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**INVESTIGATION INTO AGEING AND
THE EFFECT OF HYDRATED LIME ON
MASTICS AND MIXTURE AGEING**

By

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Abstract

Age hardening of bitumen is one of the key factors determining the lifetime of an asphalt pavement. When the bitumen is excessively aged, the asphalt mixture will become brittle and its ability of supporting traffic-induced stresses and strains may significantly reduce, which can easily cause some cracking damage to the bound layer of a pavement. As bitumen is always in contact with mineral fillers in asphalt mixtures, the mechanisms of oxidative ageing of binders are significantly influenced by the physical and chemical interaction between fillers and the bitumen.

For a long while, attempts to solve the ageing problem of asphalt binder by various methods, including polymer modification, nano-particle enhancement or functional improvement have been undertaken. Hydrated lime is one of many potential additives used in bitumen to improve the performance of asphalt mixtures. Hydrated lime in hot mix asphalt creates multiple benefits. A considerable amount of information exists in the literature on hydrated lime's ability to control water sensitivity and its well-accepted ability as an anti-stripping agent to inhibit moisture damage. However, recent studies have shown that lime acts as an active filler and anti-oxidant. These properties create multiple benefits for pavements. Although the majority of research on the use of hydrated lime in asphalt mixtures has been carried out in the USA, the beneficial effects of hydrated lime have also been reported worldwide especially in Europe. In the UK, the use of hydrated lime only started in the early 2000's and still needs a lot of research into its effect on the traditionally used asphalt materials in the UK pavement industry.

This research primarily focuses on an in-depth investigation of bitumen ageing mechanisms and evaluation. Furthermore, this research aims to investigate the

advantages of using hydrated lime to mitigate ageing in bitumen mastics and asphalts mixtures as a whole.

The full project has been broken down into three parts. The first is a pure bitumen study, the second is a mastic level ageing study and the third is a mixture level ageing investigation. The bitumen ageing study investigated the effect of different ageing methods and parameters on bitumen ageing. In addition, this study focused on the mechanisms and factors affecting bitumen ageing and attempted to develop a better understanding of ageing evaluation methods with different perspectives; basic properties, mechanical and rheological behaviour using a dynamic shear rheometer (DSR) and finally a chemical approach with Fourier transform infrared (FTIR).

The second level is the mastics level, which investigated the effect of different fillers on bitumen-filler mastic ageing. Particular attention was paid to study the benefits of using hydrated lime on ageing mitigating in the mastic phase. Furthermore, a detailed study at the mastic level was conducted to investigate the effect of hydrated lime on stiffening and ageing mitigation of bitumen mastics. Different means to evaluate this effect were implemented involving both physical and chemical properties. The evaluation testing was aimed at developing a better understanding of hydrated lime anti-oxidant effects on ageing mitigation. Moreover, special attention was paid to the interactions between hydrated lime and bitumen which affects the ageing of bitumen mastics.

The third level was the mixture ageing level. In this study, the effect of hydrated lime replacement of the natural aggregate fillers was investigated. This effect on the asphalt mixtures was investigated by different tests on their mechanical properties such as indirect tensile stiffness modulus (ITSM), indirect tensile strength (ITS) and their fracture properties using the semi-circular bending (SCB) test. Furthermore, the effect of ageing on the recovered bitumen was evaluated.

The results and conclusions from the performed studies indicate that hydrated lime slows down bitumen ageing more than granite and limestone fillers. This effect depends mainly on the bitumen type and filler concentration. In addition, the research showed that hydrated lime interacts differently with the different bitumens used in this study. This interaction affects stiffening and ageing properties of mastics and mixtures. Furthermore, results show that different ageing indices used in this project correlated well with each other and also with chemical changes.

The detailed results from the FTIR tests on recovered fillers and bitumen from the mastics, showed the ability of hydrated lime to adsorb some of the bitumen components such as carboxylic acid products. This mechanism reduces the formation of ageing products and consequently reduces the age hardening of mastics and asphalt mixtures. Unlike hydrated lime, granite filler does not exhibit this ability to react with bitumen.

Dedication

To my Parents for their unlimited love, inspiration, sacrifices and prayers. . . .

To all my brothers and sisters for their help, support and encouragement. . . .

To all my family and friends in Palestine for their friendship

I dedicate this work hoping that I made all of them proud. . . .

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Rami,

January 2018

Declaration

The research described in this thesis was conducted at the Nottingham Transportation Engineering Centre, Civil Engineering Department, the University of Nottingham between February 2014 and December 2017. I declare that the work is my own and has not been submitted for a degree from another university.

RAMI MOHAMMED S. ALFAQAWI

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List of abbreviations

BBR	Bending Beam Rheometer
C=O	Carbonyl Group (C=O)
DSR	Dynamic Shear Rheometer
FM	Fineness Modulus
FTIR	Fourier Transform Infrared
G	Granite
HL	Hydrated Lime
ITS	Indirect Tensile Strength
ITSM	Indirect Tensile Stiffness Modulus
LS	Limestone
MBV	Methylene Blue Value
PAV	Pressure Ageing Vessel
PSD	Particle Size Distribution
RTFOT	Rolling Thin Film Oven Test
RV	Rigid Voids
S=O	Sulfoxide Group (S=O)
SCB	Semi-Circular Bending
SEM	Scanning Electronic Microscopy
SSA	Specific Surface Area
TFOT	Thin Film Oven Test
TTSP	Time-Temperature Superposition Principle
WLF equation	The Williams, Landel And Ferry Equation

Chapter 1: Introduction

1.1 Overview and research motivation

The motorway and trunk road system in England consists of more than 30,000 miles. In the year 2013 local authorities in England and Wales allocated a budget of £2.9 billion for road maintenance and rehabilitation of this huge infrastructure which was 15% more compared to the previous years ([ALARM,2013](#)). Increasing traffic volumes and heavier vehicle loads have led to the accelerated wear of pavement structures resulting in increased maintenance and rehabilitation expenditure. From highway agencies' perspectives, the goal of road planning, construction and maintenance is to maximise the value of road investment. This is often equivalent to minimising the total amount of the agencies' construction and maintenance costs. For heavily trafficked roads the social costs of road closure for reconstruction and maintenance are so high that a long-life pavement is often desired. In the United Kingdom (UK), 40 years pavement design life is believed to be the most economical for highways. These pavements, are constructed with thick bound layers built upon good foundations and are expected to maintain their structural integrity for 40 years, if surface distress can be treated in a timely manner ([UK Highways Agency,2013](#)). If the magnitudes and configurations of traffic loads, climate conditions, and material properties are provided, a proper combination of thickness and mixture types can be designed to meet the limits for tensile or compressive strain requirements. However as an organic material, bitumen in asphalt mixtures is likely to undergo significant changes during its long service life. The most noticeable change is oxidative ageing. As bitumen ages, its stiffness will increase and its ductility will decrease, making it susceptible to embrittlement and cracking. Although such changes are closely related to the

mechanistic behaviour and performance of asphalt mixtures, they often receive little consideration in long life pavement design ([Yuhong et al.,2014](#)).

The ageing of bituminous binders is one of the key factors determining the lifetime of an asphalt pavement. Excessive bitumen ageing will significantly influence the durability of bituminous mixtures. When the bitumen is excessively aged, the asphalt mixture will become brittle and its ability to support traffic-induced stresses and strains may significantly reduce, which can easily cause cracking damage to the bound layer of a pavement. It can also weaken the adhesion between the bitumen and aggregate, resulting in loss of materials at the surface layer ([Wu,2009](#)). The process of ageing involves chemical and/or physical property changes that usually make bituminous materials harder and more brittle, thus increasing the risk of pavement failure. The ageing-related pavement failure modes include cracking (thermal or traffic induced) and ravelling. Cracks on a pavement surface may increase ageing of the binder because of increased exposure area to atmospheric oxygen ([Lu et al.,2008](#)).

In general, bitumen ageing takes place in two stages, short-term ageing at high temperature during asphalt mixing, storage and paving, and long-term ageing at ambient temperature in service. In bitumen ageing, two types of mechanism are involved, the main ageing mechanism is an irreversible one, characterised by chemical changes of the binder, which in turn has an impact on the rheological properties. This process includes oxidation, loss of volatile components and exudation of oily components from the bitumen into the aggregate. The second mechanism is a reversible process called physical hardening. Physical hardening may be attributed to molecular structuring, i.e. the reorganisation of bitumen molecules (or bitumen microstructures) to approach an optimum thermodynamic state under a specific set of conditions.

For a long while, attempts to solve the ageing problem of asphalt binder by various methods, including polymer modification, nano-particle enhancement or functional improvement have been undertaken. Through these methods, various anti-ageing

additives have been used such as ultraviolet (UV) absorbers, antioxidants and combinations of these ([Lerfald and Horvli,2003](#); [Wu,2009](#); [Apeagyei,2011](#); [Iwański and Mazurek,2013](#); [Cong et al.,2014](#)).

Hydrated lime is one of many potential additives used in bitumen to improve the properties and the performance of asphalt mixtures. Hydrated lime in hot mix asphalt (HMA) creates multiple benefits. A considerable amount of information exists in the literature on hydrated lime's ability to control water sensitivity and its well-accepted ability as an anti-stripping agent to inhibit moisture damage. However, recent studies demonstrate that lime also generates other effects in HMA. Specifically, lime acts as active filler, anti-oxidant, and as an additive that reacts with clay fines in HMA. These mechanisms create multiple benefits for pavements. Thus, studies investigating the beneficial effect of hydrated lime to mitigate the ageing in asphalt pavement are still being performed ([Lesueur et al.,2016](#); [Kakade et al.,2016](#); [Gundla et al.,2016](#); [Zou et al.,2013](#); [Iwański and Mazurek,2013](#); [Lesueur et al.,2013](#)).

1.2 Problem statement

As a result of long-term operation there is a lowering of surface durability. This loss in durability results in ravelling of surface materials, different types of cracking as well as permanent deformation and a loss of water and frost resistance. The main reason for this is the process of ageing.

Bitumen ageing is mainly caused by the impact of high temperatures during transport and placing of the mixture. It should be noted that the ageing of the bitumen depends on the influence of numerous external factors such as sunlight, temperature change, free oxygen, freezing and thawing cycles, and salts used for winter road maintenance. Changes in the bitumen properties which occur during the ageing process, significantly reduce the surface durability; therefore, many studies have been conducted looking for modifiers and additives to the bitumen

that could reduce the intensity of the ageing process [Plancher et al.\(1976\)](#). One such material may be hydrated lime, which has been known as an additive for asphalt mixtures for a considerable time. However, its impact is not fully recognised, especially on the ageing of asphalt mixtures. With the unique properties of hydrated lime, including particle size and surface energy, it may prove that it is an additive with a unique impact on the rheology and damage mechanics of asphalt mastics.

However, it is scientifically proven that hydrated lime has beneficial effects on the asphalt mixtures used in road construction. This has been studied in depth in the USA where hydrated lime is present in 10% of the Hot Mix Asphalt (HMA) produced each year. Unfortunately, in Europe, the functionalities of hydrated lime are still rather poorly known and thus the use of hydrated lime is less usual.

Therefore the need still exists for developing more effective antioxidant treatments for controlling oxidative hardening in paving asphalts. In order to do so, a comprehensive study to develop a better understanding of the ageing mechanisms, different factors affecting bitumen ageing, and different methods to mitigate it was undertaken. Furthermore, it is of great interest to develop a better understanding of the impact of hydrated lime on asphalt mixture ageing and to compare it to other fillers commonly used in the UK. From this, a better understanding of hydrated lime functionalities and mechanisms in asphalt mixtures is sought.

1.3 Research aim and objectives

The main aim of this research study is to develop a better and deeper understanding of asphalt ageing mechanisms and to investigate the advantages of using hydrated lime to mitigate asphalt ageing during its long life service.

In order to achieve the aim of this research, the study has the following objectives:

- To conduct a comprehensive literature review on bitumen ageing, the effect of additives and mineral fillers on ageing of asphalt mixtures and bitumen-filler mastic systems.
- To investigate the mechanisms and factors affecting bitumen ageing. In addition, to understand how to quantify the ageing effect with different ageing indices.
- To investigate the effect of using hydrated lime on the ageing properties and performance of asphalt mixtures and mastics and to quantify this effect.
- To investigate and understand the mechanisms of how hydrated lime affects and mitigates bitumen ageing.

1.4 Thesis structure and outline

This thesis is organised into eight chapters as follows:

- **Chapter 1** is the introduction, where the background to the research topic and the research motivation are presented. Identification of the research problem, objectives, significance and contributions are also included in this chapter.
- **Chapter 2** describes a comprehensive literature review, which is related to the background of the current research; several topics are reviewed in this chapter, including reviews of bitumen ageing and the effect of mineral fillers on the ageing of bitumen mastics and mixtures. Furthermore, this chapter reviews the factors affecting the ageing of bitumen, mastics and mixtures. The ageing indicators used in the past to quantify the ageing effect on bitumen, mastics and mixtures are presented in this chapter.
- **Chapter 3** summarizes the methodology followed to accomplish the objectives of this research project. It also details the characterization of raw materials used in this research study. Particular attention is given to filler characterization. This is important as different filler properties can significantly affect the aging properties of mastics and mixtures.
- **Chapter 4** studies the effect of different ageing methods and parameters on bitumen ageing. This chapter provides ageing principle investigations to be used as a base study to set up the parameters, tests and methods that will be used in the following stages. The effects of different aging methods on bitumen properties are compared and the factors and parameters affecting bitumen aging are investigated in this chapter as well.

- **Chapter 5** investigates the influence of different fillers on bitumen-filler mastic ageing. Furthermore, the effect of using hydrated lime as a replacement for these fillers was further studied in this chapter. Moreover, the effect of hydrated lime on mastic ageing was further investigated with different binders for a better understanding of bitumen-fillers interaction.
- **Chapter 6** focuses on mixture ageing level, where the effect of using hydrated lime on the ageing of asphalt mixtures prepared with different aggregates was evaluated at the mixture level through different tests (ITSM, ITS and semi-circle bending).
- **Chapter 7** provides an extensive detailed study of mastic ageing. Mastics with different fillers with different concentrations were prepared and aged to different ageing levels. A comprehensive detailed testing of mastics was conducted to better understand the interaction between bitumen and different fillers. Furthermore, this chapter investigates the effect of different fillers on mastic stiffening. Finally, the effect of hydrated lime on mastic ageing was investigated to determine the mechanism of aging mitigation that hydrated lime follows.
- **Chapter 8** contains the conclusions and recommendations based on the findings of the study and directions for future work are also suggested.

Chapter 2: Literature Review

2.1 Introduction

This chapter provides a comprehensive literature review, which is related to the background of the current project studies. The first part of this chapter provides a brief introduction to age hardening of bitumen, simulations and the factors affecting ageing. Furthermore, this part discusses the ageing indicators and ageing mechanisms. The following sections summarise the effect of the mineral fillers on the ageing of bitumen mastics and mixtures. The final part focus on the previous attempts that have been made to evaluate the effect of using hydrated lime on mastics and pavement ageing.

2.2 Age hardening in Asphalt Pavements

Hot mix asphalt (HMA), normally known as asphalt pavement, is a composition of materials which are commonly used for the construction of pavements on highways. It is generally a mixture of mineral aggregates (gravel or crushed stones and fillers) that are glued together by a bitumen binder.

Even though the bitumen is constitutes a lower percentage of the asphalt mixture than other components, its characteristics predominantly influence the performance of the whole mixture during its lifetime.

In general, for hot asphalt mixes, mixtures are fabricated by first heating about 5% bitumen by weight up to around 160°C so the bitumen viscosity is decreased then blending it with 95% aggregates.

In common with many other organic materials, bitumen can age harden during the production and service life as a result of the exposure to environmental actions;

these external influences cause it to harden, resulting in a decrease in penetration and increasing viscosity and a hardening in the bitumen, thus increasing the risk of pavement failure over time.

Ageing of bitumen has been known as one of the main reasons for the deterioration of asphalt pavements over time. The ageing process can cause stiffening and hardening of an asphalt mixture, which may result in increased cracking and reduced pavement life ([Petersen,2009](#)).

As a result of compositional changes in the bitumen during the production and its life, age hardening of bitumen occurs. These changes are not well understood, due to the complexity of bitumen, which comprises organic molecules that vary widely in composition for different crudes. In addition, more complications are faced during studying of ageing in the field, which includes uncontrolled variables and unknowns such as mixture characteristics, maintenance treatments, traffic, and climate.

However, many studies have investigated the age hardening of bitumens and asphalt mixtures, which have provided significant advances toward a better understanding of the mechanisms of age hardening ([Scholz,1995](#)).

Among the different mechanisms causing bitumen ageing and hardening, the most important are oxidation and loss of volatile components, which lead to chemical changes in the binder. The other mechanism is a reversible process called physical hardening that can be attributed to molecular restructuring.

2.3 The effect of Ageing on asphalt

As bitumen ages, its stiffness will increase and its ductility will decrease. Thus this makes it more susceptible to embrittlement and cracking. Although such changes are closely related to the mechanistic behaviour and performance of bituminous mixtures, they often receive little consideration in long-life pavement design ([Yuhong et al.,2014](#)). Excessive ageing of the bitumen will significantly reduce

durability, which contributes to various forms of cracking in the bituminous mixture. Cracking generally occurs in the form of fatigue, thermal, or reflective cracking. Fatigue cracking is the result of an accumulation of damage, arising from repeated traffic loading, which with time leads to fracture. Thermal cracking is the result of thermally-induced tensile stresses which exceed the tensile strength of the bitumen. Reflective cracking occurs in mixtures which overlay existing roadways that are cracked. Furthermore, excessive ageing can also weaken the adhesion between the bitumen and aggregate, which leads to loss of materials at the surface layer and thus more severe deterioration in the surface of the bitumen

Generally, the effect of asphalt mixture ageing takes place in two stages, short-term ageing at high temperatures during asphalt mixing and paving, and long-term ageing at ambient temperatures during in-service life.

The first stage called Short-Term Ageing: this stage describes the changes of the bitumen mixture during the mixing process and laying. The first significant hardening of the binder occurs during the mixing when hot bitumen is mixed with the hot aggregate at high temperature. Age hardening of the binder continues, although at a much slower rate, while the hot asphalt mixture is processed and transported to the paving site, laid and compacted. An increase in bitumen viscosity and hardening can be observed by increasing the mixing temperature, which accelerates the rate of bitumen oxidation considerably.

The second stage is the Long-Term Ageing: this stage refers to the oxidation of the bitumen during its service life in the pavement and on the road. Age hardening continues at a slower rate for the first few years of paving. Thereafter, the rate of hardening further decreases until some limiting value is reached.

Bitumen hardening in asphalt surface courses is affected by different factors during service life such as mixture composition, the bitumen thickness and the mix porosity (void content of the mixture) and bitumen properties. Furthermore, the age hardening of asphalt mixture during the service time depends on the local

climate. Therefore, all these involved parameters make it quite complicated to accurately describe and evaluate in-situ ageing.

2.3.1 Factors affecting ageing

The tendency for bitumen to harden during the short and long-term has been studied for many years. (Traxler,1963) identified fifteen different factors, which may influence the chemical, and rheological characteristics of bitumen, these factors are detailed in Table 2.1

He identifies the most important of the composition-related factors that govern the changes that cause the hardening of bitumen in pavements as follows: Oxidation, Volatilisation, Steric or physical factors, Loss of volatiles by exudation.

Table 2.1 Bitumen ageing Mechanisms (Traxler,1963)

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)	✓	✓	✓			✓	
Photo-oxidation (direct light)	✓	✓	✓	✓		✓	
Volatilisation	✓	✓				✓	✓
Photo-oxidation (reflected light)	✓	✓	✓	✓		✓	
Photochemical (direct light)	✓	✓		✓		✓	
Photochemical (reflected light)	✓	✓		✓		✓	✓
Polymerisation	✓	✓				✓	✓
Steric or physical	✓					✓	✓
Exudation of oils	✓	✓				✓	
Changes by nuclear energy	✓	✓			✓	✓	✓
Action by water	✓	✓	✓	✓		✓	
Absorption by solid	✓	✓				✓	✓
Absorption of components at a solid surface	✓	✓				✓	
Chemical reactions	✓	✓				✓	✓
Microbiological deterioration	✓	✓	✓			✓	✓

2.3.1.1 Oxidation

The oxidation of the hydrocarbon components in bitumen is generally accepted as the major cause contributing to the hardening and embrittlement of asphalt mixtures. The reaction of oxygen with bitumen molecules causes the formation of carbonyl species, resulting in larger and more complex molecules that make the

bitumen harder and less flexible. The degree of oxidation is mainly dependent on the temperature, period of exposure and the thickness of the bitumen film.

Hardening due to oxidation has long been held to be the main cause of ageing, to the extent that other factors have been given scant consideration. However, it has been shown that, although other factors are generally less important than oxidation, they are measurable.

2.3.1.2 Volatilisation

Volatilisation is the evaporation of the light fractions from binders and depends mainly on temperature and the exposure conditions. It is usually not a significant factor contributing to long-term ageing in the pavement where the rate of evaporation is controlled by the diffusion rate and the length of the diffusion path. Well-compacted dense asphalt will have a slow diffusion process, therefore, the amount of age hardening that results from evaporation of volatiles is usually small.

2.3.1.3 Steric or physical hardening

Steric or physical hardening is a progressive hardening due to the formation of a structure within the binder over a period of time. This hardening is attributed to a combination of reorientation or restructuring of molecules within the bitumen and the slow crystallisation of waxes. This effect is reversible and can be destroyed too by application of heat.

2.3.1.4 Loss of volatiles by exudation

Separation (exudation) hardening results from the removal of the oily constituents, resins, or asphaltenes from the bitumen caused by absorption into some porous aggregates.

2.4 Ageing indicators

2.4.1 Bitumen ageing indicators

As bitumen ages in the field during its service life or in the laboratory, some bitumen properties are changed. The changes that the bitumen undergoes during short and long-term ageing can be quantified by means of different ageing indicators.

Ageing is normally evaluated by comparing some rheological or chemical property before and after ageing. This is commonly expressed and quantified by means of an ageing index.

The effect of age hardening of the bitumen can be quantified in terms of penetration, changes in softening point and viscosity.

The ageing index is defined as the ratio of a given binder property after a given level of ageing to that before ageing. Penetration, viscosity and softening point tests are considered the most common empirical tests that are used to evaluate the consistency or hardness of bitumen and bitumen mastics.

The ageing index can be computed based on any asphalt physical property that changes with ageing. Equation 2-1 shows the generic form of the ageing index:

$$\text{Aging index} = \frac{\text{Physical property of aged asphalt}}{\text{Physical property of original asphalt}} \quad \text{Equation 2-1}$$

These ageing indices are usually used to evaluate the susceptibility of bitumen to ageing and are employed in specifications to set a limit to the level of deterioration in pavements. The higher values of the ageing index mean a higher degree of bitumen hardening.

In addition to the general form of an ageing index, the difference in softening point $\Delta R\&B$ before and after ageing has been used to evaluate the extent of hardening according to Equation 2-2

$$\text{Change in softening point } (\Delta R\&B) = T_2 - T_1$$

Equation 2-2

Where:

T_1, T_2 = the softening point before and after ageing, respectively.

The rheological properties of bitumen (complex modulus and phase angle) as a function of frequency can also be used as bitumen ageing indicators ([Bahia et al.,2001](#)). For unmodified bitumen, ageing increases the complex modulus and decreases the phase angle over a range of frequencies, indicating that the aged bitumen shifts viscous characteristics and shows an increase in stiffness

In addition to the changes in physical and rheological properties, many researchers have used the chemical changes developed with ageing as an indicator of bitumen age hardening. The increase in carbonyl and sulfoxide in the bitumen spectrum are the main indicators used to quantify the effect of ageing on the bitumen.

2.4.1.1 Fundamental tests of bitumen

It is essential to characterise binders based on testing methods and parameters that can reliably measure their contribution to resisting external damage within asphalt mixtures. The mechanical properties of bitumen for low, intermediate to high-temperature conditions, have traditionally been characterised using empirical methods. For example, Fraass breaking point, capillary viscosity, and softening point have been used to identify the low, intermediate and high in-service temperature properties, respectively. However, the empirical nature of those tests has resulted in many cases of failure to establish a good correlation between these conventional, empirical binder properties and asphalt mixture or pavement performance. In addition, these tests do not provide sufficient information about the physical and rheological properties for modified bitumens. Therefore, using more fundamental engineering properties for characterising bituminous binders has increasingly been needed to reliably predict pavement performance ([Airey and Brown,1998](#); [Airey,2002](#)). Thus, fundamental tests have been introduced to

investigate mechanical properties and viscoelasticity of binders under different environmental conditions. These tests have included Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR). A detailed description of the main elements associated with the DSR is presented below.

Dynamic Shear Rheometer (DSR)

The Dynamic Shear Rheometer (DSR) is a dynamic oscillatory test apparatus that can be used to describe the linear viscoelastic properties of bitumen over a range of temperatures and frequencies. It applies a sinusoidal shear strain to a sample of bitumen sandwiched between two parallel disks as shown in Figure 2-1. The sinusoidal load is normally applied under strain-controlled loading in which a small strain within the linear viscoelastic range is used and the resulting stress is measured. The amplitude of the stress is measured by determining the torque transmitted through the sample in response to the applied strain.

The two principal measurements of the DSR are, torque (T) and angular rotation (θ), the remaining mechanical properties are calculated by using these two parameters.

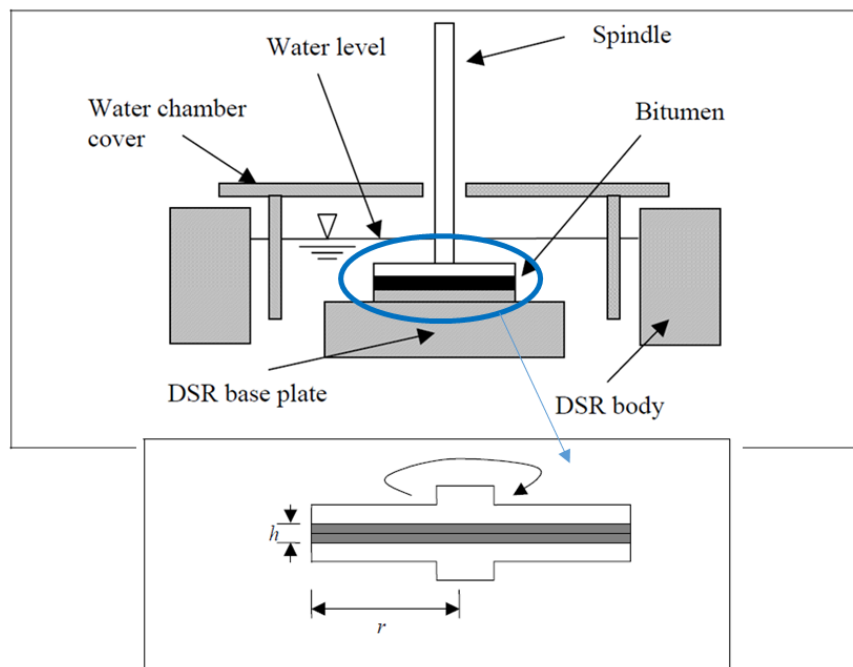


Figure 2-1 DSR testing arrangement and testing geometry

The stress and strain are calculated based on the measured torque and angular rotation as follows:

$$\tau = \frac{2T}{\pi r^3} \quad \text{Equation 2-3}$$

Where,

τ : maximum shear stress (N/ mm²)

T : torque (N.m)

r : radius of the parallel disks (mm)

$$\gamma = \frac{\theta r}{h} \quad \text{Equation 2-4}$$

Where,

γ = shear strain

θ = deflection angle (radians)

h = gap between parallel disks (mm)

Therefore, from the calculation of strain and stress, the absolute complex modulus can be calculated according to the following formula:

$$G^* = \frac{\tau_{max}}{\gamma_{max}} \quad \text{Equation 2-5}$$

The magnitudes of the shear stress and strain are strongly dependent on the geometric properties of the oscillating plate, i.e. radius of the parallel plates and gap between the upper and the lower parallel plates. Therefore, various parallel plate sizes are used in the DSR testing depending on the expected stiffness of materials, to comply with the compliance of the device. Generally, the size of the plate that should be selected to test the sample decreases as the expected stiffness of the sample increases. Plates with smaller radius are normally used at lower testing temperatures while larger radius is used at higher testing temperatures to reliably measure the viscoelastic properties of the bitumen. A number of different parallel plate geometries are used in DSR testing to measure a wide range of

bitumen stiffness. The following different plate sizes are suggested by SHRP-A-369 ([Anderson et al., 1994](#)). However, the proper choice of plate geometry or specimen size should be dictated by the stiffness of the test specimen, rather than temperature.

- Use 8-mm parallel plates with a 2-mm gap, for temperature range 0°C to 40°C, when $0.1 \text{ MPa} < G^* < 30 \text{ MPa}$
- Use 25-mm parallel plates with a 1-mm gap, for temperature range 40°C to 80°C, when $1.0 \text{ kPa} < G^* < 100 \text{ kPa}$.
- Use 40-mm parallel plates, for temperatures $> 80^\circ\text{C}$, when $G^* < 1 \text{ kPa}$

DSR Data Representation

Dynamic shear tests can be performed at different temperatures and frequencies to measure stiffness and phase angle. There are different techniques of data presentation available to represent the results graphically. The most commonly used representative methods are Isochronal Plots, Isothermal Plots and Master Curves.

Isochronal Plot

An isochronal plot is a curve, which represents the behaviour of a system at a constant frequency or loading period. In the dynamic test, the data can be presented over a range of temperatures at a given frequency. This technique has distinctive advantages as it gives a clear idea of the mechanical properties (complex modulus, phase angle) and temperature susceptibility in a single plot with different temperatures. A typical isochronal plot is shown in Figure 2-2.

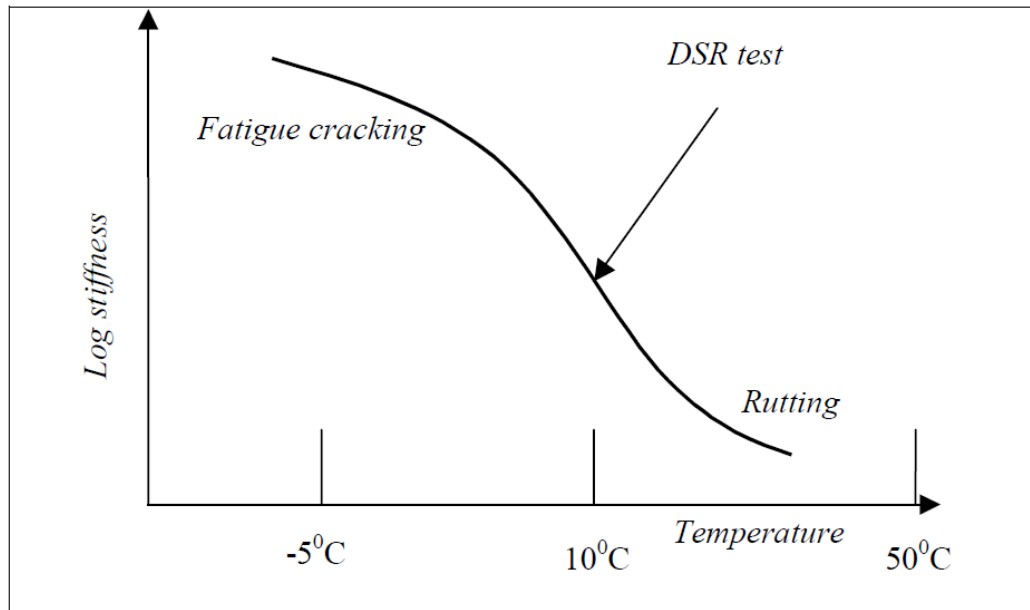


Figure 2-2 Typical isochronal plot for DSR testing data

Isothermal Plot

An isothermal plot or isotherm is an equation, or a curve on a graph, representing the behaviour of a system at a constant temperature. In this type of plot, data at a given temperature is plotted over a range of frequencies or loading durations. The curve can be used to compare different viscoelastic functions at different loading times at a constant temperature. In addition, this type of plot can be used to study the time dependency of the material. As DSR testing is only performed over a limited frequency range, it is impossible to represent a wide range of rheological properties in an isothermal plot. Therefore, master curves are used to extend the data over a wider range of loading times using the Time-Temperature Superposition Principle (TTSP).

