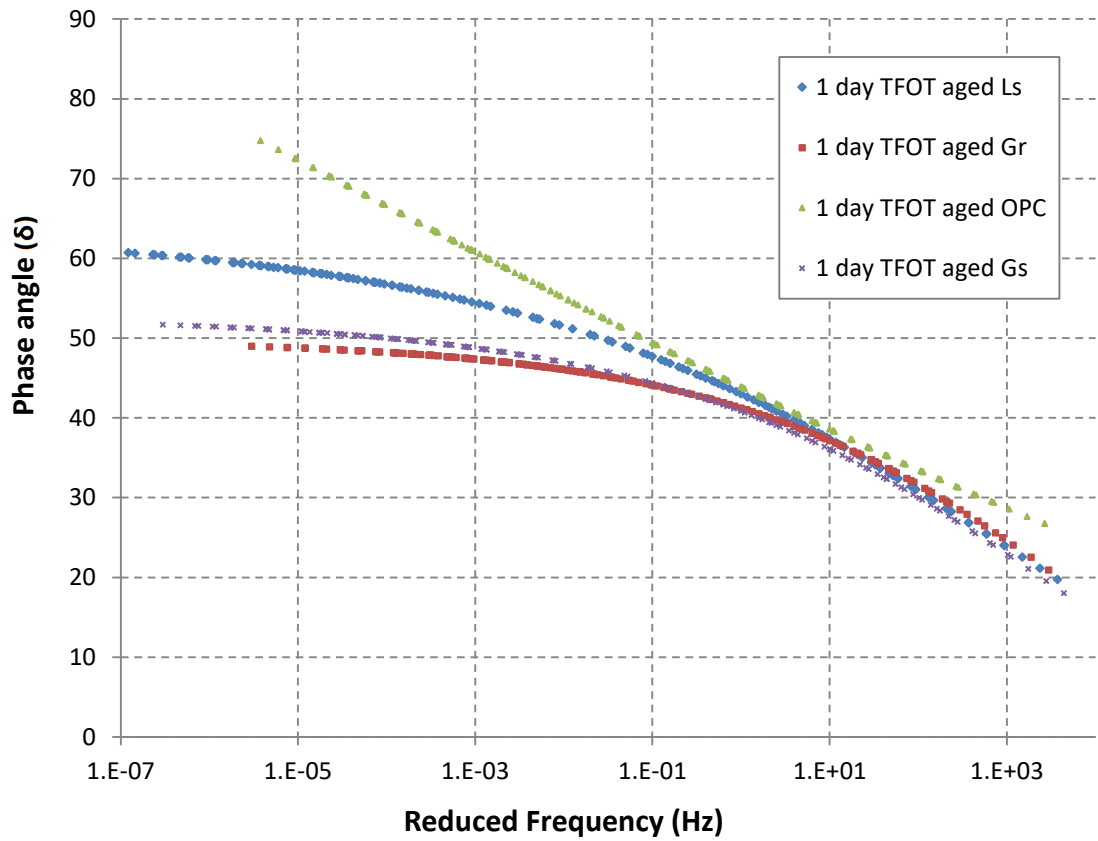


Figure 5.18: Phase angle one day ageing comparisons (29%)

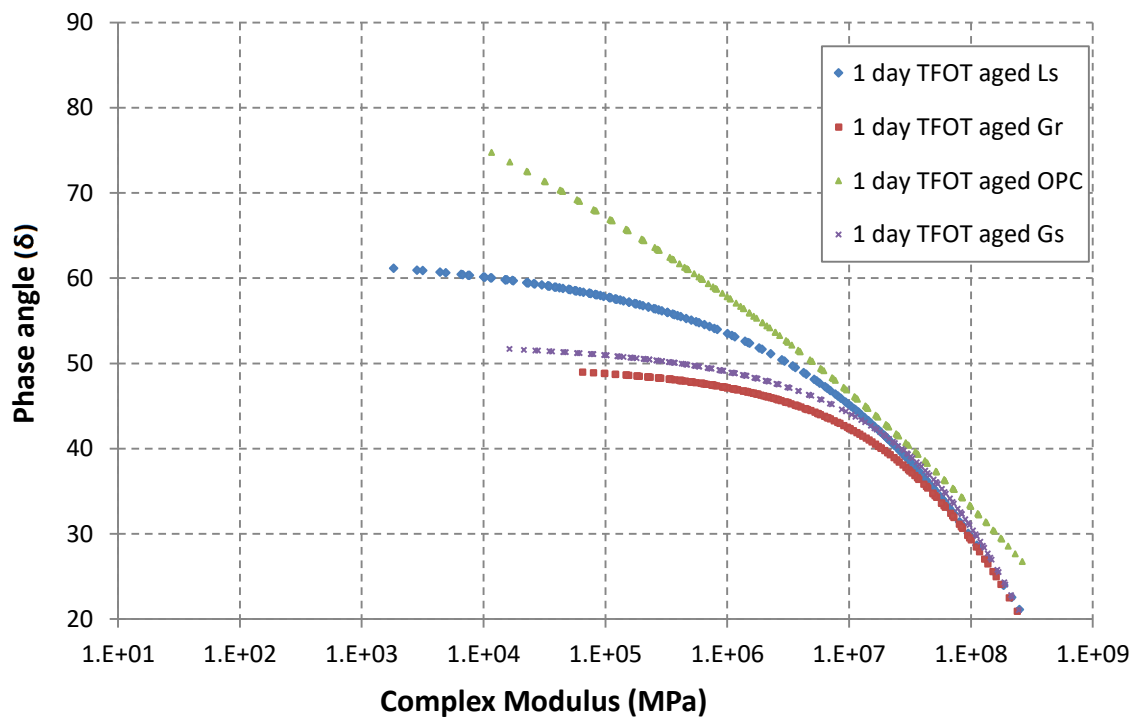


Figure 5.19: Black diagram one day ageing comparisons (29%)

The identical behaviour of granite and gritstone in unaged mastics at similar effective volume supports the assertion as stated earlier that packing plays a vital role in a bitumen-filler suspension. However, this role cannot solely be based on the packing as seen from the previous discussion on OPC. The difference of the role of filler is clear from complex modulus master curves of aged mastic. The gritstone filler has more stiffness, maybe due to its more acidic nature. A bit opposite role of granite at high temperature is due to an error in phase angle due to compliance of the machine. This is also reflected in its black diagram too.

The anomalies in the results of 40% mastic by volume are attributed to high filler content especially due to time which was too long and harsh for the binder. An example of such an anomaly is seen in the data for gritstone complex modulus from intermediate to low temperature. This point led this research to further reduce the filler concentration and ageing time to 20% and 20 hours respectively. This was to see if the trends were repeatable at lower filler content or if such trends can only be seen at high filler content. The experimentation was limited to the limestone and granite only; use of gritstone in next stage of testing was deemed unnecessary due to the similarity of its behaviour at higher ageing times and filler concentration to that of granite. In the next phase 5 hour TFOT testing was incorporated to study the effect of short-term oxidative ageing.

The anomalies in phase angle, as discussed earlier, especially at higher reduced frequency are somewhat attributed to compliance errors associated with its measurement (Airey, 2002). The next section will explore the findings, discussed so far, at a lower concentration. From a particle point of view, one possible explanation of adsorbed layer decreasing the stiffening effect is due to lowering of inter-particle van der Waals forces. This is because this adsorbed layer of binder on filler particles acts to shield the particle from its stiffening potential.

5.10 MINERALOGICAL COMPOSITION

Before assessing the effect of filler on mastics at low concentration in aged and unaged condition it was necessary to study their acidic/basic character through mineralogical analysis. XRD helps to understand the phenomenon of the nature of the particulate in bitumen-filler suspension. A summary of the presence of the important minerals and their relative proportions in limestone and granite is shown in Table 5.4, the relevant detailed XRD spectrogram is presented in Appendix B.

The composition of minerals has its effect due to complex processes that occur at the surface of mineral aggregate and their effects on its affinity both for bitumen and water. Filler particles are composed of various minerals; each of these minerals has different crystalline structure and chemical composition. Aggregate fillers can be categorised on this basis. With regard to XRD analysis, there can be hundreds of minerals in a single aggregate type depending upon its source, composition etc. In Table 5.4 only the important minerals are presented from the XRD mineralogical analysis. These minerals have effect due to their higher percentage as compared to omitted minerals present as minute fraction. In the case of granite, these main minerals were Quartz, Calcite, Vandendriesscheite and Cuprite. For limestone filler these minerals were Calcite, Dolomite, Quartz, Colusite and Tin Niobate.

Table 5.4: XRD analysis for mineralogical composition

Limestone	Granite
Calcite (72.8%)	Quartz (68.8%)
Dolomite (20.2%)	Calcite (23.7%)
Quartz (4.7%)	Vandendriesscheite (5.1%)
Colusite (1.4%)	Cuprite (2.4%)
Tin Niobate (0.9%)	-

XRD analysis shows, in granite, that quartz acts as an important mineral along with and calcite with relatively lower amounts of Vandendriesscheite and Cuprite. Quartz is a silicate mineral deriving its origin from igneous rocks. This leads to its classification as an acidic rock. Calcite is basic in its generic nature; however, the relatively higher proportion of quartz is expected to give an acidic character to the overall mineralogy of the filler.

Limestone filler has a higher presence of the calcite and dolomite as main minerals, which support its basic character. The amount of basic minerals is far less than generic minerals of OPC, which explains the stiffening behaviour of OPC notwithstanding the packing, effective volume and surface texture of its particulates.

5.11 FILLER AS LOW CONCENTRATION IN BITUMEN MATRIX

The rheological response of the mastics using filler at 20% of the volume of bitumen (17% compositional volume) was again plotted in terms of complex modulus, phase angle and black diagrams. The results indicated that addition of limestone filler did slightly increase the stiffness of the composite; this was followed by granite filler. This is consistent with discussion of high filler content mastics. Firstly, in order to explain the behaviour of the bitumen in terms of the packing, it is to be recalled that the limestone had Rigden voids or 33% while granite had 38%. In terms of the effective volume of the fillers in the mastics these values were 25% and 28% for limestone and granite. Yet this information alone is not able to explain the behaviour of these fillers. The surface activity of filler in this case is helpful to explain the behaviour. It can be deduced from the results that in the case of unaged mastics basic filler has the tendency to increase the stiffness despite its lower effective volume in suspension. Here, the packing of

the filler has less effect on the stiffening potential of the fillers than the filler's active and non-active nature in the mastic. This information is consistent with the findings of the high filler concentration section.

In terms of filler behaviour using 5 hours TFOT ageing, the differences were further reduced in terms of the stiffening effect. This is represented in Figure 5.20 which shows somewhat identical behaviour of both 5 hour aged mastics in terms of complex modulus. There seems to be little anomaly in the result for granite at lower temperature. The only possible explanation of there being little unusual behaviour in granite mastic at 5 hr ageing may be due to the presence of some microstructural agglomeration of filler in the bitumen, as which was dispersed relatively higher test temperatures leading to a uniform viscous behaviour of the bitumen. The other explanation of this could be due to the occurrence of a non-linear response at this test temperature. The occurrence of this non-linear is, however, least expected. This is because the strain limit measured at the lowest temperature was used to ensure the material response remained within the region of linear viscoelasticity. The material response was clear in terms of its properties at higher temperature so re-evaluation of the properties of the limestone at lower temperature was unnecessary. This difference between 5 hours aged limestone and granites is clearer in terms of the phase angle master curve and black diagram as shown in Figure 5.21 and Figure 5.22 respectively. The observation which can be brought forward to discussion is that the acidic character seems to come into play as mastic start ageing.

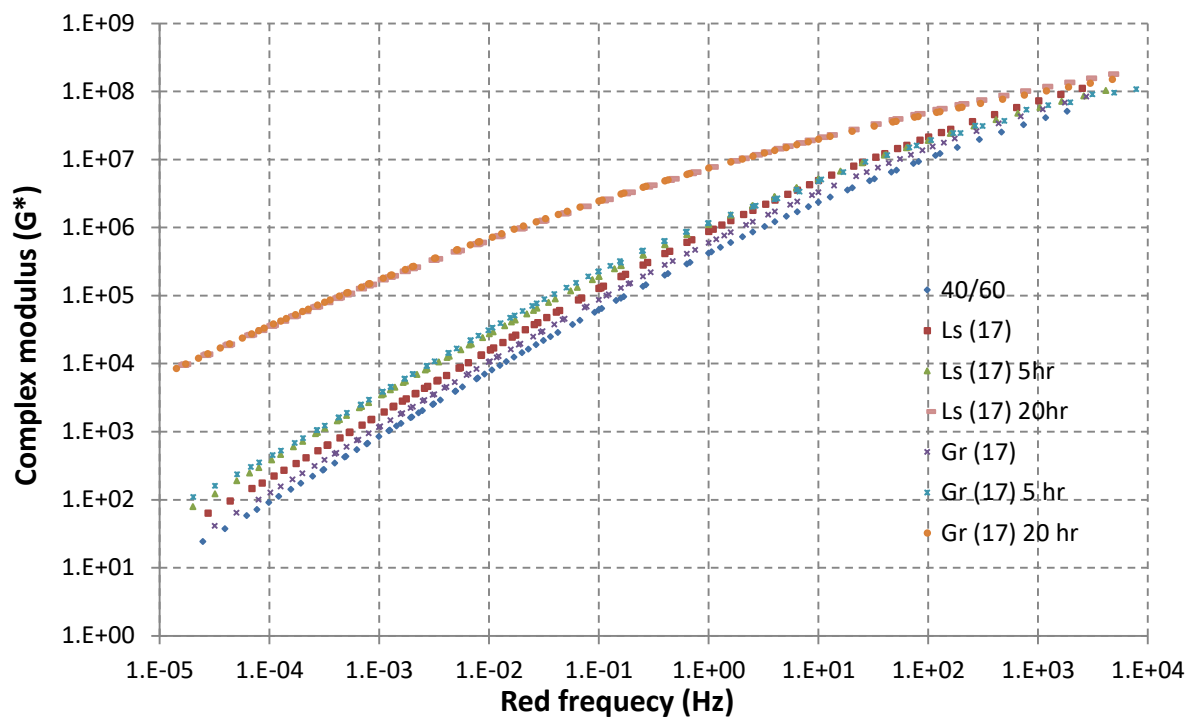


Figure 5.20: G^* mastic comparison (17%)

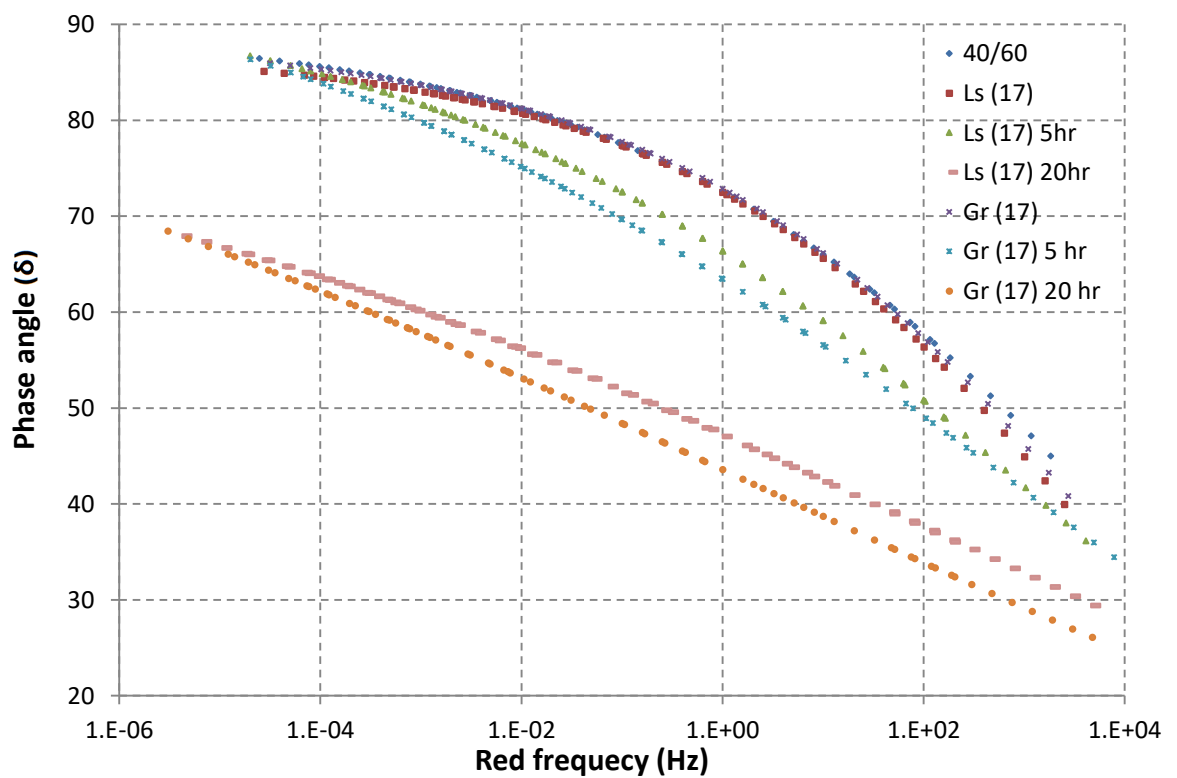


Figure 5.21: Phase angle comparison (17%)

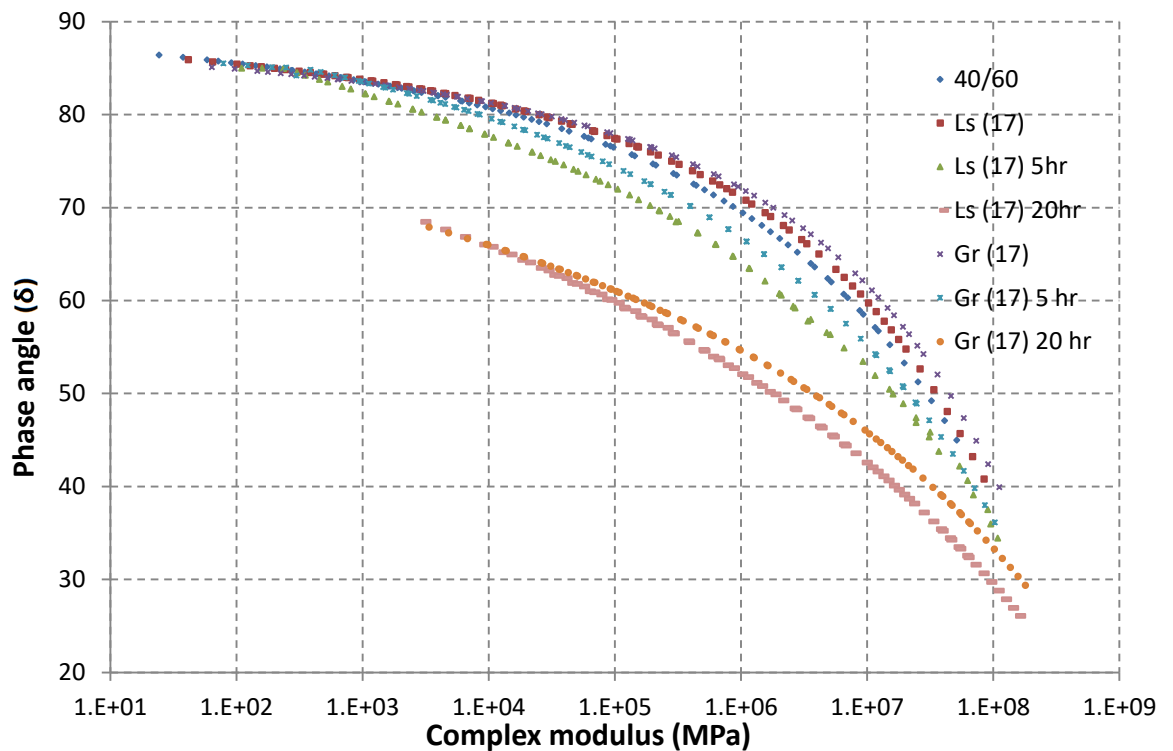


Figure 5.22: Black space diagram (17%)

The difference in stiffness between 20 hours aged limestone and granite mastic is not clear from their complex modulus master curves. It seems to be the case that there is no clear difference between the properties of the two materials as shown by their respective curves. This is further evidenced by the phase angle master curves. The curves of both mastics is divergent from the curves of the other materials in the data at high temperature, this might be due to the compliance issue with quite stiff aged mastic. The difference between the two mastic curves at 20 hours ageing regime shows that the granite mastic is less viscous than limestone mastic. This indicates that 20 hours ageing is influenced by the catalytic nature of granite.

At lower filler contents the acidic nature of the granite filler does have much effect on the ageing of mastics along with packing of the filler in mastics. As seen from the curves of unaged mastics, it was anticipated that the slightly higher effective

volume may be a contributing factor. However, it has been seen that the surface activity of the filler does play a role in terms of ageing.

The data analysis of this phase (study at 17% compositional volume) also helps to explain the behaviour of the granite at 29% compositional volume, its complex modulus and phase angle master curves. This can be summarised as both the packing and acidic/basic nature of the filler affects the properties of mastic. The packing fraction effect is more pronounced at unaged conditions. As the material ages the effect of the packing is combined with the effect of the acidic/basic nature of the particle. Acidic filler seems to act as a catalyst for the ageing while basic filler acts more as a retardant towards ageing of the mastics. The explanation of the effect of these fillers is further supported by the mineralogical analysis of the filler particles.

5.12 SUMMARY

In numerous studies positive role of filler has consistently been discussed in several aspects. Some these studies are; Traxler et al. (1933), Anderson (1987), Chen (1997), Shashidhar and Romero (1998), Lesueur and Little (1999), and Liao (2007). In this research, the effect of filler in mastic was explored especially taking into account bitumen-filler interaction. The packing of filler was emphasised keeping in view discussion of Traxler et al. (1933), Rigden (1947), and Shashidhar and Romero (1998). The packing of filler helped to understand the stiffening potential of the fillers while reducing variable to a single most important parameter, namely Rigden voids.

The important pioneering work of Rigden, despite its problems, has been highlighted by Heukelom and Wijga (1971), Anderson and Goetz(1973),

Anderson et al. (1992) and Kandhal et al (1998). An attempt was made to understand the mechanism of interaction between fillers and binders in terms of the theory of packing of the particles. It was seen that theory of packing wasn't sufficient to understand the stiffening potential of filler; additional information with respect to surface reactivity, fineness and surface texture was necessary.

In terms of complex modulus, it was seen that adding filler had less effect at low temperature. These effects were more pronounced at higher temperature. This is consistent with work of Anderson et al. (1992). It was seen that dynamic shear modulus of mastic is dependent both on bitumen and filler. This occurs because the bitumen becomes tender at higher temperature while filler remains as a rigid entity. Additionally adsorption layer also does not affect the low-temperature elastic properties, it only affects the high temperature flow properties. This can be useful in reducing the tendency of rutting in hot weather (Chen, 1997).

Few micromechanics-rheology models from colloid science were applied to calculate the theoretical stiffening ratio (a measure of stiffening potential). These models have the ability to predict stiffening potential from properties of individual ingredient. It was observed that these models produced good results at low volume concentrations with exception of Chong model. The observation was made that even Maron-Pierce model underestimated the stiffening potential of granite mastic at higher concentration. These observations and discussion on these models lead to the conclusion that it is difficult to precisely model mastic data using any single model. This is due to the presence of complex stiffening effects of filler beyond volume filling. Similar observation was made by Buttlar et al. (1999). In this regard, Shashidhar and Romero (1998) has summarized variables affecting stiffening potential.

These micromechanics based models do not incorporate physico-chemical interaction of bitumen fillers in mastics. Assumptions were made in numerical modelling of the stiffening potential of fillers regarding particle shape and unimodality. Such assumptions were found to be approximately true through mineral morphology, so no adjustment was made in this regard. This discussion was made keeping in view the work of Chen (1997). In this regard, Scanning Electron Microscopy (SEM) tests were performed.

A discussion was made with regard to the acidic/basic nature of filler. Such emphasis can be traced back to earliest work of Richardson (1915) who noted that filler role more than just void filling but also include physico-chemical interaction. Anderson and Goetz (1973) discussed reinforcement effect of filler depending upon their nature and type, Gubler et al. (1999) argued that certain filler can delay ageing. In this part of research, X-Ray Diffraction tests were performed to comment on the acidic or basic nature of the aggregate. An attempt to use FTIR to study difference in oxidation functionalities of different aged mastics. This was done to comment on the difference in stiffening potential of different fillers. However, this attempt did not yield any meaningful results.

In this research, it has been argued that in unaged mastics the basic filler results in higher viscosity of the suspension. This point has support from Winniford (1961). This holds true for unaged mastic; however, for aged mastic this does not seem to be true. In the case of aged mastics, it has been seen that acidic filler promotes oxidation and has a catalytic effect as compared to basic fillers. A past research This catalytic theory has support Petersen et al. (1974b) and is contrary to belief of Rigden (1947) who believed that ageing is independent of nature of bitumen and filler, a similar belief was expressed by Traxler (1937b).

CHAPTER 6 : COHESIVE BOND STRENGTH OF THE MASTICS

In asphalt pavements the major role of the bitumen is that of adhesive agent. This adhesive agent create bond with aggregate. The tensile strength measurement of the binder is just as important as measuring the fatigue crack resistance in order to evaluate the resistance of the asphalt mixture to the cracking. The strength of any asphalt mixture is greatly impacted the mixture mass cease to act as a coherent structural unit. This happens due to loss of adhesive and cohesive bond failure. The studies such as Bhasin and Little (2009) show that work of adhesion between bitumen and aggregate is an important parameter that influence the moisture resistance and fatigue cracking resistance of asphalt mixtures. Different researchers have tried to explain adhesion of binder on aggregate based on different theories such as mechanistic tenacity, molecular orientation, chemical reaction and interfacial forces' thermodynamic balance (Bagampadde et al., 2004). The bond is strong for bitumen coated with clean and dry aggregate. However, in most of the cases this not the case due to presence of water within the voids and within the aggregate body. The failure mechanism of bitumen-aggregate system can be both adhesive and cohesive. If aggregate is clean then this bond failure is mostly cohesive in nature.

There are numerous studies that emphasise the importance of thin film binder to evaluate its response to tensile type pull off loading based on loading rate, film thickness and temperature. Some of these studies include research by Harvey and Cebon (2003) and Poulikakos and Partl (2011). This part of research is in line with such need mentioned in literature. In this research two methods were used to pull off bond strength of mastics. A larger film thickness was used in an

attempt to isolate the cohesive strength from pure adhesive type failure. In this research study, an attempt was made to use both methods to evaluate cohesive bond strength of the materials. The first method in this part of research served as a basis to define several important parameters for the second method. In the research, the test gap assembly was modified to obtain a more uniform binder thickness for the testing. This was modification was result of the attempt to minimise errors in result of first method.

6.1 PULL OFF TEST

In this research Pull Off Test mechanisms were used to evaluate the cohesive strength of asphalt and mastics and the variable affecting them. In this chapter two existing test method were used to evaluate the bond strength. Both the methods were performed at constant rate of loading. This gave these method advantage to measure the full response of the material as compared to PATTI test where only maximum load is measured and failure surfaces can be examined.

6.2 PULL OFF TEST (METHOD 1)

6.2.1 Background

This test technique was based upon the test method developed by Jakarni (2012) in his PhD research work to evaluate the pull off strength of the binder. A modification was made to the compression device. This gap assembly was then used to achieve a more uniform film thickness.

This method is taken from PhD dissertation thesis of Jakarni (2012). The thesis was divided into three parts, in part 1, a detailed literature review of the test was

conduct for the selection of the method to assess and propose a test method. In part 2 this proposed method was subjected to evaluation using trial and error experimental approach to develop technique, its procedure, test set up, testing and data analysis. In part 3 the researcher evaluated his method using different bitumen and mastic combinations over different conditions, thicknesses, deformation rates etc. and finally proposed a draft protocol for his testing. In this research this method was re-evaluated to measure the pull off strength and extending this work to mastics and different ageing regimes.

6.2.2 Results and Discussions

The substrate plates (22.6 mm) were labelled as A, B, C, D, E, and F then relevant tests were performed, results are shown in Figure 6.1. The statistical analysis shown in Figure 6.2 indicates that the variation is independent of the plate pair used. The missing values in the Table 6.1 indicates that material had premature failure either due to handling or seating adjustment of load. These specimens were tested after 24 hour of conditioning. This condition time was selected based upon study by Copeland (2007) and Jakarni (2012).