TTSP, used in analysing dynamic mechanical data, involves the construction of master curves. Work done by various researchers has found that there is an interrelationship between temperature and frequency (or temperature and loading time) which, through shifting factors, can bring measurements done at different temperatures to fit one overall continuous curve at a reduced frequency or time scale. This continuous curve represents the binder behaviour at a given

temperature for a large range of frequencies. The principle that is used to relate the equivalency between time and temperature and thereby produce the master curve is known as the time-temperature superposition principle.

Master Curves

Master curves are used to present the extended data over a wide range of loading times and frequencies in one graph. In their simplest form, master curves are produced by manually shifting modulus versus frequency plots (isotherms) at different temperatures along the logarithmic frequency axis to produce a smooth curve at one selected reference temperature using a shift factor. The Williams, Landel and Ferry equation (WLF equation), has been widely used to describe the relationship between a_T and temperature. Figure 2-3 describes the shifting process in order to combine the curves into a smooth and continuous master curve.

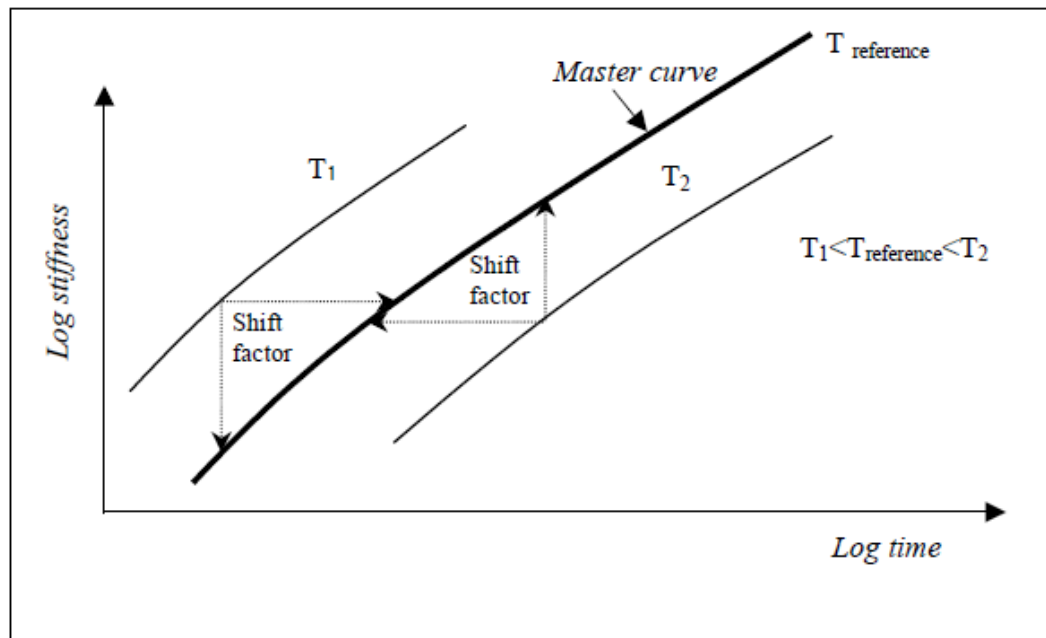


Figure 2-3 Typical isothermal plot and generated master curve

Bitumen characterisation using DSR

The Dynamic Shear Rheometer (DSR) is usually used to characterise the viscous and elastic properties of asphalt binders at high and intermediate service temperatures. The key outputs of DSR are the complex shear modulus G^* and phase angle δ , of bitumen which is measured by applying a small amount of oscillating shear strain or stress within the linear viscoelastic region on a bitumen sample, sandwiched between the fixed steel plate and oscillating spindle.

The shear complex modulus G^* is a measure of material resistance to deformation when subjected to oscillating shear stress and it is equivalent to the magnitude of a vector equal to the square root of the sum of the squares of the viscous modulus G'' and elastic modulus G' as explained in Figure 2-4.

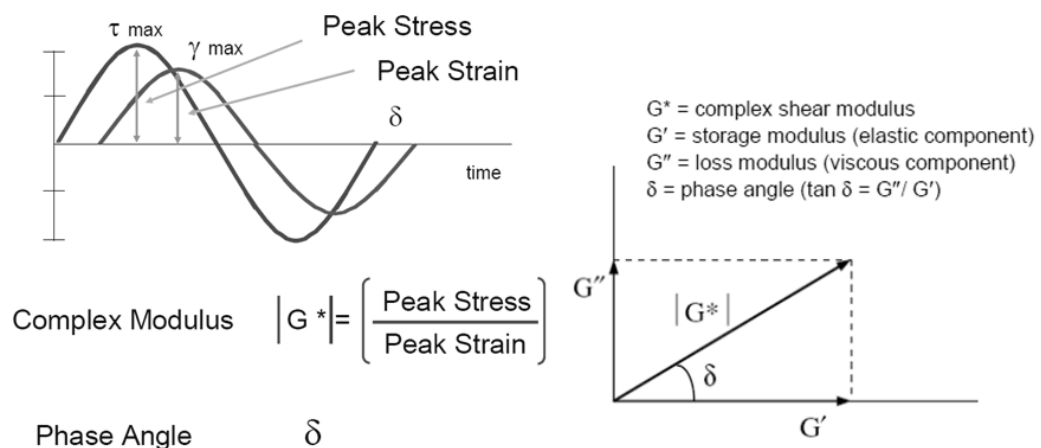


Figure 2-4 DSR oscillatory loading

The phase angle δ is the phase or the lag difference between sinusoidal stress and strain, and it gives an indication of the magnitude of recoverable and non-recoverable deformation. Materials that have 0° phase angle are considered purely elastic where the deformation is fully and immediately recovered after releasing the load, whereas purely viscous materials have 90° phase angle and the deformation is partially recovered as a time-dependent function.

2.4.1.2 Fourier transform infrared (FTIR)

One of the techniques that best describe these chemical changes in the bitumen with ageing is the Fourier transform infrared (FTIR) spectroscopy. This technique is sensitive, easy to apply to bitumen and is able to offer quick reliable information regarding aliphaticity, aromaticity and oxygenation rate happening in bitumen with ageing ([Lamontagne,2001](#)).

Many studies have adopted Fourier transform infrared (FTIR) spectroscopy to characterize the ageing behaviour. FTIR is used to observe the evolution of chemical structures of bitumen as a result of ageing ([Lamontagne,2001](#); [Ouyang et al.,2006](#); [Mouillet et al.,2008](#); [Wu,2009](#); [Marsac et al.,2014](#); [Yang et al.,2014](#)).

The FTIR test consists of exciting the material with Infra-Red light and then quantifying the different types of molecular bonds through characteristic absorption bands in the infra-red light spectrum. Carbonyl groups, characterised by C=O, are among the major functional groups formed during oxidative ageing. It has been demonstrated that the formation of carbonyl (C=O) changes the physical properties of the binder, thus many researchers have used it as an ageing index to quantify the evolution of chemical changes in the binder with ageing.([Lamontagne,2001](#); [Wu,2009](#); [Ouyang et al.,2006](#); [Mikhailenko et al.,2016](#)).

FTIR measurement principles

There are two commonly used FTIR measurement principles: transmission and reflection mode.

In the transmission mode, the infra-red (IR) beam passes through the sample. For bitumen characterisation in this method, it requires a time-consuming preparation of very low thickness bitumen films or may need the use of a solvent. At least 3 sample preparation methods can be used:

- spreading of a hot binder droplet on an IR transparent plate with a spatula,
- spreading of a solution of bitumen on the plate followed by an evaporation of the solvent to obtain a film of bitumen,
- a sample of bitumen solution.

This mode was the first used to characterise bitumen and most of the data reported in the bibliography were obtained in transmission mode ([Marsac et al., 2014](#)).

The other mode is reflection mode: with the attenuated total reflectance (ATR) technique, the beam enters a crystal with high refractive index held in contact with the sample. The beam reflects at the crystal sample interface and penetrates for just a few μm into the sample. After one or more reflections, the radiation is attenuated for the specific wavelengths absorbed by the material. For bitumen, the material must be heated to cast a droplet at the surface of a base plate.

Different methods have been used to quantify the ageing related evolution of bitumen spectrums at the main oxidation products: sulfoxide ($\sim 1,030\text{ cm}^{-1}$) and carbonyl ($\sim 1,700\text{ cm}^{-1}$). In order to overcome the effect of sample thickness and the IR radiation path length, the general principle is to normalise the absorption values obtained for these specific wavenumbers by calculating a ratio of a value obtained at a reference wavenumber which is supposed not to be significantly affected by oxidation ([Marsac et al., 2014](#)).

([Lamontagne, 2001](#)) introduced a spectrometric index calculation method to avoid using spectrum normalisation in FTIR analysis. The functional and structural indexes are then calculated from the band areas measured from valley to valley, based on which, several index types are calculated with band area ratio. Figure 2-5 shows the result for their original bitumen.

They introduce the following indices:

- Aromatic structures (Aromaticity index - $A_{1600}/\Sigma A$);
- Aliphatic structures (Aliphatic index - $(A_{1460} + A_{1367})/\Sigma A$)
- Oxygenated functions (Carbonyl index - $A_{1700}/\Sigma A$, and Sulphoxides - $A_{1030}/\Sigma A$).

The sum of the area represents:

$$\Sigma A = A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}.$$

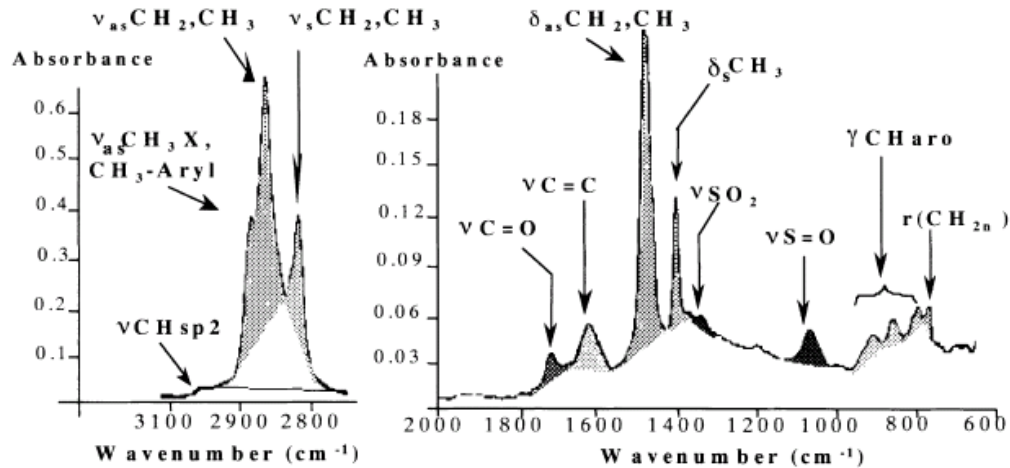


Figure 2-5 FTIR spectrum of a 4000-400 cm⁻¹ original bitumen (Lamontagne,2001)

2.4.2 Mastic ageing indicators

Due to the complex ageing behaviour of bitumen, a unique ageing indicator is not always enough to characterise the ageing behaviour. Ageing of modified bitumen or bitumen mastics should also take into account the effect of ageing on the modifier itself and the change in ageing behaviour.

Many researchers have used an intermediate material such as mastic, in order to better understand the properties of asphalt mixtures. Mastics are a combination of bitumen and fillers, thus the effect of fillers on mastic stiffening and other rheological properties needs to be taken into consideration when mastic ageing is studied.

In general, bitumen ageing indicators (viscosity, penetration, and softening point) can be applied to filler mastic ageing evaluation as well.

(Lesueur et al.,2016) stated that the difference in softening point $\Delta R\&B$ before and after ageing can be used to quantify the extent of age-hardening of the mastic.

They added that however more sophisticated rheological methods and spectroscopic technics such as FTIR could also be used as mastic hardening indicators, the softening point is already a very good indicator of the extent of age-hardening in the mastics.

Furthermore, on a study of ageing of bitumen-filler mastics by ([Wu,2009](#)), pure bitumen and mastics containing different fillers were artificially aged in the TFOT. The effect of ageing on both mastics and pure bitumen was compared using different ageing indices. He used the rheological ageing indices complex modulus and the phase angle for evaluating mastic and bitumen ageing. In addition to that, he used FTIR analysis to detect the influence of the fillers on the chemical changes in the recovered bitumen from the mastics.

In a study by ([Hagos,2008](#)), in order to investigate the effect of bitumen and mastic ageing on the cohesive characteristics of the bitumen, he used the following evaluation mechanisms to characterize the bitumen and mastic properties before and after ageing:

- Dynamic Shear Rheometer (DSR): used to determine the viscoelastic properties – complex modulus and phase angle as a function of frequency
- Gel Permeation Chromatography (GPC) and Attenuated Total Reflectance Infrared Spectroscopy (ATR-FTIR) were used to evaluate the effect of ageing on the molecular size distribution of the bitumen, and to identify the changes in functional groups associated with oxidation respectively.

Therefore, it can be concluded from the previous studies that the same ageing evaluation methods used for pure bitumen can be used as well for evaluation of mastic ageing and to quantify the effect of different fillers and modifiers on ageing.

2.4.3 Asphalt mixture ageing indicators

Mixture assessment techniques mainly deploy the ratio or comparison of resilient modulus of the aged and un-aged specimens. The indirect tensile stiffness modulus (ITSM) is commonly used to evaluate the effect of ageing of the asphalt mixture. The ratio of the aged resilient modulus to the un-aged resilient modulus is usually used as an ageing indicator for asphalt mixtures as shown in *Equation 2-6*

$$\text{Resilient modulus ratio} = \frac{\text{Resilient modulus after ageing}}{\text{Resilient modulus before ageing}} \times 100\% \quad \text{Equation 2-6}$$

Furthermore, the effect of ageing on an asphalt mixture can be quantified by measuring the changes of mixture performance and mechanical properties due to ageing. In a study by ([Hagos,2008](#)), he used the repeated load Indirect Tensile Test (ITT) in order to evaluate the effect of ageing on the mechanical performance of the mixture (strength and resistance to fracture) and to relate mixture performance with properties of the recovered bitumen.

2.5 Ageing Mechanisms

As stated before, significant ageing takes place during the first stage (short-term ageing) when the bitumen is subjected to a high temperature during mixing in an asphalt plant. The short-term ageing of bitumen involves two ageing mechanisms: oxidation and volatilization. Meanwhile the long-term ageing, which represents the hardening of the bitumen during its service period in the pavement and is mainly due to oxidation. The long-term ageing process of an asphalt pavement is significantly affected by the environmental conditions and the characterisation of the bitumen used. The type of asphalt mixture influences the ageing process as well. For example, a higher rate of ageing is expected in a porous asphalt mixture compared to dense asphalt. The reason for this higher ageing in porous asphalt is mainly attributed to the high amount of voids in porous asphalt that allows access

to oxygen and water, resulting in changes in the bitumen properties over the whole thickness within a relatively shorter time.

As a result, considerable rheological changes take place such as a decrease in penetration, and an increase in softening point and viscosity of the bitumen due to the age hardening.

Figure 2-6 presents a general trend for the ageing of dense asphalt mixtures during mixing and transportation (short-term ageing) and during the in-service period (long-term ageing) on the viscosity ratio (viscosity ageing index).

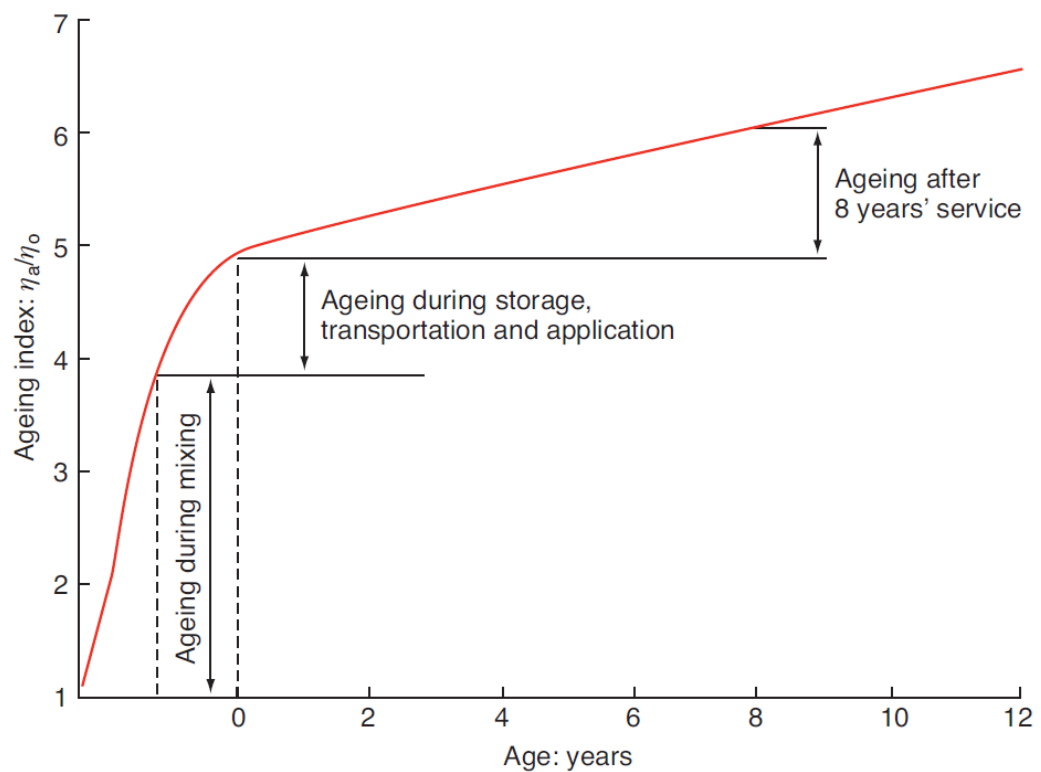


Figure 2-6 Effect of short and long-term ageing of the binder on viscosity ratio with ageing period (Hunter et al.)

2.6 Ageing simulation

Researchers have done numerous investigations over recent years to correlate accelerated laboratory ageing of bitumen with field performance. To simulate the field ageing, the methods involve increasing the temperature, decreasing bitumen film thickness, increasing oxygen pressure, or using combinations of these factors.

Those bituminous materials have to develop into a composition similar to the field aged conditions in order to accurately simulate the ageing happening in the field. Ageing of bitumen artificially in a laboratory depends upon factors and conditions, which could accelerate the oxidation and age hardening. The most important is the rise in temperature, the composition of the atmosphere (air, oxygen) and renewal of the bitumen surface in contact with atmosphere achieved when the bitumen is fluid.

Different types of tests have been developed to simulate field ageing in the laboratory, including conducting of accelerated ageing on pure bitumen, loose asphalt mixture, or on compacted asphalt specimens. Numbers of standard tests already exist to measure the effect of heat and air on bitumen and asphalt mixtures. The main aim of these tests is to identify bitumens that are too volatile or are too susceptible to oxidation to perform well in service. The following subsections present the commonly used standard tests for artificially simulating the ageing of bitumen and asphalt mixtures in the laboratory.

2.6.1 Ageing tests for Bitumen

For bitumen binder, there are three European standardised tests for short-term ageing at high temperatures to simulate ageing particularly during the mixing process in an asphalt mixing plant.

- Rolling Thin-Film Oven Test (RTFOT, [BS EN 12607-1:2014](#)),
- Thin Film Oven Test (TFOT, [BS EN 12607-2:2014](#)), and
- Rotating Flask Test (RFT, [BS EN 12607-3:2014](#)).

For long-term ageing during in-service, laboratory simulation is rather difficult. Ideally, a laboratory test should be able to predict the chemical and physical changes in the bitumen, which developed after many years in the asphalt pavement. This may be achieved by conducting an ageing test under artificially severe conditions, e.g. at temperatures higher than pavement service temperature

and at pressures higher than ambient pressure. Two European standardised long-term ageing tests are:

- Pressure Ageing Vessel (PAV, [BS EN 14769:2012](#)), and
- Rotating Cylinder Ageing Test (RCAT, [BS EN 15323:2007](#)).

Although numerous investigations have been carried out, solid data, especially field data for different types of binders under different climatic conditions, are still not sufficient to prove whether if these laboratory ageing tests are relevant or if natural ageing occurred in the pavement can be properly predicted. It is also believed that ageing of bitumen at a higher temperature may be fundamentally different from ageing at a lower temperature which more accurately simulates pavement temperature.

2.6.1.1 Thin film oven test (TFOT)

The TFOT is a standard bitumen test used for measuring the combined effects of heat and air on a film of bitumen. In this test, a 50g sample of bitumen is aged in the TFOT oven on the TFOT ageing pan. The sample is placed on the TFOT pan to form a thin layer 3.2 mm thick, which is then held in the TFOT oven at 163°C for 5 hours. It is claimed that the amount of hardening that takes place in this test is similar to that which occurs in practice during the plant mixing and placing of bituminous pavement. However, a major criticism of the TFOT is that the thick bitumen film could result in a large volume relative to the exposed surface area at aged bitumen. As the bitumen is not agitated or rotated during the testing period, there was a concern that ageing (primarily volatile loss) may be limited to the surface of the bitumen sample ([Airey,2003](#)).



Figure 2-7 TFOT ageing oven

2.6.1.2 Rolling thin film oven test (RTFOT)

In the RTFOT, eight glass containers each containing 35 g of bitumen are fixed in a vertically rotating shelf. Hot air is blown into each sample bottle periodically (usually when at its lowest position). During the test, the bitumen flows continuously around the inner surface of each container in a relatively thin film at a temperature of 163°C for a period of 75 minutes. The vertical circular shelf rotates at a rate of 15rpm and the air flow is set at a rate of 4000 ml/min. This method can ensure that all the bitumen is exposed to heat and air and continuous bitumen flow can prevent the presence of a skin that may protect the bitumen. Experience has shown that the amount of hardening in this test correlates well with that observed during asphalt pavement production. A TFOT oven is shown in Figure 2-8



Figure 2-8 RTFOT ageing oven

2.6.1.3 Pressure ageing vessel (PAV)

This method is used to simulate long-term field oxidative ageing. It involves hardening of bitumen in the RTFOT or TFOT followed by oxidation of the residue in a pressurised ageing vessel. This procedure involves ageing samples of 50 g of bitumen in a 140 mm diameter pan to form 3.2 mm bitumen film thickness in a heated vessel, pressurised with air to 2.10 MPa for 20h at temperatures ranging from 90 to 110°C. Figure 2-9 shows the PAV apparatus.



Figure 2-9 PAV ageing apparatus

2.6.2 Ageing tests for asphalt mixtures

In addition to artificially ageing pure binders, a number of methods also exist for artificially ageing asphalt mixtures. The basic procedure is to artificially age the mixture and then assess the effect of ageing on key material parameters such as stiffness, viscosity and strength. Extended heating procedures typically expose the mixture to high temperatures for a specified period of time before suitable testing. ([Bell et al.,1994a](#)) describe the methods of mixture ageing so as to simulate both short-term and long-term ageing; that is, ageing which occurs during construction

and ageing which occurs whilst the pavement is in service, respectively. The SHRP short-term oven ageing (STOA) procedure which was developed under the SHRP-A-003A project is based on the work done by ([Von Quintus,1991](#)). The procedure requires loose mixtures, prior to compaction, to be aged in a forced draft oven for 4 h at 135°C (AASHTO PP2). The process was found to represent the ageing occurring during mixing and placing. For long-term ageing of asphalt mixtures in the laboratory, the long-term oven ageing (LTOA) procedures were developed under the SHRP-A-003A project. In this method, the procedure requires that after STOA, the loose material should be compacted in specimens and then placed in a force draft oven at 85°C for 5 days (AASHTO PP2, 1994).

2.7 Ageing mitigation

Researchers have attempted to solve the ageing problem of asphalt binder by various methods, including polymer modification, nano-particle enhancement or different additives. Through these methods, various anti-ageing additives have been used such as ultraviolet (UV) absorber, antioxidant and a combination of them. Published studies concerning the ageing of asphalt binder have tried to simulate the ageing process and study the ageing mechanisms, and some works to improve ageing resistance. The effects of anti-oxidant, anti-ageing materials and UV absorber on the properties of asphalt binder have been investigated in many studies. Several antioxidants have been used in the past to control oxidative hardening in asphalt pavements. Initial laboratory investigations of these antioxidants showed some promise. However, most of these antioxidant systems for retarding oxidative hardening have not performed satisfactorily in the field due to problems such as degradation, volatility, and loss of the antioxidant from the asphalt system. Another problem associated with some of the currently used antioxidants is that their use results in tender mixes since the antioxidants often soften the binder excessively ([Apeagyei,2011](#)). Therefore the need still exists to

develop more effective antioxidants treatments for controlling oxidative hardening in paving asphalts.

However, bitumen is always in contact with fine and coarse mineral particles in the pavement; therefore, the mechanisms of oxidative ageing of bitumen are expected to be influenced not only by the characteristics of the binder but also by the properties of the mineral surface due to the molecular interaction between these two components. ([Moraes and Bahia,2015a](#)) mentioned that testing of aged bitumen alone might not appear to adequately predict the mixture performance as it neglecting the apparent mitigating and/or catalytic effect that mineral filler may have on ageing.

In this context, it comes as a surprise to see that the effect of mineral fillers on bitumen ageing has received only limited attention by researchers ([Lesueur et al.,2016](#)). In fact, some works tend to show that minerals have no effect on bitumen ageing, except for so-called active fillers such as hydrated lime.

In a review conducted by ([Anderson et al.,1994](#)), they reviewed the influence of the interaction of mineral surfaces on the oxidative ageing of bitumen, and concluded that some physicochemical interactions take place at the interface between the bitumen and the mineral aggregate. These interactions may significantly alter the oxidation mechanism and thus change the ageing rate in asphalt pavement. The review also revealed that one of the best techniques for studying this phenomenon is to use the mastics (bitumen and filler).

Mastics are a combination of bitumen and fillers; thus the effect of fillers on mastic stiffening and the other rheological properties needs to be taken into consideration when investigating mastic ageing. According to ([Lesueur et al.,2016](#)), the effect of mineral fillers on bitumen ageing remains controversial.

The effect of mineral fillers on bitumen ageing properties is reviewed in the following section.

2.8 Mineral fillers in bitumen

2.8.1 Mineral filler

The term mineral filler refers to the fraction of the mineral aggregate, which mostly passes the 63 μ m sieve. Many different materials such as limestone dust, volcanic ash, portland cement, mineral sludge, hydrated lime, diatomaceous earth and fly ash, referred to as filler types, can be described in this way. Usually, asphalt mixtures have been designed to include a mineral filler. Different filler types may be used interchangeably, and different quantities of one type may satisfy a single mixture design situation.

Using filler in the mixture is based on three main reasons: stiffening the asphalt mixture, reducing initial cost (by reducing bitumen amount), and improving the asphalt mixture performance. On the other hand, it inversely affects the performance at low temperature due to brittle behaviour, hence, crack initiation at low temperature. Therefore, it is very important to classify filler properties in terms of their importance or influence on the performance of a pavement under a specific condition.

Evaluation of mineral fillers based on their characteristics started with routine tests most of which derived from soil mechanics such as liquid limit and plasticity index. As research on asphalt mixtures progressed with more filler experience, many tests have been developed to provide satisfactory properties related more to asphalt mixtures ([Liao,2007](#)).

Filler characteristics can be classified based on their importance into three groups identified by ([Tunnicliff,1967](#)).

- Primary characteristics: particle size, shape and size distribution.
- Secondary depending on primary characteristics: void content, surface area, average void diameter.

- Secondary mineralogical characteristics: texture, hardness, specific gravity, wettability.

Particle size and shape are fundamental primary characteristics of mineral fillers. A gradation curve is a useful representation of particle sizes. A greater influence on the properties is associated with the shape. For the calculation of asphalt mixture specimen voids ratio, it is essential to determine the specific gravity of fillers. Other properties like density, PH, specific surface area are also good indicator of pavement performance against various types of distress ([Osman,2005](#)).

([Harris and Stuart,1995](#)) pointed out that a single filler property is not sufficient to fully characterise the stiffening effect and be used as a general performance indicator. They mention that the general physical properties of the mineral filler that affect mastic and asphalt mixture properties are:

- Particle size distribution
- Particle density of filler
- Specific surface area
- Voids of dry compacted filler

Void content is itself a function of particle size, size distribution, and shape. Average void diameter and surface area are also a function of void concentration. Therefore, voids content is, at its least, an indirect measurement of these characteristics.

2.8.2 Mineral filler role in bitumen Mastic

Early research programs on filler influence on mastic started by investigating the modified properties of mastic, such as viscosity, softening point, and penetration. Later, researchers investigated the change in rheological properties of mastics by adding different filler types to a particular type of bitumen by means of complex modulus. However, many researchers noticed that the stiffening effect of different fillers varies with binder types. Therefore, more attention is currently being paid to investigating the filler properties, including Rigden voids and particle size

distribution, on the performance of different bitumen mastics ([Taylor and Airey,2008](#)).

([Kavussi and Hicks,1997](#)) tested four types of filler at different concentrations added to the binder and studied their effects on the rheological properties and temperature susceptibility. Results indicated that increasing the filler content reduces temperature susceptibility by reducing the penetration and increasing the softening point. In addition, filler with spherical shape particles had less influence than angular particles. The viscosity also increased by increasing the filler content tested in a rotational viscometer device.

In another study by ([Soenen and Teugels,1999](#)), they investigated bitumen-filler interaction in the DSR. Four different binders were blended with three filler types (quartz, rhyolite, tuff) in their study. The three fillers were similar in their physical properties of density and specific area. Fillers were mixed in three different volume concentrations (30%, 45%, and 55%). Frequency sweep tests in the linear region were performed at 5°C increments. The stiffening effect of mastic was evaluated through the $\left(G^*_{mastic}/G^*_{binder}\right)$ ratio. Results from the test showed that the relative stiffening effect is only dependent on the filler volume concentration but independent of filler type and bitumen origin. They also suggested that the chemical interaction between filler and binder is low regardless of the binder type or bitumen origin.