Table 6.1: Pull off strength (method 1)

Material description	Film Thickness (μm)	Pull off strength at fracture (MPa)					
		A	B	C	D	E	F
40/60	100	2.79	1.21	1.23	2.03	1.79	1.22
40/60 (4hr aged)	100	-	2.10	-	1.29	2.56	1.89
Ls	100	1.43	1.49	-	-	-	1.90
Gr	100	1.97	-	2.09	-	1.15	-
5 hr TFOT aged 40/60	100	2.97	2.05	-	2.50	-	-
20 hr PAV aged 40/60	100	-	3.03	-	3.66	3.44	-
1 day TFOT aged 40/60	100	3.26	2.35	2.98	-	2.35	-
1 day TFOT aged Ls	100	2.97	-	-	2.67	2.48	-
1 day TFOT aged Gr	100	-	3.26	-	1.72	3.03	2.92

Table 6.2: Statistical parameters pull off testing

Material description	Film Thickness (µm)	COV (%)	Max (MPa)	Mean (MPa)	Range (MPa)	STD (MPa)	Mean +SD (MPa)	Mean -SD (MPa)
40/60	100	36.98	2.79	1.71	1.58	0.63	2.34	1.08
40/60 (4hr aged)	100	26.87	2.56	1.96	1.27	0.53	2.49	1.43
Ls 100		15.89	1.90	1.61	0.47	0.26	1.87	1.35
Gr	100	29.39	2.09	1.74	0.94	0.51	2.25	1.23
5 hr TFOT aged 40/60	100	18.43	2.97	2.50	0.92	0.46	2.96	2.04
20 hr PAV aged 40/60	100	9.34	3.66	3.38	0.62	0.32	3.70	3.06
1 day TFOT aged 40/60	100	16.61	3.26	2.74	0.90	0.45	3.19	2.29
1 day TFOT aged Ls	100	9.11	2.97	2.71	0.49	0.25	2.96	2.46
1 day TFOT aged Gr	100	25.11	3.26	2.73	1.53	0.69	3.42	2.04

The individual pair of plates show a significant variability; this leads to question the repeatability of the test method. The pull off tests always have a sympathetic note attached to them about the variability in their results. This point has further support from the literature that there is no true universally acceptable pull off test which can capture the bond strength through fundamental mechanical testing.

The main cause of variability in these methods is non-standard sample preparation method and testing protocol. Although, Jakarni (2012) has established the procedure for testing according to his test set up. The author believes that operator variability, as explained in chapter 7 plays an important role in difference of results. It is demonstrated in chapter 7 that the operator who has developed the method has good repeatability in the results as compared to operator who was trained to use this method. It is opinionated here that operator variability must be checked during different stages of testing. The second problem with this method is breaking of the samples during handling. Lot of the

samples were wasted during handling. The third problem with the method is of excessive procedural steps during sample preparation and actual testing.

Here onward an attempt has been made to interpret the results Figure 6.1. However, it is to mention early on that these results should not be used for conclusive judgement. However, this may be useful for giving idea about the tensile strength properties of the material. The first observation can be drawn from the results is that the ageing increases the pull off strength. It can be particularly seen from the difference of pull off strength between unaged and 4 hours aged bitumen. This is further supported by seeing the increase of ageing time from 4 hours to 5 hours and from 5 hours to 20 hours ageing.

The second observation is that the difference of pull off strength between 20 hours PAV and one day TFOT aged binder. The long-term PAV and TFOT aged bitumen has considerable difference when compared to the unaged bitumen and mastics (both in aged and unaged conditions). When level of severity of PAV ageing in terms of adhesive bond strength is compared with TFOT, it is more than that of TFOT ageing. The point which maybe brought forward is that PAV ageing might be resulting in adhesion promoting functionalities. Thirdly, in the results it can be seen that addition of filler has not resulted in increase of pull off strength. This is contrary to known knowledge about fillers. The literature reveals that adding filler should increase the pull off strength as seen from Chen and Peng (1998). However, in this result, the Granite mastic seems to have slightly more pull off strength than limestone filler. This is again contrary finding of chapter 5, in which limestone had more stiffening potential. Here granite seems to have more adhesion. In order to justify the more apparent pull off strength of granite, the adhesion effect just needs to be dependent on mechanical properties of binder-substrate interface without effect of chemical aspect of nature of filler and bitumen. If this is the case then the whole phenomenon of more adhesion of

granite should be based on free volume of bitumen, particle size and surface texture. The literature survey indicate that physicochemical interaction of aggregate and binder play an important part in the adhesion. In general observation limestone has good adhesive properties than granite thus it will be expected to have better tendency for physicochemical interaction. This is why It is concluded that this slight difference and apparently opposite trend of both filler is due to inherent variability of the test method.

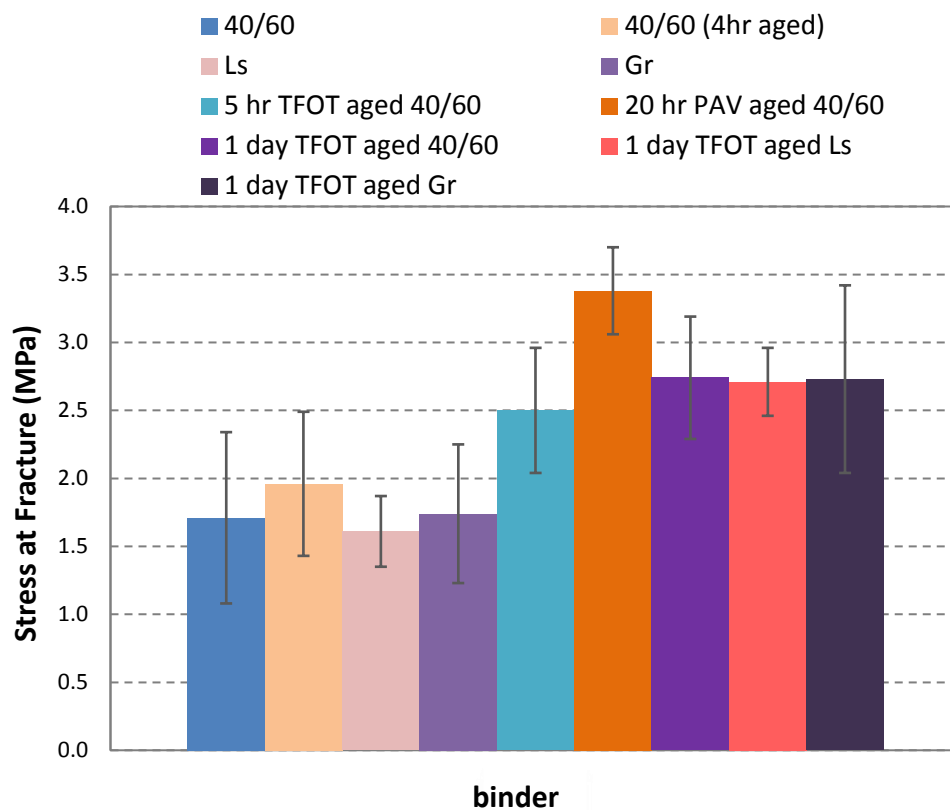


Figure 6.1: Summary of the pull off strength

In Table 6.3 the research data of this method has been compared with historical data in similar research. The tabular values of Marek and Herrin (1968), Kanitpong and Bahia (2003), Copeland (2007) are taken from the (Jakarni, 2012) PhD work and are checked for their accuracy.

The bitumen in present research was stiffer than bitumen of (Jakarni, 2012), however have closer value to that of Zhang et al. (2015). The difference of results with (Jakarni, 2012), is due to more penetration grade of bitumen. The difference of results with (Jakarni, 2012), is due to due to difference in penetration grade of bitumen.

When compared to the historical data the pull off strength, the pull off strength of the bitumen in this research has values reasonably closer to studies by Kanitpong and Bahia (2003) and Copeland (2007). The important to note here is that their bond strength is higher even with more bitumen film thickness. The reason behind this difference is mainly due to high test loading rate.

Table 6.3: Comparison with historical data

	Brief Description		Area of Contact (mm ²)	Average Film Thickness (μm)	Tensile Bond Strength (kPa)
Present study	Substrate	Aluminium	401.2	100	1806
	Binder	Conventional 40/60 grade of bitumen (Penetration at 25°C is 54)			
	Test Conditions	Deformation rate and test temperature of 10 mm/minute at room temperature			
Zhang (2015)	Substrate	Aluminium	-	20	1947
	Binder	Conventional 40/60 penetration grade of bitumen (Penetration at 25°C is 54)			
	Test Conditions	Deformation rate and test temperature of 10 mm/minute and 20°C			
Jakarni (2012)	Substrate	Aluminium	490.87	50	1306
	Binder	Conventional 70/100 penetration grade of bitumen (Penetration at 25°C is 68)			
	Test Conditions	Deformation rate and test temperature of 20 mm/minute and 25°C			

Marek and Herrin (1968)	Substrate	Aluminium	506.71	60	4075
	Binder	Asphalt cement K (Penetration at 25°C is 51)			
	Test Conditions	Deformation rate and test temperature of 25.4 mm/minute and 25°C			
Kanitpong and Bahia (2003)	Substrate	Glass	126.68	200	1982
	Binder	PG 58-28			
	Test Conditions	Deformation rate of 65.7 kPa/second at room temperature			
Copeland (2007)	Substrate	Diabase	1520.53	200	1910
	Binder	AAM (PG64-16)			
	Test Conditions	Deformation rate of 65.7 kPa/second at room temperature			

Note: All data of the test results shown here are of dry conditioning samples.

The diameter of the plate is of not much importance here as it is ultimately taken care during bond strength computation.

The values thus measured in this research by method 1 are of reasonable magnitude as compared to of historical data. When historical is compared with each other, Copeland's bitumen has lesser strength due to softer bitumen even when bonded with diabase. Marek and Herrin (1968) has much higher bond strength because of stiffer bitumen and thinner film thickness. The bond strength by Jakarni (2012) is bit lesser than historical data despite less film thickness. This might because his research was on softer grade of bitumen. This discussion leads to the need of a detailed and through evaluation of different test and material parameters. This has been discussed in great depth in chapter 7.

The pull off strength measure by of Zhang et al. (2015) seems only slightly higher to compared to the present research. The only difference seem here is of the film thickness and the test method. The uniformity of film thickness of his study is expected to be of good quality because it was achieved with Dynamic

Shear Rheometer (DSR). This leads to the conclusion that this less difference can only be attributed to different test method. The method Zhang et al. (2015) used is termed as Method 2 in this chapter. The work on this method was already in progress as when the study was published. The emphasis again is made that the two test method can generate different values on the same material under same conditions.

In next section on Method 2, it is not feasible to make comparison of both studies because two studies are further aiming in two different directions. Zhang et al. (2015) work leads more towards adhesive strength while this research will shift its focus purely on the cohesive strength. The reason of the change of the method and failure mechanism is described in next few paragraphs and summarised in conclusive remarks about this method. Before focus off conversation is changed, it is important to add that in order to compare values of different studies the test method should also be specified along with substrate type, binder specifications, and test conditions (as described in Table 6.3).

In this study visual inspection of surface, the failed specimens were made. One of the typical adhesive to mixed type of the failure is shown in Figure 6.2. It was observed during the testing that dominate type of failure was adhesive to mixed type with film thickness of 100 μm . This makes sense that with this film thickness it is hard to go either on pure adhesive type of failure or pure cohesive type of failure. It was decided to increase the film thickness to get more uniform film thickness. As the amount of time and resources spent on this method suggested that going any lower 100 μm was not a good idea. This was because it was identified that one of the possible reason for variability in this method was problem in achieving uniform film thickness.



Figure 6.2: Specimen after pull off testing (method 1)

6.2.3 Summary and warrant for Method 2

The method 1 has to be more useful in identifying the pull off strength particularly where failure mode ranges from mixed to adhesive failure. Thus making this method useful for adhesive bond strength as excessive handling of this method is expected to break the relatively weak cohesive bond due to high film thickness. Henceforth, it was thought that this this method may not be useful for testing for cohesive properties. Therefore, a different method was selected for next phase of the testing. This method was a simple with ease of operation and lesser handling of the specimen. In this chapter this method is referred as Method 2. In next phase gap assembly was modified in order to achieve a more uniform film thickness. The secondary purpose of increasing film thickness was to achieve a uniform film thickness.

6.3 PULL OFF TEST (METHOD 2)

This phase of testing purely focuses on cohesive strength of mastics. The test method used in in this part of test is based upon testing assembly developed by

Apeagyei et al. (2014). The research by the researcher measured aggregate-mastic bond strength using unconditioned and moisture conditioned specimen. The substrate-mastic joint system as shown in Figure 6.3. It is important note that this binder-substrate stand-alone system has often been referred as butt jointed and poker-chip assembly in literature.

The cohesive strength studied in this phase refer to integrity of the binder itself. This failure mechanism which occurs more within the bulk mastic than at binder aggregate interface. This cohesive failure is primarily achieved when film thickness is sufficient large.

6.3.1 Selection of conditioning time

In this method specimen were tested mainly after dry conditioning. The conditioning time was kept as 24 hours at room temperature. This was to ensure that a proper bond was achieved between the plate and bitumen. This conditioning time is more accurately referred as curing, hence for the it will be referred as curing when there is no wet or dry comparison. The term conditioning is generally used in connection with water damage or when the specimen is stored in non-standard condition. Here 24 hours is selected as curing time, this is based upon the studies; Jakarni (2012) and Copeland (2007). According to the researchers this time was sufficient for proper bond to develop.

6.3.2 Testing Phase

In this test a uniaxial steady tensile pull off load was applied to the bitumen film thickness of 500µm which was poured on to hot aluminium plates. As mentioned previously film of 500 µm was selected so that a dominant cohesive failure can be obtained.

In test set up, the plates were tied to the mould assembly using 3 screws at 120 °C, in the method 2 this three-point screw tightening mechanism was sufficient to hold the aluminium plates preventing the vertical movement of the plates. This mechanism provided sufficient grip to the aluminium plates. Aluminium was selected because the Young's modulus of the aluminium plates was very high when compared with bitumen. This is useful to mention because it prevented the deformation in control material and load was only taken by the binder. The same concept is applicable when aggregate plates are tested. The binder film thickness was prepared using silicon method of pouring.

A schematic diagram of the test methods is shown in the following figure. The uniaxial load indicates that the lateral movement has been reduced by the test mounting mechanism which holds the test assembly through a jaw type holding mechanism.

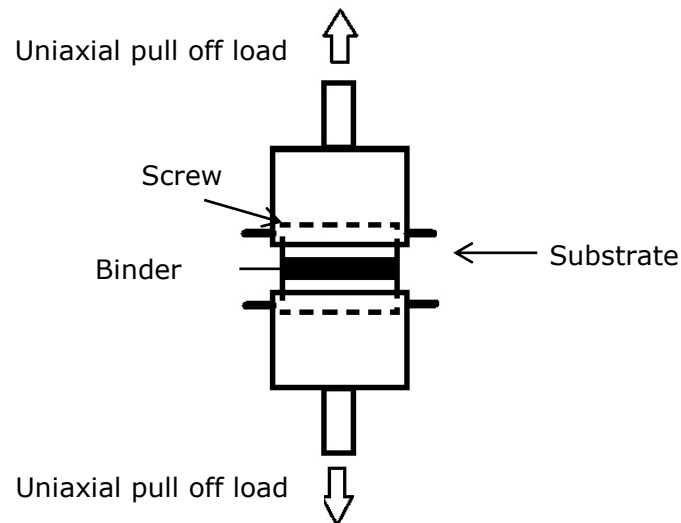


Figure 6.3: Schematic diagram of test set up

This fastening of aluminium plates with the mould assembly to hold the joined plates differed from the first pull off method. The first method used the fastening by four screws which were at 90 degrees apart while the later study used screws

which were 120 degrees angle apart. This helped to reduce the handling of the plate testing rig assembly and suggested that both tightening mechanisms were equally useful in terms of their effectiveness of securing the plates to the mould assembly. However, it was suggested that by increasing the gauge of the screw the extra handling and time of securing the plates could be minimised.

The load application was uniaxial in both studies as a universal joint mechanism was used to ensure that the lateral movement of the specimen was ruled out. The universal joint has the capability to prevent the lateral movement along the horizontal axis due to their unique design. The universal joint also has the ability to take care of the little adjustments during the seating of the load.

6.3.3 Results and Discussion

In this part of research 500µm film thickness was used with aluminium plates of diameter 25.4 mm. The Table 6.4 summarises the pull off strength at fracture and related statistical parameters for a film thickness of 500µm otherwise stated. The results are further plotted in Figure 6.4

Table 6.4: Pull off strength of mastics

Material description	Pull off strength at fracture (MPa)				COV (%)	Max (MPa)	Mean (MPa)	Range (MPa)	SD	Mean +SD	Mean -SD
	1	2	3	4							
40/60 (100 µm)	1.44	2.07	1.40	-	22.8	2.07	1.64	0.67	0.37	2.01	1.27
40/60 (500 µm)	1.08	1.20	1.17	1.37	10.3	1.37	1.20	0.30	0.12	1.32	1.08
Ls (17)	2.00	2.09	1.62	-	13.1	2.09	1.90	0.47	0.25	2.15	1.65
Ls (17) 5hr	1.51	1.68	1.67	1.60	4.81	1.68	1.62	0.17	0.08	1.80	1.64
Ls (17) 20hr	1.88	1.44	1.86	1.29	18.5	1.88	1.62	0.59	0.30	1.92	1.32
Gr (17)	1.66	2.08	1.56	1.59	14.1	2.08	1.72	0.52	0.24	1.90	1.42
Gr (17) 5hr	1.65	1.5	1.60	1.91	10.5	1.91	1.66	0.41	0.17	1.79	1.45
Gr (17) 20hr	1.22	1.24	2.12	1.70	27.2	2.10	1.57	0.90	0.43	2.00	1.14

The first important observation is that this method has lesser variability of results as compared to Method 1. It should also be noted that the gap assembly is fundamentally the same. It further affirms the previous findings that:

- The excessive handling was one of the major source of problem. In Method 2 decreased handling decreased the likelihood of the specimen break during handling.
- The second source of problem identified was that the resolution of the servo-hydraulic Instron was quite low as compared to the machine Method 2. This can be one of the reason for better results of the method 2.
- The third reason can be that the fine tuning and better resolution of in the Method 2 also decreased the breaking of specimen during load and seating.

The modified gap assembly did not play much role in improvement in the result of the Method 1. This further support the above argument for the variability in the results.

In next step graphs were drawn between load and deformation/elongation, and the area under the curve before maximum failure load. In Mechanics of Solids this is referred as ultimate tensile strength. In bond strength testing on asphalt pull off strength refers to this ultimate tensile strength. It is important to note that this ultimate strength should not be confused with fracture strength. Bitumen do take little load after ultimate tensile strength/pull off load. This load is actually taken by the dendrite of the fibrillar structure during failure of bond. However, it is so small that there is not much practical use of it in the field bituminous materials. Nevertheless, it is natural phenomena and cannot be ignored for

softening portion of stress strain curve show that material is less ductile scientific purposes. It is possible that someday someone will “make a mountain out of a molehill”.

This phenomenon is discussed in chapter 7 in more detail. The point intended is that for brittle failure in bitumen the pull off load/ultimate tensile load and fracture load is same as no fibrillar structures occur during brittle failure. However, in case of ductile failure for bitumen, the ultimate tensile strength/pull off load and fracture load are technically different.

In this analysis area under the curve before failure (peak load) was computed. This area under the curve helps to calculate energy absorbed before failure. The behaviour of bitumen after ultimate tensile load is somewhat complex. Due to this reason the area under the curve should be calculated up to peak load for analysis purposes. The discussion made here is with regards to area under the curve only and this area is area up to peak load.

In Figure 6.4 the average stress at failure for different sample is shown. The associated failure curve of dissipation energy before failure is shown in Figure 6.5. In testing, for 100 μm bitumen film thickness the failure mode is shown in Figure 6.5 (a). The failure mode is brittle supporting the adhesive to mixed failure. However, the failure for 500 μm film thickness is ductile as shown in Figure 6.5 (b), the failure was ductile. This suggested that material can elongate longer on the application of load, taking a long time to dissipate energy as compared to corresponding brittle failure. This was because after failure load some stress was taken by specimens due to elongation on ductile failure. This ductile nature of failure is represented by the negative slope of the stress-strain graph; this is shown after maximum stress. The larger the negative slope of

softening portion of stress strain curve show that material is less ductile (Poulikakos and Partl, 2011). This supports cohesive to mixed type failure of the bitumen for 500 μm film thickness. This means that the bond failure started within the molecules of the bitumen or bitumen mastic interface. This also suggests that as asphalt film thickness decreases it affects the failure mode from cohesive to adhesive. The importance of ductility or ductile failure can be seen from metals and alloys where ductility play an important. The ductility serves the purpose of a warning system in occurrence of failure. In bitumen no such warning system maybe of direct relevance. However, this ductility can be important to crack initiation and development which can ultimately be related to pavement failure.

The Figure 6.8, however indicate that overall trend for energy release of both specimens were equal. This indicate that for any pull off testing three types of information is necessary to comment on the bond strength. The first one is the maximum bond strength, second include the rate of deformation corresponding to pull off load. The third type of information need is visual and graphical analysis of the failed surface of the substrate. This lead to conclusion that normal pull off tests like PATTI might not be as useful as they provide only two types of information. This include maximum pull off strength and pictorial examination of the surface of the substrate after when elastic as well as plastic failure has occurred in the specimen.

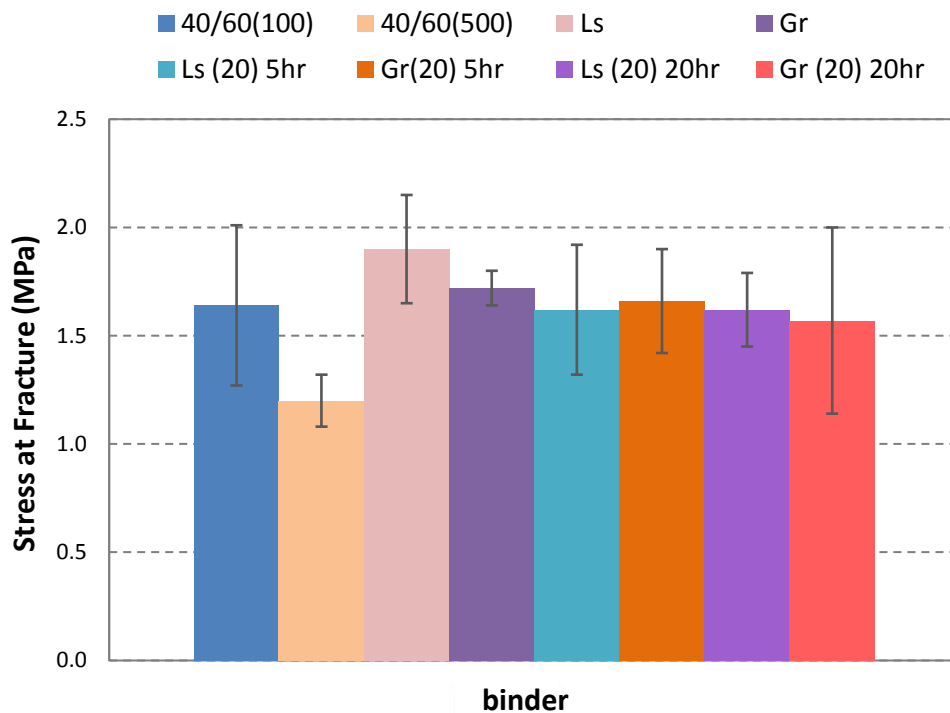


Figure 6.4: Summary of 17% mastic by compositional volume (method 2)

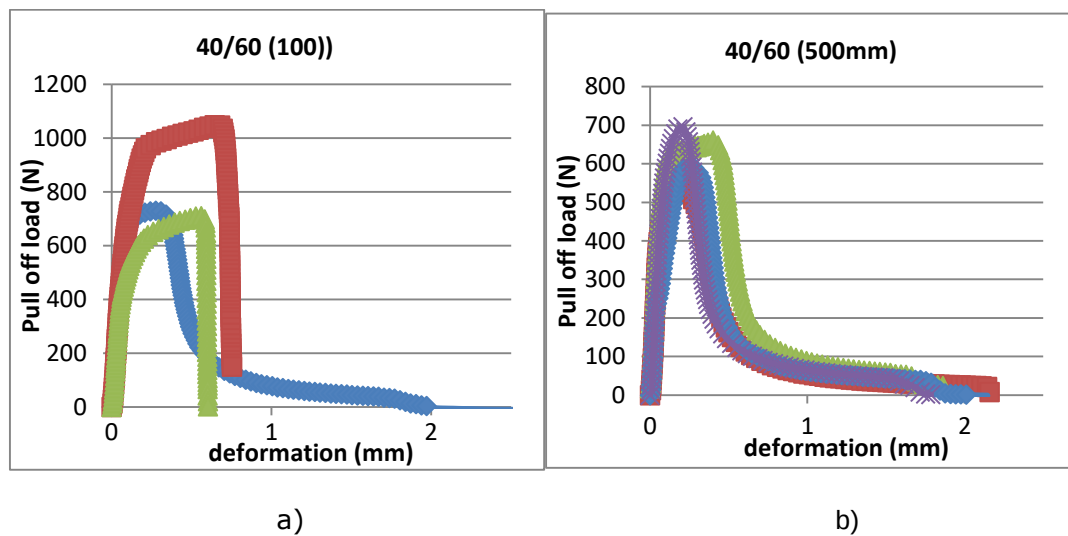


Figure 6.5: Failure curves for Pen 40/60 (100 μm)

The addition of the filler to the bitumen has significantly increased the pull off strength of the material. It is clear from the comparison of the 40/60 binder and limestone and granite mastics. The mastics has more pull off strength when compared with the equal thickness of the pure bitumen. It is also to be noted that failure mode studied indicates that for both the unaged limestone and granite

mastic the failure mode was brittle failure. The limestone has more pull off strength as compared to granite. During this stage of testing, fillers mainly play the role of stiffening agent of the binder and lesser the role of an extender. This is consistent of the findings from previous chapter, where limestone increase the stiffening potential of the mastics. The brittle behaviour of both fillers is indicated by a sharp drop in the curve which shows a quick breakage of the bond, this type of behaviour is maybe due to the adhesive to mixed type failure of the binder layer as shown in Figure 6.6.



Figure 6.6: Failure surface of Gs mastic after 20 hr ageing

After 5-hour ageing in TFOT the failure mode remained brittle as anticipated. The limestone aged show little ductile failure tendency as shown in Figure 6.7. However, the slope of the curve is very large so it can be overall taken as brittle failure. The associated variability can be attributed to inherent nature of pull off test where this little deviation is quite expected. The difference is clear from failure curves where the total energy with respect to five hours ageing is reduced.

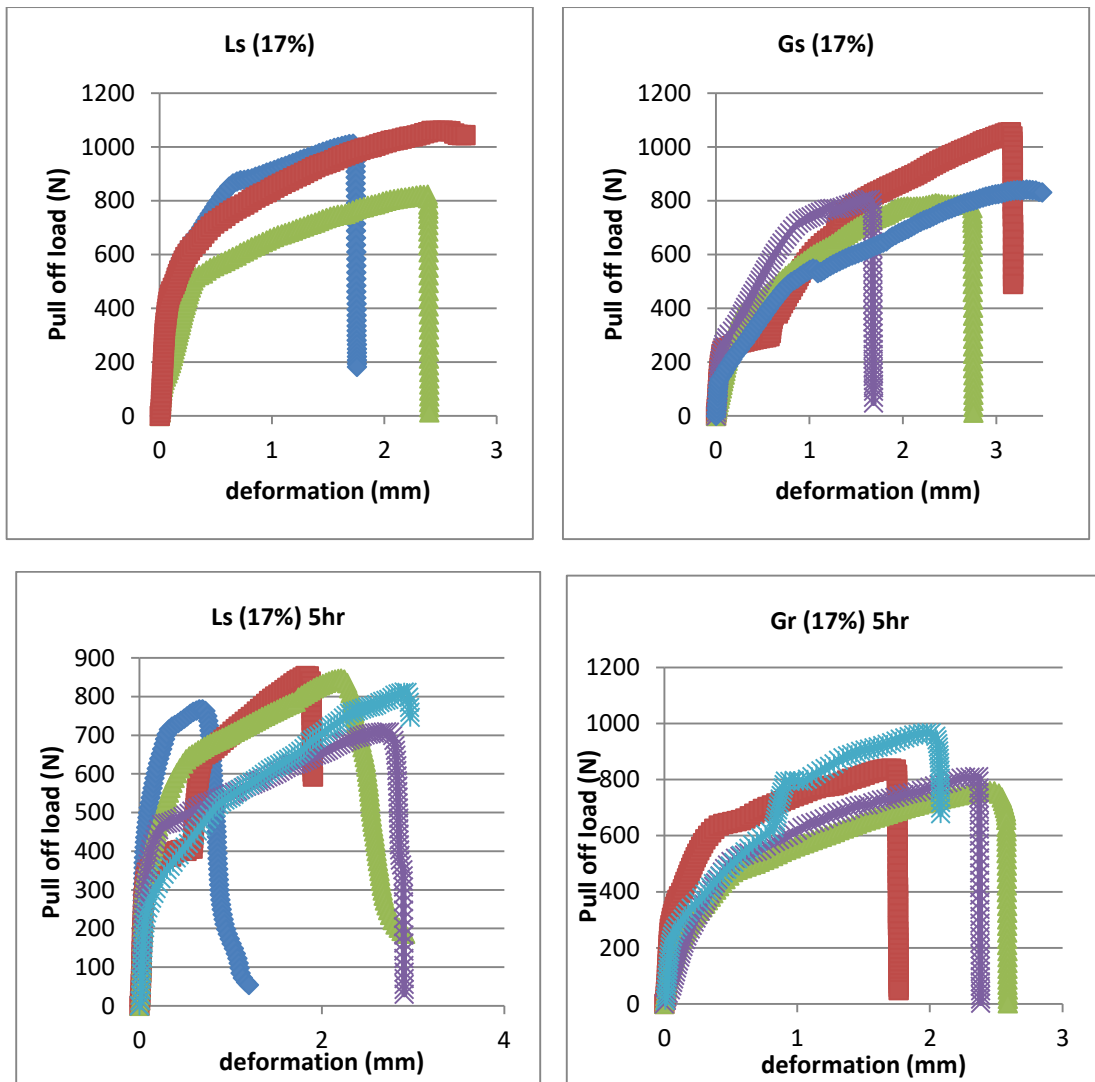


Figure 6.7: Failure mode in 20 hr aged Gs mastic

In the third stage of testing, limestone and granite mastic were aged for 20 hours in Thin Film Oven (TFO). The results of these specimen did not fit into discussion of the pull off load and neither in terms of curve behaviour. The curve behaviour was so departed from the expected behaviour that no logical explanation could be brought forward. This confusion might have occurred due to labelling or handling of the material. Due this reason results of 24 hour aged mastics were removed from the discussion.

The pull off tests is repeatable enough to use. Figure 6.8 shows the trends which are consistent with the above discussion in terms of area under the curve before failure. These values are plotted from Figure 6.5. This energy absorbed before failure is the energy released when the material fails. This discussion leads to the point that this information along with image analysis can be useful towards understanding of the failure mechanism of the aged bitumen.

Table 6.5: Area under the curve before failure

Material description						COV (%)	Max (N-mm)	Mean (N-mm)	SD (N-mm)	Mean + SD (N-mm)	Mean - SD (N-mm)
	1	2	3	4	5						
40/60 (100 μ m)	402	655	357	-	-	34	655	471	161	632	310
40/60 (100 μ m)	791	281	373	291	749	55	791	497	272	769	225
Ls (17)	1448	2077	1550	-	-	20	2077	1692	338	2030	1354
Ls (17) 5hr	609	1186	1859	1669	1784	44	1859	1421	625	2046	796
Gr (17)	1991	2254	1689	-	-	14	2254	1978	283	2261	1695
Gr (17) 5hr	1198	1488	1430	1462	-	11	1488	1395	153	1548	1242

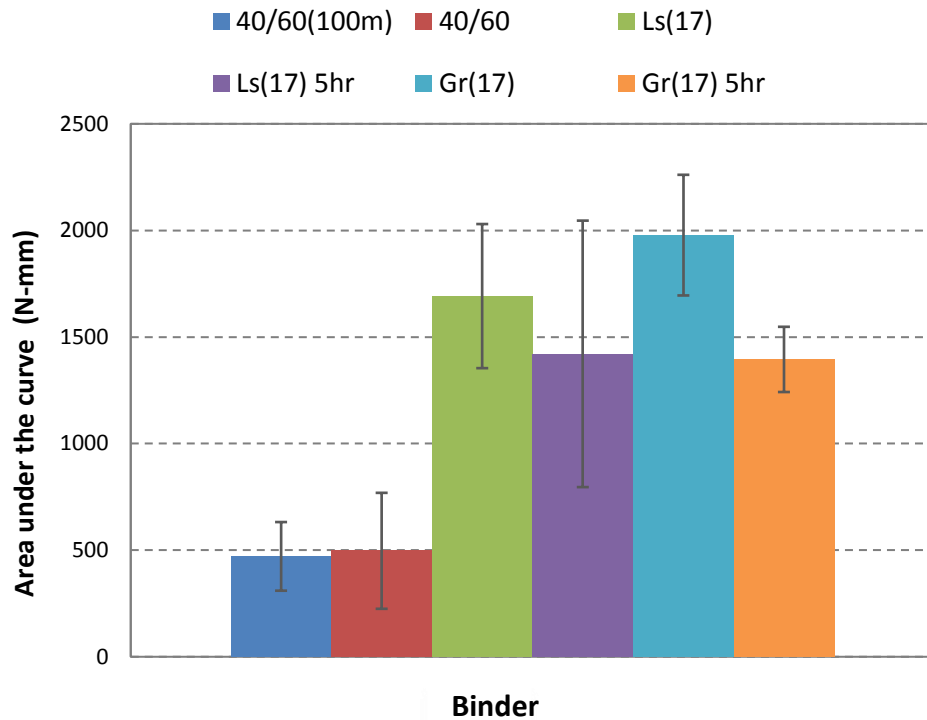


Figure 6.8: Area under the curve before failure (17% mastic)

6.3.4 Issues with Method 2

The curve behaviour and the area under the curve did not give much useful information in this test method. This method did improve the results as compared to the Method 1 in terms of pull off strength. However, a detailed analysis of the curve shows that there is not much information in terms of fibrillar structure on the curve. The curve based on this method does show ductile behaviour but does not show particular features of that occur during the formation of the fibrillar structure. According to Poulikakos and Partl (2011) the fibrillar structure has four stages: necking, voiding, filamentation and separation. The current curves do not provide much information about it.

The variability in the area under the curve and somewhat irregular behaviour of the curve from the typical (as discussed in chapter 7) show that there is further need to do some testing. A third round of testing was carried out in which major all these problems of Method 1 and Method 2 were solved.

6.4 SUMMARY

The research on pull off bond strength till now have used two methods. The first method gave quite variable results. The issues with this method are discussed. If the material handling problems of method one are solve and if tested on bit higher resolution machine, then it may produce repeatable results. It is further commented upon that this method is more useful for identifying the adhesive to mix type of failure. In order to work on cohesive strength this method might not work as good as method 2. In addition to this research could not capture any good curve behaviours.

The Method 2 solved most of the problems with the Method 2. This method showed good repeatability in terms of pull off strength and showed promising potential to evaluate bond strength of bitumen and mastics. The few advantages of the method were ease of operation, less handling of material, no requirement of trimming or any special consideration during specimen preparation. In the end few issues with Method 2 are mentioned and need for further testing has been outlined.

CHAPTER 7 : COMPRESSION PULL OFF TEST

ASSEMBLY & COHESIVE BOND STRENGTH

7.1 INTRODUCTION

In continuation of the research on pull off bond strength or simply Pull Off Strength (POS), this chapter aims to evaluate this strength and develop a better testing mechanism. This chapter further adds to the story on pull off strength through development of a new robust pull off test technique labelled as 'Compression Pull Off Test Assembly (CPOTA)'.

The prime importance of good adhesive bond between binder and aggregate has been recognised for more than a century. The story starts with the chew test in which the builders try to assess not only the consistency but also the stickiness of bitumen. It also has to be mentioned that to date, there is no standard test which can accurately determine the fundamental mechanical bond strength (Wang et al., 2014). This is because the research done to study tensile properties of thin films of bitumen has been relatively little compared to other means of evaluating its properties (Chang, 1994).

It is to be recalled that cohesion is the resultant force of the attractions between similar particles as shown by black particles in Figure 7.1, reproduced from (adhesive.org, 2010). Adhesion on the other hand refers to the resultant of the attraction between dissimilar particles. The pull off strength normally refers to both cohesive and adhesive strength. In the context of this research pull off strength has often been used for cohesive strength especially when the type of

failure was not fully known. Another term integrity also refers to cohesive strength of the binder (Bahia et al., 2012).

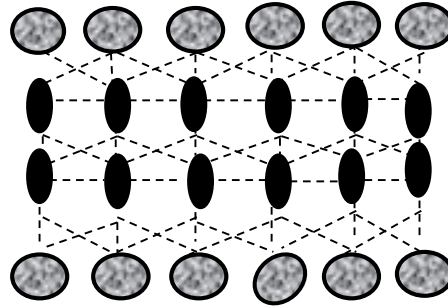


Figure 7.1: Cohesive and adhesive forces

It is important to mention here that this phase of research has been kept totally separate due to the intensity of work involved. The research methodology chapter is mainly reserved for chapter 4, 5 and 6. However several overlapping concepts and procedures are ignored here in order to avoid duplication in the thesis and references have been made to previous chapters.

7.1 THE GAP ASSEMBLY

The first step in development of a pull off testing mechanism involved manufacture of a gap assembly. This was meant to be a separate device to establish film thickness of a stand-alone binder-substrate system to be used in pull off testing. The gap assembly designed for this purpose was radically changed from previous designs. The design gave a more precise gap. The salient feature of this assembly was that the compression was applied through a separate compression mechanism and the gap was measured through a deflection gauge. This arrangement provided a statistically consistent film thickness. The gap assembly is shown in Figure 7.2 and the detailed design of the assembly (excluding deflection gauge) is presented in Figure 7.3.

The deflection gauge to measure film thickness had a sensitive of 0.05 mm and a range of 0-20mm. This was a replacement for the micrometer screw gauge. In the previous design the screw gauge was serving two purposes namely; applying compression and measuring film thickness. The data analysis showed that the new assembly gave a consistent bitumen film thickness, when installed properly. In order to minimise errors, the boundary of the whole assembly was marked. In addition to this the position of micrometer needle on the top plate was also marked. This was to ensure that each time specimens were located at the same place and pressed from the same spot. It was further ensured that the needle of the deflection gauge was perfectly vertical.

In this assembly uniform axial load is applied through a screw using hand pressure. One complete rotation of the screw produced a linear vertical distance of 1.82mm. The large handle provided the assembly with the capability to compress the bitumen layer to 50.56 micron with a 10° rotation. This calculation shows that large handle on the assembly has an advantage over the smaller head micrometer compression mechanism. In the micrometer compression assembly a 50.56-micron linear displacement can only be produced with a fine tuning of the screw. In addition to this, the new compression device applies a strong pressure to uniformly compress even a cold penetration grade bitumen 40/60 to relatively thin layer. A second difference was that the lateral movement of plates was stopped by a groove in the upper and bottom plates. In the previous design it was controlled using four guiding plates.



Figure 7.2: New compression gap assembly

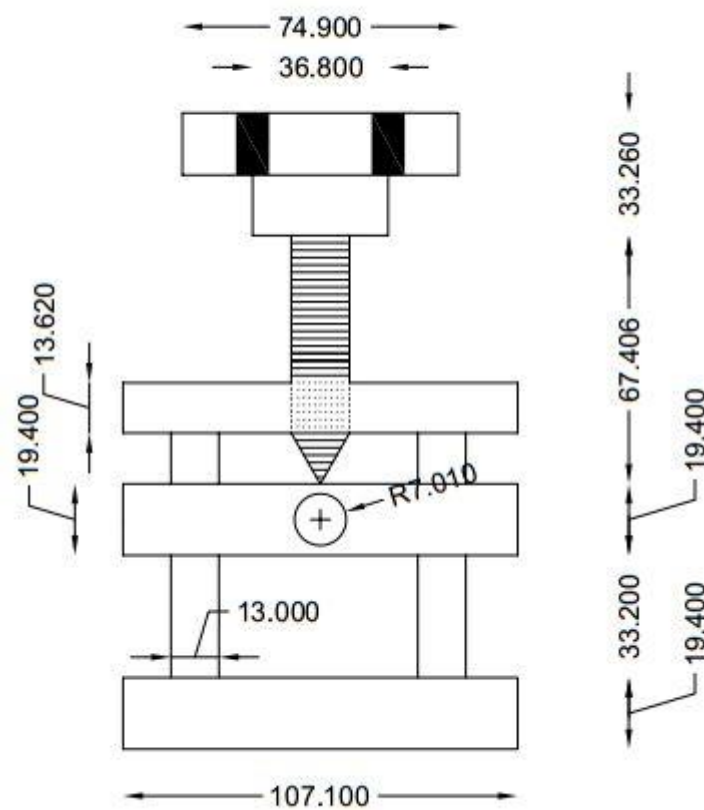


Figure 7.3: Design of the gap assembly

7.2 GAP ASSEMBLY AND OPERATOR VARIABILITY

The accuracy to achieve the film thickness of this gap assembly was checked with Vernier Calliper. The plates were assembled and a Vernier Calliper measurement was carried out before pouring. In the next step the bitumen was poured onto the plates and a film thickness of 0.5mm was achieved with the gap assembly. After curing a Vernier Calliper reading was again taken. The difference of the initial and final values gave the actual film thickness as shown in Figure 7.4. This was done on 40 specimens, four out of which were discarded.



Figure 7.4: Vernier reading before pouring

In this phase, first 10 samples were made by pouring the hot bitumen and onto a plate and then after making the butt join, the bitumen-substrate system was slightly heated and the desired thickness was achieved. This was termed 'method 1'. In the second group 10 specimen were poured with exactly the same procedure of as in method 1 except for the hot aluminium plate. In method 1 bitumen was poured onto cold plate while in method 2 bitumen was poured onto an already heated plate.

The second comparison was done between two different operators. This operator change was only in the sample preparation while the testing was performed by operator 2 in each case. The Operator 1 was more experienced and was involved in the development of the assembly. Operator 2 was less experienced and knowledgeable about best laboratory practices. In short Operator 1 had more psychomotor skills than Operator 2. Method 2 was adopted for sample preparation. The statistical comparison is shown in Table 7.1 and detailed results are presented in Appendix D. There are several conclusions that can be drawn from this study of film thickness.

- The bitumen should always be poured onto a hot substrate surface to achieve good adhesion and consistent film thickness. This is also expected to increase repeatability of the overall test method for pull off strength. Any further testing protocol should include this.
- The use of correct procedure can still lead to variability depending upon the level of experience of the operator. It is recommended that this should be reported along with the results. In the view of the author, if the proper sample preparation guidelines are prepared then these variations can be minimised to a great extent. This is evident from the fact that both operators had same experience of sample preparing on this assembly. The only difference between them was their different levels of psychomotor skills.
- This gap assembly gives quite consistent values especially when the general variability of pull off tests are considered. This shows that this assembly can reasonably be used for further pull off testing.

Table 7.1: Comparison for repeatability and operator variability

Operator	Method	Max (MPa)	Mean (MPa)	Range (MPa)	SD	COV (%)	Mean +2 SD	Mean -2 SD	Replicates
Operator 1	Method 2	0.74	0.55	0.44	0.13	23.90	0.29	0.81	10
	Method 1	0.63	0.50	0.21	0.06	12.09	0.38	0.63	10
Operator 2	Method 2	0.58	0.45	0.33	0.10	21.92	0.25	0.65	16

Table 7.2 shows results on one of the binders. This binder was tested under certain conditions; the properties of binder were defined in the material section. The variable conditions are listed in the table and the constants were; 10mm/min rate of loading or cross head speed, 0.5mm film thickness, 31.5mm diameter substrate, untrimmed specimen tested using direct method of pouring.

Table 7.2: Testing for repeatability of film thickness

Binder	POS	COV	Test condition	Replicates
Short term aged binder	1.17	13.54	Cold, dry 15 hrs, operator 1	9
Short term aged binder	1.25	8.40	Hot, wet 15 hrs, operator 1	9
Short term aged binder	1.53	14.80	Hot, dry 15 hrs, operator 2	10

The results show that operator 1 has less variability in pull off strength even in cold plate conditions and strengths are similar. The difference of values is attributed only to cold and hot pouring as the cold plate is expected to yield lower values and more variability. This was again confirmed by repeating the test. Operator 2 achieved higher pull off strength with more variability. The difference is due to the lower film thickness achieved by operator 2. A difference of 50 microns has resulted in a 22.4% increase in value of pull off strength. The only matter of advice is that an exact detailed step by step procedure should be established and that it should include all test precautions.

The above discussion leads to the conclusion that the new gap assembly is very useful in achieving uniform film thickness. This can be seen from the mean results of operator 1 (experienced) using a proper method. The operator has achieved the exact 0.50mm film thickness on average over the 10 specimens poured. The variability of pull off strength is 8.4%. This was further confirmed from the quality of the load-elongation curve comparing to the typical curve explained in section 7.9. The only matter of advice that an exact detailed step by step procedure should be established as part of the protocol for any adhesion test. This also explains why results of this research were of good quality when compared to the one achieved through method of Jakarni (2012). This is in addition to the discussion in chapter 6 about variability in results of method 1.

7.3 TEST MATERIALS

It is necessary to define test materials before discussing any test method or its design. The materials used in this phase of testing are kept separate from the research methodology chapter.

7.3.1 Bitumen

Two different sources of bitumen in Pakistan were identified and tested. These sources were from NRL Karachi and Attock Refinery. In order to avoid commercial issues these sources are concealed as 'Source 1' and 'Source 2'. The properties of these bitumen are listed in Table 7.3. This means that Source 1 may or may not correspond to the bitumen of NRL Karachi.

Table 7.3: Bulk mass properties of bitumen

Bitumen	Source 1 Pen 60/70	Source 2 Pen 40/50	Source 2 Pen 60/70
Penetration Grade (dm)	64	47	69
Specific Gravity/Density	1.04	1	1.02
Softening Point (°C)	51	56	49.5

7.3.2 Substrate

Two types of substrates were used in this phase; aluminium and limestone. The main testing regime was done on aluminium (control) because of the need for uniform film thickness for establishing fundamental parameters. Examples of variable parameters are; film thickness, test rate, operator variability etc. In addition to this, according to Marek and Herrin (1968), there was not expected to be much difference in pull off strength due to type of substrate in cohesion testing.

The use of aluminium gave advantage because of its high thermal conductivity, ease of manufacturing and malleable properties. The aggregate plates were needed for three purposes:

- In order to evaluate effect of moisture on the cohesive bond strength. Aggregate plates were selected because of their high porosity to allow better access of water to the bitumen-substrate interface or within the binder itself.
- To see difference between re-used and unused aggregate plates. This was to check if the aggregate plates can be re-used for testing. The main

reason was that aggregate plates were expensive and difficult to manufacture. A tremendous effort was put into getting them manufactured, yet the level of precision was lower than the expected.

- The third use was check see any effect of aggregate type on bond strength. The different bond strength was expected to occur due to different mechanical interlocking, surface free energies and mineral composition etc.

7.3.3 Filler

There were two options to acquire limestone and granite fillers. First option was sieving of limestone and granite dust (construction grade). The second was to acquire marble and granite dust from marble factories producing limestone and granite slabs for decorative purposes. The second option was expected to provide better quality filler free from mic content. Mica is known to adversely affect the properties of binder.

The sources of limestone and granite were Mardan and Kala Dhaka (Pakistan) respectively. The dust was collected from the marble factory near the cutter. The main use of this dust in Pakistan is for landfill. Care was taken that granite and marble dust was collected from their separate specialised factories. This was to avoid intermixing of limestone and granite particles. In this phase of testing the amount of filler was added as a percent of the mass of bitumen. The only rationale behind 'by mass' was ease of operation and simulation of field practice.

7.4 DIRECT PULL OFF TEST ASSEMBLY

In the first stage a direct tension assembly was locally manufactured. This assembly had two modifications in total. The first modification was made on the basis of joining it to the loading shaft and the base plate of a 25 kN Servo hydraulic UTM. The testing couldn't be performed on this machine due to some persistent issue. In order to avoid unnecessary details this modification has been omitted here. The second modification was made to fit into another UTM by TIRA with load carrying capacity of 10 kN. The gripping mechanism for this assembly was already manufactured for testing on polymeric materials by the respective academic department. The final test assembly (excluding clamping jaws) is shown in Figure 7.5 along with some of the resources used in this research. A few trial tests were run on the assembly. After each trial test it was ensured that the top and bottom rod of the assembly was not damaged by the holding saw tooth rig or damage it.

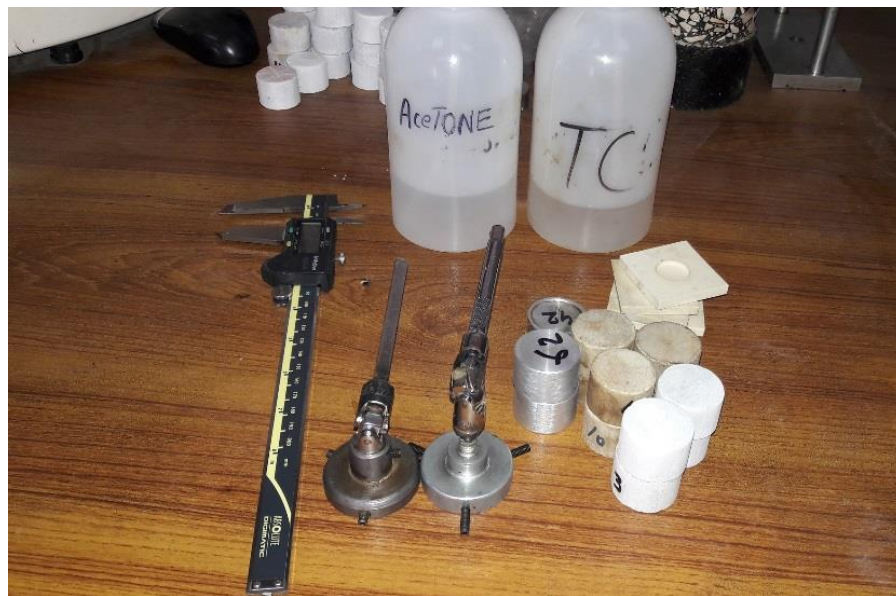


Figure 7.5: Direct pull off testing assembly

7.4.1 Sample preparation

The sample preparation was similar to the one in section 3.9.6. In order to avoid repetition of sample preparation only the differences relative to the previous method are highlighted.

- In the majority of cases bitumen was directly poured onto aluminium plates and in some cases it was poured into a silicon mould and then a disk of binder was placed onto the aluminium plates.
- In standard practice plates were preheated in an oven; however, in some cases bitumen was poured onto cold aluminium plates.
- The compression was applied with the handle bar while the thickness was read from a deflection gauge instead of a micrometer
- The boundary of the whole compression assembly was marked with a permanent marker on the table.

7.4.2 Test Procedure

The test procedure is quite similar to Method 2 of Chapter 6. For this reason, most of the details related to the direct pull off test are omitted here. The detailed procedure of method 2 is already discussed in the chapter 3 analysis.

In this method, a film thickness of 0.5mm was achieved through the gap assembly according to the procedure described in section 7.1. The sandwiched aluminium plates were gripped in the assembly with a three under-head screw mechanism. This three head mechanism was tightened with the help of an Allen

Key. The bottom and top rods of the upper plates were fixed in the saw tooth grip mechanism as shown in Figure 7.6 (left). A visual alignment of the specimen was made with marked points on each side of the plate and rod. The test parameters were adjusted in the software and the test was run. Figure 7.6 (right) shows a completed test.



Figure 7.6: Direct pull off testing assembly during and after test

7.4.3 Comment on test results

The results related to direct pull off testing are discussed in Table 7.4. The table shows pull off strengths of Pen 40/60 bitumen and an aged mastic of this bitumen. The test conditions are already described in section 7.2. The only exception is of one parameter for granite mastic that is poured onto a cold plate.

The test performed with best practices of the sample preparation indicates a variability of 16.8%. Additionally, the test performed with only one non-standard

practice yielded a variability of 33.9%. A further discussion on the results in comparison with another method is made in section 7.23. The current discussion indicates there are issues related to this which need attention.

Table 7.4: Summary of test results using direct pull off testing

Material	Pull Off Strength (MPa)	COV (%)	Plate Condition	Replicates
Source 2 Pen 60/70	0.71	16.78	Hot	6
Gr (40%) in Source 1 Pen 40/60	1.01	33.86	Cold	6

7.5 WARRANT FOR A NEW TEST SET UP

In addition to the variability of the results of previous direct pull off test and its predecessor method 2 of chapter 6, there were also some operational problems which needed consideration.

- A proper guiding mechanism is required for proper alignment of the plates and their movement during the test.
- The three-point grip was deemed insufficient in the current direct pull off test. A thorough gripping mechanism was required.
- Aluminium plates were getting damaged due to two possible reasons; Incorrect alignment creating dragging on plates during adjustment, and slip due to insufficient grip by 3 under-heads as mentioned earlier.

- It was difficult to get true failure surfaces as specimens were getting damaged. It also made it difficult to observe cavitation during testing although it was being recorded in the test.
- In addition to the above technical and operational problems, there were also laboratory resource constraints which did not favour the testing using direct pull off type testing.
- Additionally, the previous experience with this kind of mechanism and also rigorous efforts required to get repeatable results called for the need to look for some alternative mechanism for pull off testing.

7.6 COMPRESSION TEST ASSEMBLY FOR PULL OFF TESTING

This section describes the development of a new test set up. In this regard, it has been seen that compression tests are generally simple in terms of control. Additionally, the technicians in laboratories of pavement engineering are much more familiar with compression type tests than tensile type tests. This observation was taken advantage of in development of a new test assembly. The concept is discussed in the next section. However, it was anticipated that this new method would remove a lot of design flaws of the direct tension test and its predecessors.

7.6.1 The Concept and Manufacturability

In order to achieve the previously stated objective a new testing assembly was conceptualised. The basic idea behind this assembly was that “the load applied in compression in the UTM should generate a pull off load on the specimen”. In

order to translate this idea into reality a conceptual diagram was prepared as shown in Figure 7.7. The idea was found to be quite feasible in terms of manufacturability.

In order to achieve the aim, next step involved preparation of drawings. After this the assembly was manufactured locally. The 'lean manufacturing or production' method was adopted for design of the assembly. The philosophy called for developing the product to a minimum functional level then perfecting the design as per need.

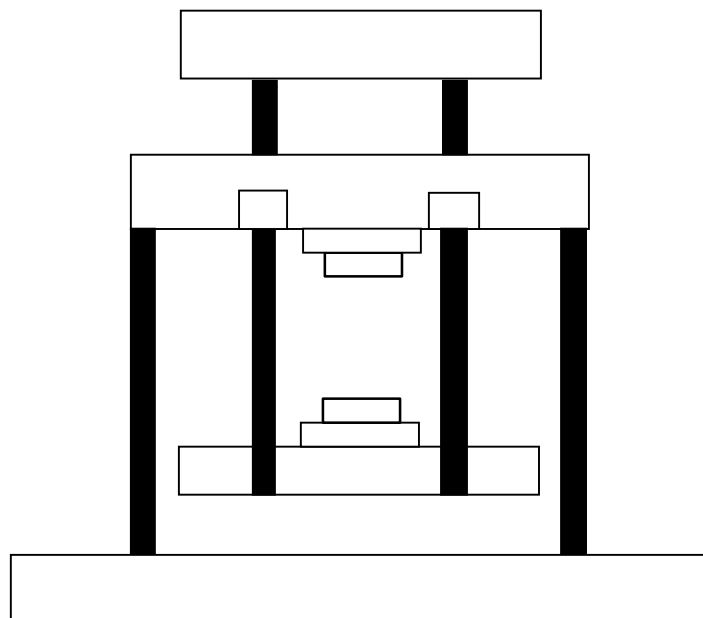


Figure 7.7: Conceptual diagram of compression device for pull off testing

The Figure 7.8 (left) shows the first complete operational assembly. In this picture two aggregate substrate are fixed by means of two sliding plates. These plates move and squeeze the substrate plates, when tightened with screws. It was noted through trial testing that this set up was very effective in giving a strong grip. The gripping involved tightening of screws with hand pressure and then applying further pressure with a small wrench. These screws were a replacement for the under-heads of previous methods. This also added a simplicity to design and ease of operation.