A project by NCHRP it studied the test methods and specification criteria for mineral filler used in HMA ([Bahia et al.,2011](#)). They investigated the properties of different mineral fillers and after the analysis of these properties and their correlation to each other, based on only two primary geometric indicators (RV and FM) and two primary chemical indicators (CaO% and the MBV) fillers were selected for mastic testing. They evaluated the effects of fillers on mastic and mixture depending on four main characteristics of the filler and mastic workability, rutting, fatigue, low temperature cracking, and moisture damage resistance. They selected

17 fillers for testing in the mastics. The fillers were blended with four different bitumen binders to create a total of 68 mastics. The mastics were produced at a 1:1 mixing ratio of filler to bitumen by mass. It is important to note that although the mastics were produced at a constant mass ratio of filler to binder, the variability in the volumetric fractions was limited to a narrow range of 26% to 32%; this is because the specific gravities of the natural fillers used were very close. To evaluate the effect of filler on mastic workability, viscosity was measured at 135°C using a Brookfield Rotational Viscometer. From the results, they concluded that filler type plays a major role in mastic viscosity for all the bitumens used. They observed that there are similarities in the trends as a function of filler type, which indicates that the influence of filler type on viscosity is more important than bitumen type and bitumen modification. The project also tested the mastic and bitumen rutting resistance which was evaluated using the Multiple Stress Creep and Recovery (MSCR) test. The results for this test showed that addition of any of the fillers increased rutting resistance. This is as expected as addition of fillers causes an increase in stiffness and hence an increase in rutting resistance. Furthermore, they evaluated mastic and bitumen fatigue resistance using the standard fatigue parameter $G^* \cdot \sin \delta$ and fatigue life as determined from a time sweep. Fatigue tests were performed at 25°C using the standard DSR testing procedure. The results showed that all mastics had relative $G^* \cdot \sin \delta$ values above one, indicating that the addition of fillers increases $G^* \cdot \sin \delta$, which is also expected due to the stiffening effect of fillers. However, fatigue life as defined by the number of cycles corresponding to a 50% reduction in initial complex modulus in a strain-controlled time sweep test for the mastic, show that addition of filler to binder has the potential to both increase or decrease fatigue life. Finally, the results from other performed tests showed that both bitumen and filler type affect stiffness of mastics at low temperatures. In a study performed by ([Wang et al.,2011b](#)) the stiffening effects of filler type and content on bitumen performance against rutting and fatigue were evaluated using the DSR. Two fillers (limestone and granite) were

added at two different contents, 25% and 50%. For fatigue performance evaluation, fatigue life was identified as the number of cycles required to reach 50% drop in G^* . For stiffening evaluation, a stiffening power is identified as $(G^*_{mastic}/G^*_{Bitumen})$. The stiffening effect on rutting was evaluated by performing repeated creep recovery. The unrecovered creep compliance at the end of the test was considered as the rutting evaluation parameter. Results from fatigue tests indicated a significant improvement with limestone in comparison with granite. However, only minor improvement was observed when filler content increased from 25% to 50%. Similarly, limestone had less non-recoverable compliance in comparison to granite. On the other hand, increasing filler content from 25% to 50% significantly improved rutting resistance.

From the studies presented above, it can be concluded that the mineral fillers play a significant role that affect the performance of bitumen mastics. This effect depends on both filler and bitumen properties. Thus, many studies still being performed to investigate and quantify the effect of different fillers on bitumen performance by different means. The following section provides a comprehensive review on the effect of fillers on the ageing properties of bitumen mastics and mixtures. a focus on hydrated lime effect on mastic and mixture ageing follows.

2.9 Effect of mineral fillers on bitumen ageing

As mentioned above, in order to study the effect of mineral fillers on bitumen ageing, the best technique is to study it using mastics (bitumen and filler combination). The mastic technique involves mixing mineral fillers with bitumen and ageing them. This technique was used in the late 1940s by researchers to investigate the benefits of using mineral fillers (called, at that time, mineral stabilizers) to prolong the lives of roofing asphalts. However, studies using this technique for ageing paving bitumen are, unfortunately, very scarce ([Anderson et al.,1994](#)).

([Schmidt,1973](#)) was probably the first to try this approach in a study on the durability of paving asphalts. He used the RTFOT to age pure bitumen for 30 minutes at 149°C, followed by 48 hours at 82°C. He concluded that there is a lack of agreement between the laboratory ageing test (RTFOT) and field age hardening which might be partly due to the absence of aggregate surfaces in the laboratory ageing tests. Therefore, he included fillers in a small part of his experiment and tried to study their effects. The results showed that there were changes in the degree of hardening, but the author indicated that subjectively the results did not match field performance.

([Gietz,1980](#)) studied the effect of three different source of baghouse fines on the ageing of two types of bitumen using the RTFOT. He observed a significant variation between different bitumen-fines combinations when aged in the thin film oven test. He concluded that the fines having the largest surface area aged the bitumen the most.

In another study by Peterson and co-workers ([Petersen et al.,1974](#)), they also used the mastic technique of ageing. Their study included several types of lime and a limestone filler. Using a newly developed thin film oven test, they studied the influence of mineralogically different fillers on the oxidative ageing of four different bitumens. They observed wide variations in the effects of the fillers on the ageing properties. The limestone filler was found to increase the ageing as measured by the relative dynamic viscosity by 37 to 80 percent, depending on the type of bitumen. On the other hand, high-calcium lime reduced the ageing by 40 to 75 percent depending on both the type of asphalt and the hydrated lime type. In addition, the improvement rate was observed to be related to the amount or volume concentration of the lime.

In a study by ([Anderson et al.,1994](#)), on the PAV ageing of mastics made with about 25 vol.% limestone, gravel, sandstone and greywacke fillers. They did not observe any measurable difference in the effect of the tested fillers on bitumen ageing properties.

In another study done by ([Huang and Zeng,2007](#)), the effect of PAV ageing up to 2,000 hrs on mastics prepared with 20 wt.% limestone or granite fillers, the researchers concluded that the use of both fillers slowed down bitumen ageing.

From the published data about the effect of fillers on mastics ageing, it can be observed that contradictory views exist. It is believed that part of this problem comes from the use of high filler content and different ageing and assessment methods. The effect of mineral fillers on bitumen ageing still remains controversial according to ([Lesueur et al.,2016](#)).

2.10 The use of hydrated lime in pavement

Hydrated lime has been known as an additive for asphalt mixtures from their very beginning. Hydrated lime has been seen to be more than a moisture damage additive. It is known to reduce chemical ageing of the bitumen. Furthermore, it stiffens the mastic more than normal mineral filler. This impacts the mechanical properties of the asphalt mixture, and strength and modulus are seen to be modified by hydrated lime. It also improves the rutting resistance. In most cases, studies focus on hydrated lime contents of 1-1.5%, and these effects are generally more pronounced for higher hydrated lime contents. Finally, the few published studies on fatigue resistance indicate that hydrated lime improved the fatigue resistance of asphalt mixtures in 77% of the reviewed cases. However, hydrated lime does not exhibit a higher stiffening effect than mineral filler at low temperature and no effect on the thermal cracking resistance is reported.

2.10.1 Hydrated lime

Hydrated lime is mainly composed of calcium hydroxide Ca(OH)_2 . It is obtained by hydrating quicklime (essentially calcium oxide CaO) using specific equipment called hydrators. Quicklime is manufactured by burning limestone of very high purity (made of calcium carbonate CaCO_3) at temperatures around 900°C in dedicated

kilns. Hydrated lime generally comes in the form of a dry white powder (Figure 2-10) with a particle density close to 2.2Mg/m^3 . Because of a high level of particle porosity. ([Lesueur,2010](#)).



Figure 2-10 Hydrated lime

Hydrated lime can be evaluated using the specifications on aggregates for asphalt mixtures which deal with fillers. The standard mainly considers the properties of the filler related to its stiffening effect on the bitumen. In particular, the voids of the dry compacted filler (Rigden air voids) and $\Delta R\&B$ are measured. Other properties used to specify mineral fillers in the asphalt industry are also listed and compared with hydrated lime properties.

Lime is available in several forms, including high-calcium quick lime, dolomitic quick lime, high-calcium hydrated lime, normal hydrated dolomitic quick lime, and pressure hydrated dolomitic quick lime. High-calcium hydrated lime is by far the most commonly used lime in the United States. Materials and Test Division, Nevada DOT, 1998 indicate the resilient modulus before and after the addition of various types of lime. The hydrated limes used in the study offered the most improvement to moisture sensitivity. The hot-mix asphalt mixture, which used quick lime, did not have a measurable resilient modulus after exposure to water and a freeze-thaw cycle.

As far as application to asphalt mixture is concerned, highly pure hydrated lime is used. This hydrated lime type is called CL90S according to EN 459-1 or referred as Type -1 according to ASTM C1097 and AASHTO M303. Also depending on its purity and use, other grades are used in different applications.

Previous studies have investigated the beneficial effect of hydrated lime on aggregates when used in asphalt mixture and showed that this effect could be in the form of surface modification and/or clay flocculation. Hydrated lime has been reported to modify the surface properties of aggregates, and it has been found more effective in asphalt mixtures with siliceous aggregate than those with limestone aggregates ([Bagampadde et al.,2011](#); [Grönniger et al.,2011](#)). Surface modification is not the only phenomenon associated with the addition of HL as this unique filler has also been reported to improve the adhesion properties between limestone aggregates and bitumen ([Huang et al.,2005](#); [Mohammad et al.,2018](#)).

Hydrated lime has been found very efficient against moisture damage for aggregates containing clay. That is the reason why in some states of the USA such as California, Nevada, Colorado and Utah, where a large amount of clay has been reported in the aggregates, HL is used for the construction of asphalt mixtures to be used in road pavements. Clay may occur naturally inside the rock and be liberated as a result of crushing. HL flocculates the clay particles, preventing them from building a water-displaceable barrier between bitumen and aggregate ([Aschenbrener,1995](#); [Little and Petersen,2005](#)).

HL is often compared to the other types of mineral fillers in the asphalt industry. European standards for asphalt mixture from EN 13108-1 till EN13108-7 clearly categorises HL as a filler and hence it can be evaluated against the standards on aggregates for the construction of asphalt pavements as detailed in EN 13043. This standard also describes the combined use HL and other fillers. This standard mainly talks about the properties of the fillers which contributes to stiffening effect in the

bitumen by measuring voids in the in dry compacted fillers and softening point using $\Delta R\&B$.

A comparison of some properties of mineral fillers and hydrated lime is presented in Table 2.2 The properties presented in Table 2.3 are just a guide as these may vary significantly depending on the source of the mineral filler.

Table 2.2 Typical properties of hydrated lime compared to mineral fillers (Lesueur et al.,2012)

Property	Method	Unit	Hydrated Lime	Mineral Filler
Particle Density	EN 1097-7	Mg/m ³	2.2	2.6-2.9
Voids in dry compacted filler	EN 1097-4	%	60-70	28-45
Delta ring and ball	EN 13179-1	°C	Not measurable	Aug-25
Bitumen Number	EN 13179-2	-	70-120	40-50
Blaine SpecificSurface	EN 196-6	cm ² /g	>10,000	7,000
Specific Surface Area	BET (nitrogen adsorption)	cm ² /g	150,000-200,000	14,000-95,000
Methylene Blue Value	g/kg	<1	0-20	g/kg

2.10.2 Hydrated lime and resistance to chemical ageing

Hydrated lime was observed early on to decrease bitumen chemical ageing. The first observations of the anti-ageing effect of hydrated lime on bituminous materials date back to the late 1960s in Utah, when C. V. Chachas and co-workers with the Utah State Department Highways observed that control specimens of bitumen recovered from hydrated lime treated asphalt mixtures were surprisingly softer than the reference materials (Chachas,1971). From then on, many laboratory studies, and several field observations on the impact of hydrated lime on bitumen chemical ageing have been performed and conducted.

However, it is scientifically proven that hydrated lime has beneficial effects on the asphalt mixtures used in road construction. This has been studied in depth in the USA where hydrated lime is present in 10% of the Hot Mix Asphalt (HMA) produced each year. Unfortunately, in Europe, the functionalities of hydrated lime are still rather poorly known and thus the use of hydrated lime is less usual ([Lesueur,2010](#)). A critical literature review report for European Lime Association (EuLA) summarises the laboratory work done on the effect of hydrated lime on asphalt bitumen and the field studies that have investigated the effect of hydrated lime on ageing resistance of asphalt mixture. The studies that have investigated the hydrated lime effect on pavement ageing mitigations and their conclusions, as reported by ([Lesueur,2010](#)) and from the most recent studies as well, are presented in Table 2.3.

Table 2.3 A review of the laboratory studies showing the effect of hydrated lime on the ageing of bitumen.

Researcher, year	Aging procedure	Tested bitumens	HL content [wt.% based on bitumen]	Main conclusions
(Plancher et al., 1976)	• Rolling thin film oven test (RTFOT) • - 75 min. at 163°C) • Rolling MicroFilm Circulating Oven RMF	4 AC10 from different locations	50 from 1/1/600 (HL/bitumen/benzene Solutions)	• Hydrated lime treatment seen to reduce age hardening (lower stiffening, lower asphaltene content, lower carbonyl-type oxidation products) • Bitumen dependent effect but all bitumen benefit from hydrated-lime treatment
(Edler et al., 1985)	• Weatherometer: 65°C with cyclic 102 min. UV and 18 min. UV + water spray (3 bars), 32.5 hrs, 73.5 hrs, 7 days, 14 days • RTFOT 163°C, 75 min. • RTFOT + POB (pressure oxygen bomb 65°C and 2.06 MPa of oxygen pressure, 96 hrs) • RTFOT + TFOT 163°C, 5 hrs viscosity, FTIR, GPC	60/70 and 80/100	6 or 12wt.% hydrated lime	• Much lower ageing with hydrated lime as noted by viscosity, almost regardless of hydrated lime content • Lower ratio of C=O for lime modified bitumens after ageing • Effect much clearer on weatherometer, almost unseen on RTFOT • Little effect on molar weight

Researcher, year	Aging procedure	Tested bitumens	HL content [wt.% based on bitumen]	Main conclusions
(Petersen et al., 1987)	Thin film accelerated aging test (TFAAT) of hydrated lime-treated materials at 113°C for 3 days	- AC10 - California Coastal - AC10 Boscan - AC10 North Slope / Maya - AC10 West Texas/ Maya	- hydrated lime 10, 20, 30 - dolomitic lime 20	- Ageing procedure similar to 11-13 years in the field 10% hydrated lime enough to neutralize most of the acids of the binders - Hydrated lime treatment seen to reduce age hardening (lower stiffening, asphaltene content, and carbonyl oxidation products) - Rate of carbonyl formation slows down for hydrated lime-treated bitumens - Rate of sulfides, sulfoxides and ketones formation not modified by hydrated lime bitumen dependent effect but all bitumen - Benefit from hydrated-lime treatment limestone filler does not have any effect on bitumen ageing
(Johansson et al., 1995)	1 + 2 weeks in pressure aging vessel (PAV) at 60°C and 2.1MPa of air pressure	8 SHRP - core bitumens	20	- Hydrated lime reduces age-hardening based on ageing index (viscosity ratio) except for bitumen AAG - Hydrated lime does not affect carbonyl or sulfoxides formation,
(Oliver, 1995)	ARRB durability test (RTFOT + thin film 20 microns ageing at 100°C)	85/100	6-26	hydrated lime improves the durability as measured by ARRB test

Researcher, year	Aging procedure	Tested bitumens	HL content [wt.% based on bitumen]	Main conclusions
(Johansson et al.,1996)	144 hrs thin film oven test (TFOT) + PAV 60°C + 80°C	- AAA-1 - AAD-1	5	- Hydrated lime suppresses the catalytic activity of vanadium compounds - no specific hydrated lime/vanadium compounds interactions observed - Mg(OH)₂ not effective as an anti-ageing compound for bitumen bitumen dependent effect
(Wisneski et al.,1996)	pressure oxygen vessel (POV) at 88, 93 and 99°C	- AAA-1 - AAF-1 Blended or not with 4 rejuvenators	1-20	- Anti-ageing effect observed both with quicklime and hydrated lime, slightly better with HL - Lime reduces asphaltene formation upon ageing and reduces carbonyl rate formation - Lime reduces the hardening susceptibility (slope of log viscosity vs carbonyl)
(Lesueur and Little,1999)	- TFOT + PAV 100°C 20 hrs	- AAD - AAM	12.5	- Hydrated lime reduces age-hardening based on ageing index (viscosity ratio) for bitumen AAD - higher viscosity increase for AAM with HL after ageing, although no increase was found in carbonyl area: part of the viscosity increase due to the kinetics
(Hopman,1998)	RTFOT (2.5 and 7 hrs)	- Venezuela 70/100 - Middle East 70/100	12.5	- Hydrated lime reduces age-hardening (penetration, R&B, asphaltene formation) - Bitumen dependent effect

Researcher, year	Aging procedure	Tested bitumens	HL content [wt.% based on bitumen]	Main conclusions
(Sainton et al.,1999)	RTFOT (normal and 7 hrs)	- Venezuela 35/50 - Middle East 35/50	12.5	- Hydrated lime reduces age-hardening (penetration, R&B, asphaltene formation) - Bitumen dependent effect
(Verhasselt and Puiatti,2004)	- RCAT 235 min. at 163°C - or 17, 65 and 140 hrs at 90°C	- Venezuela 35/50, 50/70 and 70/100 - Middle East 35/50	12.5	- Hydrated lime reduces age-hardening (penetration, R&B, asphaltene formation) - Decrease in 1700 cm⁻¹ absorbance (carboxylic groups) with hydrated lime - Bitumen dependent effect
(Huang et al.,2005)	PAV 60°C 100-2000 hrs	- AAD-1 - ABD-1	20	- Hydrated lime reduces age-hardening (viscosity ratio, asphaltene formation) - Bitumen dependent effect - Limestone filler does not have any effect on bitumen ageing
(Recasens et al.,2005)	long-term oven aging (LTOA) of mixture with 4.5% bitumen an	80/100	17-44	Hydrated lime reduces age-hardening (penetration, R&B, viscosity)
(Sewing,2008)	Recovered bitumen from field pavements	2 to 4 years aged bitumen	2	R&B of recovered bitumen between 1 and 1.7°C lower for hydrated lime modified mixes, except for one mix
(Lerfald and Horvli,2003)	- Standardised TFOT - Modified PAV test (7days at 60°C	- B180 - MB10000	10 -50	- The net effect of hydrated lime on low temperature cracking properties seems to be doubtful - Bitumen dependent effect

Researcher, year	Aging procedure	Tested bitumens	HL content [wt.% based on bitumen]	Main conclusions
(Iwański and Mazurek,2013)	SMA wearing coarse layer with the hydrated lime	50/70 + 4% SBS	HL replace 30% of filler mass	Binder with hydrated lime had a positive effect on reducing aging process of bitumen 50/70 modified with SBS polymer in SMA mixture giving the increase in resistance to the water and frost effect
(Shafiei and Latifi Namin,2014)	Mechanical properties of the lime-containing SMA mixtures	60/70 bitumen	0 – 10	- Partial substitution of the filler with hydrated lime will cause an improvement in the resistance indices like flow number, flow time as well as rutting and fatigue cracking factors of SMA. - Rutting resistance increases as the HL percent rise up to optimum amount of HL, increasing HL more than 5% changes the trend and reduces rutting indices.
(Gundla et al.,2016)	- Mastic aged in the standardized PAV at 100°C - Short term ageing -loose mix aging at 135°C for 4 hours - long-term aging for 5 days at 85°C	Unmodified PG 64-22.	1% in asphalt mixture	- HL mixes possessed higher fatigue life than control mixes and portland cement modified mixes. - The ageing mitigation of PC improved by increasing the content from 1 to 2% but, HL was ageing mitigation still better in all cases.
(Lesueur et al.,2016)	PAV performed after 25 hours	50/70N(Nynas) 50/70 (Repsol) 35/50 (Galp)	20wt.% in mastics (two types of HL)	- The two grades of hydrated lime could significantly reduce the ageing of both bitumens - Limestone and granite mineral fillers have no effect on bitumen ageing - Portland cement and hydraulic lime were also seen to reduce bitumen age-hardening, but to a lesser extent than hydrated lime.

In a study by ([Little and Petersen,2005](#)) they investigated the unique effect of hydrated lime (HL) on the performance related properties of asphalt mixtures. They compared the effect of HL to similarly sized filler comprised of calcium carbonate, limestone. They performed extensive laboratory testing, including rheological testing of mastics, bending beam rheometer tests on mastics and some tests on mixtures such as fatigue testing, and permanent deformation testing. The results confirmed that when hydrated lime is added to bitumen as a filler, the level of effect will range between that equal to other mineral fillers to a substantially greater effect, depending on the physicochemical interaction that develops between the bitumen HL. This interaction level has proven to be different when different bitumens are used. The effects of HL are reduced as the temperature is lowered, and the HL acts similarly to an inert filler. At very low temperatures, below about -20°C , the stiffness increase due to the addition of HL is similar to that of any other filler with a similar particle size distribution. In addition, they reported that, the inclusion of HL filler particles toughens the mastic, making it more resistant to fracture and crack propagation. Aged bitumen modified with 20% by weight of HL (equivalent to 1% by weight based on typical pavement mixtures) showed greatly increased toughness and elongation to break as compared with unmodified bitumens or bitumens modified with 20% of limestone (LS) of the same particle size gradation. The result of DSR tests performed on intermediate temperatures, demonstrate that both fillers increase stiffness (G^*), but the HL filler was much more effective in extending fatigue life and increasing the degree of damage prior to failure than the limestone filler.

General conclusions from different experiments comparing hydrated lime and limestone as fillers are that the hydrated lime is more effective than the limestone and that the degree of effectiveness of the HL (and thus the degree of difference between the two fillers) is bitumen dependent.

2.11 Chapter summary

This chapter has provided a comprehensive literature review about the age hardening of bitumen and the effect of different mineral fillers on ageing of asphalt pavements. The ageing simulation tests and the factors affecting ageing were presented. Furthermore, the ageing indicators and ageing mechanisms that control the ageing process were discussed. The second part of the literature review summarized the effect of the mineral fillers on the ageing of bitumen mastics and mixtures. The final part focussed on the previous attempts that have been made to evaluate the effect of using hydrated lime on mastics and pavement ageing.

It was shown in this chapter that there are different ageing indicators that can be used to evaluate the age hardening in bitumen, mastics and mixtures. These indicators try to evaluate the ageing by looking at the results from different perspectives: basic properties, mechanical and rheological behaviour and through the chemical changes in the bitumen. Thus, these indicators could rank bitumen ageing differently. Therefore, a comprehensive study to compare these different ageing indicators at different levels is sought.

The literature showed that in Europe, the functionalities of hydrated lime are still corporative poorly known and thus the use of hydrated lime is less usual. From this, it is of great interest to develop a better understanding of the impact of hydrated lime on asphalt mixture ageing and to compare it to other fillers commonly used in the UK. Furthermore, a better understanding of hydrated lime functionalities and mechanisms in mitigating the ageing in asphalt mixture is of great importance.

Chapter 3: Methodology and Materials

3.1 Introduction

This chapter consists of two main parts. The first part summarises the methodology followed to conduct the objectives of this research project. The second part characterises the main materials used in this research study. The methodology outlines briefly the work done in each stage of the current research. A flowchart representing the work plan followed in this research is presented. The second part provides the essential characteristics of the materials used. Particular attention is paid to the filler description and characterisation as it is related to the principal theme of this study.

3.2 The methodology

This research study attempts to provide an improved understanding of the factors affecting the ageing process and the effect of different fillers on the ageing of asphalt mastics and mixtures, especially the effect of using hydrated lime on bitumen-filler mastics and asphalt mixtures. The benefits of hydrated lime to mitigate oxidative ageing were extensively investigated. In order to accomplish the aim of this research, the methodology utilised in this research comprises the following stages:

Stage I: This stage includes conducting a comprehensive literature review, materials preparation, characterisation and initial laboratory investigation.

Stage II: Comprises a pure bitumen ageing investigation to be used as a base study to set up the parameters, tests and methods that will be used in the following stages. The effect of different ageing methods on bitumen properties was compared in this stage. The factors and parameters affecting bitumen ageing were investigated as well.

Stage III: Ageing of bitumen mastic to study the influence of different fillers on bitumen-filler mastic ageing was carried out. The effect of using hydrated lime as a replacement for these fillers was further studied. The mastics were artificially aged in the laboratory at different ageing levels and then the chemical and rheological changes after each level of ageing were tested and compared to show the effect of the fillers on mastic ageing properties. Special attention was given to evaluating the beneficial effect of using hydrated lime to mitigate asphalt ageing. Moreover, the effect of hydrated lime on mastic ageing was further investigated with different binders for a better understanding of the bitumen-filler interaction.

Stage IV: Involved mixture ageing, where the effect of using hydrated lime on the ageing of asphalt mixtures was evaluated at the mixture level through different tests such as ITSM, ITS and semi-circular bending.

Stage V: An extensive detailed study of mastic ageing was carried out. Mastics with different fillers and at different concentrations were prepared and aged for different ageing levels. Comprehensive detailed testing of mastics was conducted to better understand the interaction between different fillers and binders and the mechanisms of ageing mitigation of different fillers. Furthermore, this stage investigated the effect of different fillers on mastic stiffening.

Figure 3-1 illustrates the methodology followed in conducting this research.

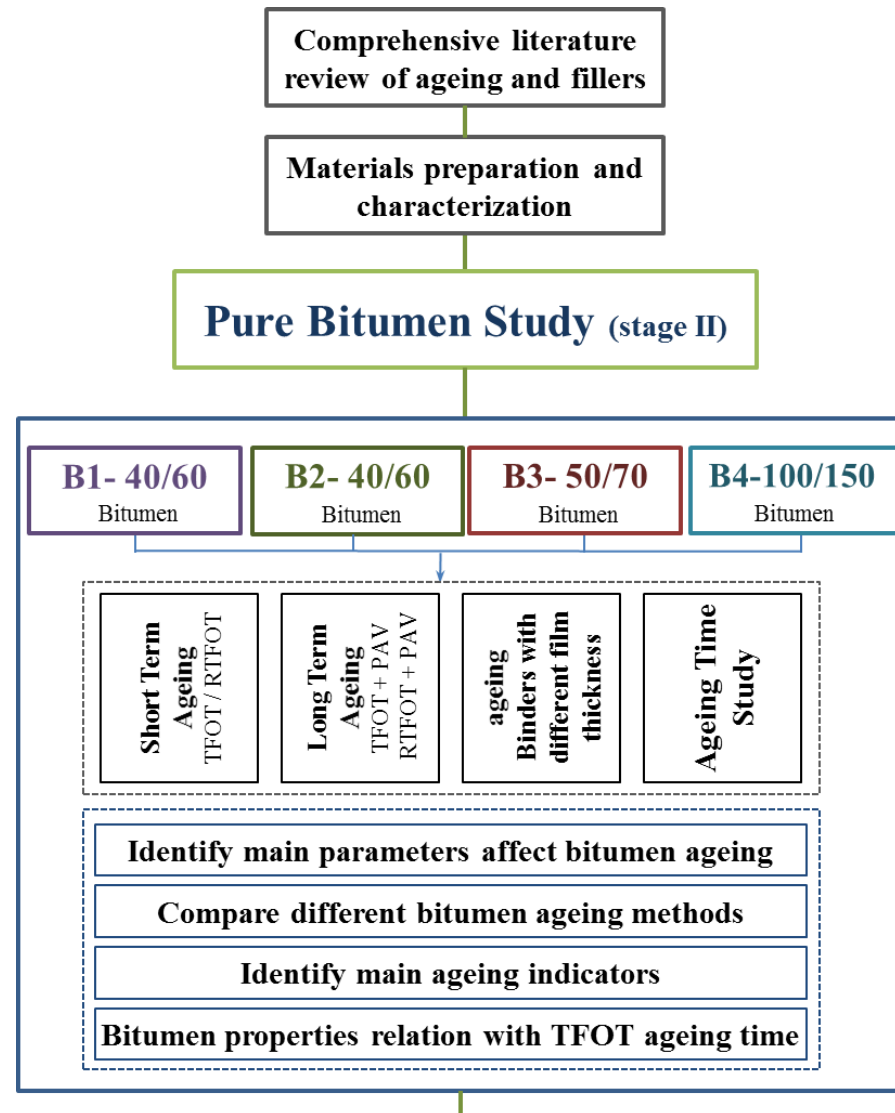


Figure 3-1 Continues

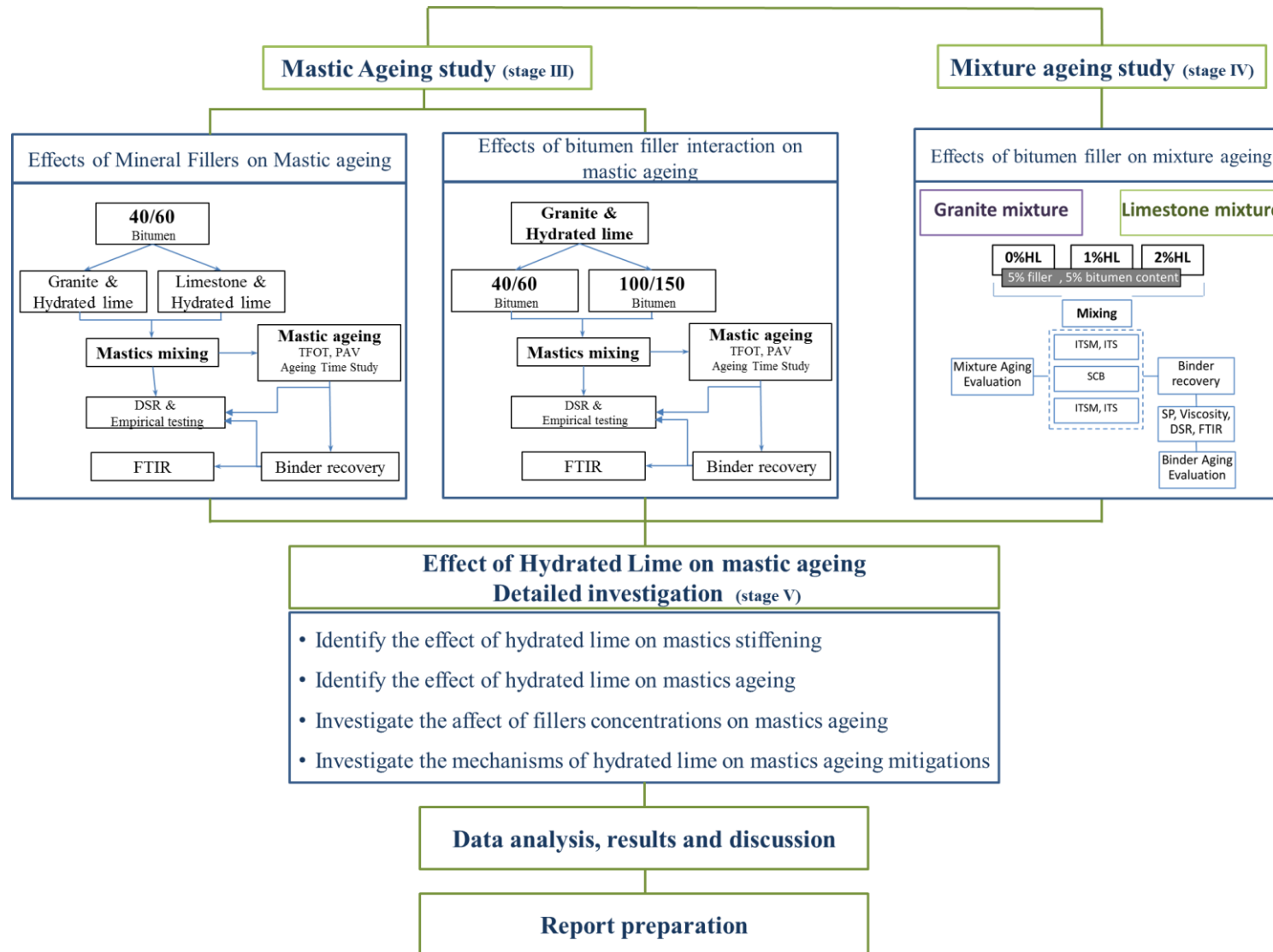


Figure 3-1 Flowchart of the research methodology

3.3 Materials Characterisation

This section discusses the characterisation of the materials used in this study. Alongside the bitumen binders and the aggregates, special attention will be given to filler characterisation as the filler properties play a significant role in the performance of asphalt mastics and mixtures. The asphalt–filler interaction also depends on physical and chemical properties of fillers. In addition to the physical mechanism of filler modification, the chemical mechanism of active fillers and the filler-bitumen interaction should be considered within the bitumen and filler combinations. Chemical compositions and the nature of the filler could control the interaction at the interface between the filler and the bitumen. Therefore, it is very important to characterise fillers for their properties prior to using them in any combination with bitumen. The main materials used and their properties are discussed in the following subsections.