Figure 7.8 (right), shows the three further design improvements which were added step by step. The first modification is addition of two springs below the upper yellow arm. During trial testing the upper moving part was striking the bottom plate. It was seen that this striking was detrimental to the durability of the assembly. This needed further care as the whole assembly was made of aluminium. This lead to the addition of two springs around the bars. The testing revealed it to be a very effective design modification.

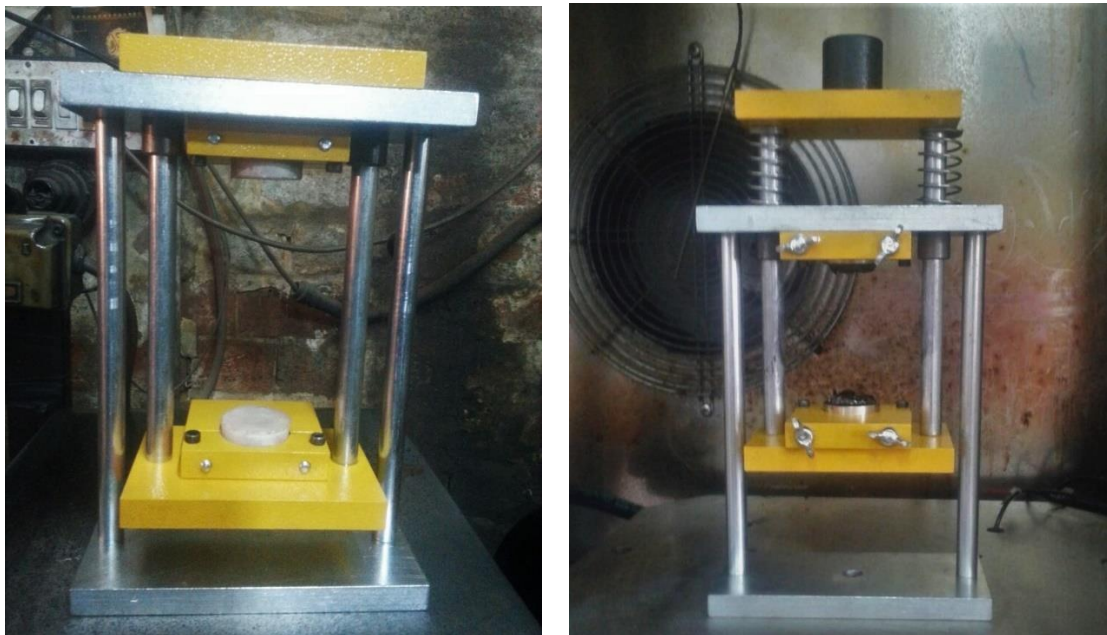


Figure 7.8: First and final design of compression pull off test assembly

The second design modification was introduction of a shaft that helped to properly centre the upper moving arm of the Universal Testing Machine. A few further trial tests were performed, and it was observed that the upper arm of UTM and shaft were not making proper contact (Figure 7.9). The solution was taken from the indirect tensile stiffness modulus assembly design. In ITSM mould a semi-circular metal piece is used for the seating adjustment which helps to introduce a true axial load. The detailed seating mechanism of this testing is presented in

Appendix E. The third modification was introduction of a hole in the bottom plate for alignment purposes. After the third modification no further enhancement was needed.

This assembly was named with the seemingly paradoxical term 'compression pull off test assembly'. However, here this term means a test assembly that takes compression load from an external source and translates it to a uniform axial pull off load on a binder-substrate system. Throughout this chapter it is termed as 'compression pull off test assembly'. The diagrammatic description of this assembly is presented in Figure 7.10.

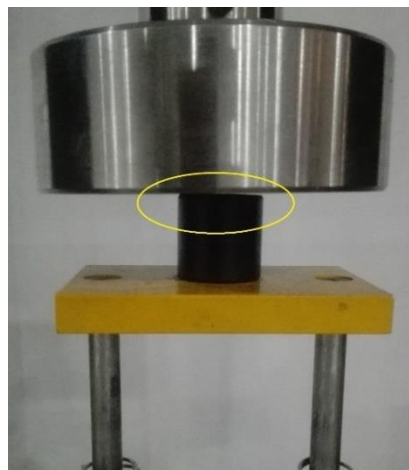


Figure 7.9: Modification needed for seating adjustment

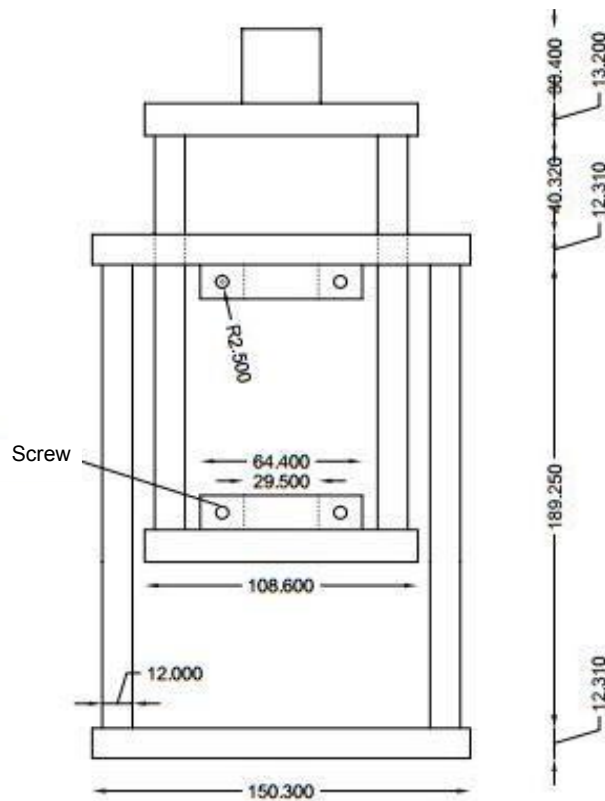


Figure 7.10: Compression pull off test assembly design

7.6.2 Test Procedure

The testing with the compression pull off test assembly is quite simple, most of the steps have already been covered previously while testing with earlier methods. However, the procedure includes the following steps:

- The first step involves installing the butt-jointed specimen with the upper plate. The substrate plate is slide into the assembly lower plate so that the butt-joint fits into the groove.
- In the second step, plates are not fastened with a screw but just held with support of hand. This is done to make sure both substrate plates are

thoroughly inserted into the plates. After this all four screws are tightened until the plates are thoroughly gripped.

- Lastly, in order to ensure firm gripping, a small pressure i.e. one step more than hand pressure is applied with a small wrench. It is important to note; no specimen was broken due handling during sample preparation or testing. This was found to be true throughout testing. It is to be explicitly state here that, the breakage of samples due to handling was a big issue with the previous methods.
- Now the specimen is ready to be placed under the loading arm. The butt-jointed specimen in the assembly is shown in Figure 7.11. This figure however is of a slightly misaligned specimen. It is worth mentioning here that slight misalignment of a specimen does not have major impact on the pull off strength. There was no cleavage type failure in this test method if non-uniform film thickness is achieved (Ebnesajjad, 2008).
- Before testing, basic testing information is entered into the software and testing parameters are adjusted. This includes defining the loading direction (compression or tension) and setting load and elongation limits for safety purpose. The cross head speed is specified and specimen dimensions are entered.
- In the next step, the contact is made by slowly lowering the upper arm until it is in soft yet full contact with the semi-circular disk (as shown in Appendix E). It is to be noted that during this process the seating load should not exceed more than few Newtons (say 10 N). However, during testing some cases included accidental application of a 100-250 N load. This was due to negligence of the operator and so they were discarded.



Figure 7.11: misaligned plates

7.7 OBJECTIVES FOR TESTING WITH COMPRESSION PULL

OFF TEST ASSEMBLY

Before the start of the testing few stepwise objectives were defined. Each objective is dependent on the achievement of the previous objective. The objective of this testing are given below. It has to be kept in mind that that prime aim is to check the validity of the test over major conditions.

- To compare the effect of different variable and explanation of thier behaviours through literature.
- To describe the failure mode and failure behaviour in pull off load in general and cohesive failure in particular.
- To make an attempt to fill the gaps in the body of knowledge, if the effect of one parameter is not thoroughly or conclusively known or commented upon.

7.8 CONSTANT AND VARIABLE PARAMETERS

In order to start testing, it was necessary to establish a few constant and variable parameters in order to stay focused on the stated objectives. The important variables which need to be evaluated were grouped into three main classifications as A) Plate geometries related variables B) Testing mechanism variables C) Material variables. An uncategorised list is given as; 1) test geometry 2) film thickness 3) rate of loading 4) conditioning time 5) pouring method 6) source of bitumen 7) grade of bitumen 8) effect of filler 9) ageing 10) moisture damage.

In addition to this one parameter was universally kept constant because of limitation of resources. This parameter was test temperature. This meant that all the specimens were tested at room temperature (20 °C). The effect of long term ageing was also not considered for the same reason.

It is important to comment of the effect of the constant parameters of this testing phase. Tensile strength decreases with increase in test temperature as per Marek and Herrin (1968) and Herrington et al. (1994). Secondly long term ageing increases the pull off bond strength and makes the material brittle more prone to cracking.

7.9 TYPICAL COHESIVE FAILURE CURVE

In the pull off testing in the compression pull off test assembly, it was identified that the binder failure followed a certain pattern which can be seen in Figure 7.12. This was typical for all the properly prepared mastics. It is to be noted that in the case of the compression pull off test assembly, a deviation from this trend was attributed to an anomaly of some sort. This could be due to problems

in specimen preparation, improper curing/conditioning, non-uniform film thickness, non-homogenous mixing of filler particles (in case of mastics) and slipping of the plate during or after the test etc. The discussion about deviation from typical behaviour has been of importance throughout this chapter.

The Figure 7.13 shows the curve during a direct pull off test load. The behaviour of this curve before peak load seems different due to different mechanisms happening during initial build-up of loading. The behaviour for both curves after failure is the same. The difference in the second curve is due to seating adjustment. In case of CPOTA, the major seating adjustment has already been taken care off with mechanism the shown in Appendix E for seating. The difference in both curves is present due to alignment of the specimen.

The analysis suggests that in order to properly analyse the failure behaviour, the curve in the second case must be normalised. This is not however the case with the pull off test in the compression device. The curve of this research can directly be analysed. Currently literature seems to be void of this discussion about curve behaviours of different methods related to tensile type testing on binder. This is due to the tendency to stick to the conventional direct tensile type testing methods.

In both cases the failure mode is ductile. This mode is identified from the ability of the material to take load after failure. Due to this reason a slow drop is observed. The next important stage in the curve is where the curve tends to straighten out but then there happens to be kink. This straightening and then sharp drop is linked with the phenomenon of cavitation discussed in the next section.

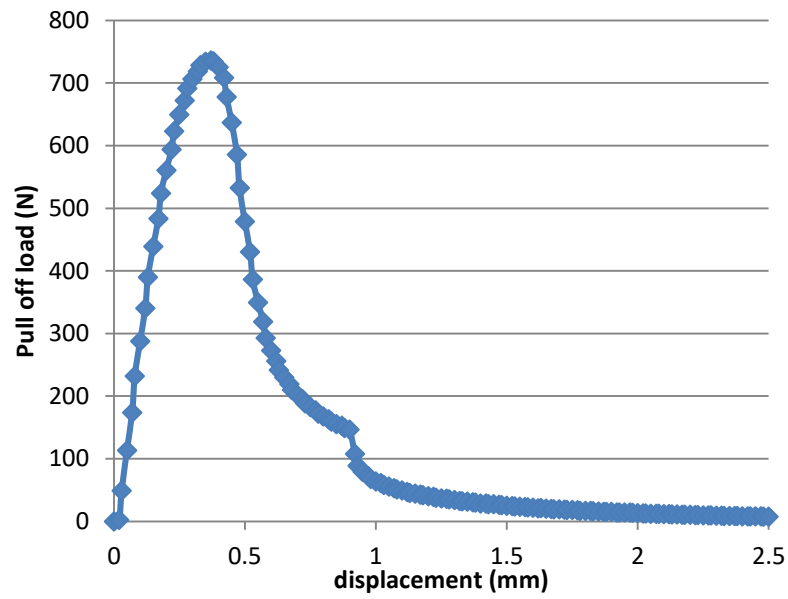


Figure 7.12: Typical ductile failure with Compression Pull Off Test Assembly

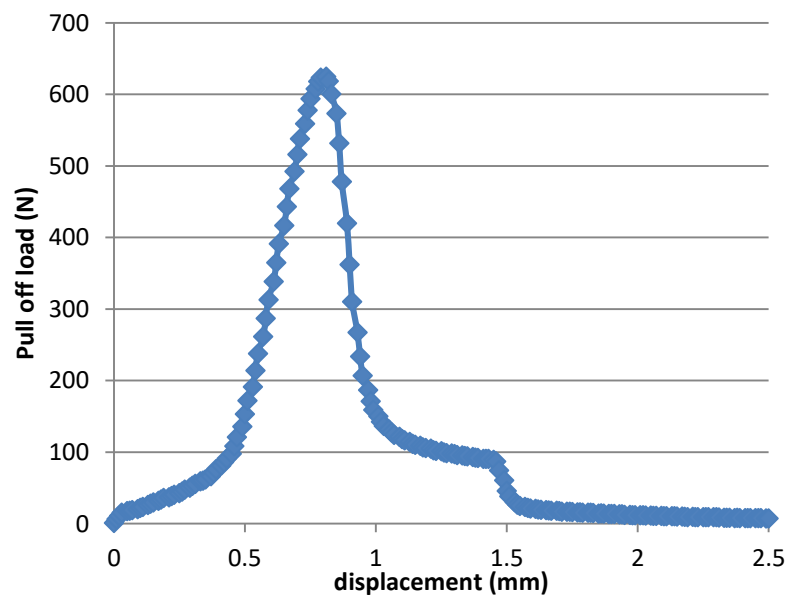


Figure 7.13: Typical ductile failure with direct pull off testing

Further discussion of the curve identifies a few important curve shapes. These frequently occurring curves can help to identify any problem in testing and

sample preparation. This discussion will be a valuable addition to studies of pull off strength of bitumen.

In this regard, both curves shown in Figure 7.14 reveal that plate slipping has occurred. It is irrespective of whether bottom plate has slipped or the top plate has slipped. As the loading started a drag force initiated on the outer side of the substrate making contact with the test assembly. Once all the gripping/frictional forces are overcome and the specimen start moving and there is reduction in the load carrying capacity. It gradually decreases as the plates are slipping. Curve two has some similarity with result of a Peel Test. Here the aspect ratio is very large so practically no peeling can be expected. Thus the only possible explanation is slipping of the plate. This was also verified with visual inspection during the test.

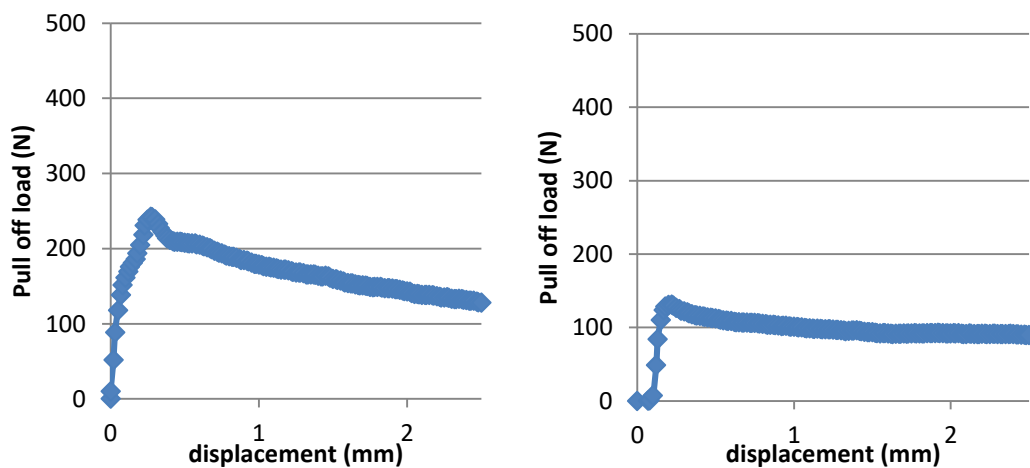


Figure 7.14: Curves associated with slipping

This slip phenomenon was further thoroughly investigated. In total 40 specimens were prepared using four different criteria. The set of 10 plates were prepared by pouring bitumen onto cold a plate and then conditioning in a dry state. The next

10 involved dry conditioned bitumen poured onto hot plates. The third set was bitumen poured onto hot plates and water conditioned. The final set was tested in a dry state under standard conditions.

It was observed that 17 out of 20 dry conditioned bitumens gave the typical ductile failure curve. In particular, all specimens in the second decade of specimens from 11 to 20 gave a very good failure curve quality. However, 10 out of 10 wet conditioned bitumens gave the curve behaviour shown in Figure 7.15. This was an indication that there was some phenomenon going on which needed further explanation. Here, it is important to note that these were aluminium plates. It was hypothesised that this trend was due to slip. It is further added that this slip only occurred in wet conditioned specimens. This means somehow that water was present on the side of the plates. Alternatively, it was trapped somewhere near the bitumen film somehow. The aluminium plates were dried before testing. This point further confirms that water was present near the film layer. Either water had diffused into the layer to some degree or it remained present somewhere near the film layer.

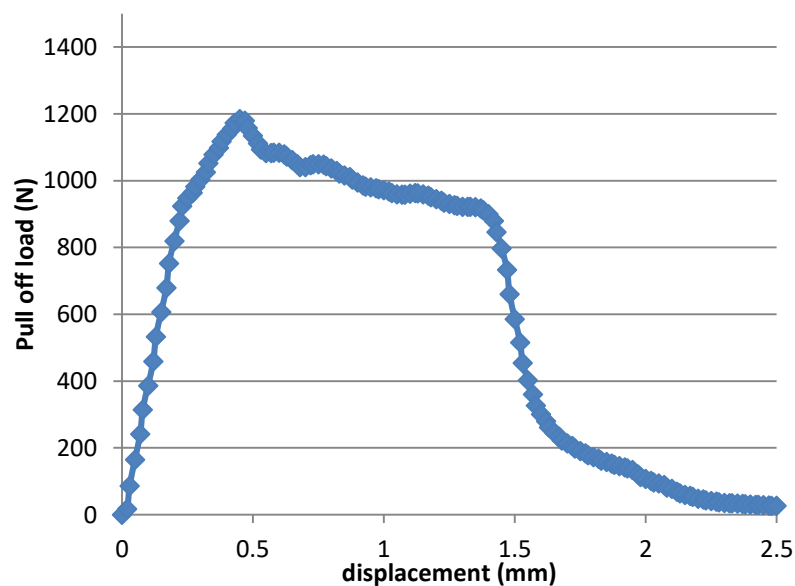


Figure 7.15: Slipping behaviour in wet conditioned specimens

Now based on the above explanation, the curve behaviour again needs to be discussed. It can be said that as the load started elongation also started to happen. As the specimen was elongated it allowed the water content to escape the bitumen layer and somehow reach the aluminium surface. This water acted as lubrication and now the plate also started to slip. This means that now the specimen was carrying the load and also that part of this force was acting as a drag force. Hence, ultimately a point came when load on the specimen was utilised to cause slip.

This is merely an explanation of the phenomenon; it needs further explanation. Currently time limitation does not permit further work on this phenomenon. Nevertheless, this discussion will provide the foundational work for any further work to find the micro-level explanation of this phenomenon

7.10 DUCTILE VS BRITTLE FAILURE

The discussion about curve type logically demands a detailed discussion to be made on the failure type. In the previous section, ductile failure mainly has been discussed. This ductile failure has consistently happened in almost all the sample due to large film thickness (0.5mm) corresponding to more likelihood of failure due to loss of cohesion. It is further stated, that observation related to film thickness has led to the conclusion that ductile failure is the predominant mechanism associated with cohesive strength. A similar observation was made by Woodhams (1998) during a study of steady cohesive peeling in dry condition.

According to Herrington et al. (1994) four types of failures mode are observed in pull off testing on butt joints/poker chips. The failure types were; brittle fracture, tenacious rupture, semiflow rupture and failure by flow. This identification was

made based on the curve behaviour and nature of surface of the fractured specimens. The current discussion is limited to ductile and brittle failure only. This is because in the current testing for cohesive strength the predominant failure has been ductile. The discussion on the intermediate stages will be of no use as the brittle failure mode is almost absent.

The results of this research show that during the dry and wet state the failure mode was ductile. This means the failure has occurred within the mass of bitumen/mastic rather than at the interface of binder and substrate. This meant a cohesive failure has happened in most of the cases. We know from the literature that water should have increased the embrittlement (Cui et al., 2014). However, the ductile behaviour of moisture damaged specimens in this research can be well explained. The film thickness used in testing was sufficiently large, so it resulted in ductile failure even after water damage. This does make sense if we recall that it takes a longer time for water to diffuse through bitumen than through aggregate. This explains that in the case of aluminium substrate water couldn't affect the bitumen-plate interface. It was also difficult for water to diffuse through bitumen in this short time. This explains the reason for ductile failure in the case of control testing.

The Figure 7.16 show a brittle and ductile behaviour of a same material. These are graphs of two specimens of the same material. One material has failed in ductile mode while the other material has failed in brittle mode. This plot shows perfect overlap of the load curve before maximum load. This surprising overlap of the curve shows a good credibility of the test method.

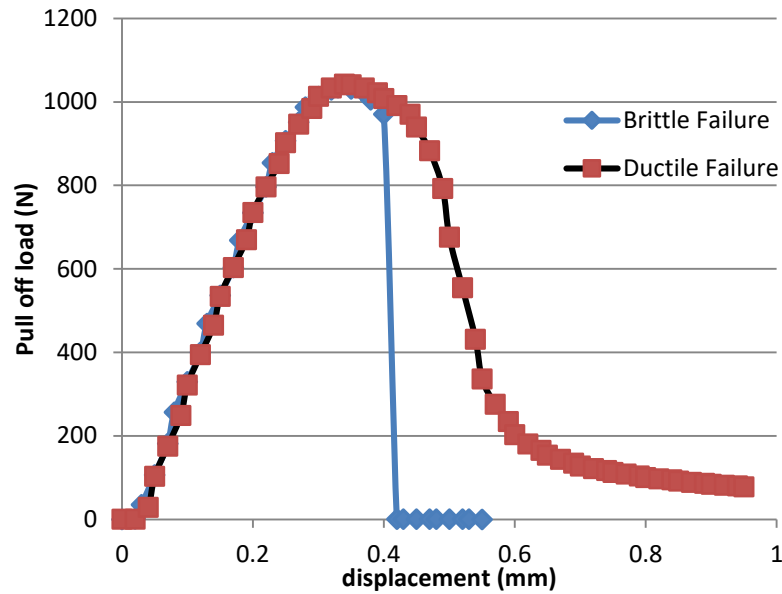


Figure 7.16: Comparison of brittle and ductile failure

7.11 CAVITATION

In order to carry further the discussion on failure mode, the next step requires explanation of the behaviour of the curve after failure. This becomes of great importance in the case of ductile failure. The brittle failure would give a sharp drop and there are not many interesting details after failure. In the case of ductile failure, the interesting phenomenon of cavitation happens which needs to be further studied. According to (Fond, 2001) cavitation “allows the genesis of multiple voids”.

It is well known from the field of polymer science that when soft adhesive joined between rigid surfaces fails, it normally nucleates. This nucleation takes the overall form of cavitation (Sultana, 2014; Gent and Lindley, 1959). One of the earliest observation of this phenomenon related to tensile type loading in bitumen was made by Budgett and later by Kumler (Chang, 1994). The possible reasons for the start of the cavitation in bitumen are micro-cavities present in the binder

due to mixing and pouring. The second reason in this regard can be breaking of the bond at the interface of bitumen and aggregate or a micro-crack.

The significance of cavitation is that it has a significant impact on the energy dissipation during crack growth. This cavitation in bitumen is advantageous in stability as compared to rubbers (Fond, 2001). In the case of bitumen viscous fingering happens and as a result of this a dendritic pattern occurs. This pattern gives the overall formation of the fibrillary structure for energy dissipation. This overall fibrillary structure is also referred as craze, which is also a sign of plastic deformation.

Figure 7.17 shows the typical curve behaviour when cavitation happens in a bitumen sample tested under tensile load. This curve behaviour will be related with the crack development, but before that it is necessary to describe few observations related to cavitation. The observations made in this research related to cavitation are further discussed with support from similar observations by other researchers. It was found that with increase of pull off strength the number of cavities increased, however the size of each cavity became smaller. In the literature a similar observation was made by Sultana (2014). This means that distribution of cavities was more associated with ductile and brittle nature of the material. As described earlier brittle material did not show any cavitation (Marek and Herrin, 1968).

Secondly the intensity of cavitation is more at the centre of the specimen as compared to the edges (Chang, 1994). It is also observed that ageing and addition of filler affects cavitation. The cavities become smaller although total number of cavity may increase as indicated by Harvey and Cebon (2003). Additionally the thin film thickness also affects cavitation through uniform stress

distribution (Chang, 1994). The result of this is less adhesive fracture energy (Blackman et al., 2013).

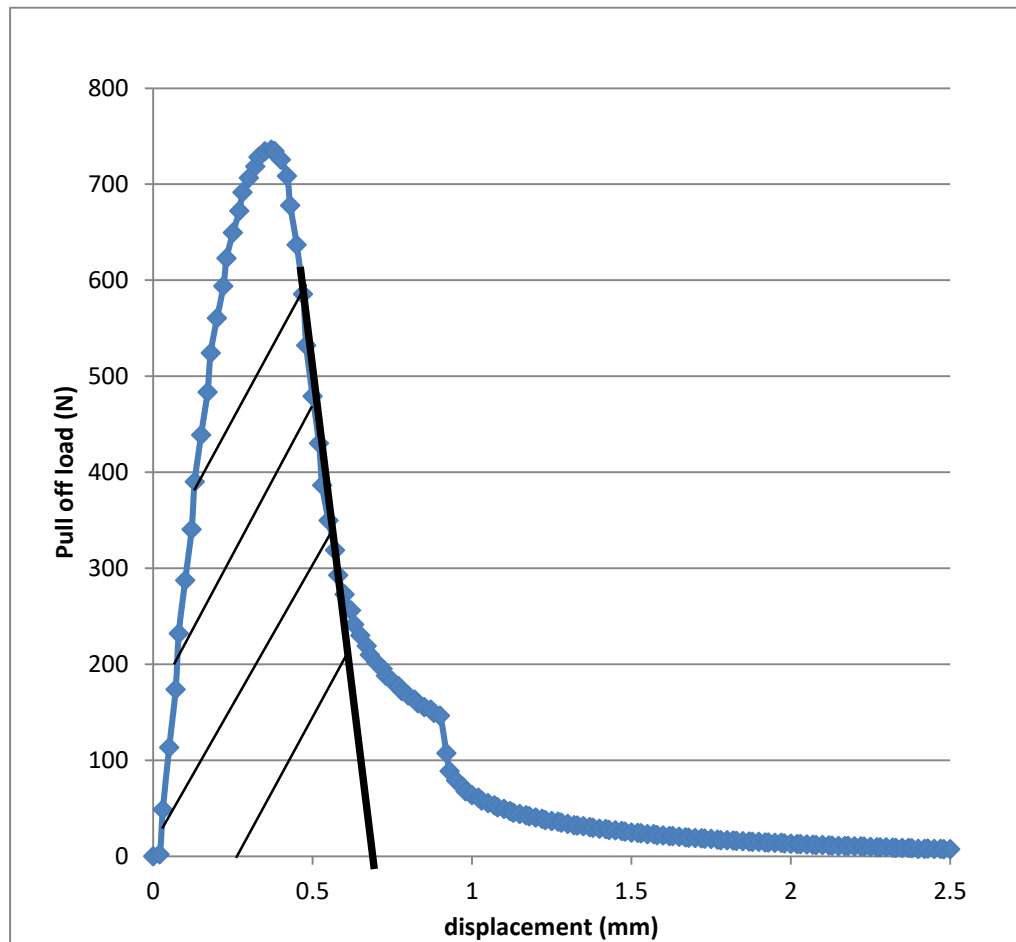


Figure 7.17: Typical curve involving cavitation

The curve indicates that voids started happening even before peak load. After peak load the development of craze did not allow the specimen to completely separate. It struggled to carry some load but because of occurrence of plastic deformation it could not resist the load. Then there was a final drop in the load (shown in the form of a step). This point shows the ultimate rupture of the binder. After this point the trend of the curve merely seems a matter of separation of the plates. There are two important points to discuss in relation to

the curve; first one is the point of void nucleation and the second is the point of final rupture. This seems to be consistent with the discussion made by Harvey and Cebon (2003) on ductile failure in butt joints specimens.

It has to be noted that in order to find the true or effective fracture energy, the area under the curve needs to be calculated before the intersection of the black line with abscissa as shown in Figure 7.17. However, the inherent variability of tensile type testing methods for a complex material such as bitumen, makes it difficult to give a uniform failure pattern after peak load. This reason has led to researchers working on the pull off testing to use peak load for quantitative analysis. In this research area under the curve before peak load (ultimate load) was taken for calculation of the fracture energy.

7.12 EFFECT OF TEST PARAMETERS

In the research maximum tensile load was used to compute pull off strength. In adhesive technology this notation has been used consistently. It is important to mention that in the testing phase several factors were being tested at once. Due this reason the results are broken down into micro tables to identify their effects on pull off bond strength.

7.13 REPEATABILITY OF TEST METHOD

Test conditions included: binder was poured onto aluminium plates to achieve 0.5mm film thickness using the silicon method of pouring on aluminium. The

specimens were trimmed, dry conditioned and tested under 10mm/min loading rate at room temperature.

The second set of test was performed with 0.5mm film thickness using the direct method of pouring on aluminium, the specimens were untrimmed and tested under 10mm/min loading rate at room temperature.

Table 7.5: Tests to check repeatability of the test method

Material	Pull Off Strength (MPa)	COV (%)	Replicates	Difference (MPa)
Source 2 Pen 60/70	0.70	9.67	5	0.03
	0.67	17.58	3	
3-hour oven aged Source 1 Pen 40/50	1.4	13.35	9	0.05
	1.45	11.04	8	

The test results reveal a very small difference between the two sets of tests on the same material. The results obtained for two different materials reveal good repeatability under intermediate precision conditions. This mean it It can be used throughout the testing regime should be evaluated using the same method in the same laboratory.

7.14 EFFECT OF PLATE GEOMETRY

The first thing in this testing phase was to evaluate the parameters related to the control substrate. The control in this testing was aluminium. The only variable related to plate geometry was the difference in diameter of a few plates because

they were manufactured at an early stage of testing.

The POS for plates having 31.5 mm diameter was 0.77MPa with COV as 6.82%, while for the plate 30.5 mm it was 0.70 with COV as 9.7%. These results of source A 60/70 Penetration grade bitumen are slightly different due to the inherent nature of the Pull Off Test.

Secondly results were evaluated in terms of aspect ratio. Aspect ratio (AR) is defined as the ratio of diameter of the film to its thickness (Harvey and Cebon, 2005). This definition is consistent throughout adhesive material research. The observation made in this research is that 0.5mm film thickness has almost half the variability of its thinner counterpart. It has been observed that higher aspect ratio resulted into less cavitation (Sultana, 2014). The aspect ratios used in both cases of this research were 63 and 61 which were quite similar and higher than the threshold of 40 as per (Sultana, 2014). In the light of her work it meant that tensile stresses and failure mode for thin films are similar as long as the corresponding aspect ratio limit is greater than 40. In this regard, Figure 7.18 from the test data shows specimens with different aspect ratio. The left specimen has lower aspect ratio than the one on the right. There seems to be not much difference in cavitation due to very small difference in aspect ratio.

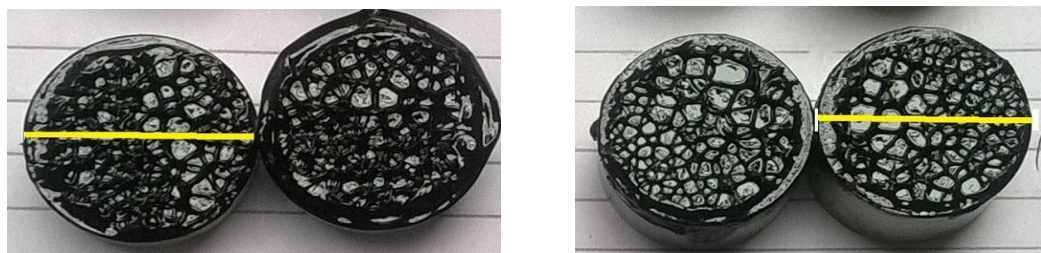


Figure 7.18: Different aspect ratio specimen

In the case of the lower aspect ratio, cavitation mainly occurred at the inner side of the specimen as shown in Figure 7.19. This central cavitation indicates less uniform distribution during application of the load. The size of cavities was reduced by increasing the aspect ratio (Harvey and Cebon, 2003). This observation shows that it makes excellent sense for cohesive failures to show more test variability than adhesive failures.



Figure 7.19: Central cavitation for lower aspect ratio

7.15 EFFECT OF SPECIMEN PREPARATION METHOD

The first parameters related to specimen preparation were direct pouring and the silicon (indirect) method of pouring. The direct method was pouring of fluid bitumen directly onto either a heated substrate or cold substrate. Then the second plate was placed over the bitumen and a butt joint was made by pressing

by hand. Later this was introduced into the gap assembly to achieve a given film thickness.

This heated or unheated substrate throughout is referred to as plate condition. Initially it was thought that the 'direct pouring' method might result in excessive heating of bitumen while pouring onto different plates. However, at a later stage this heating was minimised by pouring bitumen onto hot or cold plates simultaneously. After pouring bitumen on five or seven plates, a butt joint was made by placing and pressing aluminium plates over the poured bitumen. It was noted during the testing that for an achievement of a good bond pre-heating of the plate is necessary. This is because heating of the control plates helps to overcome hydrogen bond, π - π bonding and Van der Waals forces. These forces reduce the wetting of the substrate (Bagampadde et al., 2004).

In the second method, binder was poured into a 25mm silicon mould and was allowed to cool down to room temperature. The second step involved; placing of the binder chip onto the substrate plate, followed by joining of the second plate to form a butt-joint.

Table 7.6 shows the result for both methods of pouring. The constant variables were film thickness (0.5mm), rate of loading (10mm/min), cold plate, bond cured for 24 hours and use of aluminium as a substrate. The term 'untrimmed' has exactly the same meaning as that of the use of term in DSR testing. It refers to removing the bulged binder around the perimeter after it has been compressed to achieve required film thickness.

Table 7.6: Pull off strength to evaluate pouring related variables

Test	Material	Pull Off Strength (MPa)	COV (%)	Replicates	Variable Testing conditions
Round 1	Source 2 Pen 60/70	0.77	6.82	8	Direct pouring and un-trimmed
	Source 2 Pen 60/70	0.70	9.67	5	Silicon pouring and trimmed
Round 2	RTFO aged Source 1 Pen 60/70	1.00	11.63	7	Silicon pouring and trimmed
	RTFO aged Source 1 Pen 60/70	1.26	8.35	9	Direct pouring and trimmed

This parameter was evaluated in two rounds. In the first round penetration grade 60/70 bitumen from source 2 was tested with two variables. These variables were pouring method and trimming of the specimen (discussed in next section). Pull off strength decreased with silicon pouring and trimming. It is hard to separate two effects, as trimming is expected to affect the pull off strength too. It can be seen that direct pouring on an un-trimmed specimen yielded less variability among specimens.

In round two one variable was eliminated and the explicit effect of the method of pouring was seen. This testing was done on RTFO aged Pen 60/70 of Source 1. It can be seen from the results that silicon pouring is giving significantly lower pull off strength than the direct pour method. Silicon pouring also seems to have a higher co-efficient of variance. It can further be seen from Table 7.6 that in round 2 the strength has decreased to 20.6% just by changing method of pouring. On other hand round 1 shows only a decrease of 9.1%. This apparent difference can be attributed two factor namely ageing and trimming. The unaged bitumen seems to be less affected by trimming.

7.16 SELECTION OF CONDITIONING TIME

Firstly, the use of terms curing and conditioning fundamentally mean two different things. Curing was done to improve the bond strength in a more controlled environment. The term conditioning was reserved to study the effect of moisture damage and that of corresponding control. The curing time was selected as one hour after pouring and also one hour before testing of wet conditioned specimens.

The conversation here is divided into two sub section: conditioning time for dry pull off strength only and conditioning time for wet (and its corresponding dry specimen).

7.16.1 Dry conditioning time

In order to see the effect of dry conditioning few parameters were kept constants namely; film thickness (0.5mm), test rate (10 mm/min) on RTFO samples of Source 1 Pen 60/70. In relation to the results, Table 7.7 shows Pull Off Strength arranged according to its increasing curing time. This table also shows the test conditions in increasing order of their severity. Before this point is to be elaborated further, it should be noted that direct pouring, pouring on hot plate, un-trimmed specimen all are favourable conditions to achieve good bond. The unfavourable conditions to achieve good bond are Silicon method of pouring, pouring on cold plate, and trimming the specimen. The conditioning was done at room temperature as shown in Figure 7.20.



Figure 7.20: Curing of butt-jointed specimens

In the light of the above points, it can be seen in Table 7.7 that the reason for higher POS for Test A was that it was performed in under favourable condition. The next Test B was done with only one unfavourable condition i.e. pouring bitumen on cold plates. As indicated in the previous section this reduced POS. Test C was done with one additional unfavourable condition and that is trimming of the specimen after conditioning. Despite the presence of two unfavourable conditions Pull Off Strength has increased. The only inference that can be drawn here is that increase of curing from 15 to 24 hours has resulted in an increase of POS.

Test D was performed with three unfavourable conditions. There is not much change especially when 65 hours of conditioning is considered. The thing that can be speculated here is that changing the conditioning time from 24 hours to 65 hours did not change or slightly increased POS. However, POS has decreased here to due to the silicon method of pouring.

Table 7.7: Selection of dry conditioning time

Test	Curing Time	POS (MPa)	Replicates	Testing conditions	Number of unfavourable conditions
A	15 hours	1.25	5	Direct pouring on hot plate, un-trimmed,	0
B	15 hours	1.17	9	Direct pouring on cold plate, un-trimmed	1
C	24 hours	1.26	7	Direct pouring on cold plate, Trimmed	2
D	65 hours	1.19	6	Silicon pouring on cold plate, Trimmed condition.	3

The discussion can be summarised as increasing the conditioning time from 24 to 65 hours did not change the POS much. However, reducing the conditioning time by 9 hours had considerable effect because even with the presence of two unfavourable conditions its value is still slightly higher than with 15 hours curing. This further lead to the conclusion that 24 hours is sufficient curing time for a proper bond to develop. This conclusion is consistent with discussion made by Jakarni (2012) according to whom the effect of dry conditioning become constant after 24 hours. The same use of conditioning time has been reported in literature by various researchers (Marek and Herrin, 1968; Copeland, 2007; Apeagyei et al., 2014; Apeagyei et al., 2015; Zhang, 2015).

7.16.2 Wet Conditioning Time

It was also necessary to select an appropriate wet conditioning time before involving moisture damage into the equation. The conditioning time is important

because it can not only result in loss of pull off strength but it can also affect the failure mode (Moraes et al., 2011). The main objective here was to establish conditioning time which can give a hint about the capability of the test method to capture effect of water damage.

It is important to note that in this testing wet conditioning was done by immersing the specimen in a water bath at 25 °C for a designated period of time as shown in Figure 7.21. Distilled water was used for this purpose to avoid possible attack of salts.



Figure 7.21: Conditioning in water bath

First a few results from testing are reported here (Table 7.8); the next step will involve detailed discussion about them. These are results on short term aged bitumen and mastics. The first observation is that the variability has increased significantly after conditioning. This variability can be compromised because of the inherent nature of pull off tests and; complexity in material behaviour due to addition of filler, ageing and moisture damage.

The second observation can be divided into two further points. The first point is the short term water damage (15 hr) of aged bitumen has resulted in only 18% strength loss. The same specimen has resulted in 41% over the time of 65 hours.

The effect of dry strength is not of concern here. The difference between the two dry strengths is because of silicon pouring and use of cold plate as discussed in previous sections.

The next point is related to aged mastics. The water conditioning for 24 hours has resulted in 19% strength loss on aluminium plates (Test C) and 41.3% for aggregate plates (Test D). It is to be noted that the same materials tested on aluminium and aggregate yield different degrees of water damage. The difference is because of the high coefficient of diffusion of limestone ($3.96 \times 10^{-9} \text{ m}^2/\text{s}$ from Blackman et al. (2013) giving easier access of water to the binder.

Table 7.8: Selection of conditioning time for POS testing

Test ID	Material	Dry Condition		Wet condition		Time (hrs)	POS % decrease	Replicate	Plate Condition
		POS (MPa)	COV (%)	POS (MPa)	COV (%)				
A	RTFO aged Source 1 Pen 60/70	1.25	8.4	1.53	14.8	15	18.3	4	Aluminum substrate with silicon pouring in cold state
B	RTFOT Source 1 Pen 60/70	1.19	12.2	0.7	27.3	65	41.2	4	Aluminum substrate
C	RTFO aged Ls (40%) in Source 1 Pen 40/50	1.86	10.7	1.51	11.6	24	18.8	8	Aluminum substrate
D	RTFO aged Ls (40%) in Source 1 Pen 40/50	1.38	11.5	0.81	16.1	24	41.3	6	Aggregate substrate

The previous discussion demands a logical explanation from literature too. The selection of conditioning time has been argued against by Woodhams (1998). The present research confirms his argument that 24 hours is not a very effective time to study the full potential of water damage. However, in another study by Bahia et al. (2012) it was observed that a small conditioning time of 6 hours changed the failure mode from adhesive to cohesive failure. Their argument also make sense in the light of the present study where 15 hours water conditioning showed sufficient water damage to change failure mode. Blackman et al. (2013) have argued that water diffusion coefficient for limestone aggregate is $3.96 \times 10^{-9} \text{ m}^2/\text{s}$ while for bitumen it is $1.96 \times 10^{-13} \text{ m}^2/\text{s}$. This, according to him, meant limestone will take 10 hours for water absorption; however, bitumen does not take moisture in high concentrations even during 10 days of immersion (Blackman et al., 2013). This time was in accordance with the work of Jakarni (2012) and Copeland (2007). A total conditioning time more than 24 hours was considered to be too severe as per Copeland (2007).

The above discussion can be summarised as:

- Binder joined by aluminium substrate does show some degree water damage. This means use of control (aluminium) can be made to study the potential of water damage, even if it cannot yield detailed quantitative evaluations.
- The above point leads to further conclusion that proper quantification of water damage should be done with aggregate plates only.
- Water conditioning time can give an idea about water damage potential. However, conditioning should be done over an extended period of time in a controlled environment to study quantification of water damage

- A uniform and well explained specimen preparation technique must be adopted and developed for general testing as well as moisture conditioning. This is of utmost importance as water damage tend to increase testing variability.

7.17 EFFECT OF BITUMEN RELATED PARAMETERS ON COHESIVE STRENGTH

In this section two bitumen parameters are discussed namely: source of bitumen and effect of its consistency on the cohesive bond strength.

7.17.1 Source of Bitumen

In this research two sources of bitumen were tested. It is seen from the results that Penetration grade 60/70 from Source 1 has more POS as compared to the same grade from the other source. Source one also gave a more consistent graph. The explanation for this can be attributed to the difference in asphaltene content of the two bitumens. Source 1 seems to possess more asphaltene content which subsequently results in more tensile strength. The same explanation can be found in the very earliest work on POS by Marek and Herrin (1968). Source 1 will be further evaluated for effect of penetration grade on properties of bitumen.

TFOT ageing showed that there was no correlation between tensile strength and the source of the bitumen or its composition. Changes in bitumen composition were not significant enough to show the contribution that the individual components made to the tensile strength of bitumen.

7.17.2 Bitumen Grade and Cohesive Strength

In this section two grades of bitumen are evaluated for their integrity. This parameter was based on the discussion made by Grenfell et al. (2014). According to them cohesive strength of bitumen varies with bitumen grade. Here it is observed in accordance with Grenfell et al. (2014) and Marek and Herrin (1968) that grade of bitumen greatly affects the cohesive bond strength. As consistency is a bitumen dominant property so its effect is more pronounced than any other material parameter.

It can be said that 40/50 grade of bitumen source 1 has twice the cohesive strength of its sister Pen 60/70 and 25% more POS than that of Pen 60/70 from source 2. Hence the order of ranking would be POS of 40/50 (source1) > 60/70 (source 2) > 60/70 (source 1). It can be further said that consistency of bitumen is a more dominant factor for cohesive strength as compared to its source. In relation to effect of grade on adhesive strength, it has already been mentioned in the literature that the effect of bitumen is more dominant on adhesion performance than that of aggregate.

7.17.3 Effect of Film Thickness

A little introduction has been indirectly given under the heading of aspect ratio. The complete effect of bitumen film thickness was kept vague so that it can be properly be addressed at right place. In this research reducing the film thickness by 40% gives more than double the pull off strength compared to 0.5 mm film thickness. The mode of failure in the first case (0.5mm) was cohesive while for second case (0.3mm) it was mixed to adhesive. In terms of failure mechanism, the former has ductile failure while later showed mixed behaviour between ductile and brittle.

Table 7.9: Effect of loading rate on bond strength

Material	Mean Pull Off Strength (MPa)	COV (%)	Film Thickness (mm)	Failure mechanism	Replicate
Source 2 Pen 60/70	1.66	8.20	0.3	3 samples showed brittle failure	3
Source 2 Pen 60/70	0.71	16.78	0.5	Ductile Failure	6

Test Condition: Standard except cold plate

The earliest work on film thickness is reported by McBain and Hopkins (1924) with their adhesives. In pavement engineering, the pioneering work of Marek and Herrin (1968) clearly states the effect of film thickness on tensile strength. This effect has been studied by several researchers (Chang, 1994; Fond, 2001; Harvey, 2003; Harvey, 2005; Poulikakos, 2011; Jakarni, 2012; Sultana, 2014).

It can be seen from Table 7.9 that decreasing the film thickness increases the pull off bond strength. In table, the mode of failure of thinner films is suggested to be adhesive (Moraes et al., 2011). This shift of mode is further accompanied by brittle failure (Liantong, 2009). In this research 0.5mm was adopted as 'standard condition' for cohesive bond strength.

7.18 RELEVANCE OF LOADING RATE

The loading rate also known as cross head speed was tested for its effect on the pull off strength and the ability of the test to accurately capture this variable was evaluated. The increase in loading rate result in an increase of Pull Off Strength

as shown in Table 7.10. The failure mechanism remains ductile in all cases. The test rate of 10mm/min was adopted as the standard condition for further testing.

Table 7.10: Effect of loading rate on bond strength

Material	Mean Pull Off Strength (MPa)	COV (%)	Loading rate (mm/min)	Failure mechanism	
Ls (40%) in Source 1 40/50	1.13	9.33	20	Ductile failure in all cases	8
Ls (40%) in Source 1 40/50	1.07	14.57	10	Ductile failure in all cases	6
Gr (40%) in Source 1 40/50	0.89	12.2	10	Ductile failure in all cases	6
Gr (40%) in Source 1 40/50	0.73	15.09	5	Ductile failure in all cases	5

Test Condition: Standard except cold plate

7.19 MASTICS AND PULL OFF STRENGTH

7.19.1 Addition of filler and its type

Table 7.11 shows the difference between plain bitumen and mastic with 40% filler by mass of bitumen. The results show that addition of filler has resulted in an improvement in the pull off strength. In one case this difference seems less; this is when bitumen has been tested by hot plate pouring while mastic has been poured onto a cold aluminium plate. It is clear from the discussions in section 7.15 and also from the results of Table 7.11 that difference of pouring method results in change of pull off strength. The second observation here is that addition of filler is affecting the quality of result. This could be as simple as addition of further complex natural forces in the bitumen itself. Secondly it could more appropriately be due to improper mixing/remixing of mastic.

Table 7.11: Pull Off Strength of mastics

Material	Mean Pull Off Strength (MPa)	COV (%)	Plate condition	Failure mechanism	Replicates
Source 1 Pen 40/50	1.03	7.77	hot	Ductile failure in all cases	5
Ls (40%) Source 1 Pen 40/50	1.07	14.57	cold	Ductile failure in all cases	6
Ls (40%) Source 1 Pen 40/50	1.25	14.85	hot	Ductile failure in all cases	6
Gr (40%) Source 1 Pen	1.23	25.51	hot	Ductile failure in all cases	7

Standard conditions except mentioned in table

The result shows that there is good increase in the properties of the bitumen upon addition of the filler. The bond strength has improved without affecting the failure mechanism. The mode of failure remains cohesive failure and the material behaviour is ductile. This shows that addition of filler is improving the material properties as intended. These results are in accordance with those obtained in the rheological part of the thesis (Chapter 5). The results of this research are further supported by the work of Copeland (2007). The filler percentage was almost of same magnitude. He also reports the increase of bond strength without affect in failure mode in dry condition.

The above discussion was further evaluated in terms of effect of filler type on bond strength. It can be seen from the previous table that change of filler type is not resulting in any considerable change in terms of pull off strength. Limestone shows slight increase but due to degree of variability as compared to difference does not allow any inference to be made from it. The result is actually elaborated in Table 7.10. In this table limestone mastic shows more pull off strength as compared to granite under the same conditions. This is in a sense in agreement

with the findings of the chapter 5, where it has been discussed in great depth that different filler types have different stiffening potential.

7.20 AGEING AND PULL OFF STRENGTH

7.20.1 Bitumen Ageing

The laboratory ageing of bitumen is expected to improve the pull off strength of bitumen-substrate butt jointed specimens. In order to move further, the point is to be made that the ageing increases the pull off strength but on the other hand it results in embrittlement of failure mode due to physical hardening. This is in accordance with the observation of Wang et al. (2014), according to whom adhesion fatigue life for a bitumen aggregate system reduces with long term ageing.

In Table 7.12 shows the change in pull off strength with different ageing conditions. The observation is clear that ageing has resulted in an increase of pull off strength. The first effect is evaluated in terms of standard ageing test namely RTFOT. An additional test was performed on simply oven aged or oven hardened bitumen. This bitumen was remixed before preparing samples for pull off testing. In terms of pull off strength its effect seems to be similar to that short term ageing.

Table 7.12: Effect of ageing on Pull Off Strength

Material	Mean POS (MPa)	COV (%)	Specimen condition	Failure mechanism	Replicates
Unaged Source 1 Pen 60/70	0.42	17.58	Silicon Trimmed Cold	Ductile failure in all cases	4
RTFOT Source 1 Pen 60/70	1.26	8.35	Trimmed	Ductile failure in all cases	4
3 hours Oven aged Pen 40/50	1.45	11.04	Standard Conditions	Ductile failure except one	6

Standard conditions except mentioned in table

The curve showed ductile behaviour for unaged and RTFOT aged samples. Only two samples of 3 hours oven ageing shown some brittle failure. This is the only binder that has showed some brittleness. This demonstrates that cohesive failure is happening which is further verified by visual inspection of the failed surface.

7.20.2 Ageing of mastics

The ageing of mastic is expected to be different from bitumen ageing due to bitumen-aggregate interaction. As noted in Chapter 5, certain filler can accelerate the ageing effect compared to others fillers. It was noted that granite acts as an ageing catalyst when compared to limestone. Table 7.13 shows apparently not much difference in ageing behaviour of limestone and granite filler. This is consistent with previous discussion that this effect is not much pronounced during short term ageing. Current resource limitation did not allow long term evaluations. This catalytic effect of aggregate on the oxidation of bitumen has also been studied by Hefer et al. (2005). The conclusion of this discussion is that

the effect of filler type on pull off strength during short term ageing is not considerable.

Table 7.13: Comparison of ageing of mastics

Material	Mean POS (MPa)	COV (%)	Repliates
RFTO aged Ls mastic 40% by mass (Source 1 Pen 60/70)	1.86	10.70	7
RFTO aged Gr mastic 40% by mass (Source 1 Pen 60/70)	1.83	14.74	9

Standard test conditions

The observation made seems particularly true for cohesive strength. The failure mode for short term aged specimen was cohesive and ductile. This was true for almost all tested specimen. The role of filler up to short term age, in terms of bond strength seems to be that of an extender.

7.21 MOISTURE DAMAGE

The effect of moisture damage is discussed under three sub headings here. The first section is a general discussion about bonding mechanism. The second section explores the effect of moisture in the presence of aggregate plates. Additionally, an attempt was made to re-use already used aggregate plates. The third section discusses the problems associated with the moisture damaged specimens.

7.21.1 A comment on interfacial binding mechanism

In this section it is necessary to reject a predisposed proposition related to fractions present at the interface. A long held belief states that due to absorption

of bitumen at the aggregate surface, lower molecular weight and smaller fractions of bitumen get absorbed into the pores of the aggregate. On the other hand, large molecular weight fractions remain available at the surface of the binder. This would make the bitumen more brittle. This phenomenon is known as 'selective absorption' of bitumen. There is no such evidence from any experimental work in this regard. However, the opposite of this is true when studied through GPC elution. This is called 'selective adsorption' a surface phenomenon instead of a size exclusion phenomenon. According to this heavy fractions are attached to surface and maltene or other lighter fractions are freely available (Curtis, 1993). This makes heavier fractions to be adsorbed thus affecting pull off strength on ageing and during moisture damage. This will make the understanding of further results easier.

7.21.2 Re-use of aggregate plates and effect of substrate

The manufacturing of aggregate plates was a laborious task in terms of the effort involved. This meant that in the course of this research aggregate plates were a valuable resource. An attempt was made to see the difference of POS in terms of use of new and used aggregate plates. This was to evaluate whether these plates can be used more than once.

Table 7.14 summarises the results of these aggregate plate tests. The tests were performed on aggregate plates of RTFOT aged samples Source 1 Pen 40/50. The first set of plates was washed with acetone and then dried in the oven for a short period of time. The second set was reused plates cleaned with methylated spirit and then carefully washed with acetone and then dried in an oven.

It was seen that the pull off strength of the re-used surface was considerably lower than that of the new surface. This is due to the presence of less active surfaces for proper bonding. This reduction in active sites could be due to irreversible adsorption of bitumen on the substrate. Thus, eventually reducing the capacity for mechanical interlocking and physicochemical interactions. It will result in weaker adhesive bond. In this regard, used aggregate plates specimens show huge variability in test results. This observation makes used aggregates plates unfit to study the adhesive as well cohesive strength of mastics. Alternatively, there is need find some more better method to clean aggregate plates. The results included pull off strength after dry and wet conditioning for 24 hours.

The results show that the strength of mastic has significantly decreased in the presence of water. The mastic was preferred to evaluate the effect of moisture rather than virgin bitumen. It was anticipated that mastic would allow easier access of water within the mass of bitumen and to the interface. It seems that the effect has been captured. The dominant type of failure was to adhesive to mixed although cohesive failure was achieved in some. The adhesive to mixed type of failure is shown in Figure 7.22.



Figure 7.22: Failure at interface of binder and substrate

A comparison of the results with control (aluminium) in dry conditioning shows that pull off strength of mastic-aluminium and mastic-aggregate substrate systems is different. The strength in case of aggregate substrate should have been higher. This is because aluminum plates are relatively polished as compared

aggregate. The aggregate surface is supposed to have rougher surface that will result into better mechanical interlocking, also more surface area for binder-aggregate surface interactions. It was decided to evaluate the material behaviour with both substrate before any surface roughness evaluation.

Table 7.14: Aggregate substrate for pull off testing

Material	Mean Pull Off Strength (MPa)	COV (%)	Conditioning	Plates	Replicates
Short term aged Ls 40% in Source 1 Pen 40/50	1.86	10.7	Dry	Control	6
Short term aged Ls 40% in Source 1 Pen 40/50	0.96	33.31	Dry	Used	5
Short term aged Ls 40% in Source 1 Pen 40/50	0.81	16.15	Wet	New	6
Short term aged Ls 40% in Source 1 Pen 40/50	1.38	11.53	Dry	New	6

The results show a behaviour contrary to expected i.e. control having more POS. This deviance from the expected behaviour can be due to several factors. A source of error in terms of procedures can be due to dust particles as shown in Figure 7.23 (ineffective washing by acetone) or non-uniformity in achieving binder film thickness. The reason can also be explained at the micro level. At the micro level the decreased pull off strength in dry cases of aggregate substrate can be explained in terms of speculation by Thelen (1958).

According to Thelen (1958), many aggregates strongly adsorb moisture due to electrochemical attractions. During the ageing/heating of aggregate surface the outermost molecules become partially replaced by organic contaminants in the air. These contaminants may include fatty acids and thereby can affect the stripping potential of aggregate. This is because of reduction in free radicals and reactive sites on the surface of the aggregate.