3.3.1 Bitumen

Four different bitumen types were chosen for the experimental work in this study:

- B1, B2: 40/60 Penetration Grade
- B3: 50/70 Penetration Grade
- B4: 100/150 Penetration Grade

Bitumens B1 and B2 have the same Penetration Grade, but they have some differences in their initial rheological properties. B4 is a softer bitumen, chemically and rheological different binder from B1 and B2. As an intermediate stiff bitumen B3 was used as well. These binders with different chemical and rheological properties were selected in order to better understand the ageing effect on bitumen and to compare different changes happening during ageing.

An extensive characterisation of these bitumens was carried out prior to the mastic stage; the characterisation included the following tests: Penetration, Softening point, Viscosity and Rheological characterisation using the DSR.

Bitumen characterisation:

Penetration, viscosity and softening point tests are considered the most common empirical tests that are used to evaluate the consistency or hardness of bitumen. In this study, the values of penetration, rotational viscosity and softening point were determined according to the British standards [BS EN 1426:2007](#), [BS EN 13302:2010](#) and [BS EN 1427-2015](#) respectively. The results are shown in Table 3.1.

Table 3.1 Bitumen basic properties

Bitumen	Penetration (dmm)	Softening point (°C)	Viscosity at 135 °C (mPa.s)
B1	46	51.6	445
B2	45	52.7	544
B3	59	50.2	451
B4	119	44.2	283

In order to better understand the behaviour of bitumen, there has been a considerable rise in the more complex testing of bitumen with the aim of better characterising the rheological behaviour of bitumen and the resulting behaviour of the asphalt mixture. Dynamic Shear Rheometers (DSRs) are used to measure the rheological characteristics of bitumen. Typically, dynamic tests are performed and the parameters that are determined are the complex modulus and phase angle from which the viscoelastic properties of the bitumen can be evaluated. The DSR has become an accepted testing tool for determining the dynamic mechanical properties of bitumen in the linear region ([Airey,1997](#)). The rheological properties, complex modulus and phase angle, were determined at different temperatures and frequencies. The results at a frequency of 0.4Hz and at two temperatures, 20°C and 40°C, are presented in Table 3.2.

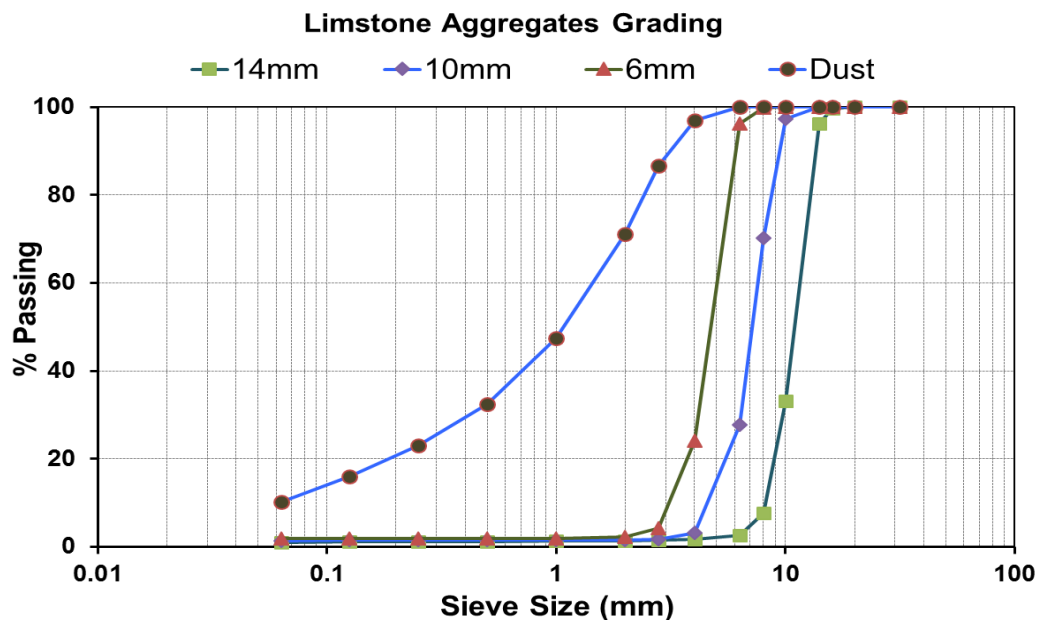
Table 3.2 Rheological properties of bitumen

Testing temperature	20°C		40°C	
Binder	G* (KPa)	δ (°)	G* (KPa)	δ (°)
B1	1032.4	65	21.4	79
B2	1545.0	63	37.9	77
B3	822.7	65	24.9	77
B4	437.6	68	8.7	83

3.3.1 Aggregates

Two different aggregates were used in this study at the mixture level: limestone aggregate and granite aggregate. The aggregates used consist of the following nominal sizes: 14mm, 10mm, 6mm and dust.

The properties of these aggregates are shown in Figure 3-2 for both granite and limestone. Combination of percentages of these nominal sized aggregates is used to construct the final gradation curve of the mixture as will be discussed in the mixture ageing study.

**Figure 3-2 Aggregates nominal size gradings**

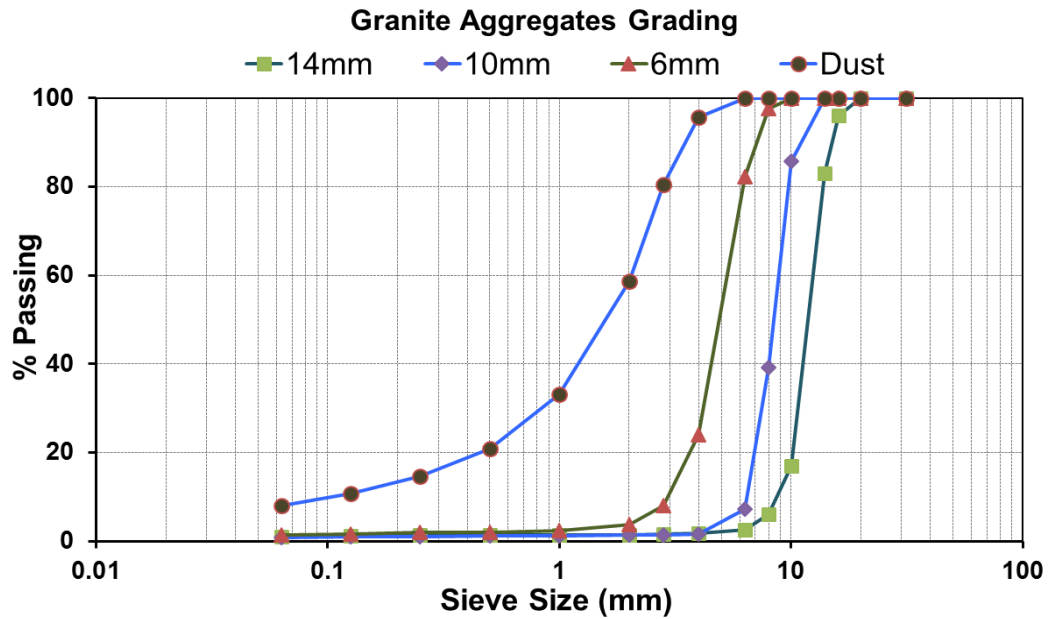


Figure 3-2 continued

3.3.2 Filler characterisation

Among the different mechanisms causing bitumen ageing and hardening, the most important are oxidation and loss of volatile components, which lead to chemical changes in the binder. The other mechanism is a reversible process called physical hardening that can be attributed to molecular restructuring. Generally, bitumen ageing takes place in two stages, short-term ageing at high temperatures during asphalt mixing and paving, and long-term ageing at ambient temperatures during in-service life. ([Moraes and Bahia,2015a](#)) showed that, even though binder ageing in pavements always occurs when the binder is in contact with aggregates and mineral filler, in most ageing studies, asphalt binders are individually aged without taking into account the effect of mineral fillers. ([Anderson et al.,1992](#)) stated that the properties of the fine fraction dominate in terms of physicochemical interactions between the bitumen and the mineral surface, as the fines are embedded in the bitumen and the majority of the surface area is generated by the fine minerals. Therefore, the mechanisms of asphalt mastic and mixture ageing are significantly influenced by the characteristics of the asphalt binder and the mineral filler

properties, in addition to the interaction between them. The type and nature of mineral filler appeared to have an important effect on the properties and performance of bitumen mastics and mixtures. Several studies investigated the effect of fillers on the performance of bitumen mastic and mixture ageing. These studies indicate that the acidic or basic nature of the filler could influence the ageing behaviour of asphalt mixtures. Furthermore, the characteristics of fillers including gradation, particle shape, void content, and surface area, play a major role to influencing the properties of asphalt mixture and its ageing resistance. In addition to that, the interaction between filler and bitumen has an effect on the mechanical properties of mixtures by influencing the workability, compaction characteristics, and the stiffness ([Kavussi and Hicks,1997](#); [Kandhal et al.,1998](#); [Hagos,2008](#); [Moraes and Bahia,2015b](#); [Cardone et al.,2015](#); [Lesueur et al.,2017](#)). For these reasons, it is very important to characterise the fillers to better understand the ways in which they improve the performance of the asphalt mixture. It is important to investigate the effect of the morphology and physical properties of the fillers on bitumen mastics and mixtures.

Three different types of filler will be used in the studies performed in this research. These fillers are granite fillers (G), limestone fillers (LS) and hydrated lime (HL). The hydrated lime was supplied by the British Lime Association (BLA). The detailed Specification of the hydrated lime are summarised in Table 3.3

Table 3.3 Hydrated lime specification

CALCIUM HYDROXIDE - Ca(OH)_2			
Grade CL90 S			
1. CHEMICAL			
		Typical Analysis	Specification
Calcium Hydroxide	Ca(OH)_2	96.00%	95.00% Min
Calcium Carbonate	CaCO_3	2.77%	4.00% Max
Magnesium Oxide	MgO	0.24%	0.30% Max
Iron Oxide	Fe_2O_3	0.05%	0.09% Max
Aluminium Oxide	Al_2O_3	0.04%	0.09% max
Silica	SiO_2	0.40%	1.50% Max
Manganese	Mn	130 ppm	150 ppm Max

Sulphur	S	<0.01%	0.02% Max
Lead	Pb	2 ppm	10 ppm Max
Arsenic	As	<1 ppm	1 ppm Max
Free Moisture		0.54%	1.00% Max
Available Lime (as Ca(OH) ₂)		97.15%	96.00% Min
Neutralisation value (as CaO)		74.98%	74.00% Min
2. PHYSICAL			
Grading % passing	200µm	99.80%	98.00% Min
	90µm	96.50%	93.00% Min
Bulk Density	Loose	560 Kg/m ³	
	Fully Compacted	670 Kg/m ³	

The main properties of the fillers characterised in this study are shown below:

(1) Particle size distributions

Particle size distributions (PSD) were assessed by a grading test. In this study, a Beckman Coulter Laser diffraction particle size analyser (LS200) was used to measure the particle size of granite and limestone fillers. In this device, a flux curve is generated, which is a composite of the flux curves for all the filler particles that pass through a laser beam during a sample run. The LS200 system converts the composite flux curve into a particle size distribution. This device uses water as a liquid dispersant, where the sample of filler to be tested has to be in contact with water. So this method was not suitable for testing the hydrated lime filler as there is a reaction between water and the hydrated lime Ca(OH)₂. Therefore, using a Malvern Mastersizer 2000, the particle size distribution of hydrated lime filler was determined by the supplier with the use of Methanol as dispersant instead of water. The particle size distribution curves of the fillers are presented in Figure 3-3.

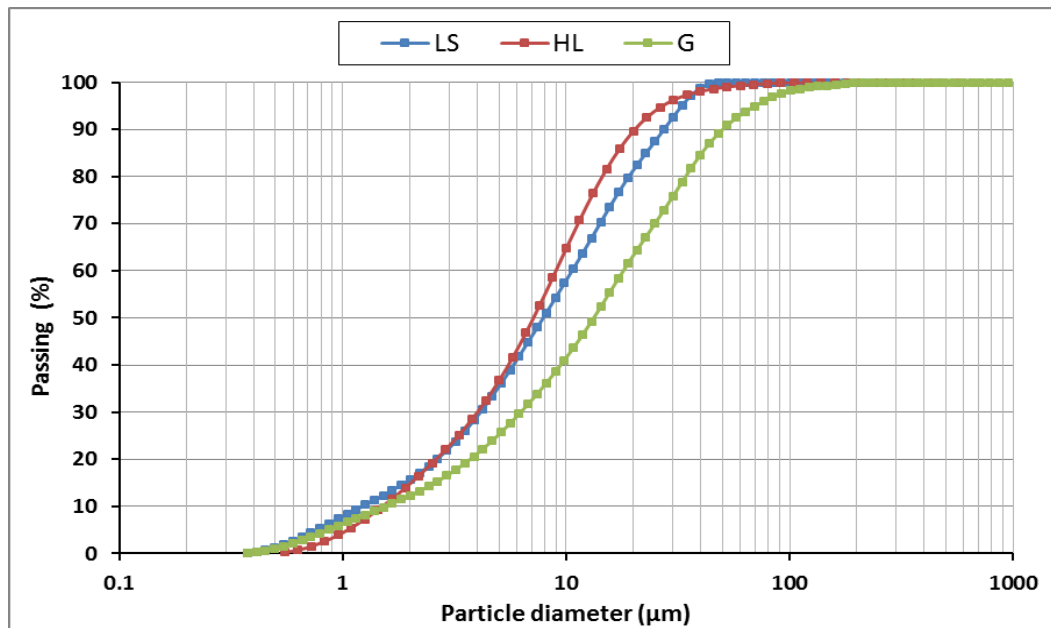


Figure 3-3 Particle size distribution of fillers

Looking at the gradation curves of the fillers, it can be seen that hydrated lime and limestone fillers have almost the same gradation, but the granite filler is somehow coarser. However, more than 95% of the granite filler particles are smaller than 63μm. In order to allow more convenient comparisons between different fillers' PSD, a mathematical description of the PSD curves such as D10 (diameter at which ten percent by volume of particles are smaller), D50, D90 and Coefficients of Uniformity are used. A summary of these results is given in Table 3.4.

Table 3.4 summary of the PSD results

	Granite (G)	Limestone (LS)	Hydrated Lime (HL)
D10	1.705	1.346	1.509
D50	14.580	8.670	7.137
D90	55.100	30.050	20.272

A previous study by ([Kandhal et al.,1998](#)) indicated that the effect of fillers on stiffening the mixture and mastics appears to be high. The smaller the size of the filler the more the binder is modified. This is because the finer fillers have more absorption potential in binders and thus they produce the highest viscosity values (more stiffening effect) at a given temperature. This study gave special attention to the finer fillers, especially at D10. They also reported that the finer the filler

(lower D₁₀), the more significant the effect on the retained tensile strength ratio (TSR). TSR increases as D₁₀ decreases. Furthermore, decreases in D₁₀ increased the resistance to stripping as well. The results in Table 3.4 reveal that the fillers used in this study have very similar D₁₀ values. In addition, the limestone and hydrated lime have almost the same PSD characteristics; however, they are different from the granite filler. The outcomes of the research should therefore reflect the effect of the mineral filler properties and interaction with bitumen rather than the stiffening effect due to the particle size difference.

(2) Particle density

The particle density or Specific Gravity (SG) is very important to control the volumetric properties of mastics for better comparison between different mastics. The Specific Gravity (SG) was measured in this study by the pycnometer method in accordance with [BS EN 1097-7:2008](#). For each filler, a small sample was oven dried to constant mass at 105°C, weighed and placed in a small pycnometer. The pycnometer was filled with distilled water at 20°C (for measuring granite and limestone filler densities; for hydrated lime another liquid that does not interact with hydrated lime was chosen) and the total mass was recorded. The pycnometer was then emptied and washed and dried. The volume of water in the pycnometer is then measured by filling with distilled water at 20°C and the density calculated as the mass of filler divided by the volume of filler measured by displacement. The results of SG for the fillers are presented in Table 3.5. The results show that hydrated lime has a lower SG than granite and limestone fillers. However, limestone and granite have almost the same SG.

Table 3.5 Filler particle densities

Filler	Specific Gravity (Mg/m³)
Granite	2.66
Limestone	2.65
Hydrated Lime	2.22

(3) Specific surface area (SSA)

The specific surface area (SSA) was determined to evaluate the stiffening effect of the filler relative to its SSA. It is well known that there is an increase of SSA with an increase in fine particle content, thus creating a larger SSA. For larger values of SSA, more bitumen is expected to be adsorbed by the filler. Consequently, the filler stiffening effect should increase with SSA. In this study, the specific surface area (SSA) was taken from the laser diffraction determination of particle size distribution for the granite and limestone fillers. For HL, the preferred method is by nitrogen adsorption using the Brunauer Emmett Teller (BET) method due to its high internal porosity ([Lesueur et al.,2013](#)). The results are shown in Table 3.6.

Table 3.6 Fillers' specific surface area

Filler	Surface area (m ² /g)
Granite	1.26 *
Limestone	1.58 *
Hydrated Lime	2.24 **

* (Particle size analyser)

** (mastersizer2000)

The results reveal that hydrated lime has a higher surface area compared to granite and limestone. Although limestone and hydrated lime have similar grading curves, the specific surface area of hydrated lime is significantly larger. Granite filler has the lowest SSA and that is backed up by the results from PSD curves, as granite fillers are coarser. These differences in SSA for the fillers are very important. They could give a better understanding and indication of the ability of fillers to adsorb/absorb bitumen fractions, and consequently their ability to affect mastic stiffening and the ageing properties.

(4) Voids in dry compacted filler -Rigden voids (RV)

The voids in dry compacted filler or Rigden voids (RV) were determined with the Rigden equipment in accordance with [BS EN 1097-4:2008](#). A filler sample is first compacted in a mould with the defined compaction system, and then the void

content is calculated considering the compacted volume and the filler particle density calculated earlier. The results for Rigden voids of the fillers are presented in Table 3.7.

Table 3.7 Rigden voids for used Fillers

Filler	Rigden voids (%)
Granite	46.94
Limestone	39.82
Hydrated Lime	61.62

It can be noticed that hydrated lime has a very high Rigden voids compared to the other fillers. This high value of RV could be related to the higher porosity of the hydrated lime particles as many earlier studies have mentioned. For mineral filler, the porosity generally comes from the voids between the particles; however, for hydrated lime, the porosity inside the particles, adds to the porosity between the particles, hence leading to a much higher value ([Lesueur et al.,2012](#)). The porosity and surface texture of hydrated lime is discussed in the following subsection. The stiffening effect of filler is dependent on the Rigden voids of the filler. These voids in the compacted filler (RV) reflect the effects of particle shape and particle size distribution which are well correlated with the Rigden voids. These unique properties of hydrated lime on the stiffening effect of asphalt mastics and mixtures will be discussed in the following chapters.

(5) Particle shape and texture

The filler particle shape was determined by Scanning Electron Microscopy (SEM) imaging with the objective of identifying shape morphology differences between different fillers. This may explain the differences in the geometrical/physical properties and the effect of filler on bitumen mastics and mixture stiffening properties. Figure 3-4 presents the SEM images at different resolutions for the fillers used in this research.

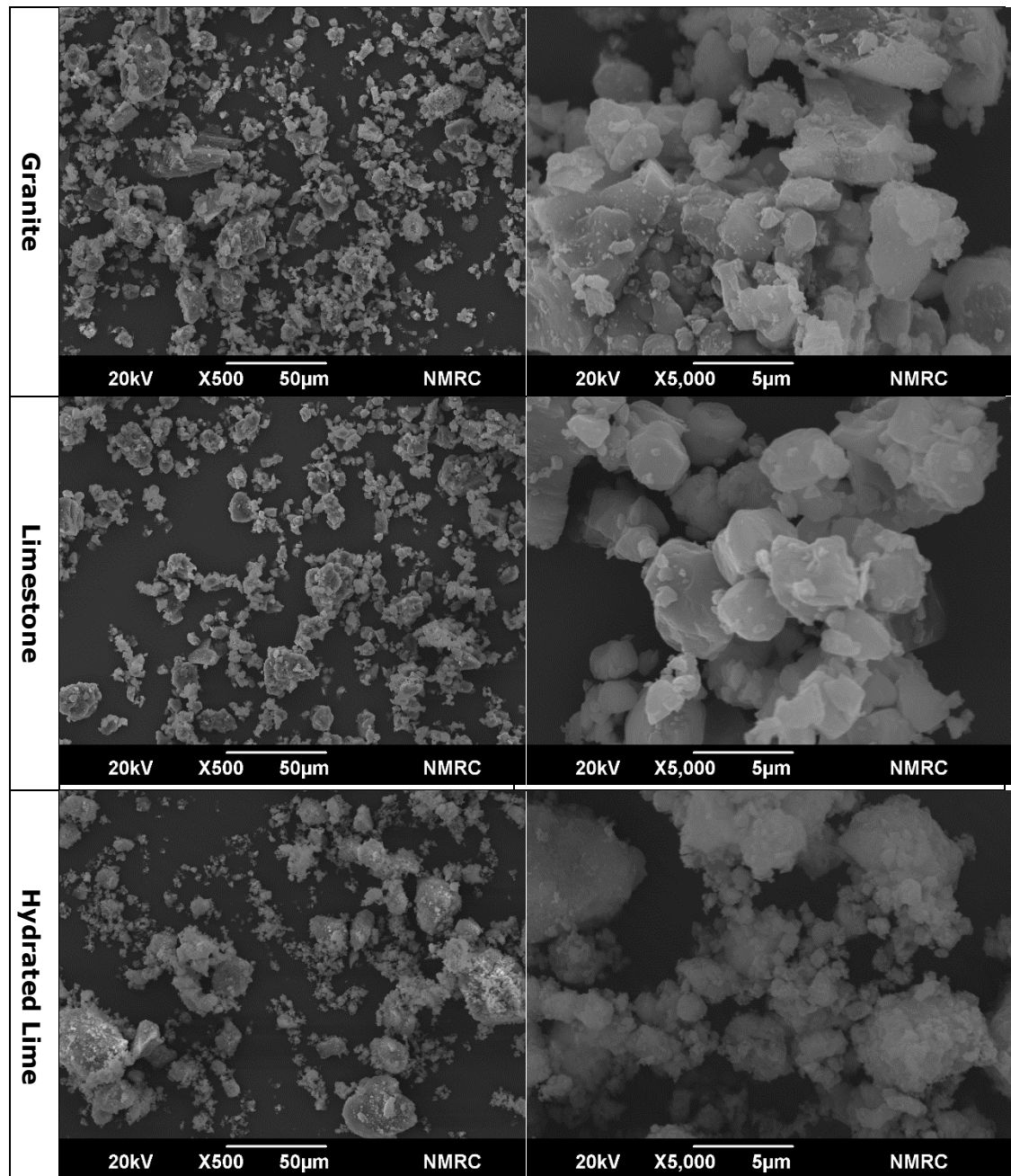


Figure 3-4 Filler particle shapes and textures

It can be seen from the microscopic morphology of the filler particles by SEM imaging that hydrated lime has mostly granular type particles with a very rough texture. However, granite and limestone fillers have mostly angular type particles with smooth to slightly rough texture. A closer SEM image with a 1µm resolution of hydrated lime is shown in Figure 3-5 which shows more closely the rough texture of the hydrated lime particle surface. The SEM imaging results can be correlated with the other filler tests. The larger value of the specific surface area (SSA) and

RV of hydrated lime are consistent with the granular shape of particles. The higher SSA of hydrated lime could be related to the internal pores of the hydrated lime particles and its rough surface compared to limestone and granite fillers. Thus, it is important to understand these properties and their effect on the mastics and mixtures in order to analyse the data in mastic and mixture phases accordingly.

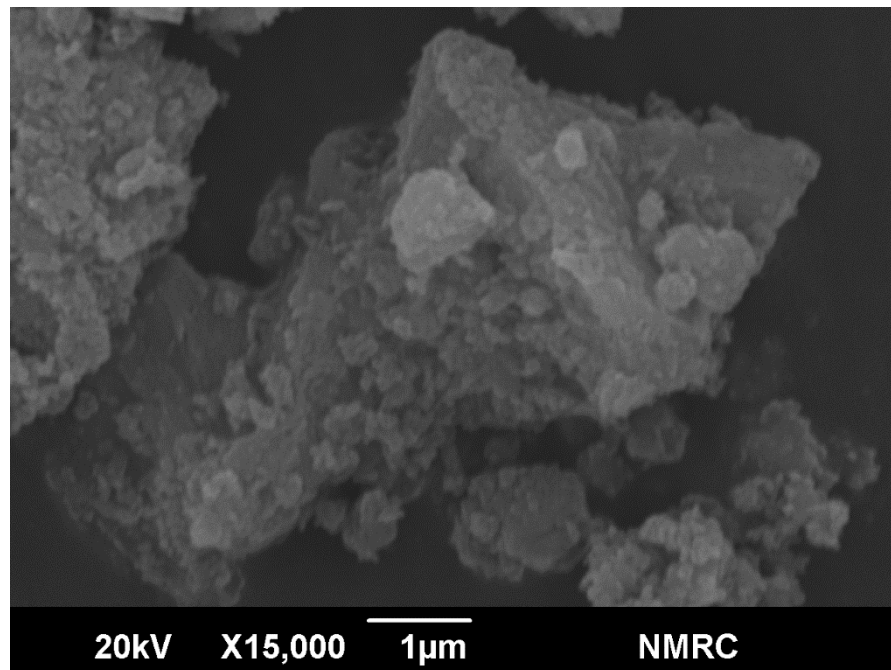


Figure 3-5 High magnification SEM image of hydrated lime particles

Filler characterisation summary

A summary of the filler properties characterised in this chapter is shown in Table 3.8.

Table 3.8 Summary of filler properties

	Granite (G)	Limestone (LS)	Hydrated Lime (HL)
Specific Gravity (Mg/m³)	2.66	2.65	2.22
Surface area (m²/g)	1.26	1.58	2.24
Rigden voids (%)	46.94	39.82	61.62
D10	1.705	1.346	1.509
D50	14.58	8.67	7.146
D90	55.10	30.05	20.33

3.4 Chapter summary

This chapter has outlined the methodology and materials used in this research. The methodology utilised in this research comprises five stages as discussed earlier in this chapter. Each stage will be discussed in more detail in the following chapters. Since this research emphasis is on the effect of the fillers on the ageing properties of mastics and mixtures, particular attention was paid to the characterisation of fillers and how the difference in these properties would affect the ageing mechanisms and influence the performance of asphalt mastics and mixtures. The following remarks are made:

- All fillers are fine and well graded and less than 63 μ m in size. Granite filler is coarser than the other fillers. Hydrated lime and limestone have almost the same gradation.
- The particle densities of granite and limestone are almost the same and the hydrated lime has a lower density. Thus, attention should be paid to the stiffening effect and volumetric properties when comparing mastics with high filler concentrations.
- Hydrated lime has mostly granular type particles with a very rough texture. However, granite and limestone fillers have mostly angular type particles with smooth to slightly rough texture.
- The results show that, although the hydrated lime and limestone have almost the same grading and particle size, HL has significantly higher Rigden voids and specific surface area (SSA) compared to both the limestone and granite fillers. This could be due to its finer particles, rough surface texture and its internal pores.

Chapter 4: Ageing of Bitumen: Initial Study

4.1 Introduction

Ageing of bitumen has been known as one of the main reasons for the deterioration of asphalt pavements over time. The ageing process can cause stiffening and hardening of bitumen and asphalt mixture, which may result in increased cracking and reduced pavement life. Although pure bitumen ageing does not take account of the influence of aggregates and fine fillers on ageing, it is easier to undertake than asphalt mixture ageing techniques and can be correlated to field performance ([Airey,2003](#)). Therefore, bulk ageing of pure bitumen is still widely used by researchers, and it provides a good reference base to the study the influences of fillers and aggregates on ageing.

The effect that oxidative ageing has on asphalt binders is critical in evaluating the long-term performance of an asphalt pavement. Therefore, for better understanding of the nature of the ageing mechanism and factors affecting this process, a variety of testing procedures and standards have been developed.

There are different mechanisms causing bitumen ageing and hardening, the most important of which are oxidation and loss of volatile components, which lead to chemical changes in the binder. The other mechanism is a reversible process called physical hardening that can be attributed to molecular restructuring. Generally, bitumen ageing takes place in two stages, short-term ageing at high temperatures during asphalt mixing and paving, and long-term ageing at ambient temperatures during in-service life. Due to the fact that the life cycle of asphalt is many years,

several testing procedures have been developed for rapidly ageing bitumen in the laboratory to simulate real field ageing for a shorter period of time. These can be separated into short-term and long-term ageing.

Most of the research into the ageing of bitumen utilises a thin film subjected to extended heating or hot moving air. The most common test procedures are the rolling thin film oven test (RTFO) and thin film oven test (TFOT) to simulate short-term ageing. The pressure ageing vessel test (PAV) is used for long-term ageing simulation.

This chapter studies the effect of different ageing methods and parameters on bitumen ageing. A comparison between RTFOT and TFOT for short-term ageing methods for different binders was performed. The PAV test was performed after short-term ageing on both the TFOT and RTFOT residue.

The effect of ageing on binders was quantified as an Ageing Index (AI) for different properties. These ageing indices encompassed the change in initial properties (penetration, softening point, and viscosity). The rheological and chemical changes of bitumen with ageing were also used to quantify the ageing effect. The Ageing index for different properties was calculated and compared. In addition to the traditional ageing methods, the effect of bitumen film thickness in the TFOT and PAV was investigated and the effect of ageing was quantified using different ageing indices. Furthermore, an ageing time study was performed using different binders in the TFOT oven for an extended ageing time to study the rate of ageing on bitumen. The relation between ageing time and the ageing rate was investigated and the effect on different binders was compared. The results and methodologies used are explained in the following sections.

4.2 Materials

In order to compare the effect of different ageing methods and ageing factors on the bitumen ageing, four different binders were used in this study. The binders have different pen grades; B1 and B2 are 40/60 pen binders, and B3 is a 50/70 pen binder. B4 is a softer binder with a penetration of 100/150.

The main fundamental specifications of these binders were tested and are presented in Table 4.1

Table 4.1 - Binder specification

Binder	Penetration (mm)	Softening Point (°C)	Viscosity at 135°C (mPa.s)
B1	45	51.6	445
B2	45	52.7	544
B3	59	50.2	451
B4	119	44.2	283

4.3 Ageing methods

Laboratory accelerated ageing involves different mechanisms in terms of increasing temperatures, the surface area being exposed to air or oxygen, environmental pressure, and different film thicknesses. Therefore, ageing analysis should consider the conditions and the understanding of ageing mechanisms involved in the ageing methods used. Thus, the aim of this study is to compare the effect of different ageing methods and factors on aged bitumen properties. The different ageing simulation methods used in this study are presented below.

4.3.1 Standard short and long-term ageing simulation

The effect of different ageing simulation methods was compared. The standard Thin Film Oven Test (TFOT) and The Rolling Thin Film Oven Test (RTFOT) methods were used for the short-term ageing simulation. For the long-term ageing, the Pressure

Ageing Vessel (PAV) was used, where the short-term ageing of bitumen in the TFOT or RTFOT was followed by PAV ageing. The Thin Film Oven Test (TFOT) is a standard binder test used for measuring the combined effects of heat and air on a film of bituminous binder. The purpose of the test is to simulate the effect of ageing on binders due to short-term ageing during mixing in an asphalt mixing plant. The test was carried out according to [BS EN 12607-2:2014](#). In this test, bitumen samples with the same volumes were placed in a TFOT pan to form a thin layer of the same thickness, which was then held in the TFOT oven at 163°C for 5 hours. The rolling thin film oven test (RTFOT) was also used for the short-term ageing simulation. In the RTFOT, eight glass containers each containing 35 g of bitumen were fixed in a vertically rotating shelf in the RTFOT oven. Hot air is blown into each sample bottle when it is at its lowest position. The samples were aged at a temperature of 163°C for a period of 75 minutes, according to [BS EN 12607-1:2014](#) standards.

The Pressure Ageing Vessel (PAV) ageing procedure was used to simulate long-term ageing in accordance with [BS-EN 14769:2012](#). In this procedure, samples were aged in a vessel pressurised to 2.1 MPa and heated for 20 hours at 90°C in the PAV oven after short-term ageing in the TFOT or RTFOT oven.

A comparison between these methods was performed. The ageing effect in terms of severity of the method used on different bitumen binders was investigated. In addition, the response and behaviour of each bitumen under different ageing methods was studied.

4.3.2 Effect of film thickness on ageing

From the literature of oxidative ageing, it is well known that oxidation of bitumen involves a diffusion mechanism. Thus, the film thickness is expected to play a major role in the ageing and must be controlled when studying the relative ageing of different binders ([Anderson et al.,1994](#)). So in order to investigate the effect of binder film thickness on the ageing, different binders were aged with different

thicknesses ranging from 1.8mm to 4.2mm in the TFOT oven and then followed by PAV ageing to simulate the short and long-term ageing respectively. The binder ageing effect was evaluated with different ageing indices as will be discussed in the following sections. The ageing susceptibility and the relationship between the ageing index and bitumen film thickness were investigated.

4.3.3 Ageing time study

As it was felt that only one ageing point from the TFOT for an ageing study is not enough to describe the whole situation, this study shows the evolution and changes of the chemical and physical properties of the bitumen developed during oxidative ageing with time. These results were also used as a base for following studies in the mastic phase to show the effect of mineral filler on bitumen ageing rate.

([Wu,2009](#)) stated that the intensity of the influence of the mineral on ageing keeps changing as the ageing simulation continues due to the changes in its adsorbing and catalysing abilities. This phenomenon will be discussed in detail in Chapter Five. However, in this chapter an ageing time study for the pure binders was performed, where it combines the effect of the extended ageing time in the TFOT oven on bitumen ageing and the effect of the bitumen film thickness. In this study, the different binders were aged in the TFOT oven for different ageing times of 2, 5, 10, and 20 hours, with two different ageing bitumen thicknesses; 3.2mm and 2.2mm. The effect of ageing was quantified and compared after different ageing stages.

Figure 4-1 summaries the ageing methods used in this study.

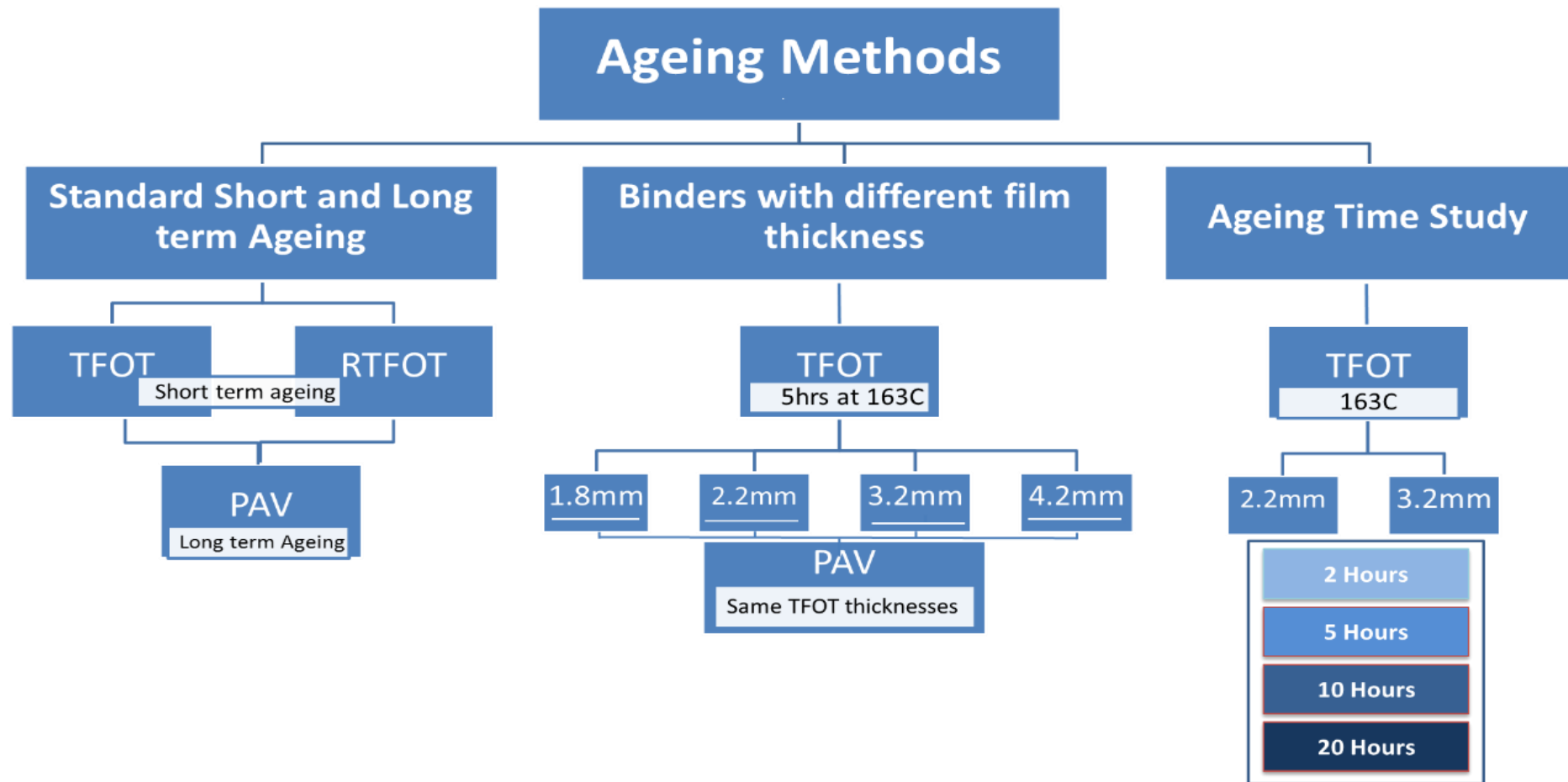


Figure 4-1 Ageing methods used for pure bitumen studies

4.4 Ageing evaluation

After ageing bitumen in the laboratory, some bitumen properties are changed. Ageing is normally evaluated by comparing some rheological or chemical property (e.g. penetration, softening point and viscosity) before and after ageing.

Due to the complex ageing behaviour of bitumen, a unique ageing indicator is not always enough to characterise the ageing behaviour. Ageing analyses of modified bitumen or the effect of filler should also take into account the effect of ageing on the modifier itself and the change in ageing behaviour.

In this section, the different tested binders with different ageing levels were evaluated by looking at the results from different perspectives:

- Basic properties: penetration, softening point and rotational viscosity
- Mechanical and rheological behaviour using dynamic shear rheometer (DSR).
- Chemical approach with Fourier transform infrared (FTIR) spectroscopy.

The ageing of bituminous material is commonly expressed and quantified by means of an ageing index. The ageing indices used to quantify the ageing effect on the binders were calculated after each ageing stage and compared. The following equation shows the general form of the ageing index:

$$\text{Ageing index (AI)} = \frac{P_{AGED}}{P_{UN-AGED}} \quad (1)$$

Where:

P_{UNAGED} = a physical property (e.g. viscosity, Softening Point, complex modulus) of the unaged bitumen;

P_{AGED} = the same physical property as measured on the unaged binder but performed after the ageing of the material.

In addition to the general form of an ageing index, the difference in softening point $\Delta R\&B$ before and after ageing was used to evaluate the extent of hardening according to equation (2)

$$\text{Change in softening point } (\Delta R\&B) = T_2 - T_1 \quad (2)$$

Where:

T_1, T_2 = the softening point before and after ageing, respectively.

In addition to the changes in physical and rheological properties, the chemical changes developed with ageing were investigated. The increase in carbonyl and sulfoxide index measured by the FTIR were calculated and correlated with other ageing indices used in this study.

4.4.1 Basic properties (Empirical tests)

Penetration, viscosity and softening point tests are considered the most common empirical tests that are used to evaluate the consistency or hardness of bitumen and bitumen mastics. The four different binders were aged with the different ageing methods and the ageing indices (the change in empirical tests viscosity and softening point) were calculated. High-temperature viscosities have been determined by using the Brookfield rotational viscometer at a temperature of 135°C according to [BS EN 13302:2010](#). The softening point was performed according to [BS EN 1427:2015](#). The results are shown in Table 4.2 and represented graphically in Figure 4-2. These results are the average of three replicates for viscosity and two repeats for softening point and the results were repeatable.

Table 4.2 –Ageing indices for binders aged with different ageing methods

Ageing method	Viscosity at 135°C (mPa.s)				Softening point (°C)			
	B1	B2	B3	B4	B1	B2	B3	B4
Un-aged	445	544	451	283	51.60	52.70	50.20	44.20
TFOT	622	660	692	402	56.80	57.20	55.40	50.60
RTFOT	651	825	670	379	56.80	59.40	56.40	49.60
TFOT+PAV	840	987	893	504	62.00	62.20	60.60	54.80
RTFOT+PAV	845	987	939	485	63.00	63.80	62.00	54.00
	Viscosity (AI)				ΔR&B			
T/ Unaged	1.40	1.21	1.53	1.42	5.20	4.50	5.20	6.40
R/ unaged	1.46	1.52	1.49	1.34	5.20	6.70	6.20	5.40
T+P/Unaged	1.89	1.81	1.98	1.78	10.40	9.50	10.40	10.60
R+P/unaged	1.90	1.81	2.08	1.71	11.40	11.10	11.80	9.80

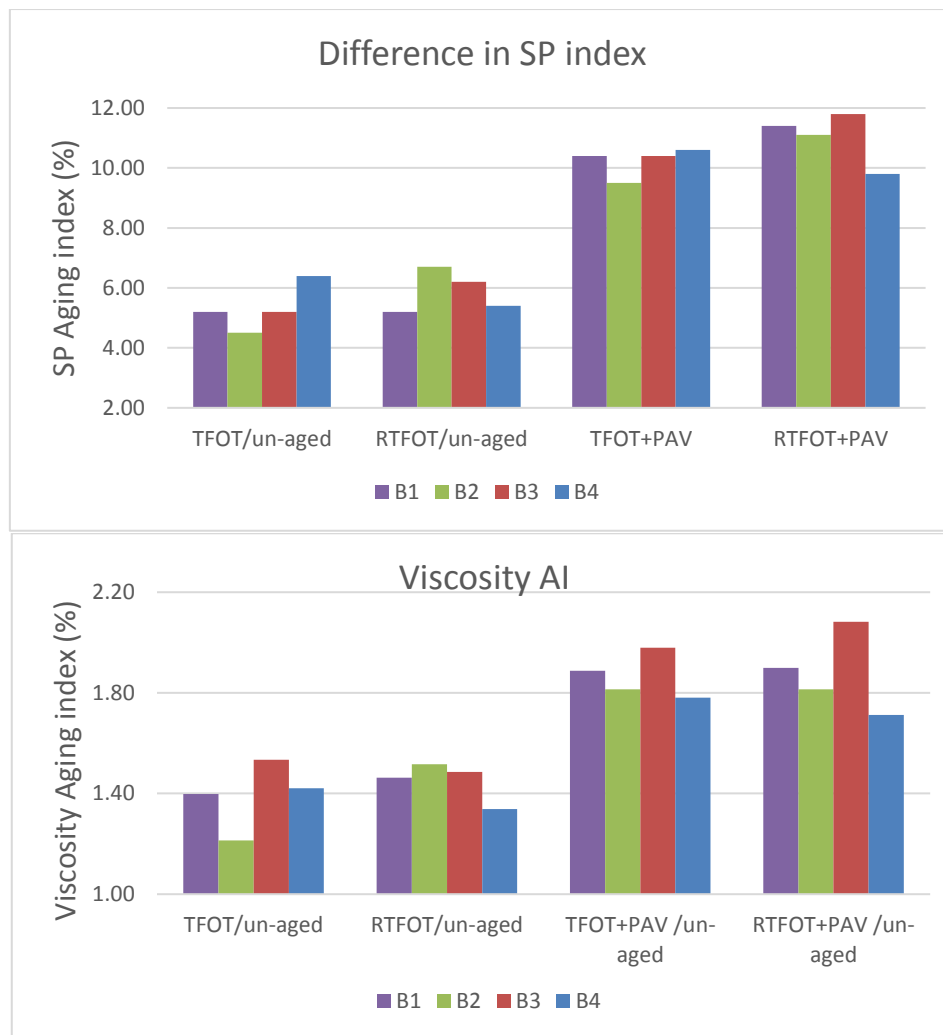


Figure 4-2 Ageing index from viscosity and softening point

It can be seen from the table and figures above, that the short-term ageing methods (TFOT and RTFOT) have almost the same effect on the viscosity and the softening point. However, it is binder dependent as it can be seen for binder B2 that the RTFOT is more severe and has more increase in both viscosity and softening point after short-term ageing. This is illustrated more clearly in Figure 4-3 and Figure 4-4. In general the effect of ageing on softening point changes; it increases by 5 to 7°C after short-term ageing and after long-term ageing, it increases by in the range of 9 to 12°C. Moreover, the PAV results reveal that although, there was some difference in viscosities and softening point values after short-term ageing for some binders, after these binders were PAV aged, they had more or less the same softening points and viscosity values. This may indicate the

possibility that the ageing mechanisms in the RTFOT and TFOT tests do differ and the ageing sensitivity is bitumen dependent. These results are in line with a previous study by ([Lu and Isacsson,2002](#)). In this study, different ageing indicators were compared after TFOT and RTFOT ageing. A strong correlation was observed between TFOT and RTFOT, regardless of the type of the parameters measured and the two ageing procedures showed a similar severity of ageing.

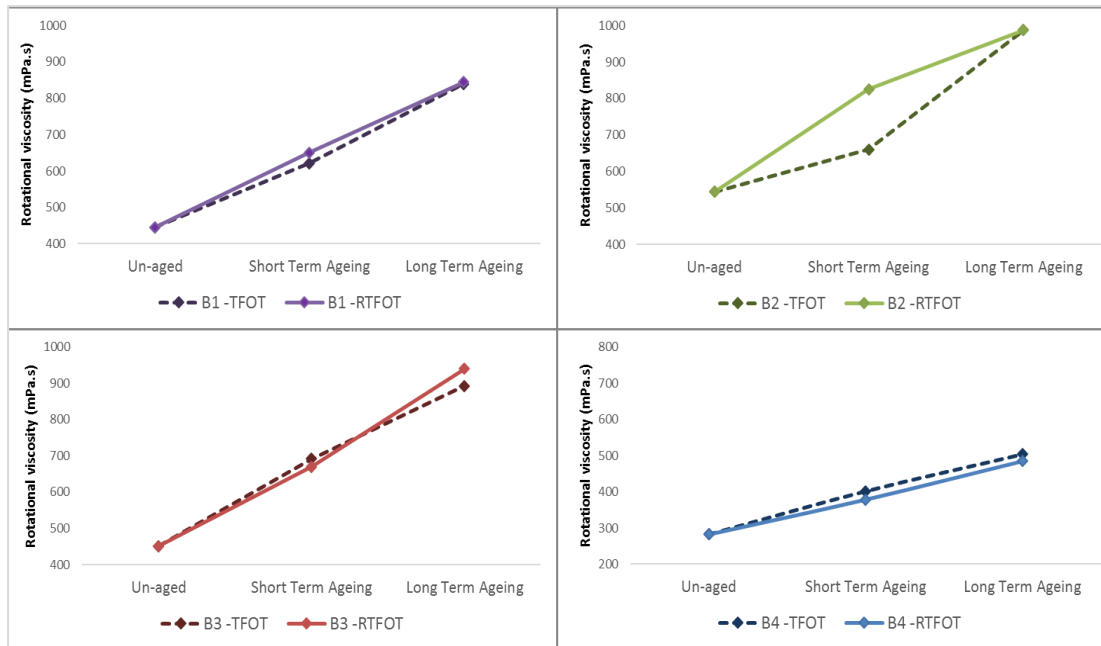


Figure 4-3 TFOT and RTFOT ageing effect on different binders (viscosity change)

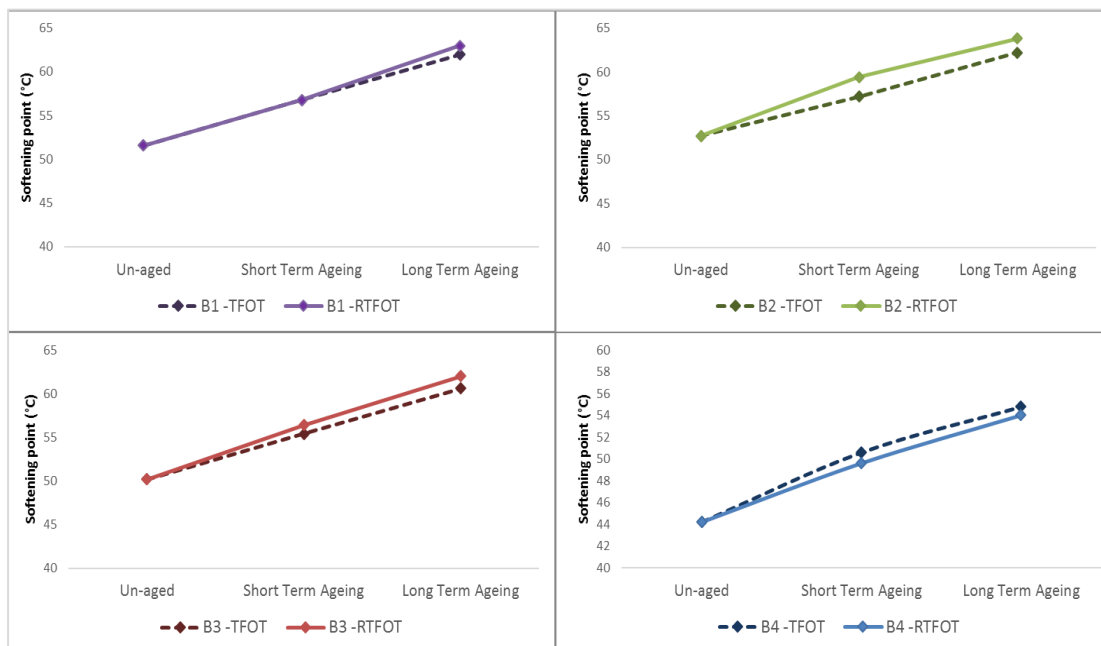


Figure 4-4 TFOT and RTFOT ageing effect on different binders (softening point change)

4.4.2 Changes in rheological properties

Although the measurement of empirical properties did reflect the ageing effect on bitumen, it was not possible to apply a certain factor to comprehensively characterise the ageing behaviour as the effect depends on a single point measurement. Therefore, using a fundamental rheological parameter in order to classify and evaluate bitumen binders according to their performance properties would lead to a better understanding of bitumen behaviour which occurs when subjected to different temperatures and loading conditions. In order to have a complete characterisation of the bitumen, as a viscoelastic material, bitumen must be tested over a wide frequency range (loading times) and temperatures related to actual traffic loads and pavement temperatures. Therefore, Dynamic Shear Rheometers (DSRs) are used to measure the rheological characteristics of bitumen. The parameters that are determined are the complex modulus and phase angle from which the viscoelastic properties of the bitumen can be evaluated. The rheological behaviour of bitumen and mastics can be measured using the DSR over a wide range of temperatures and frequencies. The results are usually presented in the form of master curves. Compared with empirical properties, i.e. viscosity and softening point, master curves reflect a rheological spectrum over a wide frequency or temperature range. Therefore, the use of master curves is becoming more and more popular in characterising a bitumen's rheological properties.

In this section, rheology has been applied to evaluate the properties of different bitumen binders before and after ageing with different methods.

The rheological properties of the bitumen were evaluated by the "Bohlin Gemini 200" model DSR. The following test conditions were used for the rheological characterisation by frequency sweep tests at different ageing stages:

Mode of loading: Controlled-strain,

Temperatures: 0 to 80°C,

Frequencies: 0.1 to 10 Hz,

Plate geometries: 8 mm diameter with a 2 mm gap (0°C to 30°C) and 25 mm diameter with a 1 mm gap (30°C to 80°C).

The results of frequency sweep DSR tests at different ageing stages for different binders are the average of two replicates but the difference between them was less than 10% in all cases. The results have been presented as complex modulus (G^*) master curves (at reference temperature of 30°C), phase angle (δ) master curves at 30°C and Black diagrams, and the results are shown in Figure 4-5 to Figure 4-7

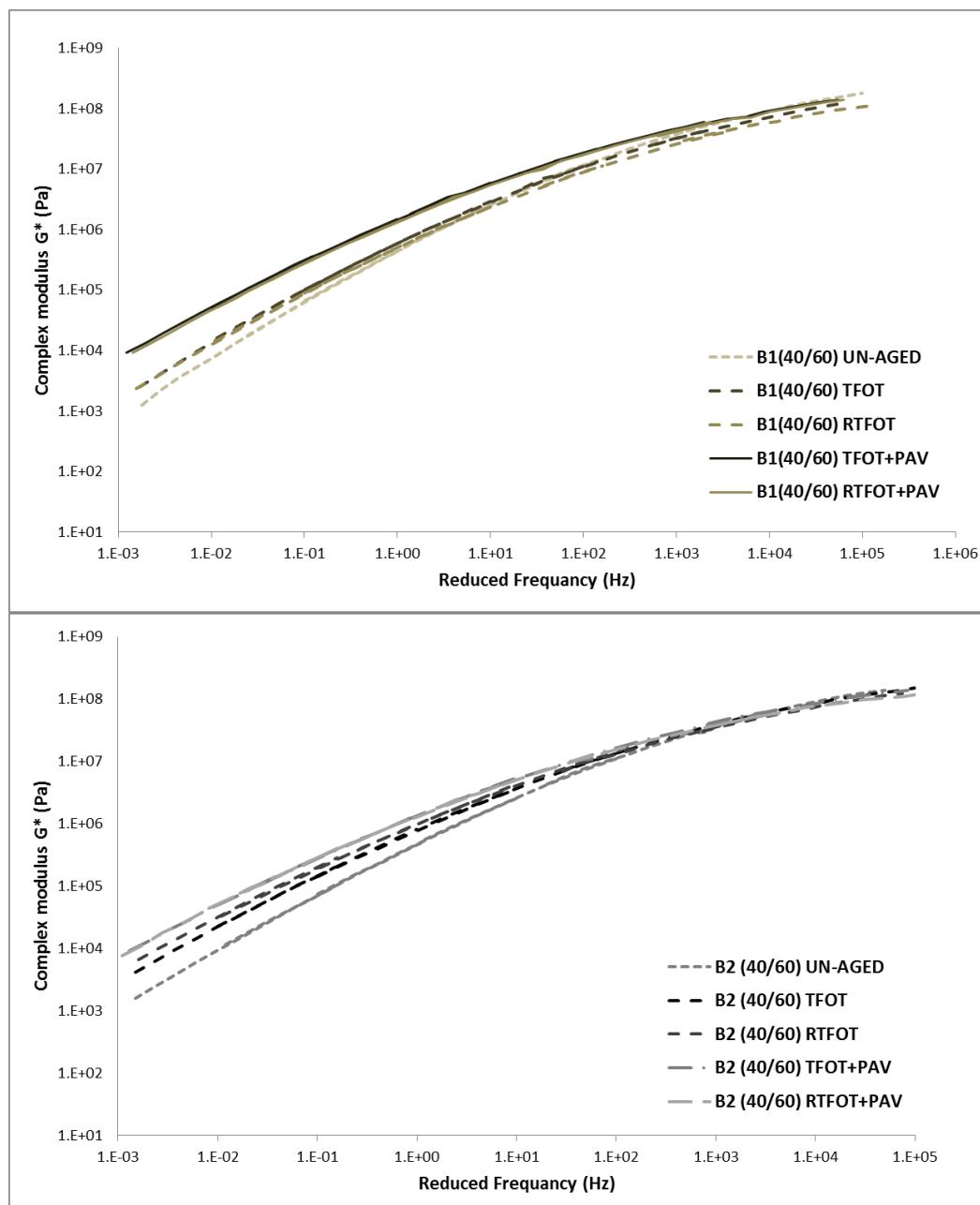


Figure 4-5 DSR Complex modulus master curves for bitumen B1 and B2 (40/60)

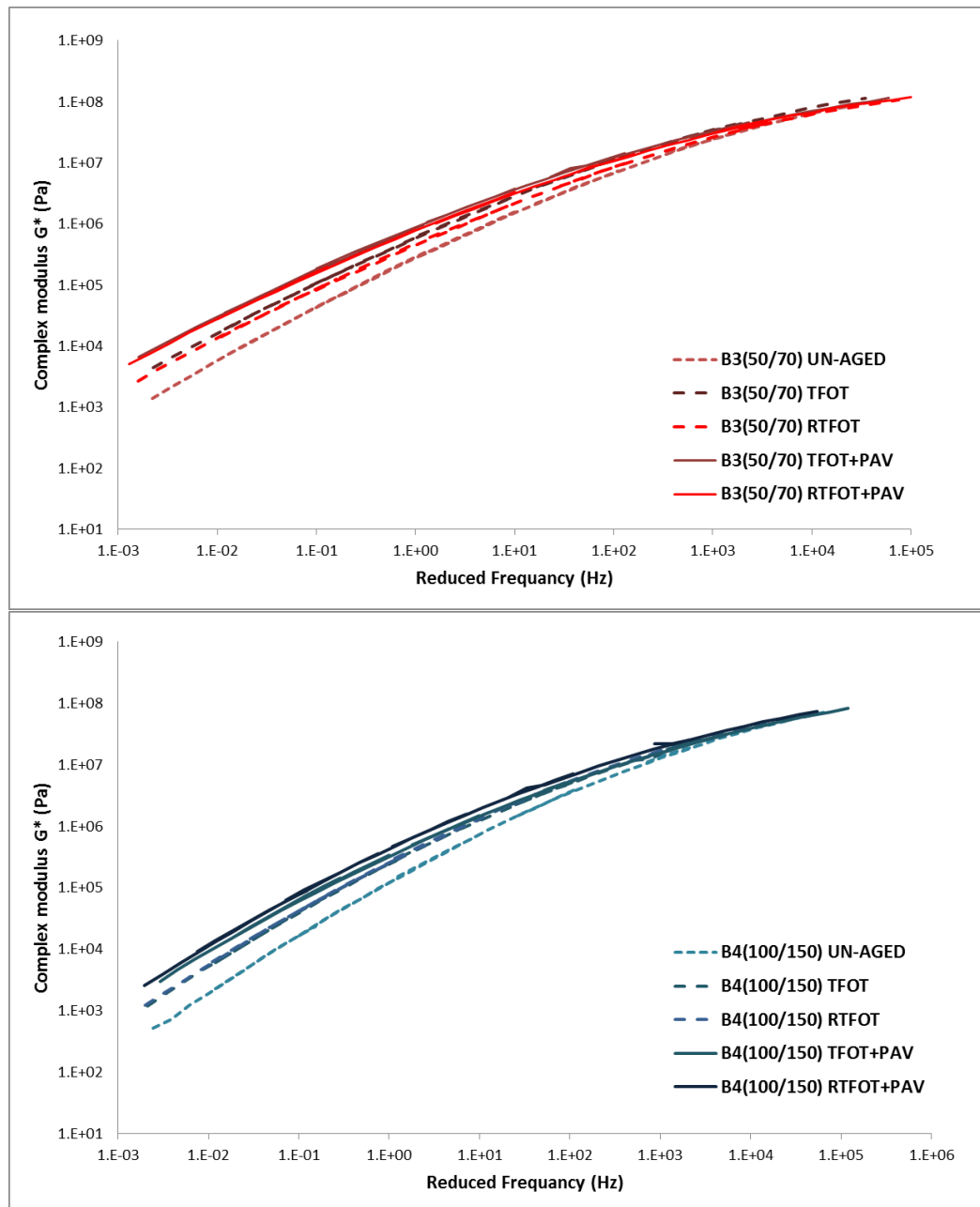


Figure 4-6 DSR Complex modulus master curves for bitumen B3 and B4

As shown in Figure 4-5 and Figure 4-6, the complex modulus master curves of pure bitumen are constructed using the WLF shifting method at a reference temperature of 30°C after different ageing stages. As seen, all binders exhibited a higher complex modulus G^* over the tested frequency range after ageing. However, it is clear that a bigger increase in the complex modulus is observed at lower frequencies (higher temperatures) whereas minor changes were observed at high frequencies. The master curves also show that both ageing methods (TFOT and

RTFOT) have almost the same severity on the bitumen ageing as they show a consistent increase in stiffness for binders either after short-term ageing in the 'TFOT' or 'RTFOT' or long-term aged with TFOT+PAV or RTFOT+PAV procedures. This can also be confirmed by the behaviour of the phase angle master curves and Black diagrams (Figure 4-7 for Bitumen B1 as an example). As can be seen, after ageing with different methods, phase angle master curves for both ageing methods show almost the same decrease with ageing, corresponding to an increase in the elasticity of the bitumen and a reduction of its flow characteristics after ageing.