Figure 7.23: Failure due to dust coating

In the light of the above explanation, the new aggregate surfaces have already absorbed moisture from air (in addition to presence of dust as well). Later insufficient drying of the new aggregate surface has resulted in reduced bond strength. This is consistent with the observation made by Blackman et al. (2013). In the case of re-used aggregate plates the damage has already been done due to washing by methylated spirit and accumulation of oily components by adsorption of previously used bitumen. These two reasons have reduced the active surfaces in addition to the problems of dust and non-uniformity in film thickness.

The testing with aggregate substrate showed three types of failures namely; adhesive, cohesive and mixed type. Visual inspection has shown that almost half the samples have shown adhesive to mixed type failure. This was true for both dry and wet conditioned samples. The adhesive to mixed failure for wet conditioned specimens make lot of sense as has been seen from the amount of water damage previously. The adhesive to mixed failure for samples which clearly have shown cohesive failure with control plates seems odd here. A logical explanation can be drawn from the previous discussion. The possible reason for such failures could be either due to poor film thickness or due to poor bonding (Tarrer and Wagh, 1991). The poor bonding makes a lot of sense here as seen with the specimen failing due to surface dust. The dust combined with thin film thickness has resulted in mixed to adhesive failure. This explanation can be

related to the observation of Tarrer and Wagh (1991) that cohesive strength is only completely available if the interface bond between binder and aggregate is of good quality.

In addition to this, the aggregate substrates' rough surface texture and larger area of contact is expected to provide good adhesive bond. This is because of better interlocking of the binder with aggregate in the dry state. On the down side the rough texture can lower the coatability as compared to a smooth surface, secondly this can provide a "safe heaven" for moisture (Bagampadde et al., 2004). In this regard sample preparation was done with extreme care to ensure good coating for improved binder-substrate bond (Tarrer and Wagh, 1991). However, despite these considerations apparently a 'proper bonding' was not achieved. Next discussion serves the purpose to explain the reason for lower pull off strength as compared to control specimens for the same material.

7.21.3 Substrate Slip Due to Moisture Damage

The observation of failure curve of wet conditioning specimens revealed that some phenomenon was happening that resulted into a curve showing behaviour similar to that of slipping of plates. This same curve behaviour was observed before and sometimes after the peak load. In both cases, the only possible explanation is that slipping of the plate has occurred during the load application.

It seems that binder was trying to carry the load and at the same time partial load was being utilised to overcome drag force between the substrate and the test assembly interface. It leads to two scenarios. In the first one if the plate stopped slipping due to whatever reason (adjustment), the specimen solely took the load and eventually failed. This should be clear from curve B of Figure 7.24.

The second scenario is of curve A in Figure 7.24. The specimen was carrying load and there was no movement of the plate although a drag force was being generated in stealth mode. As the load reached certain peak load, the plate movement along with binder elongation started happening. Eventually this peak dropped as true slipping started happening. The drop in load happened because the load binder was carrying was removed; for this reason, a sharp drop in the curve happened. These points are being explained throughout this section.

The explanation of the curve behaviour was further verified. The verification was done by marking a line around the periphery of the plates and simultaneously observing the curve behaviour. The line position after testing was again marked.

The discussion is included in section of moisture damage because this phenomenon mainly happened in wet conditioned specimen. Examination of the failure curves of dry specimens did not show this behaviour. This indicate that the bitumen during the conditioning might have entrapped some water. This water might have been released during testing and wetted the plate sides. This water could have acted as a lubricant and might have caused slip.

A comment on the curve type is to be recalled, namely that a bell type curve. The typical curve meant that everything is going right. The sharp vertical rise or drop in a curve also meant things were going right. The only deviation can be due to brittle mode of failure or reduction in fibrillary structure. On the other hand, a horizontal line (inclined at 45°) before start of cavitation meant that something went wrong. However, as a matter of principle the tests on slipped specimens were repeated.

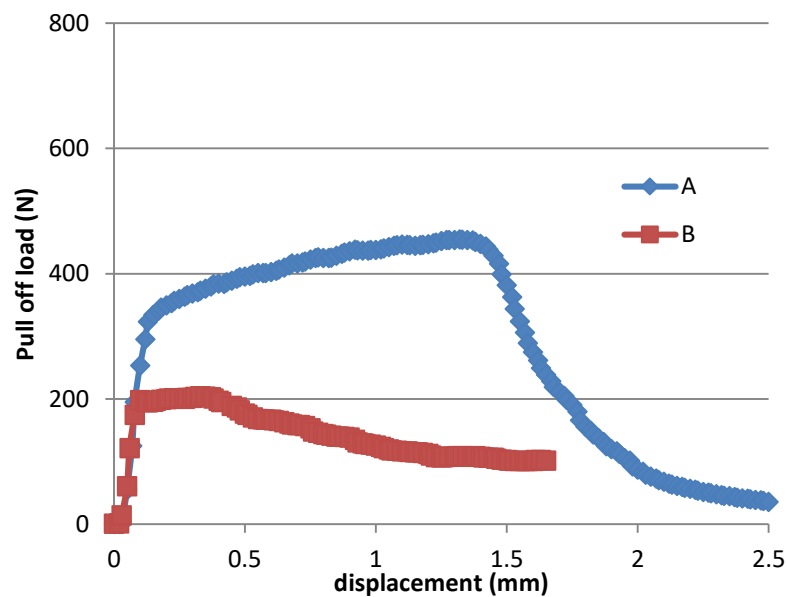


Figure 7.24: Slip before and after peak load

In Figure 7.24, both types of slips are shown. The graph is for the same test condition and same material in wet condition. It is interesting to note a very nice initial build-up of the curve; this shows the good repeatability of the test method.

One of the suggestion here is to do a dry conditioning of the wet specimen for some time. The testing done in this phase has shown that towel drying and one-hour dry conditioning is not enough. In this matter, a longer dry condition may provide a panacea to the problem.

7.22 MOISTURE DAMAGE AND AGEING

The conversation in this section will be kept concise as the relevant tabular values are already discussed in section 7.23 on conditioning 7.16.2 and section 7.21.1 on aggregate plates. One of the further possible explanation of large percentage loss of pull off strength after water damage could be due to use of aged binder. It is to

be noted that both the aluminium (after 65 hours) and aggregate (after 24 hours) showed great loss of strength. It is clear that for the aluminium specimen that the only source of water entry was laterally.

The effect of moisture on aged asphalt pull off strength was noted in the work of Moraes et al. (2011). The ageing/oxidation of bitumen promotes likelihood of micro-cracks. These micro-cracks become pathways for the water to penetrate at binder-aggregate interface. This phenomenon accelerates the process of moisture damage Aguiar-Moya et al. (2015). Once the water is at the interface it tries to remove carboxylic acids, sulphoxides and anhydrides on the surface. These strongly adsorbed functional groups are the major oxidation products along with ketones. It is to be noted that these products except ketones tends to get easily removed from the substrate under the action of the water. Especially carboxylic acid which has weaker bond as compared to hydrogen bonding of water with some of the aggregate surfaces (Robertson, 2000) and (Bagampadde et al., 2004). However, having identified one of the causes and providing relevant explanation, there is still a need for further testing on aged binders to verify this hypothesis.

7.23 COMPARISON WITH OTHER TEST METHODS

This section compares the testing technique developed in phase of testing. It also makes an effort to compare this method with previous methods qualitatively. The first Table 7.15 shows the results of the two newly manufactured test assemblies. It is clear from the variability of test results from the Compression Pull Off Test Assembly (CPOTA) that this method is quite effective in evaluating bond strengths. The variability of the Direct Pull Off Test with all good pouring procedures is 2.5 times the variability of the former, even when poured onto a

cold a plate (deliberately used to cause variability in results). In the next step, testing of mastic under the same conditions, this variability is 2 times.

Table 7.15: CPOTA Vs Direct Pull Off Testing Assembly

Method	Material	POS (MPa)	COV (%)	Condi tions	Repli cates
Compression Pull Off Test Assembly (CPOTA)	Source 2 Pen 60/70	0.77	6.82	Cold	8
	Gr (40%) in Source 1 Pen 40/50	0.89	12.2	Cold	6
Direct Pull Off Test Assembly	Source 2 Pen 60/70	0.71	16.78	Hot	6
	Gr (40%) in Source 1 Pen 40/50	1.01	33.86	Cold	6

A comparison of the two test methods developed as a part of this new testing phase is given in Table 7.16. This table also includes comparison with other methods, where specified. The comparison is made stepwise ranging from sample preparation to examination of the failed surface. This comparison establishes the usefulness of this method for evaluating pull off by minimising material handling, ease of operation, and instalment in UTM etc.

Table 7.16: Comparison of CPOTA other methods

Parameter	Direct Pull Off Test Assembly and other methods	Compression Pull Off Test Assembly
Comparison with Pull Stub type tests	Pull stub type tests such as PATTI do not capture complete useful data for pull off testing	Captures complete range of data required for testing of a fundamental mechanical property
Breakage during sample handling	Specimen breaking is a big problem handling	Out of hundreds of specimen tested not a single broke due to handling

	especially during clamping in UTM	
Fitting into UTM rig	Requires careful clamping and unclamping in the jaw of machine	Only requires placing the CPOTA under shaft and making an easy to do contact. Removing does not even require any unclamping. It can be removed straight away.
Time required for achieving required film thickness	The gap assembly used by Jakarni (2012) and method adopted by Zhang et al. (2015) are relatively slow	Speedier and does not require any sophisticated machine. Additionally, powerful compression mechanism makes it easy to handle even less workable binder
Time required during testing	These methods require more e.g. at least six screws needed for clamping of substrate	Speedier than previous two used methods due to improvement in clamping mechanism i.e. only four screws required for clamping
Gripping of aggregate plates	The conventional mechanism explored in this research were not good enough to account for variation in plate diameter. The second problem was gripping of imperfect circular plates.	Easier to account for larger variation in diameter as well as ability to accommodate imperfect circular plates
Damage to aluminium substrate	Three-point clamping damaged the aluminium plates	The clamping mechanism did not damage any plate
Start of load curve	May or may not start from zero elongation depending upon manual adjustment.	User controlled, it can easily be started from zero elongation.
Curve adjustment	Curve correction is needed by plotting a tangent to the initial curve.	No curve correction needed under this method once manual seating is done.

Full material behaviour	No curve in the reported literature has shown a step in the leg due to ductile failure	This is study seems to be first of its kind to show a full material behaviour for bitumen.
Cavitation	During testing its difficult to observe and fully capture phenomenon of cavitation	Cavitation was clearly captured during test and in the result plots
Failed surface	The fail surface can easily get damaged during the testing.	The plates are nicely separated there is no such issue

7.24 SUMMARY

This chapter has summarised the development of two test methods namely; direct pull off test assembly and Compression Pull Off Test Assembly (CPOTA) test. The latter method removed major problems of the first method of this phase and of methods used in chapter 6. Historically direct pull off test assemblies and its variations have been used. In this research, direct pull off test approach was abandoned because of the problems associated with it.

A new compression assembly was developed to achieve desired uniform film thickness. There overall goal of this phase was achieved through development of a compression gap assembly for achieving required film thickness and Compression Pull Off Test Assembly (CPOTA). In gap assembly, previously micrometer screw guage was being used for compression as well as film thickness measurement. In new assembly a separate mechanism to compress and measure film thickness was used. The film thickness achieved through this method was consistent when verified through vernier caliper.

This method was successful to identify both ductile and brittle type failures. The resulting failure curve behaviour was explained in detail. It was also discussed that how failure curve help to accept or reject any test on specimen. The phenomenon of cavitation was discussed in context of bitumen and mastics. It was observed that this method was more useful to analyze phenomenon of cavitation than previous and historical methods.

A detailed test programme for cohesive bond strength was conducted for all the major test variables needed for any pull off tests.

The variability of CPOTA testing was discussed and its usefulness for pull off testing was commented upon. The usefulness was addressed through certain test parameters. These parameters were divided in three domains; effect of plate geometry, effect of binder; and effect of testing rate.

In testing, the effect of plate geometry on pull off testing was evaluated. A detailed discussion was made on effect of changes in specimen preparation on pull off testing. The selection of conditioning and curing and conditioning time was commented upon. In bitumen related parameters, the effect of bitumen source, grade, and film thickness was evaluated. The last parameter evaluated was effect of loading rate.

In relation to mastics, role of the filler was observed to be enhancing the pull off strength. The ageing, itself, resulted in increase of POS but on the other hand shifting failure mode towards brittle. The type of the filler did not have any effect on POS after short term ageing.

The use of aggregate plates is quite necessary to study effect of moisture. The moisture conditioning reduced the POS and resulting into a more mixed to adhesive type failure. In this regard, use of re-used aggregate substrate for POS was found to be ineffective. In moisture conditioning specimen the slip of the plates from the testing assembly was a major problem. The curve behaviour helped to address this issue. It was highlighted that proper cleaning of the aggregate plates was necessary. In addition to this longer dry conditioning time was suggested for moisture conditioned aggregate specimen prior to pull off testing.

In the end, results of this phase were analysed and explained in the light of existing knowledge in the area of binder ageing, moisture damage and bitumen chemistry and pull off strength. In the course of testing several interesting observations were made and explained. It was demonstrated that that this method can be successfully used for further testing for cohesive as well as adhesive strength.

CHAPTER 8 : CONCLUSIONS AND RECOMMENDATIONS

8.1 SUMMARY

The binding materials bitumen and mastics were used in this research. Three ageing techniques were studied and the use of Thin Film Oven Test for the long-term oxidative was explored. The effect of filler's properties on the mastic was discussed in terms of packing fraction and acidic/basic character of mineral aggregate.

The bitumen-filler particulate suspension provides more realistic depiction of the aggregate as the mastic coated material. This led this research to incorporate mastics as the binding material along with bitumen to study mineral aggregate properties effects.

The scope of research involved physical, rheological testing on bitumen and mastics using different ageing techniques to evaluate their effect on oxidative ageing and potential use of TFOT for long-term oxidative ageing of the bitumen and mastics. This involved a study to understand the oxidative ageing mechanism of bitumen.

The research was extended to study the adhesive/cohesive bond strength of the binder using pull off testing techniques. The main motive was to use of most fundamental material property i.e. 'tensile strength' to evaluate material

properties. The emphasis was made on the cohesive bond strength of bitumen and mastics. This pull off strength was evaluated using two locally available and cost effective pull off tests techniques. These test techniques were developed due to lack of well-established pull off test method to evaluate adhesive/cohesive bond strength. The detailed testing regime indicated few issues with these methods.

In order to solve these issues a radical design modification was conceptualised. The concept was assessed for manufacturability and lean manufacturing approach was used develop the test technique. The test was evaluated in terms of usefulness for evaluating pull off strength. The promising results led to a detailed testing programme. The test successfully evaluated all the test parameters. This not only established the robustness of the test but also paved the way to establish 'good practices' for any pull off test.

The aim of the successor of this research should be to further minimise the test variability. There is need to prepare a detailed test protocol. In order to make it more robust there is need to carry out a detailed testing programme for pure adhesive failure.

8.2 CONCLUSIONS

The conclusions are drawn from three aspects of research namely; ageing techniques, effect of filler properties and cohesive bond strength. The cohesive integrity of the mastics was studied through three pull off test techniques. The research leads to following conclusion:

1. In relation to chapter 4, the use of Thin Film Oven (TFO) for long-term oxidative ageing of bitumen apparently indicates its potentially promising use. This seems to be true at least in case of rheological testing. However, the FTIR tests (described in 4.7) show counter intuitive result (explained in 4.8). The results indicate that maximum oxidation in binder has happened till a specific time. The maximum increase in carbonyl and sulfoxide has already happened during this time. After this material is undesirably hardening as the oxidation functionalities seem to flatten out (see Figure 4.17) This further lead to following conclusions:

- A. The results lead to conclusion that ageing mechanism of PAV and TFOT seem to be different (section 4.5). This is because of different level of formation of oxidation functionalities. (section 4.8).
- B. Such attempts, should establish a clear ageing profile over different temperature and ageing times to select appropriate ageing time for any methods to be compared (section 4.5 and 4.6)
- C. It can be seen in this research that comparison of ageing effect at extreme limits should not solely be based on rheological testing as some undesirable hardening has also happened. Such studies should be supplemented with study on chemical functionalities also (as explained in 4.8).
- D. The observation also indicates need for a more fundamental material property (such as tensile strength) to study the ageing effect. This is because favourable results from rheological testing and unfavourable results from FTIR. This result is derived from overall results of chapter 4 and chapter 7.

2. A precise description of the findings from chapter 5 is that for any unaged mastic the packing fraction seems have dominant effect to explain stiffening

potential (section 5.4 and 5.5); however, with the progression of ageing the catalytic effect of aggregate play more important role (section 5.9).

3. The acidic fillers tend to increase the ageing effect as compared to basic aggregate fillers. This conclusion led to the conclusion that in order to understand the complete behaviour at aged and unaged conditions, it should include test techniques that can provide additional information regarding acidic/basic character of the fillers using state of the art techniques such as XRD (as outlined in section 3.5.3 and explained in section 5.10).
4. Even in unaged condition the complex phenomenon of stiffening potential should not be solely based on packing fraction. There is need to incorporate other filler's aspects too such as their dispersion, mixing, agglomeration, morphology (particle size, surface texture) and interfacial properties and surface activity. It has been seen that basic fillers result in slightly stiffer suspension (section 5.4 and 5.6).
5. In this research, some micromechanics-rheology models from colloid science were applied to calculate the theoretical stiffening ratio (a measure of stiffening potential). A one by one detailed discussion of these models is made in section 5.8. These models produced good results at low volume concentrations. However, these models do not incorporate physico-chemical interaction of bitumen filler in mastics. These models' basic assumption was partially fulfilled regarding particle shape and unimodality through mineral morphology. The research outlines their potential benefit in this regard, there is however need to carryout detailed investigation in this regard. The incorporation of properties of bitumen and nature of aggregate surface can improve the predictions of these models. The results of the application of these models and their comparison with experimental data is given in section 5.8.10.

6. The techniques of Jakarni (2012) in section 6.2 and Apeageyi et al. (2014) in section 6.3 shows their robust nature and usefulness as compared to pull stub type tests. Among these two methods the first technique was deemed to be more useful to identify adhesive to mixed/hybrid bond strength only. The second method was found to be comparatively more robust in nature because of its usefulness in evaluating both cohesive and adhesive failure.
7. The discussion in section 6.2 leads to the conclusion that there is need to further reduce the material handling in method of Jakarni (2012). This was evident both from both on-hand practice and test data. The gap assembly of this method was used for method 2 (section 6.3) with slight improvement.
8. The problems of method 1 lead to the use of the method of Apeageyi et al. (2014). This method has shown to be a better technique to evaluate cohesive bond strength of the binders (section 6.3). However, results of this method showed some problem to differentiate materials at same level of treatment i.e. difference between limestone and granite mastics in aged and unaged condition (section 6.3.3). The improvement in gap assembly, explained in section 3.9.2, of method 1 (section 6.2) provided more film thickness control but overall test procedure did not improve the test variability. The deviation of the failure curve from ideal behaviour show problems due to slipping, imperfect alignment, sensitivity to material handling etc., as described in section 6.3.4.
9. A new novel test method was devised to measure cohesive bond strength based on the principle of 'tensile strength evaluation'. This method has shown good potential to evaluate bond strength (cohesive/adhesive) as seen in its detailed testing regime described in section 7.12 to, 7.20. This method provides panacea to many problems faced in the historical test methods (as summarized in table 7.16).

10. The test method devised in this research provides a useful insight into investigating material behaviour. The material response in terms of load elongation curve has been more elaborated than any other method in the literature as can be seen in section 7.9 and 7.10. The related kink in the failure leg through this method has been elaborated in section 7.11. Thus this method makes it easier to further understand this phenomenon of fibrillary nucleation in bitumen and mastics as discussed in 7.11

8.3 RECOMMENDATIONS

This section provides not only the direction for the immediate extension to this work but also sets foundation for the further important research work in this regard. The recommendations are made through the detailed experimental programme and respective literature review. The areas of focus in following points are ageing, mastics, pull off testing, and cohesive strength.

1. The ageing method comparison should be made by reducing the ageing time and temperature and making attempt to minimise the effect of undesirable hardening in TFOT ageing.
2. The conclusive statement in this regard is that, for comparison of ageing techniques should be made on three grounds namely; rheological testing, functional group analysis and pull off testing.
3. It is recommended to evaluate the effect of physicochemical interactions on the oxidative ageing of mastics along with the stiffening potential of the fillers. It may be useful to include mechanical and physical tests to evaluate the primary and secondary properties and bond evaluation.

4. It is recommended for future studies to study the effect of moisture damage on the cohesive bond properties through extended periods of conditioning of the bitumen through longer conditioning periods. This can further be incorporated with the effect of ageing to combine the ageing and moisture damage mechanism on cohesive bond strength.
5. The next logical approach in use of CPOTA or similar testing on integrity of bitumen should be to focus purely on adhesive bond strength. Only slight modifications needed in the gap assembly to accurately measure thin film thickness less than 100 micrometer.
6. It is suggested to study the integrity of mastics to correlate with important bitumen chemistry parameter namely bitumen compatibility. This can be achieved through bitumen fractionations techniques with or without use of pull off tests.
7. A more detailed testing regime can be tried to correlate complex modulus with pull off bond strength in an attempt to formulate some correlation between binder rheology and tensile strength.
8. Three material aspect are recommended to be evaluated namely; polymers, antistripping agent and adhesion promoters. The specific difference between fillers and polymers can be made in terms of cohesive strength. This should be done in attempt enhance filler role towards adhesion/cohesion. This test technique can even be used to explore mechanisms such as self-healing and moisture damage. In this regard, a starting step can be re-joining failed specimen and later classifying them based on film thickness using vernier caliper.

9. The use of detailed image analysis in evolution of filler properties and examination of the failure surfaces in pull off testing is recommended. The X-ray tomography or any other microscopic techniques maybe useful to provide any insight in this regard.
10. The evaluation of pull off strength through robust tests such CPOTA can result into inclusion of tensile strength towards binder specification to evaluate its crack resistance.
11. The above point further leads to the application of fracture mechanics through use of the binders. There is an ongoing research on fracture mechanics in pavement engineering through tests on asphalt mixtures. There is great potential of fracture mechanics in the domain of binder too.
12. It is highly recommended to carry out a detail evaluation of fracture energy for brittle as well as ductile failure. There is need to streamline the hide and seek which is often happening in reporting of the pull off test results in various publications. The past researchers are somewhat justified because of the inherent variability of the pull off test results. A successful attempt in this regard can provide breakthrough in establishing a robust standard test method.

GLOSSARY

Adhesive Strength: The resultant of intermolecular forces between dissimilar particles. The bond between binder and substrate is referred as adhesive bond strength.

Aliphatic: This term mainly refers to open chain structure of hydrocarbons, like alkanes, alkenes and alkynes and is used to differentiate them from aromatic compounds.

Aromatics: A generic fraction of bitumen obtained by SARA analysis. It is distinctive as the term aromatic refers to compounds which have benzene in its ring structure.

Aromaticity: The property of aromaticity is generally about a significant extra stability associated with a resonance delocalised structure.

Bitumen grading: There are three grading systems for identifying and specifying bitumen and includes: **Penetration**, **Viscosity** and **Performance grading**.

Blown bitumen (Oxidised bitumen): Bitumen used in a wide variety of 'industrial' applications including roofing, flooring, pipe-coating etc. They are produced by passing air through soft bitumen/flux mixtures under controlled temperature conditions.

Carbonyl group: Carboxylic acids, esters, anhydrides, acylalides, amide and quinines, aldehydes and ketones are collectively are called carbonyl group.

Cohesive strength: The pull off strength due to intermolecular forces between the same material i.e. binder.

Cyclic: Hydrocarbons having a ring of atoms. If all atoms in ring are all the same it is called homocyclic; if atoms are involved it is heterocyclic.

Fibrillar structure: It is a failure mode which is characterised by presence of large number of fibrillars. Fibrils are very fine finger like dendrites. These are created during tensile type loading on thin films.

Filler: Mineral matter composed of particles (e.g. limestone dust, Portland cement or stone dust) smaller than 63 μm .

FTIR: Fourier transform infrared spectroscopy to identify functional groups in an organic or inorganic compound.

Fused aromatic ring: A molecular structure in which two or more aromatic rings have two carbon atoms in common, while aromatic refers to compound having Benzene in its structure and aromatics is a fraction of SARA fractions.

H/C: Hydrogen to carbon ratio

Loss shear modulus (G'') the complex shear modulus multiplied by the sine of the phase angle expressed in degrees. It represents the component of the complex modulus that is a measure of the energy lost (dissipated) during a loading cycle.

Mastic: The bitumen and mineral filler joined together to form mastic where mineral filler is aggregate passing sieve 200 or size less than 0.063mm.

Naphthenic structure: The hydrocarbons which contain less or no n-alkanes and mainly contain cyclohexane (saturated ring structure, C_nH_{2n}) in a molecule are called naphthenic. The oils which contain paraffinic carbon content less than 55-60% are called as naphthenic.

PATTI Test: It is a pull off type test commonly used to find bond strength of the binders. In this test rate of loading cannot be controlled.

Phase angle (δ) in radians or degrees is the lag between applied strain (sinusoidal) and the resultant sinusoidal stress in a controlled-strain testing mode, (or between the applied stress and strain in a controlled-stress testing mode.)

Polar molecules: Describe molecules that have a permanent dipole moment.

Pull Off Bond Strength: The ultimate tensile strength of a butt jointed or a poker-chip specimen.

Saturates: A generic fraction of bitumen obtained by SARA analysis.

Shear modulus (also called complex modulus) (G^*), is the ratio of peak stress to peak strain and is said to be resistance in deformation when shear loading takes place.

Solubility parameter: The solubility parameter is a numerical value that indicates the relative solvency behaviour of a specific solvent.

Storage shear modulus (G'): The complex shear modulus multiplied by the cosine of the phase angle expressed in degrees. It represents the in-phase

component of the complex modulus that is a measure of the energy stored during a loading cycle.

Sulphoxides are generally represented with the structural formula $R-S(=O)-R'$.

Surface free energy defined as the excess energy at the surface of a material compared to the bulk. Free energy on surface of material is the result of intermolecular forces difference acting on the surface as compared to these forces acting on molecules inside the bulk material. Surface molecules get attracted to the bulk material.

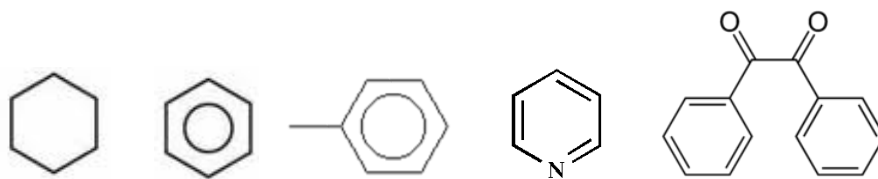
Resins: A generic fraction of bitumen obtained by SARA analysis.

Rheology: The study and evaluation of the time/temperature dependent response of materials, which are stressed or subjected to an applied force.

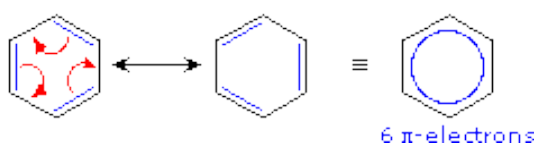
$\phi_{\max}$ Maximum packing fraction, the maximum packing fraction is defined as the solid volume content of a suspension at which the viscosity of the suspension becomes infinite. The combined effects of particle size distribution, particle size, shape and density are encompassed in this key property of fillers. In this dissertation packing refers to packing fraction computed using Rigden voids test method.

ϕ The *solid phase volume* is the volume of solid particles within a suspension. It is expressed as the volumetric ratio of solid volume to the volume of the suspension. For bitumen-filler mastics a ratio by weight has often been employed, with 2:1 ratios of filler to bitumen being commonly employed to investigate the effects of filler in bitumen.

Important molecular structures used in bitumen chemistry



Molecular structure of Cyclohexane (saturated ring structure), Benzene (unsaturated ring structure), Toluene, Pyridine and Benzil respectively.