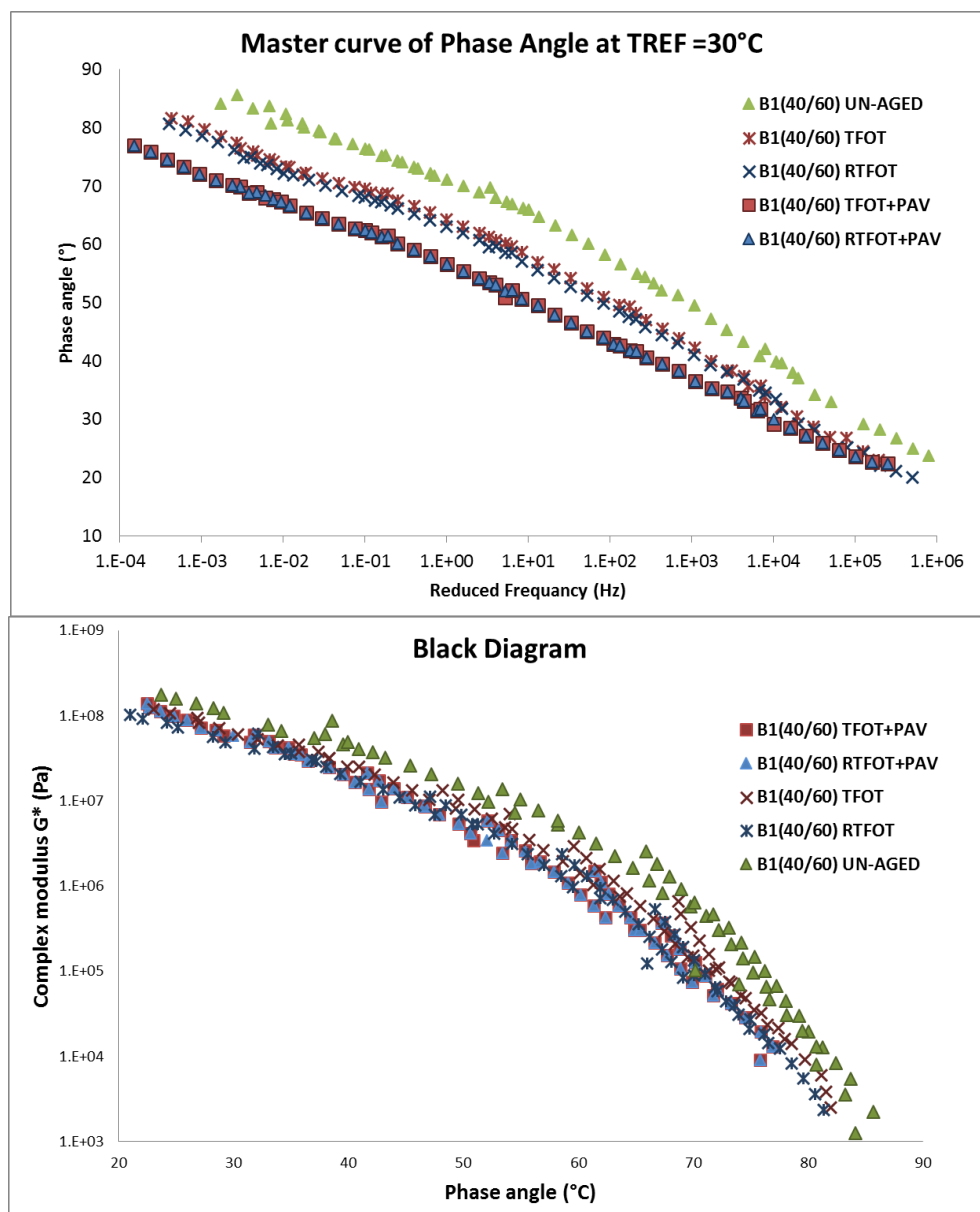


Figure 4-7 Phase angle and Black diagram for B1 (40/60) at different ageing stages

Furthermore, all ageing methods used in this study caused a decrease in phase angle especially at low frequencies (high temperatures), which in combination with the increase of complex modulus, is an indication of embrittlement of the binder and the degree of change is bitumen dependent. Since different compositions of bitumen result in different rheological properties, they also influence the bitumen sensitivity to ageing. To make the comparison more clear the ageing index derived from the rheological properties will be discussed in the following subsection.

4.4.2.1 Ageing index from complex modulus

Bitumen ageing is usually evaluated by means of an ageing index, which is defined as the ratio of a physical/rheological parameter of the aged bitumen to that of the original bitumen. The higher values of the ageing index indicate a higher degree of bitumen hardening. In order to show the rheological results in a clear and more quantitative way, the complex modulus (G^*) values are selected to compare the change of rheological properties of different binders after ageing at different testing temperatures and frequencies. The complex modulus ageing index (AI) is defined as:

$$\text{The ageing index (AI)} = \frac{G_{aged}^*}{G_{unaged}^*} \quad (3)$$

where,

G_{aged}^*, G_{unaged}^* = the complex modulus of the bitumen before and after ageing at the same temperature and frequency, respectively.

The behaviour of the bitumen after short and long-term ageing was compared at different temperatures and frequencies. The AI curves for Bitumen (B2) as a function of temperature at different chosen frequencies (0.1Hz, 0.4Hz, 1.59Hz, and 10Hz) after TFOT and PAV ageing are presented in Figure 4-8. It can be seen that at high frequencies (1.59, and 10Hz) the AI values increased with increasing test temperature up until 50°C, after which the AI became almost stable. With respect

to low frequencies (0.1Hz, 0.4Hz), there was a peak on the curve between 40°C and 60°C. The AI values at different frequencies became closer at very low temperatures 0°C and at temperatures higher than 60°C. A reason for this could be due to the fact that the bitumen at these temperatures almost reached its glassy or fluid state at which the sensitivity of the ageing index to temperature and frequency reduces. The same trend was observed for all used bitumens in this study.

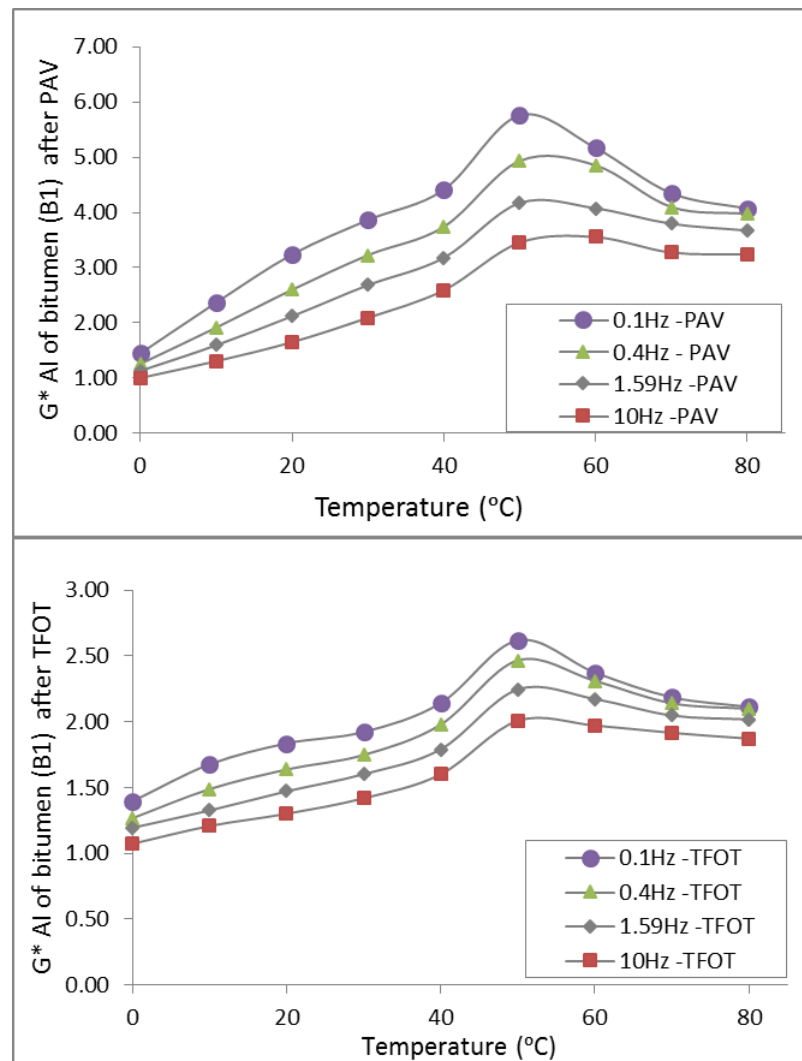


Figure 4-8 G* Ageing index for bitumen (B2) as a function of temperature at different frequencies after TFOT and PAV ageing

The change in the trend of these curves indicates that the AI of the base bitumens is more sensitive at a low frequency and at non-extreme temperatures. Therefore, a frequency of 0.4Hz was adopted to characterise the ageing properties of binders

and mastics. This frequency has also been adopted by other researchers who have studied the ageing effect on bitumen and mastics ([Wu,2009](#); [Rahman,2004](#)). Thus, the results of this study can be compared with these previous studies.

The results of Aging Index (AI) calculated at 20°C and 40°C and 0.4 Hz are presented in Figure 4-9 for complex modulus and Figure 4-10 for phase angle (δ). From Figure 4-9 it can be seen that the complex modulus (G^*) ageing index has almost the same trend after different ageing methods for both chosen temperatures. However, it is noticeable that the ageing index at 40°C is higher than that for 20°C. In addition, it can be noticed that at both temperatures the ranking of bitumens according to the degree of ageing with the two different ageing methods (TFOT and RTFOT) are similar.

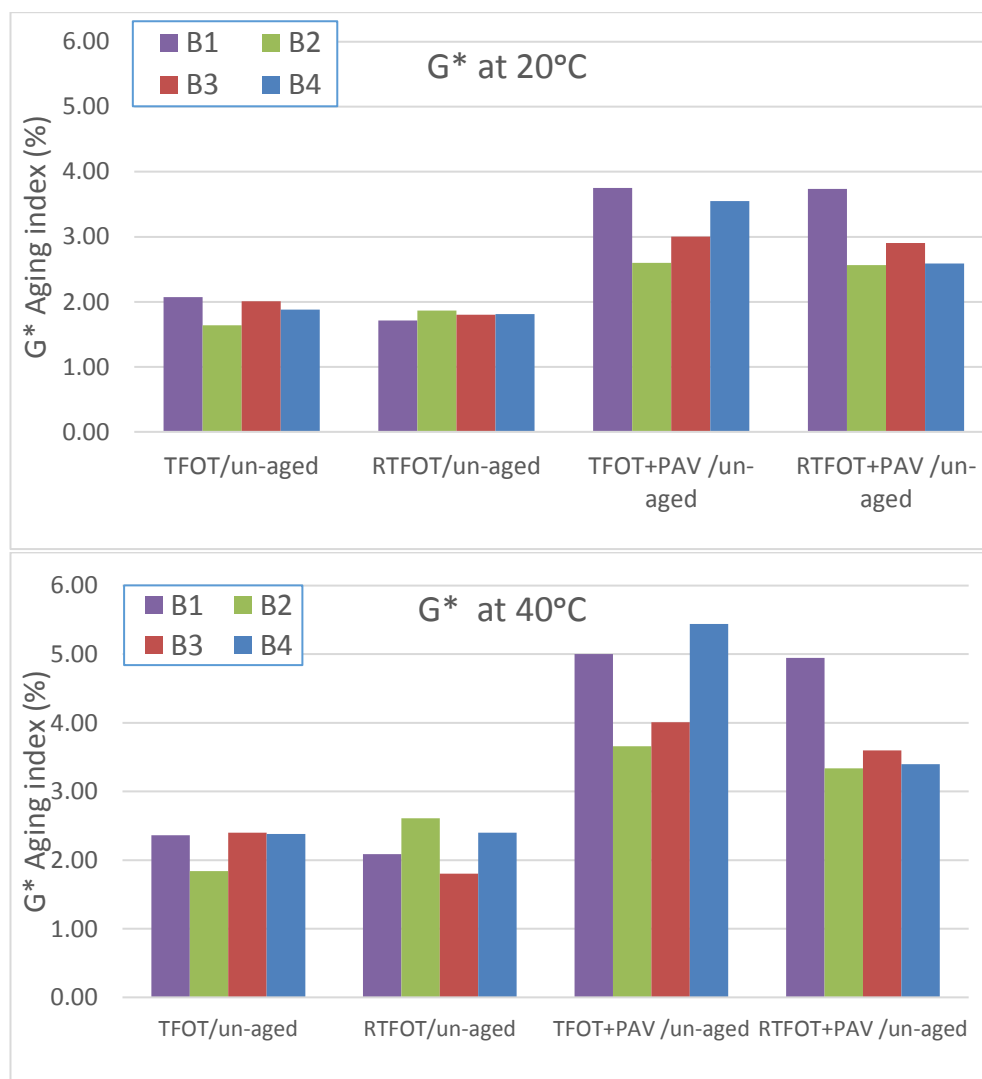
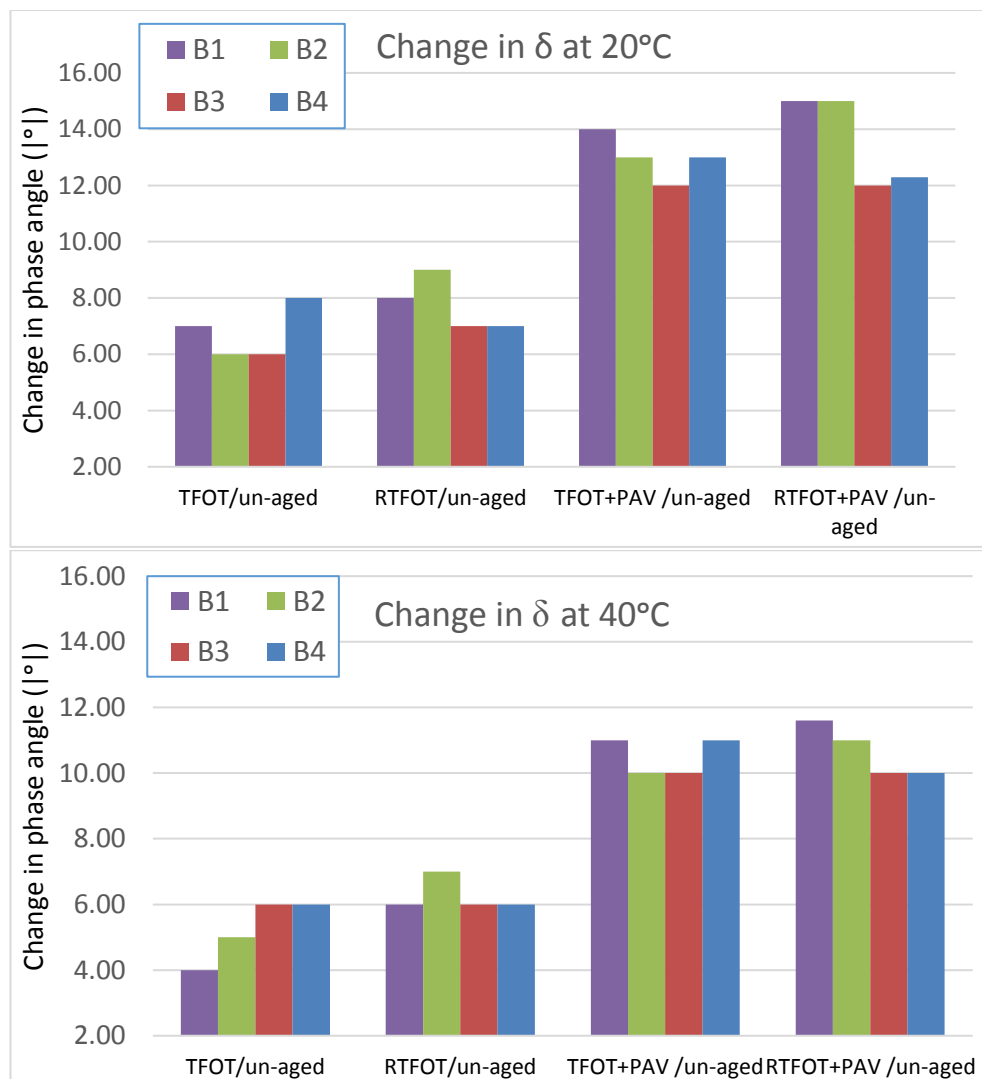


Figure 4-9 Complex modulus ageing index at 20°C and 40°C

Also from Figure 4-10, the same conclusion can be made according to the change in the phase angle with ageing. However, in contrast to the complex modulus, the change in phase angle is higher at the lower temperature of 20°C. The results also show that the complex modulus (G^*) increases and the phase angle (δ) decreases with ageing which indicates that ageing makes the properties of the bitumen more solid-like.

**Figure 4-10 Change in Phase angle at 20C and 40C**

In addition, it is noticeable that the magnitude of the changes is bitumen dependent as well as depending on the evaluation conditions. For example after short-term ageing, at 20°C and 0.4Hz, the complex modulus may increase by 63% (B2) to

107% for B1. After long-term ageing, it ranges from 156% (B2) to 275% (B1). In comparison, at 40°C and 0.4Hz, the increase in complex modulus range between 80% (B3) and 160% (B2) after short-term ageing. In addition, the increase ranges from 233% (B2) to 444% (B4) after long-term ageing. Therefore, these results indicate that the ageing had minimal effect on dynamic modulus at lower temperatures. These conclusions also can be supported by the master curves of the binders presented in Figure 4-5 and Figure 4-6 as they show clearly that at higher frequencies (low temperatures) the changes in complex modulus are very low compared to the changes at lower frequencies (higher temperatures). In contrast, the decrease in phase angle after long-term ageing measured at 20°C ranges from 18% to 24%. However, this change ranges between 12% and 15% at 40°C.

Moreover, since the phase angle is a measure of the ratio between loss modulus and storage modulus ($\tan(\delta)=G''/G'$), the decreased phase angle implies that ageing leads to a greater increase in storage modulus than in loss modulus. However, at high temperatures, the increase in complex modulus is mainly attributed to the increased viscous component (G'').

4.4.3 FTIR analysis

Many studies have adopted Fourier transform infrared (FTIR) spectroscopy to characterize ageing behaviour. It has been used to observe the evolution of chemical structures of bitumen as a result of ageing ([Lamontagne,2001](#); [Ouyang et al.,2006](#); [Mouillet et al.,2008](#); [Wu,2009](#); [Marsac et al.,2014](#); [Yang et al.,2014](#)). The FTIR test consists of exciting the material with infra-red light and then quantifying the different types of molecular bond through characteristic absorption bands in the infra-red light spectrum. Carbonyl groups, characterised by C=O, are among the major functional groups formed during oxidative ageing. It has been demonstrated that the formation of carbonyl (C=O) changes the physical properties of the binder; thus many researchers have used it as an ageing index to quantify the evolution of chemical changes in the binder with ageing ([Lamontagne,2001](#); [Wu,2009](#); [Ouyang et al.,2006](#); [Mikhailenko et al.,2016](#)).

In this study, an FTIR spectrometer was used to determine the functional characteristics of the bitumen before and after ageing. The FTIR analysis was performed using a Bruker Tensor 27 infrared machine. The spectra used were the average of 32 scans (per sample) with a 4 cm^{-1} resolution and a band range of $4000\text{--}500\text{ cm}^{-1}$. For the bitumen, around 0.5 g is placed (at ambient temperature) on the FTIR crystal as a solid and the scan conducted, the average of the 32 scans being recorded. The crystal was cleaned with ethanol before each test. Carbonyl C=O and Sulfoxide S=O were used as ageing indices to evaluate the effect of ageing on binders after different ageing methods. The analysis can be monitored either relative to the area of the functional bands or by calculating structural indices in order to avoid the effect of the film thickness of the tested samples.

In this study, ageing indices were used. They were calculated as follows:

$$\text{Carbonyl index (C=O)} = A_{1700}/\Sigma A,$$

$$\text{Sulfoxide index (S=O)} = A_{1030}/\Sigma A$$

Where:

The sum of the area ΣA represents: $A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}$

The FTIR Spectra of the bitumen binders before ageing are presented in Figure 4-11. In addition Figure 4-12 shows the FTIR scan results for bitumen (B4 as an example) before ageing and after ageing by different methods. The calculated carbonyl and sulfoxide indices are presented in Table 4.3.

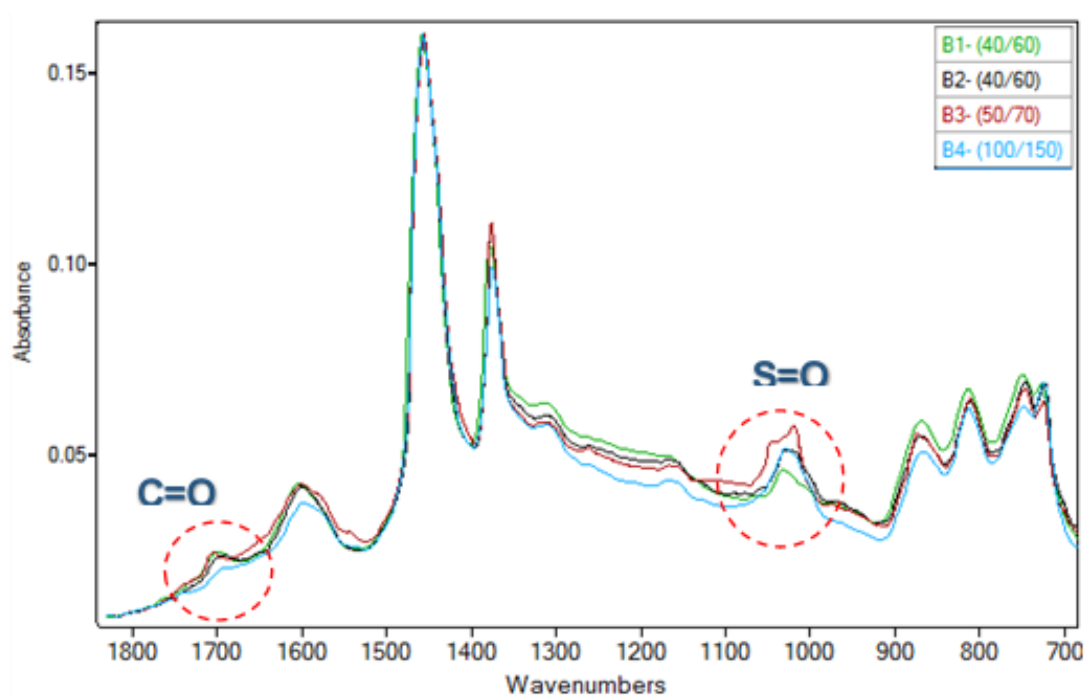


Figure 4-11 FTIR Spectra of differen bitumen binders before ageing.

From the FTIR spectra in Figure 4-11, it can be noticed that the softer binder (B4 -100/150 pen) has the lowest carbonyl area, the other binders have similar carbonyl areas which are significantly higher compared to B4 (100/150) bitumen. Furthermore, a quantitative comparison between different binders was performed depending on the carbonyl and sulfoxide ageing indices.

A quantitative comparison between the effect of different ageing methods on the changes in carbonyl and sulfoxide indices was calculated after ageing bitumens using different methods and the results are presented in Figure 4-12 and Table 4.3.

Regarding the effect of different ageing methods on bitumen ageing, it can be seen from Figure 4-12 that the absorbance values at wavenumbers representing carbonyl and sulfoxide increase as the ageing simulation proceeds. This indicates that the amount of the oxidation products in bitumen increased during the ageing process and this means the bitumen stiffness increased.

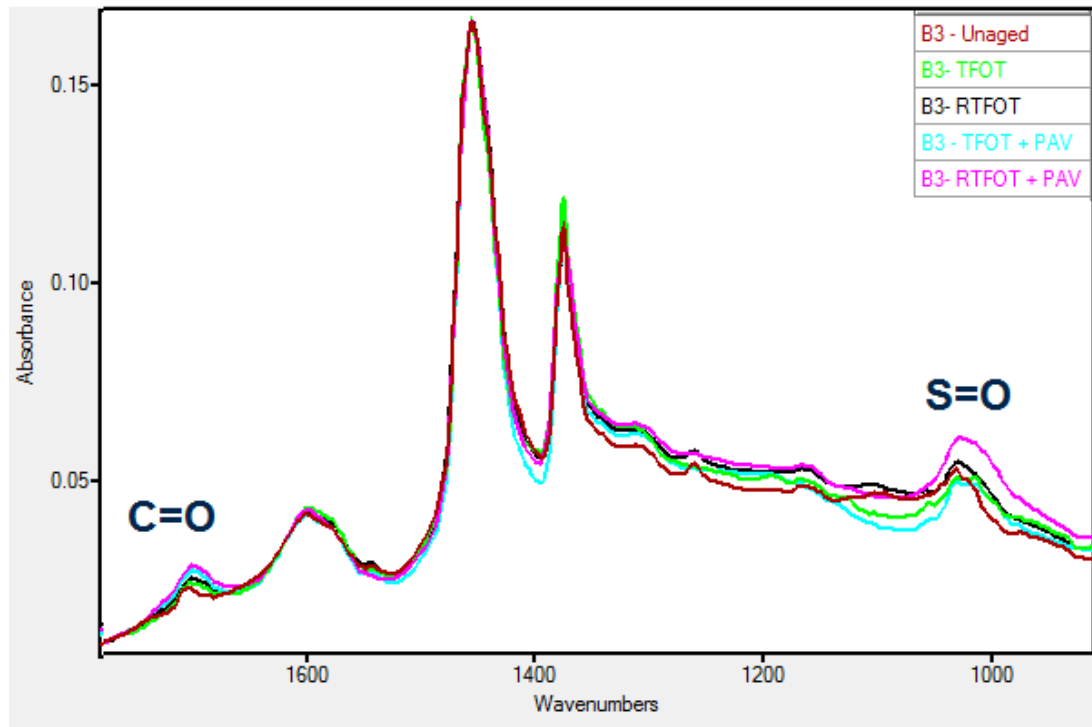


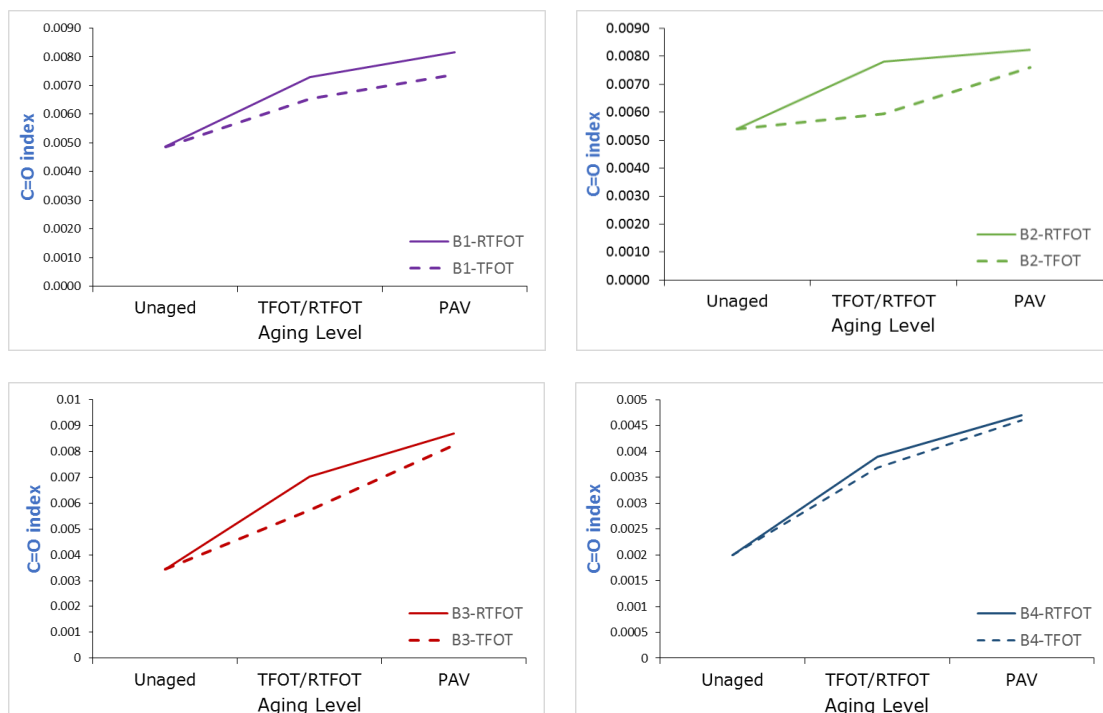
Figure 4-12 FTIR Spectra of Bitumen (B4) at different ageing levels.

In addition, the carbonyl and sulfoxide indices were calculated after applying different ageing methods and presented in Table 4.3. These results show there is a correlation between the increase in carbonyl area and bitumen stiffness. This can be correlated to the physical properties of the bitumen (softening point, viscosity and complex modulus). However, the sulfoxide ageing index is less correlated. These results are in agreement with some previous studies ([Lu and Isacsson,2002](#); [Yut and Zofka,2014](#); [Abdullah et al.,2013](#); [Lu et al.,2008](#)).

Table 4.3 –Carbonyl and sulfoxide ageing indices for binders aged with different ageing methods

Ageing method	Carbonyl Index				Sulfoxide Index			
	B1	B2	B3	B4	B1	B2	B3	B4
Un-aged	0.0049	0.0054	0.0034	0.0020	0.026	0.019	0.035	0.038
TFOT	0.0065	0.0059	0.0057	0.0036	0.036	0.035	0.039	0.039
T+PAV	0.0074	0.0076	0.0082	0.0046	0.048	0.044	0.048	0.048
RTFOT	0.0073	0.0078	0.0070	0.0039	0.039	0.026	0.041	0.041
R+PAV	0.0082	0.0082	0.0087	0.0047	0.054	0.039	0.051	0.051

The results in Table 4.3 reveal that the effect of the different ageing methods on the carbonyl index for different binders used in this study is correlated to the other physical properties tested in this study. However, the results also can show that the carbonyl index for the RTFOT aged bitumen is slightly higher than the TFOT aged bitumen as can be seen more clearly in Figure 4-13. This result is expected due to the different ageing mechanisms that could occur in the two ageing methods.

**Figure 4-13 Carbonyl index for binders aged with different methods**

The RTFOT ageing includes blowing hot air into samples during ageing; therefore, the RTFOT ageing simulation ensures that all the bitumen is exposed to heat and air, which increases the oxidation rate of the bitumen. Thus, more oxidation products such as carbonyls are generated by this method than the TFOT ageing. This effect appears to be bitumen dependent. Moreover, the results show that after PAV ageing both methods give almost similar carbonyl indices. In general, the FTIR test performed on bitumen aged with different methods shows that the carbonyl index is a good indicator of bitumen ageing. The carbonyl index can rank the bitumens according to their ageing degree as with correlation to other rheological and physical ageing indices. Figure 4-14 show the correlation between carbonyl index with viscosity and softening point where a good correlation coefficient, $R^2=0.88$ and $R^2=0.90$ were obtained respectively.

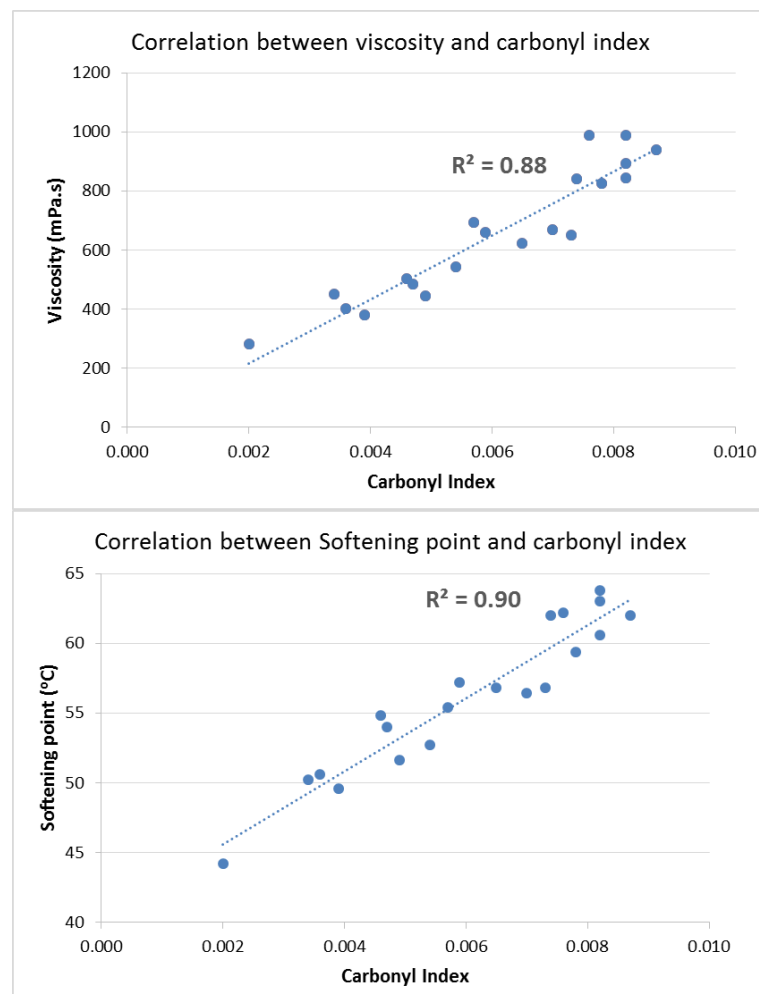


Figure 4-14 Correlation between carbonyl index and viscosity and softening point.

4.5 TFOT ageing with different film thicknesses

Studies have been done to investigate the effect of film thickness on the laboratory ageing of bitumen. These studies have highlighted the important influence of the bitumen film thickness on bitumen ageing. From the literature review of bitumen oxidation in the PAV, it became apparent that oxidation of bitumen binders involves a diffusion mechanism. Thus, the film thickness is expected to play a major role in the ageing process and must be controlled when studying the relative ageing of different binders ([Anderson et al.,1994](#)). So in order to investigate the effect of binder film thickness on ageing, different binders were aged in the TFOT and this was followed with PAV oven ageing with different thicknesses and the ageing effect was then evaluated by different ageing indices as discussed in previous sections. A thicker binder film is believed to result in stronger resistance to oxidation, resulting in delayed hardening and improved fatigue resistance. The reason, according to ([Heslop and Catt,1997](#)), is that a thick binder film keeps binder hardening to a minimum because of the longer time required for oxygen to penetrate the thicker binder film. Binder film thickness plays an important role in the oxidation process of the bitumen since oxidation is a chemical process that is a function of the diffusion of oxygen, which varies with the consistency or viscosity of the binder. Temperature and pressure are factors that affect the rate of diffusion of oxygen and thus the ageing rate ([Anderson et al.,1994](#)).

In order to find the effect of bitumen film thickness on the laboratory ageing of binders, four different binders were aged in the TFOT pans with different thickness (1.8, 2.2, 3.2 and 4.2mm) for the normal 5hrs TFOT ageing at 163°C. This was followed by PAV ageing with the same thicknesses as used in the TFOT. The PAV ageing was done according to [BS EN 14769:2012](#). The samples were aged for 20 hours at 90°C under a pressure of 2.1MPa. The relationship between the bitumen binder thicknesses and the ageing has been observed in the four different binders.

The ageing index after each stage of ageing was calculated and the film thickness to ageing index relationship was derived as well. Figure 4-15 and Figure 4-16 presents the relations between ageing and binder thickness after TFOT and PAV ageing respectively. These results are the average of three replicates for viscosity and two for softening point and complex modulus, the results were repeatable. The percentage deviation with respect to the mean value representing all the replicates tested was less than 15%.

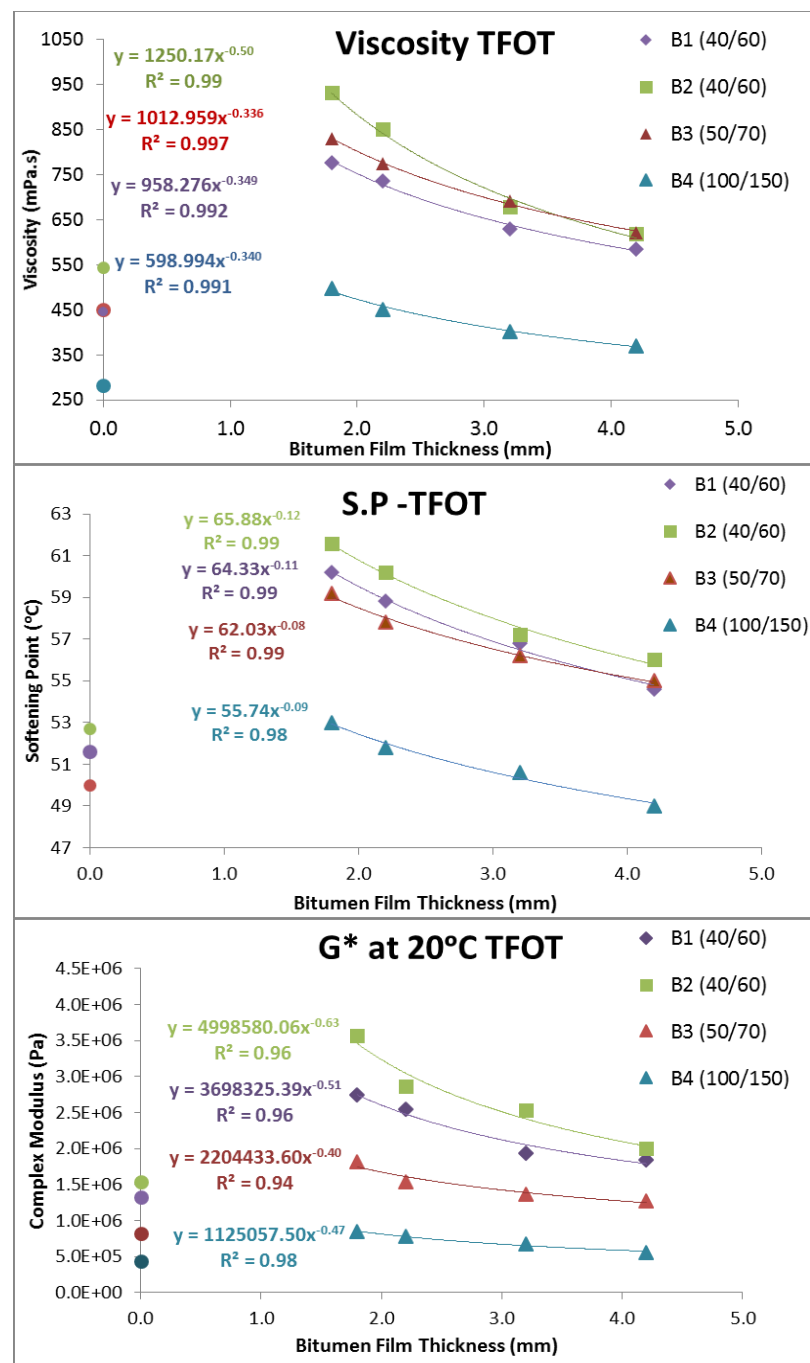


Figure 4-15 Ageing binders with different thicknesses -TFOT

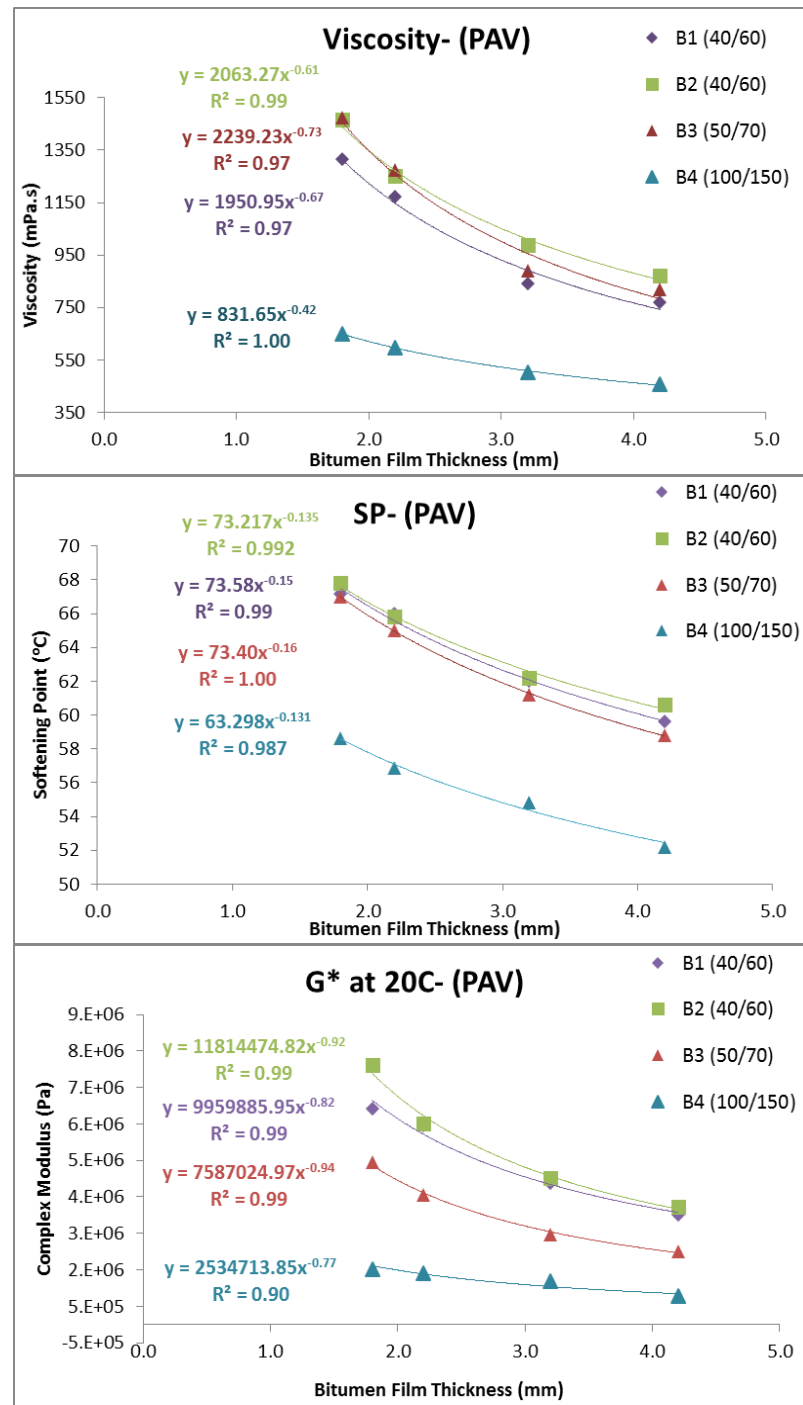


Figure 4-16 Ageing binders with different thicknesses - PAV

The results confirm the important effect of the film thickness on bitumen ageing and it can be seen that the influence is highly bitumen specific. It is clear that the bitumen film thickness is well correlated with the change in physical properties (Viscosity, Softening point and Complex modulus). It can be seen that the results show that a power law describes the trend of change of these properties with film thickness. As the bitumen film decreases, the viscosity, softening point and

complex modulus increase after ageing. Some previous studies have shown the relations between the bitumen film thickness and the ageing effect. (Anderson et al.,1994) observed that there is a linear relationship between log viscosity after ageing in PAV and the square of the film thickness. Recently (Moraes and Bahia,2015a) investigated the film thickness effect during ageing in the PAV. Their study showed that a power law describes the relationship between the ageing index and film thickness. In order to see the effect of film thickness on the ageing index for different tested properties, ageing index was calculated as discussed in section 4.4. This relation with ageing index is presented in Figure 4-17.

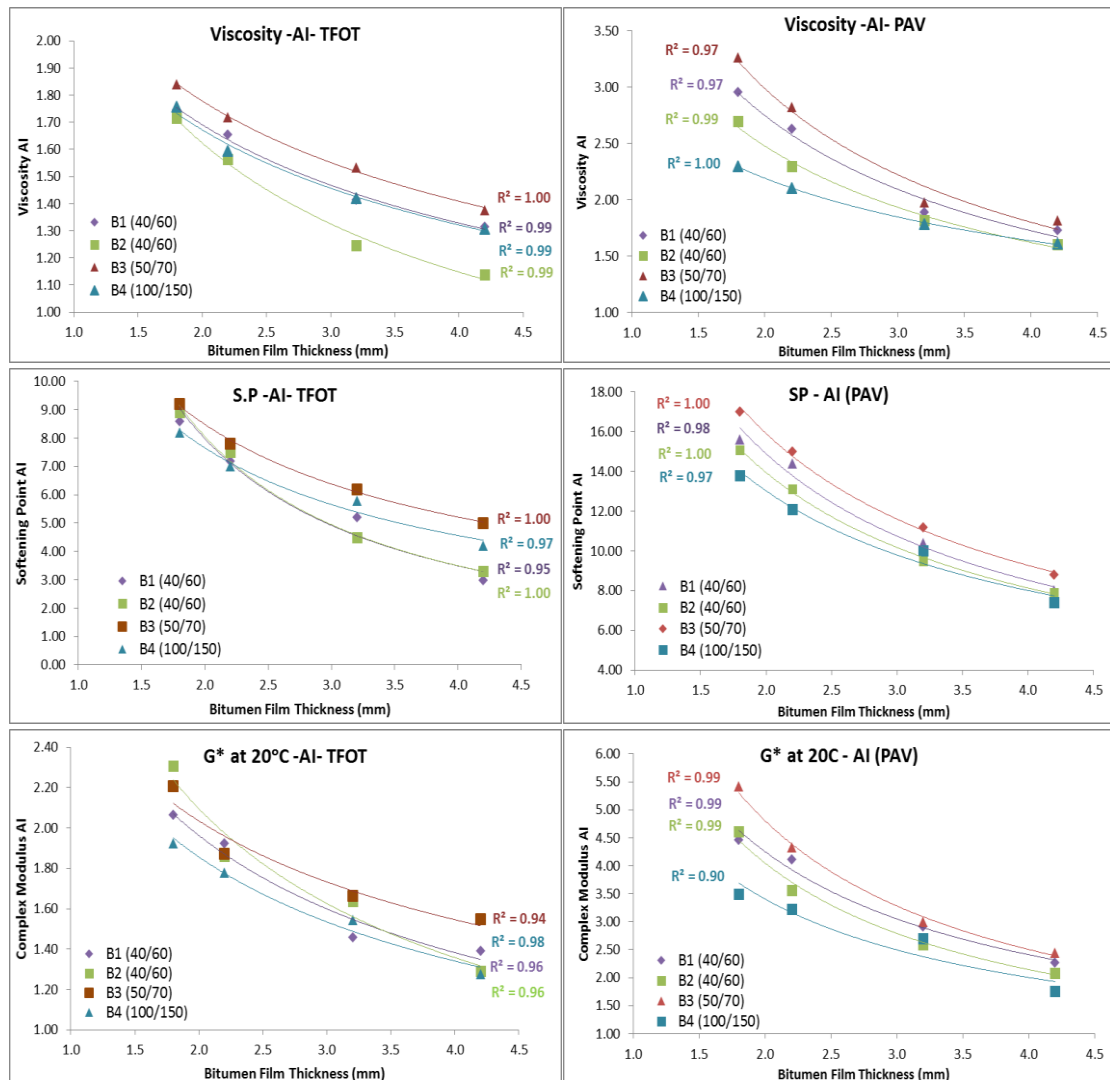


Figure 4-17 Relationship between film thickness and ageing index

The results above show that the ageing index decreases by increasing the bitumen film thickness. In addition, they show that a power law describes the trend against film thickness. The results of this study are in agreement with the finding of ([Moraes and Bahia,2015a](#)) and furthermore, it has been applied to different binders and other ageing indices. It can also be seen from the PAV results that the ageing index range decreases with the increase of bitumen film thickness. It can be noticed after PAV ageing at 4.2mm thickness, the ageing indices for different binders are much closer to each other. It means that the range of ageing indices is smaller, this could indicate that the sensitivity of bitumen to ageing in the PAV decrease with the increases of bitumen film thickness.

4.6 The ageing time study

The ageing time study was performed in order to study the rate of ageing and the change in bitumen properties with extended ageing times. This was done as it was felt that only one ageing point from the TFOT for an ageing study is not enough to describe the whole situation and to show the evolution and changes of the chemical and physical properties of the bitumen developed during oxidative ageing. This ageing time study combines the effect of extended ageing time in TFOT oven oxidative ageing on bitumen in addition to the effect of bitumen film thickness. In this study, the different binders were aged in the TFOT oven for different ageing times, 2, 5, 10, and 20 hours, with two different bitumen thicknesses 3.2mm, and 2.2mm. The effect of ageing was quantified by different ageing indices as discussed earlier. The effect of TFOT ageing time on softening point and viscosity increases and the complex modulus for different binders aged at 3.2mm thickness is shown Figure 4-18.

It is clear from the relationship between the ageing time and the increasing rate of different properties that an exponential relation controls this rate of increase for all these properties. The rate is also bitumen dependent, as it is related to the ageing index. Thus in order to show this effect on the ageing index for the tested properties, the ageing index was calculated and the relation between ageing index and the TFOT ageing time was derived and the results are shown in Figure 4-19. The results of the ageing index relationship with TFOT ageing time shows that the viscosity and complex modulus ageing indices as calculated in this study increase exponentially with TFOT ageing time. However, for the softening point ageing index ($T_{aged} - T_{unaged}$), it can be noticed that a linear relationship more accurately describes the increase in softening point ageing index with TFOT ageing time. Furthermore, the results show that the different ageing indices rank bitumen similarly according to the ageing effect.

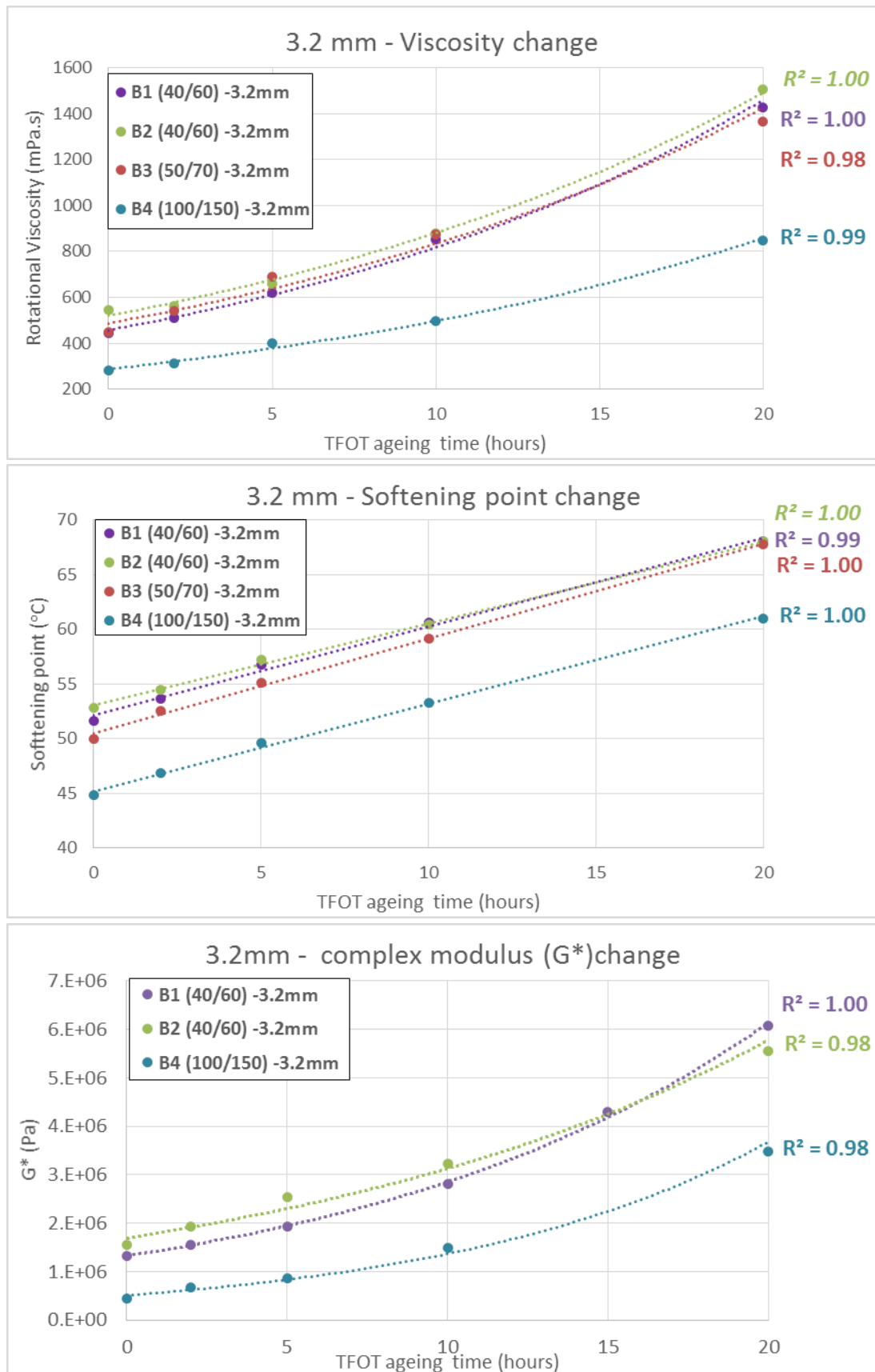


Figure 4-18 Effect of TFOT ageing time at 3.2mm film thickness on bitumen properties

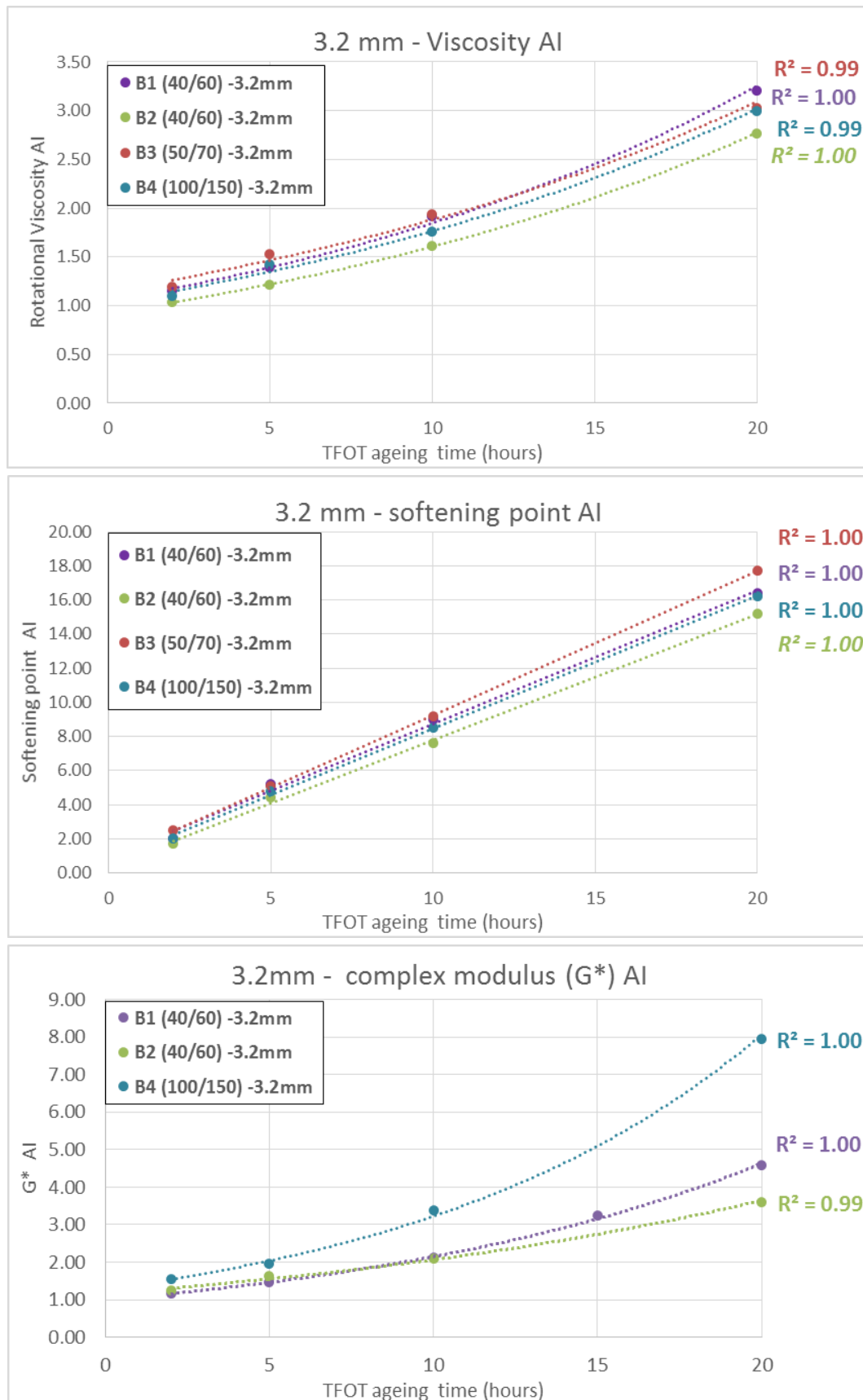


Figure 4-19 Effect of TFOT ageing time at 3.2mm on AI

Furthermore, a comparison between the effects of different ageing film thicknesses on the TFOT ageing rate for different bitumens was also performed. The relationship between the increase in viscosity, softening point and the complex modulus was derived. This relationship is shown in Figure 4-20.

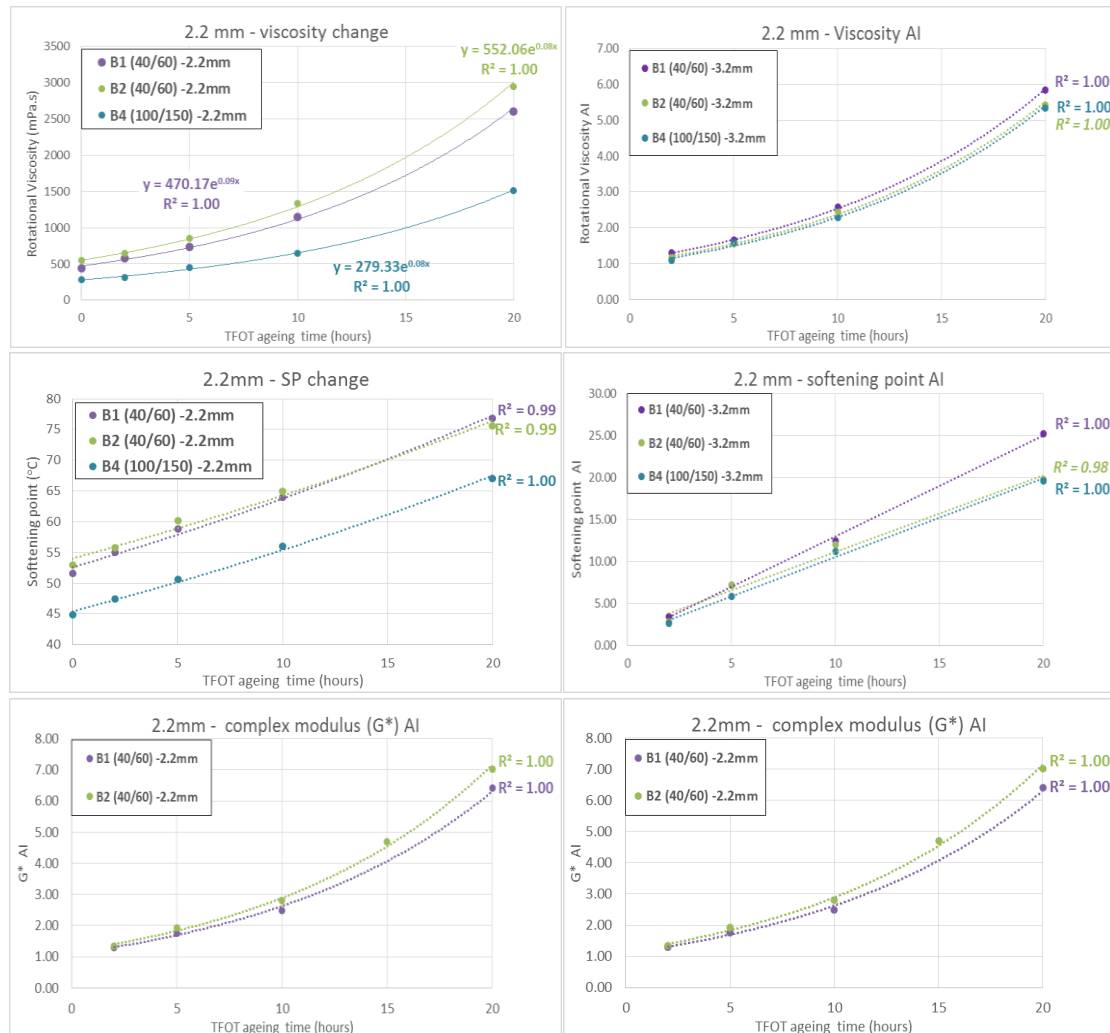


Figure 4-20 Effect of TFOT ageing time at 2.2mm thickness on bitumen

From both Figure 4-19 and Figure 4-20, it can be concluded that the effect of extended ageing time in the TFOT oven on different bitumen binders does not change with the thickness. In addition, the relationship between the changes in different physical properties measured in this study remains the same with the two different thicknesses used in this study. However, the effect at lower film thickness is more intense but of the same form. These comparisons are shown in Figure 4-21.

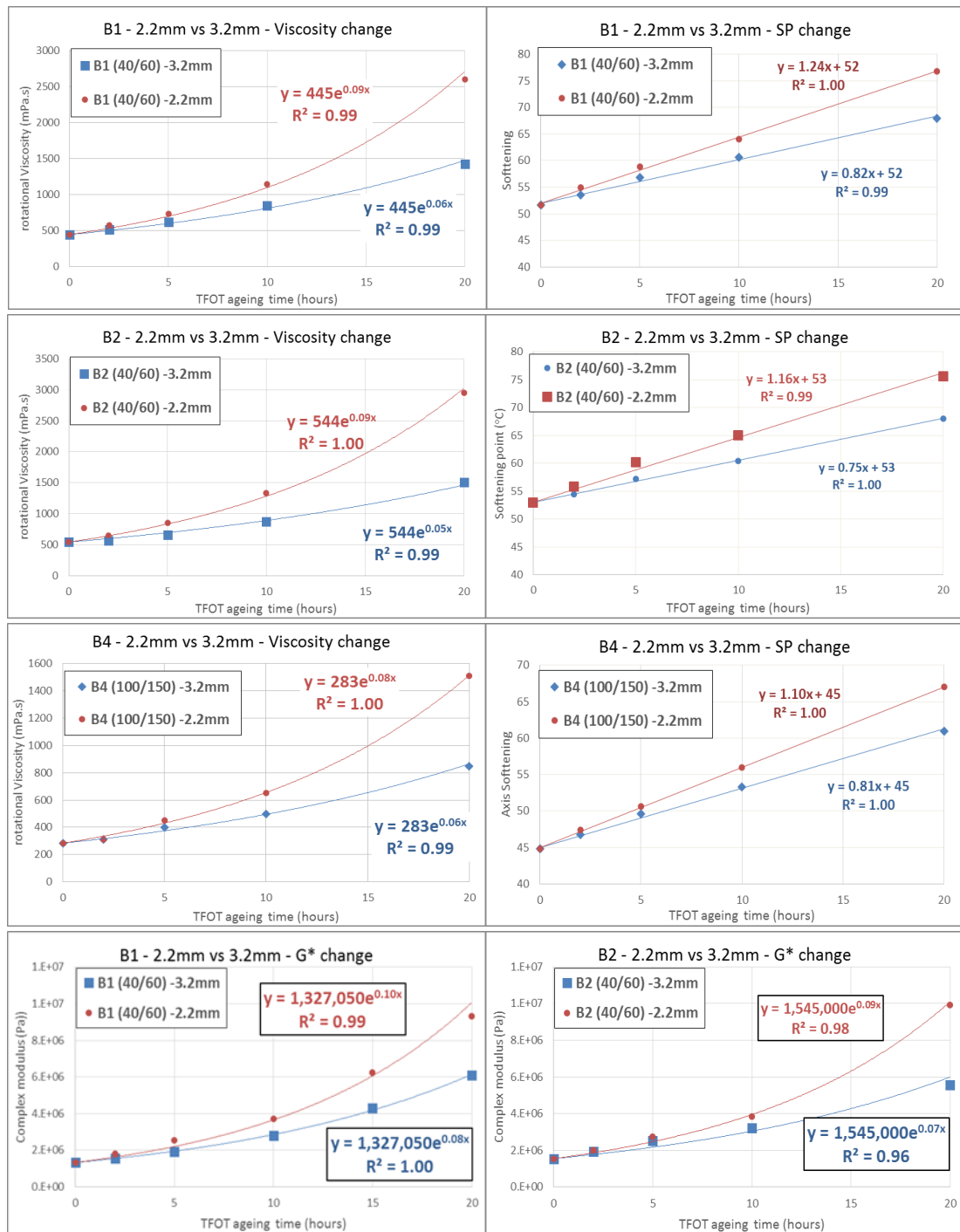


Figure 4-21 Comparing the effect of TFOT ageing time at 2.2mm and 3.2mm thickness on bitumen properties

4.7 Chapter conclusion

The main aim of this chapter was to study the effect of different ageing methods and parameters on bitumen ageing. A comparison between short and long-term ageing methods was performed. The effect of ageing on binders was quantified as Ageing Index (AI) for different properties such as softening point, viscosity and complex modulus and using FTIR to study the chemical changes in bitumen with ageing. In addition to the traditional ageing methods, the effect of bitumen film thickness in the TFOT and PAV was investigated and the effect of ageing was quantified using different ageing indices. Furthermore, an ageing time study was performed using different binders in the TFOT oven for an extended ageing time to study the rate of ageing on bitumen. The relation between ageing time and the ageing rate was investigated and the effect on different binders was compared. The conclusions from the study can be summarized as follows:

- The effect of TFOT and RTFOT ageing on short-term ageing of different binders almost the same.
- The ageing indices calculated from different physical properties, viscosity and softening point, are well correlated with the change in rheological properties and the complex modulus ageing index calculated in this study. In addition, they both rank bitumen ageing similarly.
- The complex modulus (G^*) ageing index calculated at different temperatures and frequencies in this study ranked the bitumen ageing similarly. However, the difference is greater at temperatures from 40-60°C and at lower frequencies. Furthermore, the change in phase angle (δ) is more pronounced at lower temperatures.