Resonance structure for benzene

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Appendix A

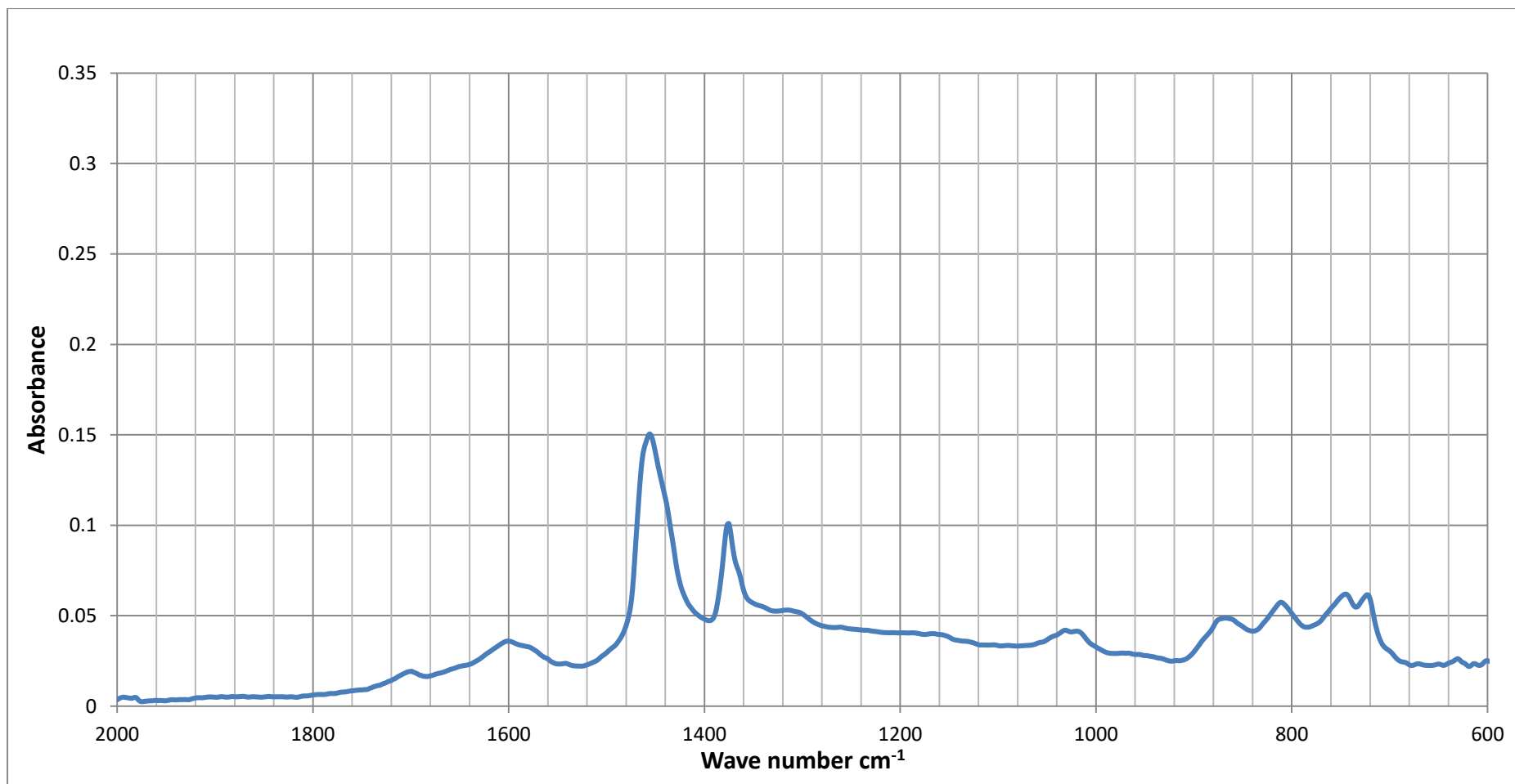


Figure Appx A.1: FTIR results PAV 40/60

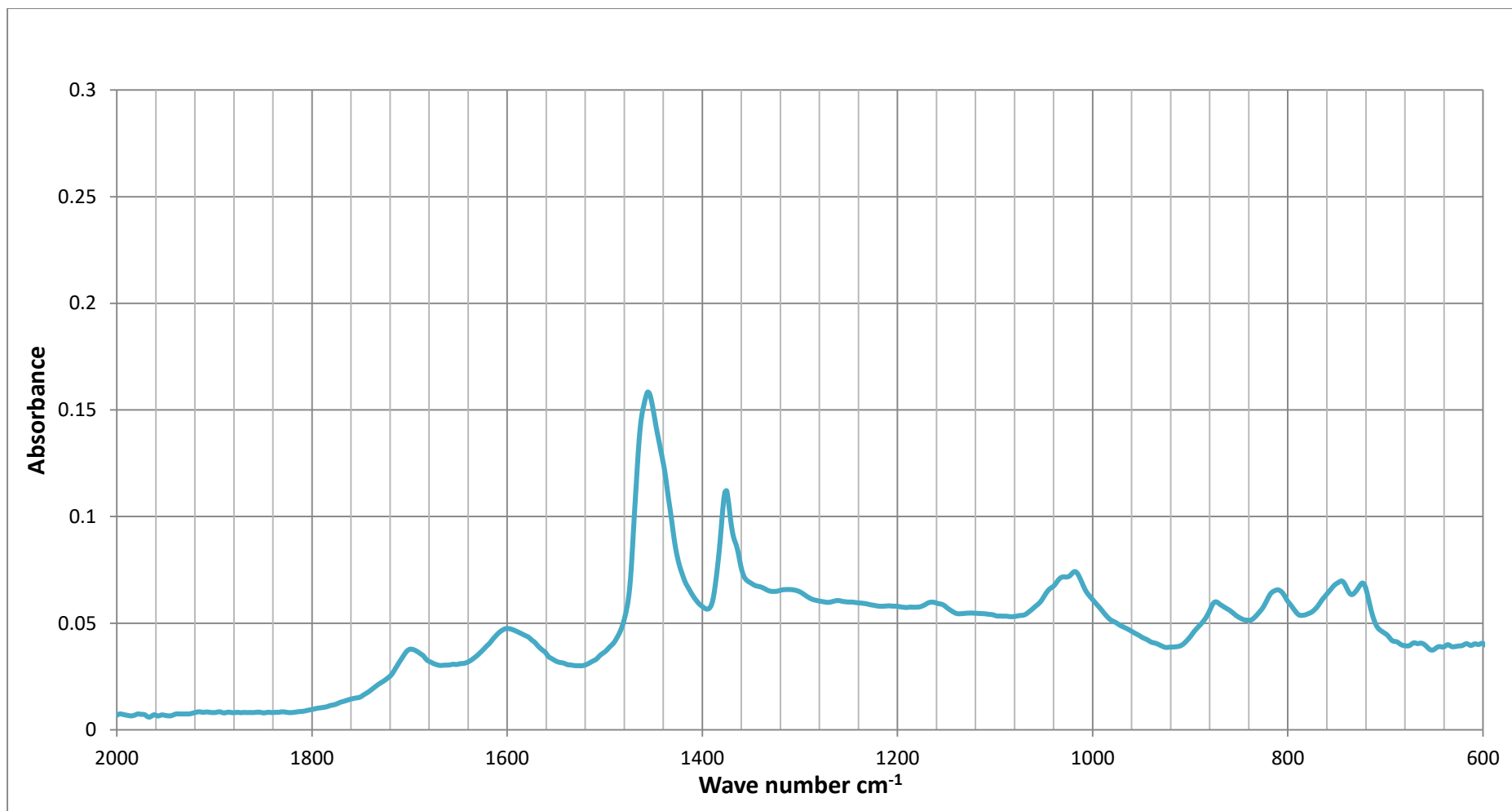


Figure Appx A.2: FTIR results of 2 days aged 40/60

Appendix B

$$\log |G^*(f, T)| = \delta + \frac{\alpha}{1 + e^{\beta + \gamma (\log f_r)}}$$

Table Appx B.1: Shape factors of Generalised Sigmoidal function curves for binders

Material	Difference b/w upper and lower asymptote	Shape Coefficients	Lower asymptote	Shape Coefficients
	α	β	δ	γ
40/60	14.81	-0.91	-4.94	-0.26
Ls(17)	14.52	-0.92	-4.61	-0.27
Ls(20)5hr	8.21	-1.33	-0.43	-0.46
Ls(20)20hr	21.43	-1.85	-11.63	-0.18
Gr(17)	12.73	-0.85	-2.98	-0.30
Gr(20)5hr	14.78	-1.12	-5.10	-0.26
Gr(20)20hr	21.51	-1.72	-11.35	-0.17
40/60	16.46	-0.98	-6.39	-0.24
5 hr TFOT 40/60	16.39	-1.11	-6.52	-0.24
1 day TFOT 40/60	22.46	-1.69	-12.57	-0.19
20 hr PAV	21.27	-1.63	-11.49	-0.20
2 day TFOT 40/60	25.30	-2.06	-15.69	-0.16
Ls	15.07	-0.99	-4.96	-0.26
1 day TFOT Ls	21.29	-1.43	-10.00	-0.12
Gr	14.83	-0.93	-4.60	-0.26
1 day TFOT Gr	20.70	-0.92	-7.67	-0.09
Gs	14.29	-0.95	-4.22	-0.27
1 day TFOT Gs	21.04	-1.67	-10.34	-0.13
OPC	14.69	-1.05	-4.67	-0.27
1 day TFOT OPC	20.95	-1.80	-10.76	-0.17

Appendix C

Table Appx C.1: Maron-Pierce's Model

Material	G_b	G_m	ϕ_2	ϕ_m	G_m/G_b predicted	G_m/G_b	SSE
Limestone	19700	19700	0.000	0.555	1.000	1.000	0.000
	19700	43000	0.167	0.555	2.043	2.183	0.004
	19700	60100	0.231	0.555	2.930	3.051	0.002
	19700	79900	0.286	0.555	4.248	4.056	0.002
				$\phi_m =$	0.555	$\Sigma =$	0.008
Granite	19700	19700	0.000	0.766	1.000	1.000	0.000
	19700	37000	0.167	0.766	1.928	1.878	0.001
	19700	51005	0.231	0.766	2.665	2.589	0.001
	19700	75300	0.286	0.766	3.694	3.822	0.001
				$\phi_m =$	0.5956	$\Sigma =$	0.003

Table Appx C.2: Nielsen's Model

Mat erial	G_b = M_1	G_{mastic} = G_c (MPa)	G_c/G_b	φ_2	B	C	A	M_c / M_1 (predic ted)	M_c/M_1 (measur ed)	SSE
Limestone	19700	19700	1.000	0.000	0.000	2.101	4.242	1.000	1.000	0.000
	19700	43000	2.183	0.167	1.000	2.101	4.242	2.203	2.183	0.000
	19700	60100	3.051	0.231	1.000	2.101	4.242	3.010	3.051	0.000
	19700	79900	4.056	0.286	1.000	2.101	4.242	4.075	4.056	0.000
					A =	4.24	$\varphi_m =$	0.49	$\Sigma =$	0.000 3
Granite	19700	19700	1.000	0.000	0.000	2.893	2.074	1.000	1.000	0.000
	19700	37000	1.878	0.167	1.000	2.893	2.074	1.787	1.878	0.002
	19700	51005	2.589	0.231	1.000	2.893	2.074	2.404	2.589	0.005
	19700	75300	3.822	0.286	1.000	2.893	2.074	3.331	3.822	0.017
					A =	2.07	$\varphi_m =$	0.44	$\Sigma =$	0.024 0

Table Appx C.3: Krieger-Dougherty's Model

Material	G_b	G_m	φ_2	φ_m	K_E	G_m/G_b (Predicted)	G_m/G_b (measured)	SSE
Limestone	19700	19700	0.000	0.468	3.394	1.000	1.000	0.000
	19700	43000	0.167	0.468	3.394	2.012	2.183	0.006
	19700	60100	0.231	0.468	3.394	2.943	3.051	0.001
	19700	79900	0.286	0.468	3.394	4.472	4.056	0.011
		$K_E =$	3.394		$\phi_m =$	0.468	$\Sigma =$	0.018
Granite	19700	19700	0.000	0.462	3.006	1.000	1.000	0.000
	19700	37000	0.167	0.462	3.006	1.861	1.878	0.000
	19700	51005	0.231	0.462	3.006	2.615	2.589	0.000
	19700	75300	0.286	0.462	3.006	3.811	3.822	0.000
		$K_E =$	3.006		$\phi_m =$	0.462	$\Sigma =$	0.000

Table Appx C.4: Mooney's Model

Material	G_b	G_m	φ_2	φ_m	K_E	G_m/G_b (Predicted)	G_m/G_b (measured)	SSE
Limestone	19700	19700	0.000	0.807	3.321	1.000	1.000	0.000
	19700	43000	0.167	0.807	3.321	2.009	2.183	0.006
	19700	60100	0.231	0.807	3.321	2.925	3.051	0.002
	19700	79900	0.286	0.807	3.321	4.345	4.056	0.005
		$K_E =$	3.321	0	$\phi_m =$	0.807	$\Sigma =$	0.013
Granite	19700	19700	0.000	0.746	2.887	1.000	1.000	0.000
	19700	37000	0.167	0.746	2.887	1.858	1.878	0.000
	19700	51005	0.231	0.746	2.887	2.623	2.589	0.000
	19700	75300	0.286	0.746	2.887	3.805	3.822	0.000
		$K_E =$	2.887		$\phi_m =$	0.746	$\Sigma =$	0.000

Table Appx C.5: Chong's Model

Material	G_b	G_m	φ_2	φ_2	G_b	G_m	ϕ_2	SSE
Limestone	19700	19700	0.000	0.485	5.661	1.000	1.000	0.000
	19700	43000	0.167	0.485	5.661	1.555	2.183	0.083
	19700	60100	0.231	0.485	5.661	2.538	3.051	0.028
	19700	79900	0.286	0.485	5.661	4.664	4.056	0.023
		$K_E =$	5.661		$\varphi_m =$	0.485	$\Sigma =$	0.133
Granite	19700	19700	0.000	0.395	3.000	1.000	1.000	0.000
	19700	43000	0.167	0.395	3.000	1.397	2.183	0.129
	19700	60100	0.231	0.395	3.000	2.206	3.051	0.077
	19700	79900	0.286	0.395	3.000	4.478	4.056	0.011
		$K_E =$	3.000		$\varphi_m =$	0.395	$\Sigma =$	0.217

Table Appx C.6: Robinson's Model

Material	G_b	G_m	φ_2	φ_m	G_m/G_b (Predicted)	G_m/G_b (measured)	SSE
Limestone	19700	19700	0	0.525	1	1	0
	19700	43000	0.166	0.525	2.198	2.182	4.92E-05
	19700	60100	0.230	0.525	3.019	3.050	0.000107
	19700	79900	0.285	0.525863	4.071914	4.055	1.57E-05
		$K_E =$	4.910	$\phi_m =$	0.525	$\Sigma =$	0.000172
Granite	19700	19700	0	0.418	1	1	0
	19700	37000	0.166	0.418	1.866	1.878	3.9E-05
	19700	51005	0.230	0.418	2.608	2.589	5.62E-05
	19700	75300	0.285	0.418	3.813	3.822	5.82E-06
		$K_E =$	3.130	$\phi_m =$	0.419	$\Sigma =$	0.000101

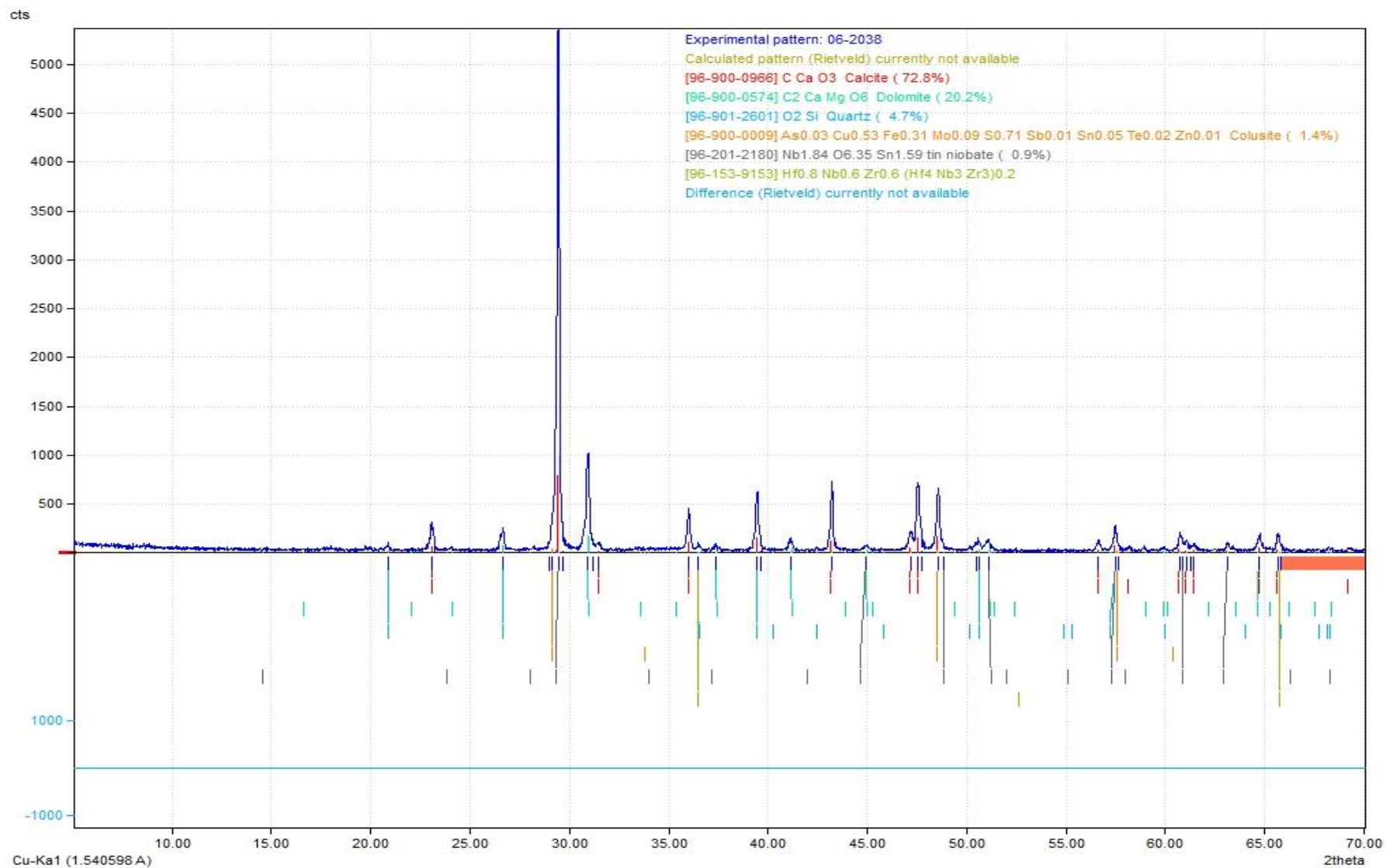


Figure Appx C.1: X-ray Diffraction analysis of limestone filler

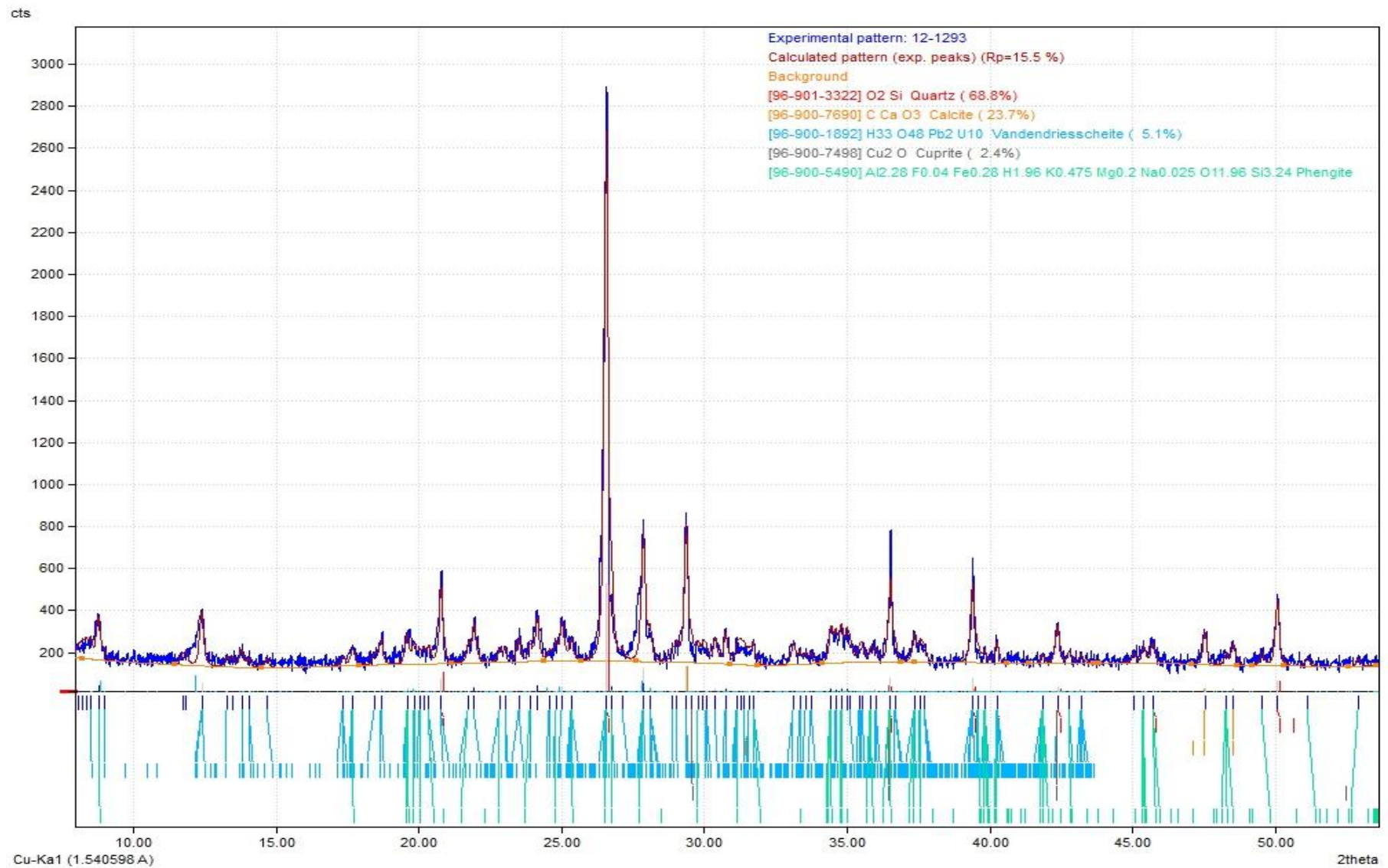


Figure Appx C.2: Diffraction analysis of granite filler

Appendix D

Procedure for Pull off testing (Method 1)

- Take out the pair of plates from conditioning cabinet and carefully remove the four rods at each corner of the pair of plates.
- Place the pair of plates in between the top and base plate of the rigid testing rig and secure the test setup by inserting and tightening the bolts.
- Attach the universal joint attachment to the test setup by fastening to the top plate of the rigid testing rig.
- Turn on the hydraulic pump and INSTRON servo hydraulic frame.
- Set the test cabinet of the INSTRON servo hydraulic frame to the required test temperature.
- Place the test setup (i.e. pair of plates, rigid testing rig and universal joint attachment) on hydraulic ramp (i.e. lower part) of the INSTRON servo hydraulic frame and secure the position using two carver clamps.
- Follow the following procedures for operating the built-in software of the INSTRON servo hydraulic frame. (Note: To be used as guidelines only and might vary depending on the version and types of the built-in software).
 - Select Icon Rubicon.
 - Click Run > Click Start Manual > Select Stroke > Click OK.
 - Press the up symbol on the controller attached to the INSTRON servo hydraulic frame (Note: Enable manual control for the movement of up and down of hydraulic ramp (i.e. lower part) of the INSTRON servo hydraulic frame).
 - Adjust the position of the hydraulic ramp to enable the universal joint attachment to be fastened to the upper part of the INSTRON servo hydraulic frame.

- Ensure that hydraulic ramp (i.e. lower part) of the INSTRON servo hydraulic frame has sufficient space (i.e. at least 10 mm) to allow movement during testing.

(Note: Condition the test setup (i.e. pair of plates, rigid testing rig and universal joint attachment) in the test cabinet of the INSTRON servo hydraulic frame for at least 15 minutes prior to testing)

- Click Command > Click Ramp > Click 1
- Input as follows:
 - Control Mode: Stroke
 - End point: +10.000 mm
 - Checkbox Relative
 - Rate/Time: (Insert the required deformation rate)
 - Next: Manual
 - Profile: Linear
 - Checkbox Maxima > Checkbox Minima
 - Targets 1: If REL STROKE $\geq$ +10.000 then FREEZE
 - Targets 2: If ABS LOAD $\geq$ +20.000 kN then FREEZE
- Click Overview (Note: Ensure that all parameters are correctly inserted) > Checkbox Select Ramps (i.e. at the right hand bottom)
- Click Run > Click X-Y Plot
 - Click Finish Logging > YES
 - Click Select Axis > (Select Y= Load) > (Select X=Stroke) > OK
 - Click Save Data Into File > OK (Select destination to save the file)
- Click Start New Test > Click Test Setup > Checkbox Threshold

- Checkbox Load > Load = 500 N
- Checkbox Other Sensor > Stroke = 50 μm
- Click GO > (Are You Ready to Start New Test: YES)
- Once completed, click Finish Logging
- Convert file to ASCII Format
- Re-write file name
- Exit X-Y Plot
- Regain control of the hydraulic ramp

Click Start Manual > Click Stroke

- Testing is now completed. Carefully remove the test setup (i.e. pair of plates, rigid testing rig and universal joint attachment) from the INSTRON servo hydraulic frame.
- Carefully remove the separated pair of plates from the top and base plate of the rigid testing rig.



Ls(17)



Ls(17)5hr



Gr(17)5hr



Ls(17)20hr

Figure Appx D.1: Few failed surfaces of Method 2 (Chapter 6)

Appendix E

Table Appx E.1: Film thickness variability

Method	sample #	stress	Quality of curve	Film Thickness	Max	Mean Film Thickness	Range	SD	COV	Mean - 2 SD	Mean + 2 SD
Operator 1 Method 1	1	1.54	-	0.55	0.74	0.55	0.44	0.13	23.90	0.29	0.81
	2	1.77	Good	0.45							
	3	1.15	Good	0.63							
	4	1.00	-	0.61							
	5	1.28	Good	0.3							
	6	1.06	Good	0.58							
	7	1.13	Good	0.48							
	8	1.03	Good	0.68							
	9	1.18	Good	0.44							
	10	1.12	Good	0.74							
Operator 1 Method 2	11	1.28	Good	0.54	0.63	0.50	0.21	0.06	12.09	0.38	0.63
	12	1.19	Good	0.43							
	13	0.94	Good	0.48							
	14	1.26	Good	0.49							
	15	1.13	Good	0.63							
	16	1.40	Good	0.47							
	17	1.10	Good	0.54							
	18	1.45	Good	0.52							
	19	1.22	Good	0.42							
	20	1.39	Good	0.52							
Operator 2 Method 2	21	1.67	Good	0.51	0.58	0.45	0.33	0.10	21.92	0.25	0.65
	22	1.37	-	0.33							
	23	1.73	Good	0.52							
	24	1.82	Good	0.58							
	25	1.30	-	0.41							
	26	1.26	Good	0.39							
	27	1.54	-	0.55							
	28	1.39	-	0.5							
	29	1.25	-	0.39							
	30	1.24	Good	0.29							
	31	1.15	Good	0.44							
	32	1.03		0.25							
	33	1.44	Good	0.51							
	34	1.55	Good	0.53							
	35	1.15		0.52							
	36	1.54	Good	0.53							

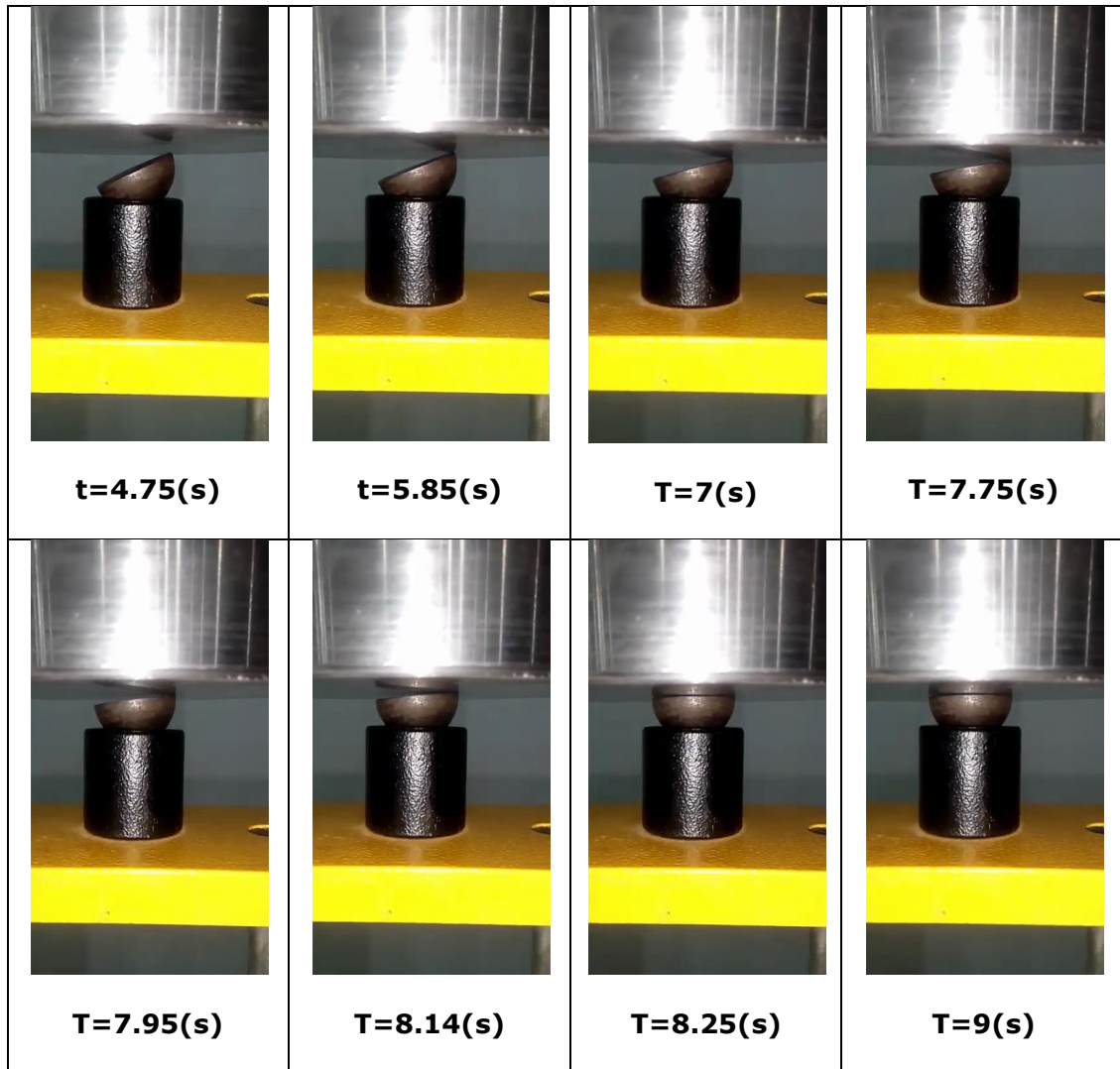


Figure Appx E.1: Seating adjustment in CPOTA

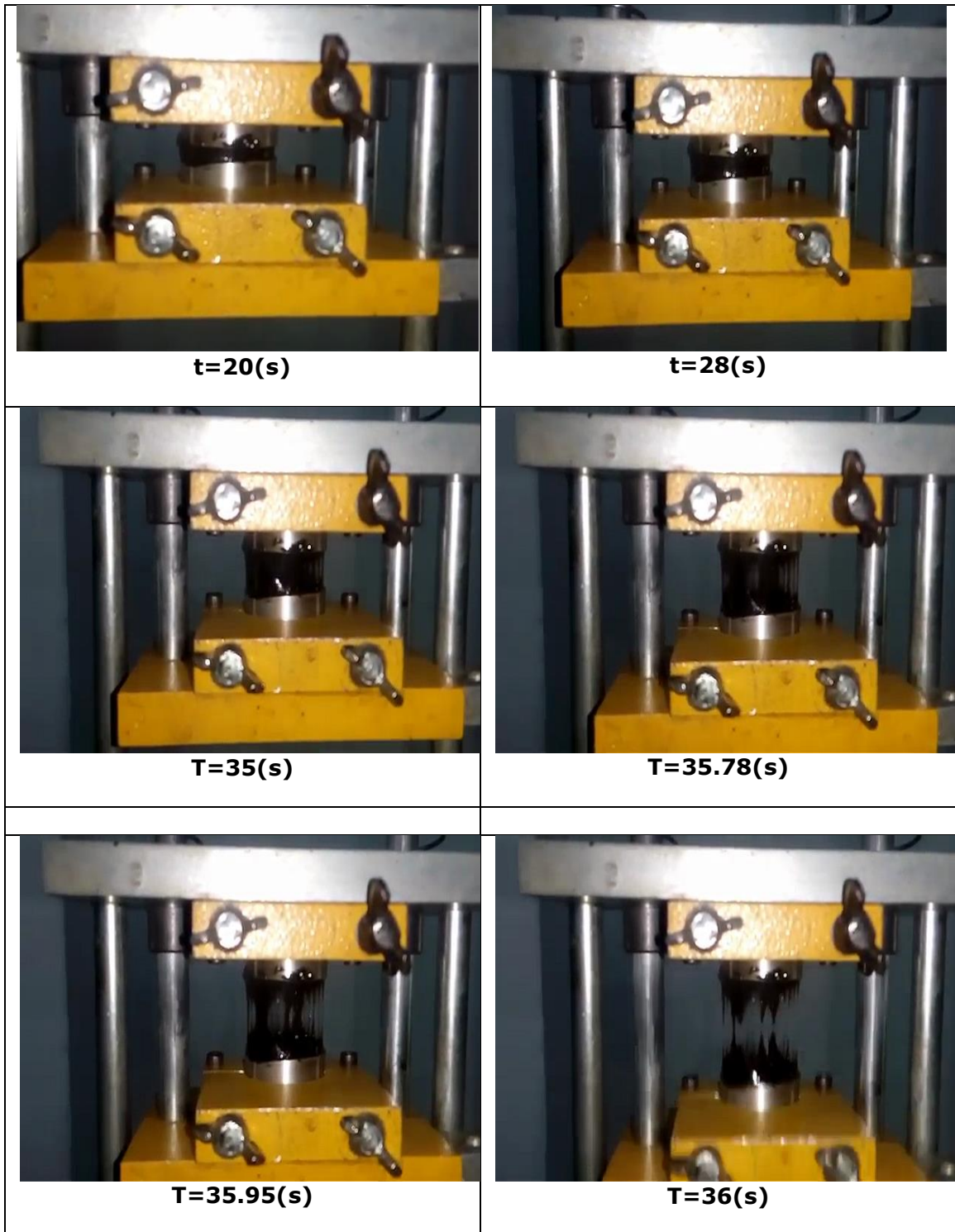


Figure Appx E.2: Ductile Failure and Fibrillar Structure

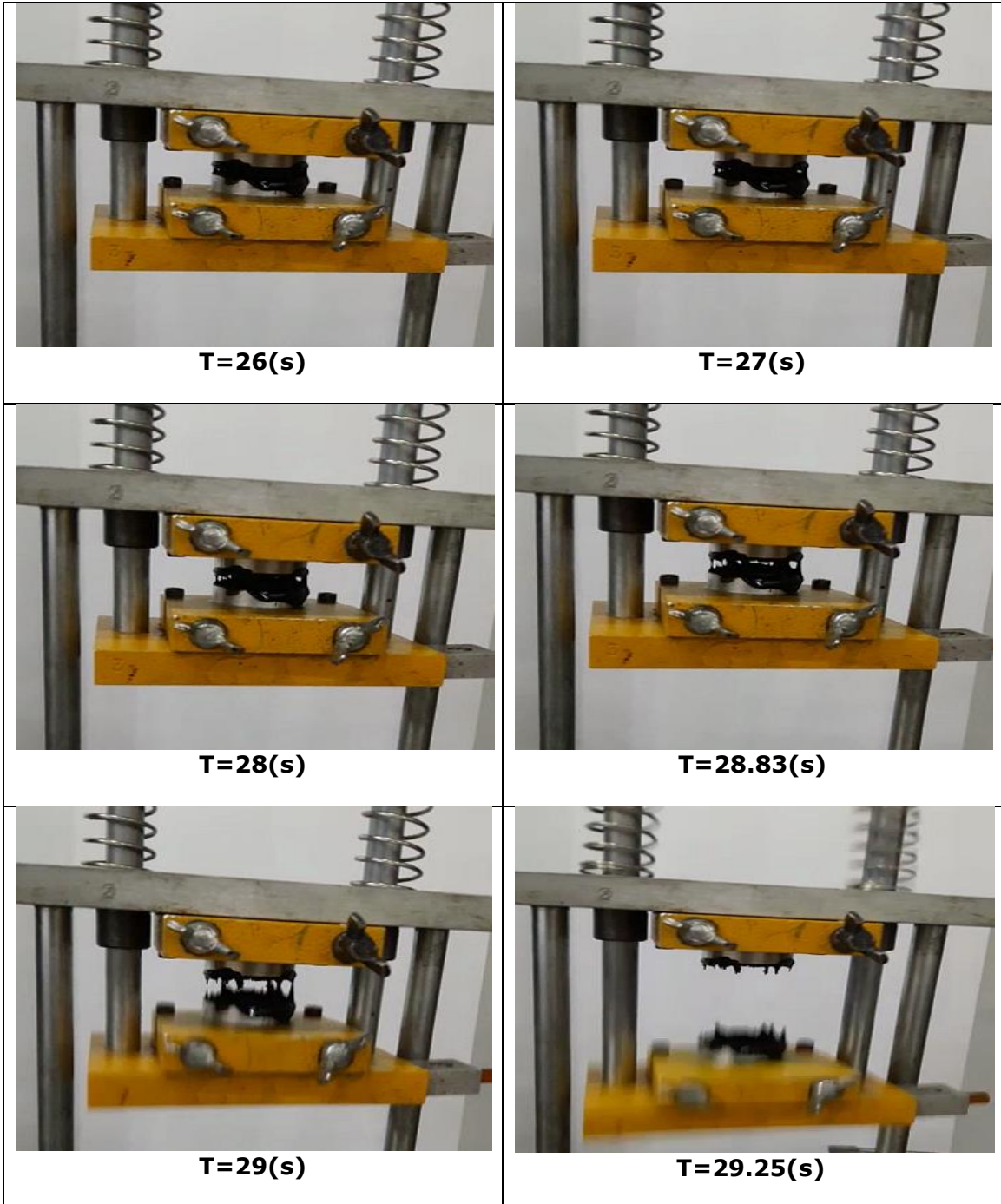


Figure Appx E.3: Brittle Failure

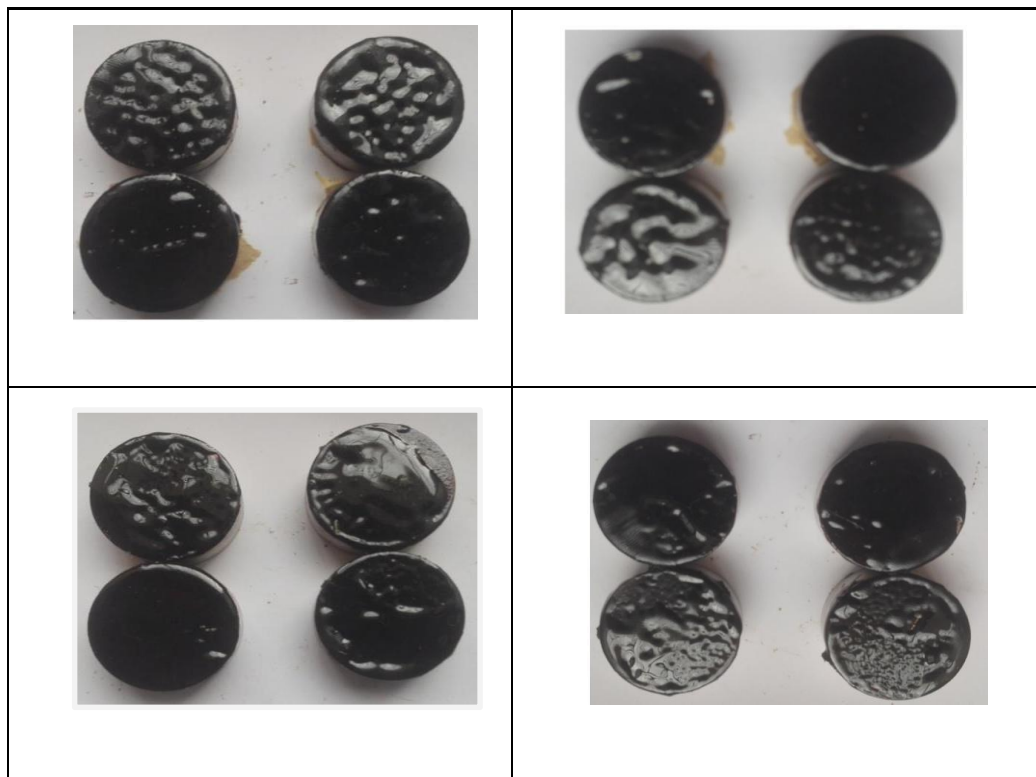


Figure Appx E.4: Drawback of delay in capturing of failed surface

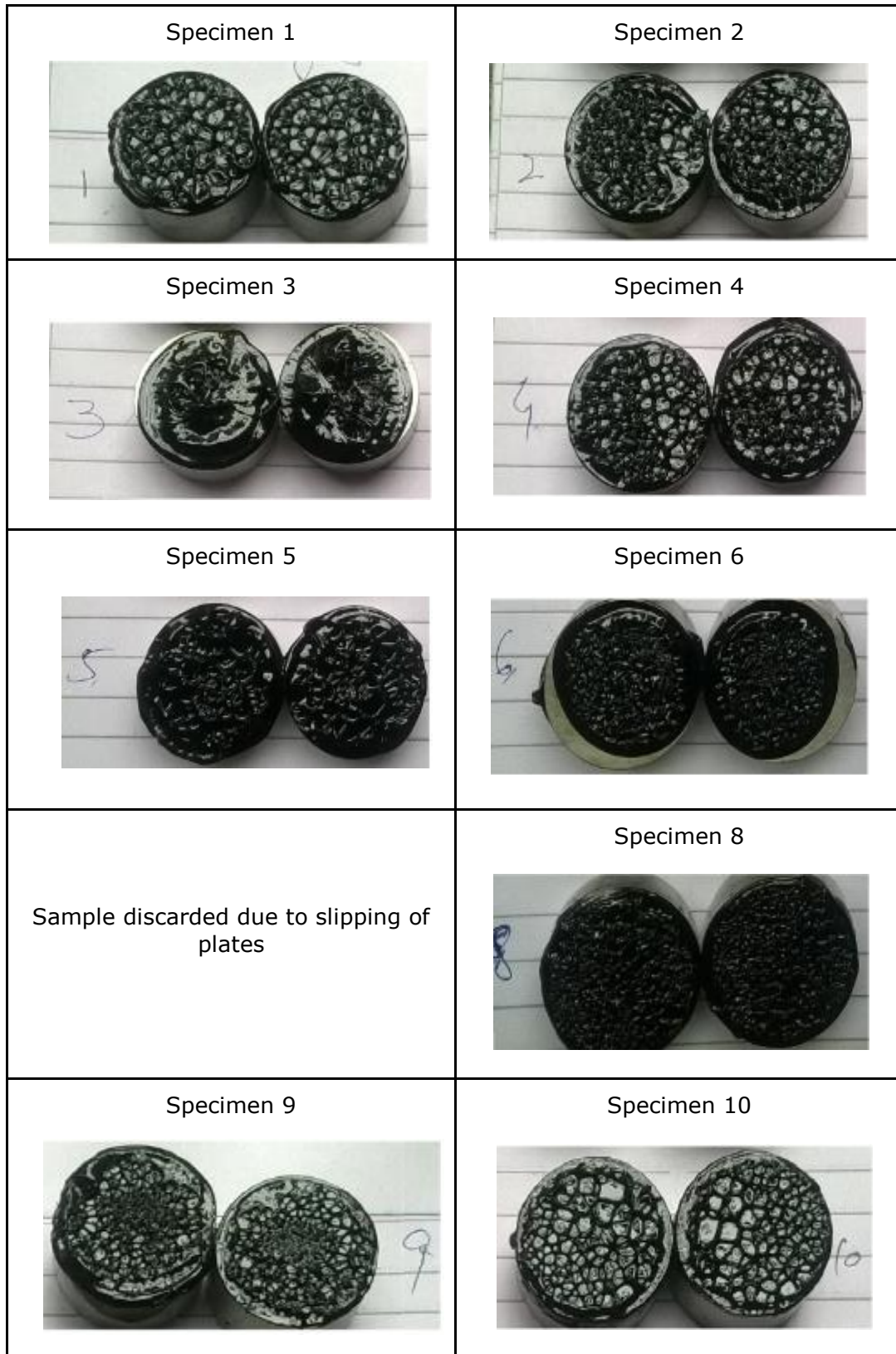


Figure Appx E.5: Failed surfaces of Penetration grade 60/70 (Cavitation)

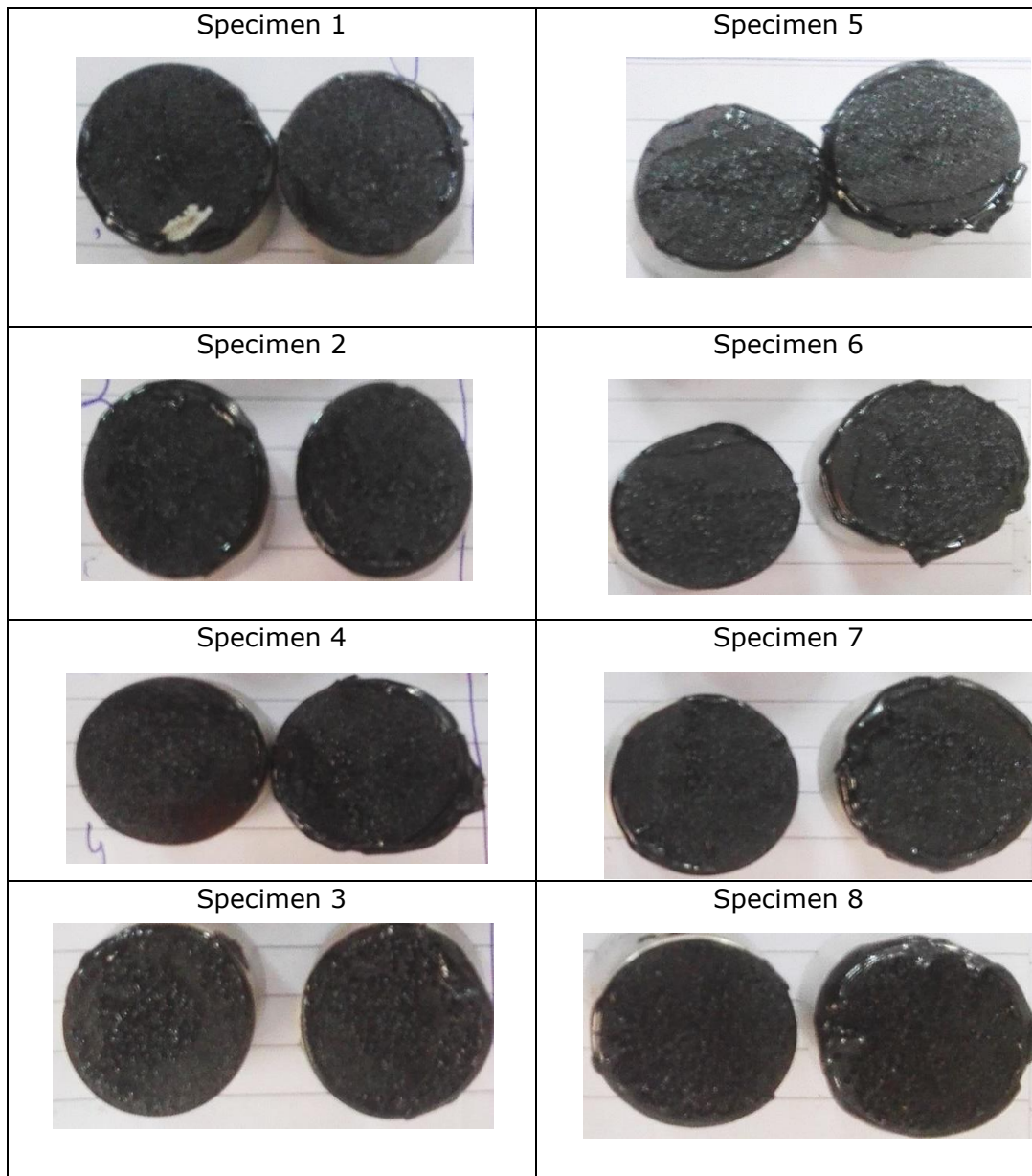


Figure Appx E.6: Failed surfaces of Penetration Limestone mastic (40%)

Sample 12 (Wet) 	Sample 13 (Wet) 
Sample 14 (Wet) 	Sample 15 (wet) 
Sample 16 (dry) 	Sample 17 (wet) 
Sample 18 (dry) 	Sample 19 (dry) 
Sample 20 (wet) 	Sample 21 (dry) 

Figure Appx E.7: RTFOT Ls mastic (40%) in Pen 40/50 of Source 2

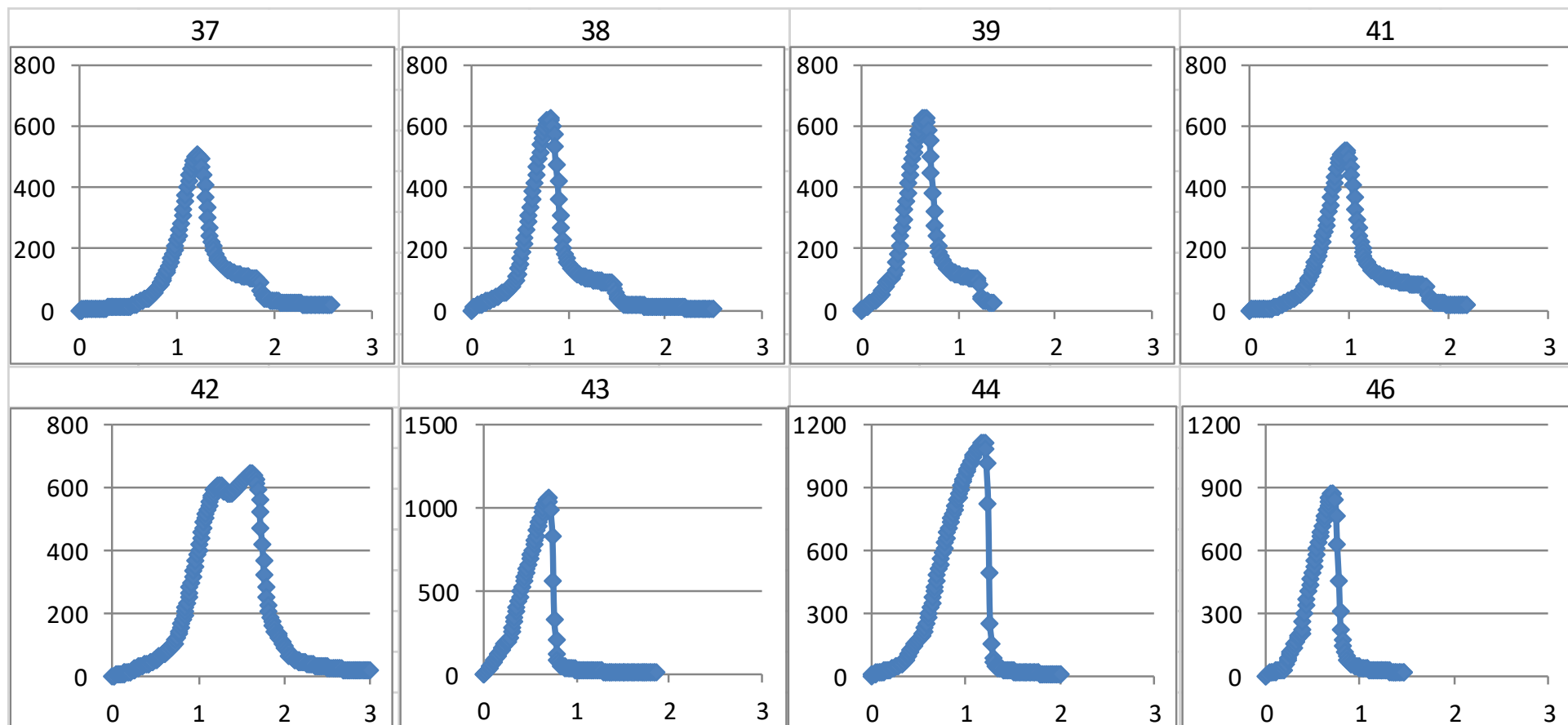


Figure Appx E.8: Load (N) - elongation (mm) curves with Direct Tension Test (ductile and brittle failure)

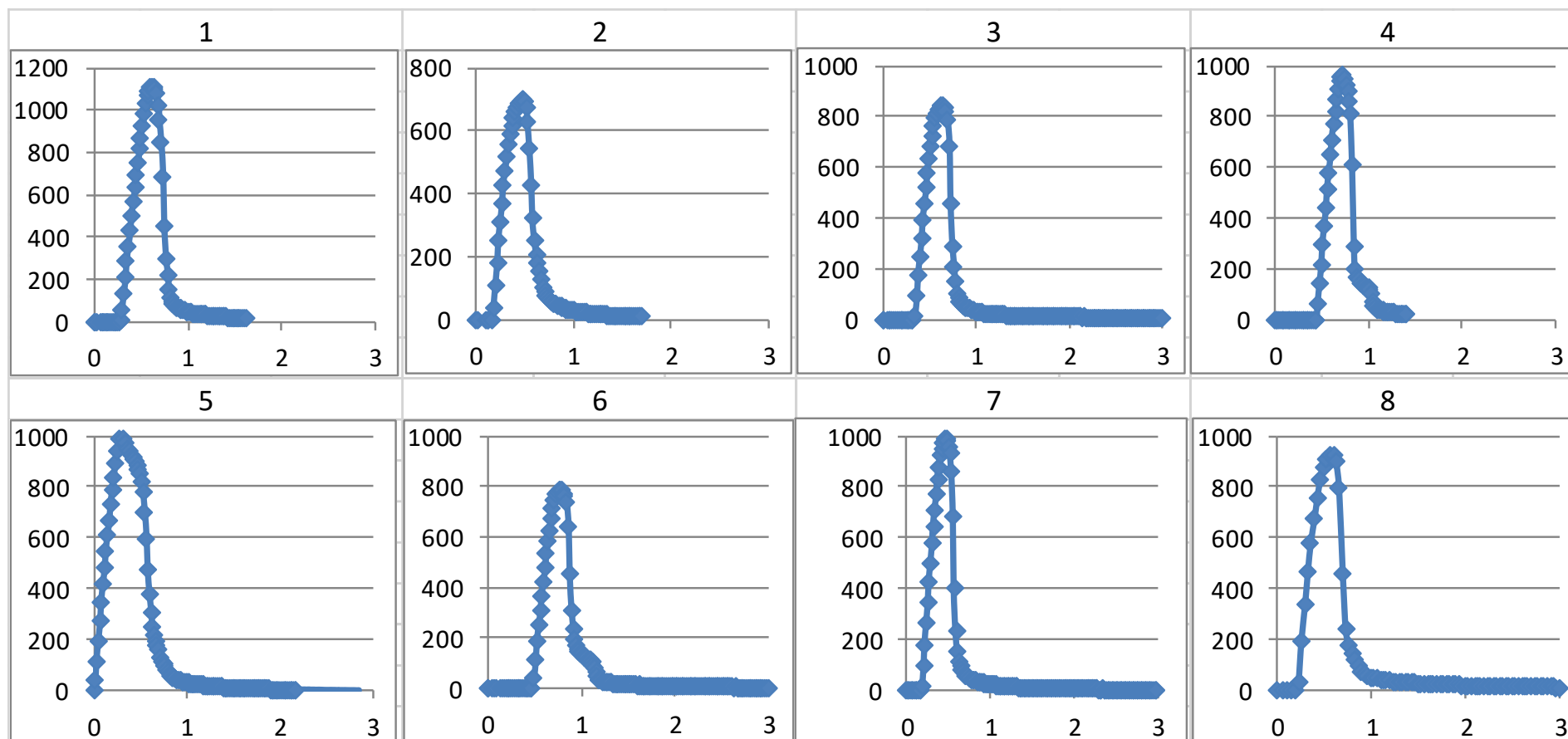


Figure Appx E.9: CPOTA Load (N) - elongation (mm) curves for Ls (40%) Source 2 Pen 40/50