- The FTIR test on bitumen showed that the carbonyl index is correlated to the stiffness and hardening of the bitumen better than the sulfoxide index. Thus, the carbonyl index can be used as an ageing indicator rather than the sulfoxide index.
- The FTIR test performed on the bitumen aged with different methods in this study showed that carbonyl index is a good indicator of bitumen ageing. The carbonyl index can rank the bitumen according to their ageing degree as well as being correlated to other rheological and physical ageing indices. However, the result showed that the formation of carbonyl is greater during short-term ageing and the rate is slower for the long ageing.
- The results from ageing bitumen with different film thicknesses show that the ageing index decreases by increasing the bitumen film thickness. In addition, it shows that a power law describes the trend of ageing index changes with film thickness. This conclusion applies to both TFOT and PAV ageing.
- From the PAV results for bitumen aged at different thicknesses, it was noticed that the ageing index range decreases with the increase of bitumen film thickness; this indicates that the sensitivity of bitumen to ageing in the PAV decreases with the increase of bitumen film thickness.
- The ageing time study for different bitumen in the TFOT reveals the relationship between the changes in different physical properties measured in this study remains the same with the two different thicknesses used in this study. However, the effect at lower film thickness is more intense but with the same relation.

- The results of the ageing index relationship with the TFOT ageing time show that the viscosity and complex modulus ageing indices as calculated in this study increase exponentially with TFOT ageing time. However, for the softening point ageing index ($T_{\text{aged}} - T_{\text{unaged}}$), a linear relationship more accurately describes the increase in softening point ageing index with TFOT ageing time.

Chapter 5: Ageing of Mastics (bitumen and filler)

5.1 Introduction

According to ([Moraes and Bahia,2015a](#)), even though binder ageing in pavements always occurs when the binder is in contact with aggregates and mineral filler, in most ageing studies, asphalt binders are individually aged without accounting for aggregate-induced interactions. It is important to recognise that the most intimate contact between bitumen and aggregate in a paving mixture involves the fine aggregate and filler.

([Anderson et al.,1992](#)) stated that the properties of the fine fraction dominate in terms of physicochemical interactions between the bitumen and the mineral surface. The fines are embedded in the bitumen and the majority of the surface area is generated by the fine minerals. Therefore, the mechanisms of asphalt mastic ageing are largely influenced by the characteristics of the asphalt binder and the mineral filler properties, in addition to the molecular interaction between them. The chemical and rheological changes associated with ageing are well understood for neat bitumen as the result of much research on this subject ([Read and Whiteoak,2003](#)), ([Petersen,2009](#)). However, for the ageing of asphalt mastics, many topics in this research area still need to be investigated.

Therefore, in order to develop a better understanding of the way by which mineral fillers can affect bitumen ageing, an ageing study on bitumen-filler mastics was performed.

Mastic ageing has its advantages compared to asphalt ageing. As mentioned above, the surface area of fillers is much larger than the coarse aggregate, which will make the adsorbing and catalysis phenomenon more obvious. In addition, as the fillers in mastics can be viewed as being embedded in the binder, the effects of air void content and binder film thickness, which were concerns during the mixture ageing studies, can be avoided in mastic ageing.

The main aim of this study was to investigate the effect of different fillers on bitumen-filler mastic ageing. Particular attention was paid to studying the benefits of using hydrated lime on mitigating the ageing effect in the mastic phase. The ageing was quantified after different ageing stages (short-term ageing, long-term ageing and after extended ageing in the TFOT oven). Different ageing indices were used for quantifying the ageing effects on mastics as discussed earlier in Chapter 4. The experimental programme and the research results are presented in the following sections.

5.2 Materials and experimental programme

This bitumen-filler mastic ageing study was carried out in two stages. The first stage was carried out to study the effects of mineral fillers on mastic ageing and to investigate the effect of hydrated lime on mitigating the ageing of mastics with different fillers. The second stage investigated the effect of hydrated lime on the ageing of mastics prepared with different binders in order to study the hydrated lime interaction with different binders. The detailed testing programme for each stage will be discussed separately in the following sections.

5.3 Effects of mineral fillers on mastic ageing

The main aim of this study is to better understand the effect of different fillers on the ageing of bitumen-filler mastics, and in addition, to quantify the effect of ageing on different mastics including different percentages of hydrated lime. The first part

of the study utilised the standard TFOT to simulate short-term ageing of mastics, and the PAV was used for long-term ageing simulation. In the second part, an ageing time study was performed in order to show the effects of different fillers on the ageing rate of bitumen-filler mastics.

5.3.1 Materials

Three types of filler were used in this study: granite filler (G), limestone filler (LS), and hydrated lime (HL). All fillers were substantially finer than 63µm in particle size.

One type of bitumen, a 40/60 Pen bitumen (B2) with a penetration of 45dmm and a softening point of 50°C, was used to prepare the mastics. The properties of the fillers are summarised in Table 5.1.

Table 5.1 Filler properties

	Granite (G)	Limestone (LS)	Hydrated Lime (HL)
Specific Gravity (Mg/m³)	2.66	2.65	2.22
Surface area (m²/g)	1.26	1.58	2.24
Rigden voids (%)	46.94	39.82	61.62
D10	1.71	1.35	1.51
D50	14.58	8.67	7.15
D90	55.10	30.05	20.33

5.3.2 Mastic preparation

The mixing was done as explained below (see Figure 5-1):

- The amount of bitumen required was at first heated at 160°C in the oven in a small container.
- In another container, the required amount of filler was prepared; it was put into a 160°C oven for 24 hours to ensure a moisture-free particle surface.
- The tin containing the bitumen was then placed on a hot plate maintained at 160°C, the bitumen was stirred by hand and the accurate mass of filler was

added slowly while the stirring was continued until the mastic became homogenous (mixing takes approximately 5 minutes).

- The mastic was continuously stirred as it was cooling down until the temperature became low enough to prevent the filler from settling.
- The mastics were stored for later testing; before each test the mastics were heated to a liquid and stirred to ensure homogeneity.

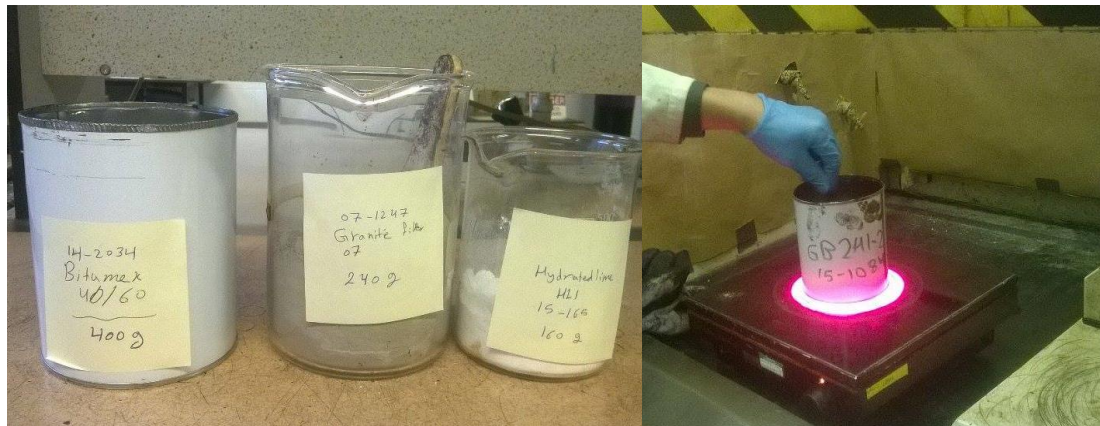


Figure 5-1 Mastic mixing and preparation

For each mastic set, in order to guarantee that the fillers were homogeneously distributed within the mastics, samples were taken from different parts of the mastic after each mixing process, and tested for softening point to ensure their consistency and compared to each other. The results show that the hand mixing was reliable and repeatable and the fillers were homogeneously distributed within the mastic.

The bitumen-filler mastic combinations in this study were prepared as follows; first, granite (G) or limestone (LS) fillers were mixed with 40/60 bitumen to produce mastics with 50% filler by mass. Then the filler (granite or limestone) was replaced by hydrated lime at percentages of 10% and 20% by mass to produce the six different mastic combinations in Table 5.2.

Table 5.2 Bitumen-filler mastic combinations

Mastics of Granite and Hydrated Lime				Mastics of Limestone and Hydrated Lime			
% by mass				% by mass			
Mastic ID	Bitumen	Granite	Hydrated Lime	Mastic ID	Bitumen	Granite	Hydrated Lime
50G	50%	50%	0%	50LS	50%	50%	0%
40G+10HL	50%	40%	10%	40LS+10HL	50%	40%	10%
30G+20HL	50%	30%	20%	30LS+20HL	50%	30%	20%

■ Bitumen ■ G ■ HL

Mastic ID	Bitumen (%)	Granite (%)	Hydrated Lime (%)
50G	50	50	0
40G+10HL	50	40	10
30G+20HL	50	30	20

■ Bitumen ■ LS ■ HL

Mastic ID	Bitumen (%)	Limestone (%)	Hydrated Lime (%)
50LS	50	50	0
40LS+10HL	50	40	10
30LS+20HL	50	30	20

5.3.3 Testing programme

To study the effects of mineral fillers on mastic ageing, the testing programme was carried out in two stages. In the first stage, the mastics were short-term aged in the TFOT (5 hours, 163°C) at a thickness of 2.2mm on the TFOT plate, followed by PAV ageing at 90°C for 20 hours to simulate the long-term ageing. Softening point, rotational viscosity and DSR tests were carried out on the mastics before and after different ageing stages to investigate the effect of ageing on different mastics and to quantify the effect of hydrated lime on mastic ageing. Also, FTIR tests were performed to investigate the chemical changes in the recovered bitumen from mastics after short and long-term ageing. The ageing indices were calculated and compared for different mastics. The second stage was carried out in order to study the effects of different fillers on the ageing rate. Mastics with proportions as in the first stage were aged in the TFOT oven (163°C, 2.2mm thickness) for different ageing times, 1, 2, 5, 10 and 20 hours. The same tests and calculations as in the

previous stage were applied in this stage as well. Figure 5-2 illustrates the testing programme used in this study. All the results in this chapter are the average of three replicates for viscosity and FTIR ageing indices and two replicates for softening point and complex modulus; the results were repeatable. The percentage deviation with respect to the mean value representing all the replicates tested was less than 10%.

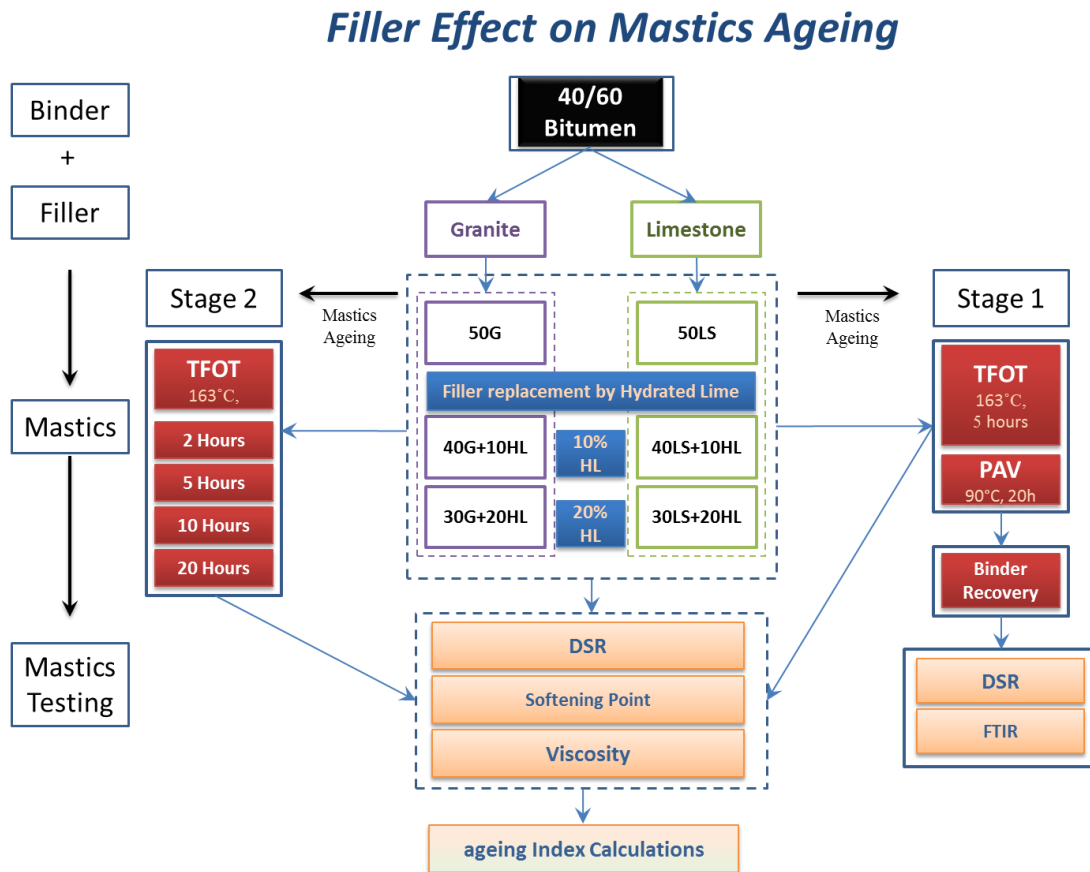


Figure 5-2 Filler effect on mastic ageing testing programme

5.3.4 Stiffening effect of fillers on mastics

The effect of the filler on mastics was firstly examined by means of the stiffening effect that the fillers have on the mastic. The stiffening effect is the change in properties of mastics compare to the same property of the base binder. The stiffing effect of fillers was evaluated with different means after mixing the mastics; increase in viscosity and softening points. This effect is presented in Figure 5-3. It

can be seen that the addition of filler increases the viscosity and softening point. In addition, it can be noticed that the granite filler has more stiffening effect than limestone filler at the percentages used in this study.

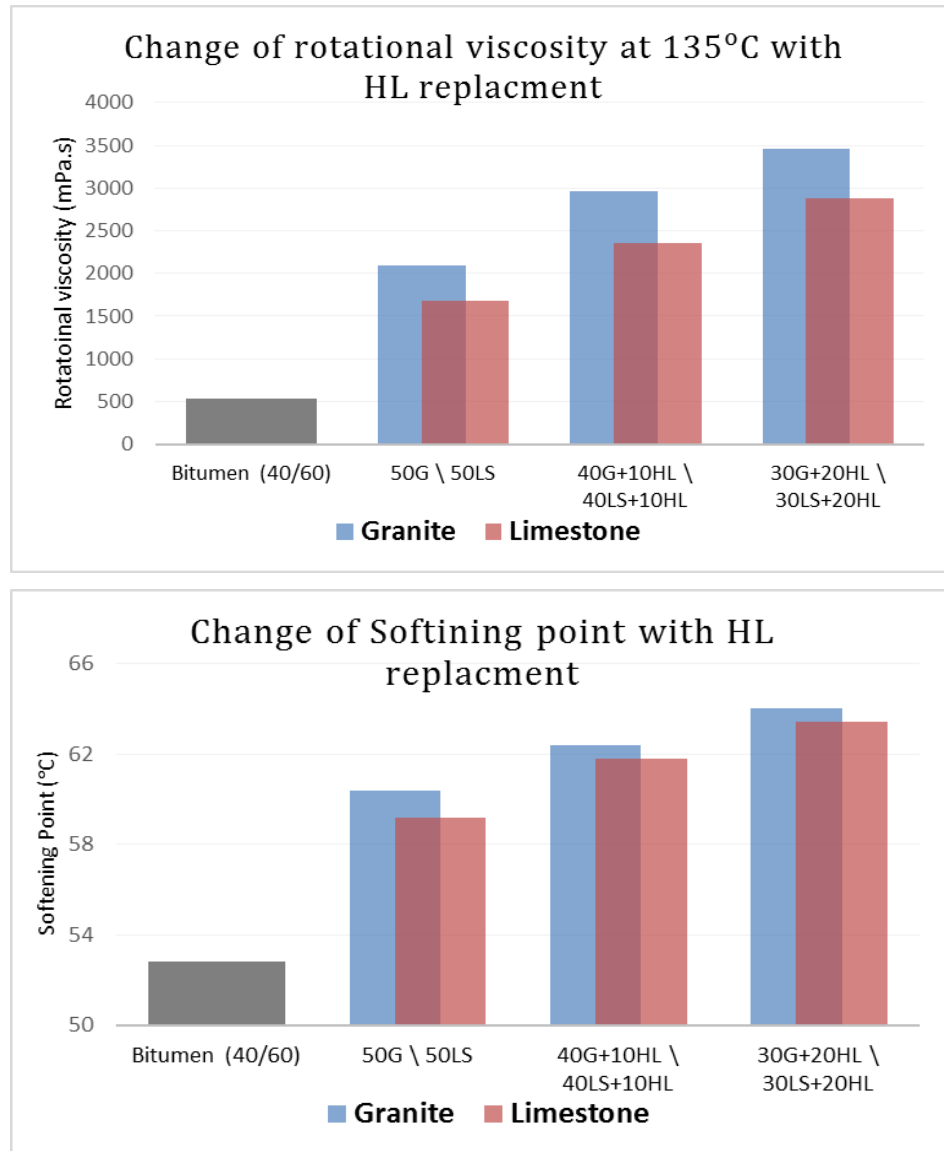


Figure 5-3 Stiffening effect of fillers on mastics

The higher stiffening for the granite filler could be due to its higher Rigden Voids (RV) compared to the limestone filler, as many studies indicate that the stiffening effect of filler is significantly related to the Rigden voids of the filler. These voids in the compacted filler reflect the effects of other properties such as particle density, particle shape, and particle size in the filler fraction. In addition, Figure 5-3 reveals that hydrated lime replacement of the filler at 10 and 20% increases the stiffening

effect on the mastic. This effect was expected as hydrated lime has higher Rigden Voids and specific surface area. Some previous studies attributed this higher Rigden voids to the higher porosity of the hydrated lime particles and to its rough surface texture. This increases its ability for adsorption and consequently increases the stiffening effect. This was clear for the hydrated lime particles used in this study as discussed earlier in Chapter Three about the filler properties. Moreover, the combined RV for the filler combinations used in this study was evaluated according to [BS EN 1097-4:2008](#) and the results are presented in Table 5.3. The results show that the mastics containing HL and G having higher RV.

Table 5.3 Rigden voids for filler combinations

<i>Material</i>	<i>Rigden Voids (%)</i>			
	Trial 1	Trial 2	Trial 3	<i>Average</i>
Limestone	40.26	39.78	39.42	39.82
Granite	47.22	47.00	46.62	46.94
Hydrated Lime	59.99	62.67	62.21	61.62
<i>Combined Rigden Voids (%)</i>				
<i>Granite + Hydrated lime</i>				
10% HL in mastics 40G+10HL	49.64	48.70	46.42	48.25
20% HL in mastics 30G+20HL	55.61	55.02	53.98	54.87
<i>Limestone + Hydrated lime</i>				
10% HL in mastics 40LS+10HL	46.21	46.39	47.76	46.79
20% HL in mastics 30LS+20HL	51.76	51.02	51.39	51.39

5.3.5 Ageing evaluation of mastics

The ageing effect on mastics was evaluated using different ageing indices as mentioned earlier in Chapter Four. The rotational viscosity and complex modulus ageing indices were used in this study. In addition, the change in the softening point ($\Delta R\&B$) was used for ageing evaluation in this study. The results obtained for the ageing indices of mastics are presented in Figure 5-4. The results show that the mastics made with 50%G showed higher ageing indices even compared to bitumen ageing in some cases. On the contrary, all other combinations showed a reduction in ageing indices. In addition, the effect of hydrated lime is clear. Replacing fillers with hydrated lime showed a lower ageing index compared to the original mastics and to the neat bitumen as well.

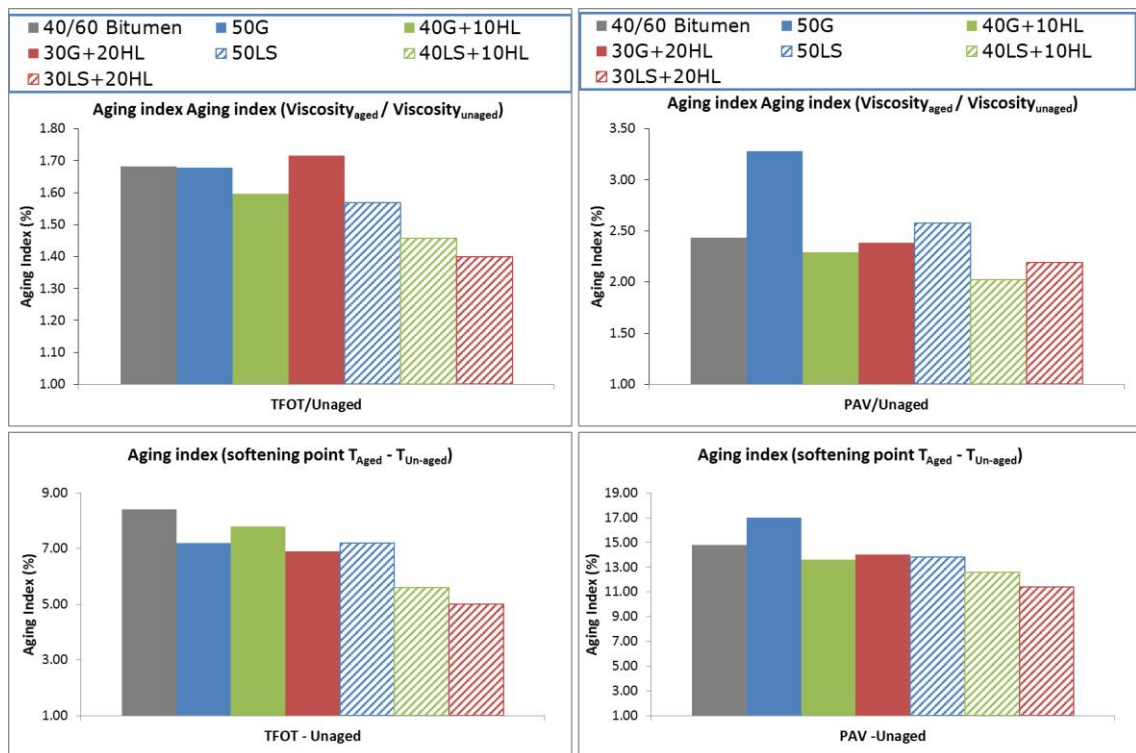


Figure 5-4 Different ageing indices (AI) for mastic ageing evaluation

Furthermore, the above results show that replacing 10 or 20% of the fillers by hydrated lime has a strong impact and reduces the age hardening of the mastics as shown by the reducing ageing indices. This effect is more pronounced after the long-term ageing. However, there was a slight modification on the short-term

ageing after TFOT. In addition, it could also be noticed, that replacing 20% of filler with hydrated lime does not give significantly different results from the 10% hydrated lime replacement especially for the granite filler mastics.

Generally, it is clear that by replacing up to 20% of filler by hydrated lime can reduce the effect of ageing on the mastics by up to 30% after long-term ageing as calculated by the viscosity ageing index. It was also noticed that the combination of LS+HL fillers after short-term and long-term ageing always gives softer mastics than with G+HL fillers. This means that the LS+HL combination reduces the rate of ageing and oxidation within the mastics more. Furthermore, the results in Figure 5-4 show that there is an agreement between the different ageing indices used in this study in ranking the mastics according to their ageing susceptibility. In addition, all the ageing indices used show the benefits of using HL replacement of base fillers in reducing the ageing effect on the mastics. This effect of HL on ageing mitigation as quantified by the ageing indices ranges from 11 to 30 % depending on mastic filler combinations and the ageing index used. These results confirm earlier findings that hydrated lime slows down bitumen ageing.

The results obtained in this study are in agreement with previous findings of hydrated lime effectiveness to reduce ageing effects ([Little and Petersen,2005](#); [Lesueur et al.,2012](#); [Lesueur et al.,2013](#); [Iwański and Mazurek,2013](#); [Lesueur et al.,2016](#)). However, more investigation is still needed to understand the relationship between the change in the physical and rheological properties and the chemical changes within the bitumen mastics. Also, better characterisation of the bitumen is required along with a better explanation of hydrated lime and bitumen interactions. The following subsections discuss the effect of hydrated lime on rheological changes and chemical changes during mastic ageing.

5.3.6 Effects of fillers on the rheological properties of mastics ageing

5.3.6.1 Complex Modulus Master Curve

The rheological properties of the mastics were characterised in this study with a Bohlin Gemini 200 Dynamic Shear Rheometer. The data of rheological parameters were generated using a frequency sweep. The frequency sweep testing was performed on the bitumen and bitumen-filler mastics under strain controlled loading conditions by applying a sinusoidal angular displacement of constant amplitude within the linear-viscoelastic domain. The test parameters were as follows: 0.3% strain amplitude over a range of 0.1 to 10Hz and a temperature range from 0 to 50°C. The Bohlin Gemini 200 DSR was used to measure the dynamic shear modulus (G^*) and phase angle (δ) of the bitumen and bitumen-filler mastics.

The resulting complex shear modulus $|G^*|$ and phase angle (δ) data were used to produce master curves using the time-temperature superposition principle, with shift factors following the Williams-Landel-Ferry (WLF) equation. The selected reference temperature for the master curves was 30°C.

Figure 5-5 shows the complex modulus master curves for the base bitumen and bitumen-filler mastics. It can be seen that the addition of the filler has an effect on the overall complex modulus at all test temperatures due to the stiffening effect of mineral filler. As noticed, the addition of mineral filler to bitumen shifted the curve toward higher frequencies without changing the slope, thus giving a more elastic response, which is expected due to the addition of elastic filler particles.

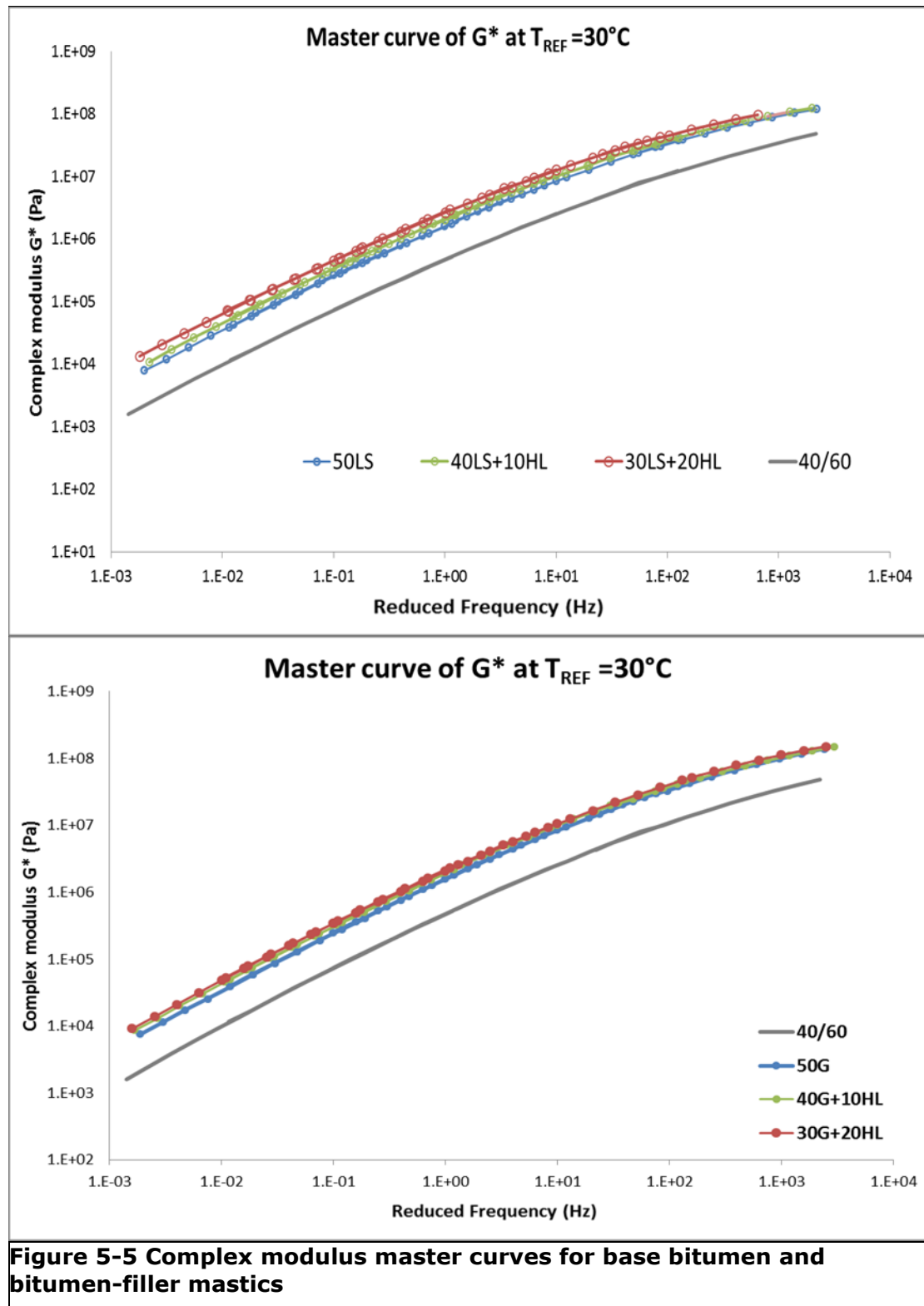


Figure 5-5, shows a slight increase in the complex modulus for mastics when 10 and 20% of fillers were replaced by HL. This stiffening effect of HL replacement is more pronounced at lower frequencies (higher temperatures) and with the LS filler replacement. The reason for the higher stiffening effect of the HL replacement of

limestone fillers is that the difference in RV between these two fillers is more than that between granite and hydrated lime fillers. As presented earlier in Table 5.3, at 20% replacement of LS filler by HL, the increase in RV for this combination is up to 30% compared to LS initial RV. However, for 30G+20HL the RV increased by only 17%. Therefore, in order to show the stiffening effect of the fillers on mastics more clearly, the relative increase in the complex modulus compared to the base bitumen at different temperatures was calculated and presented as G^* stiffening ratio in Figure 5-6.

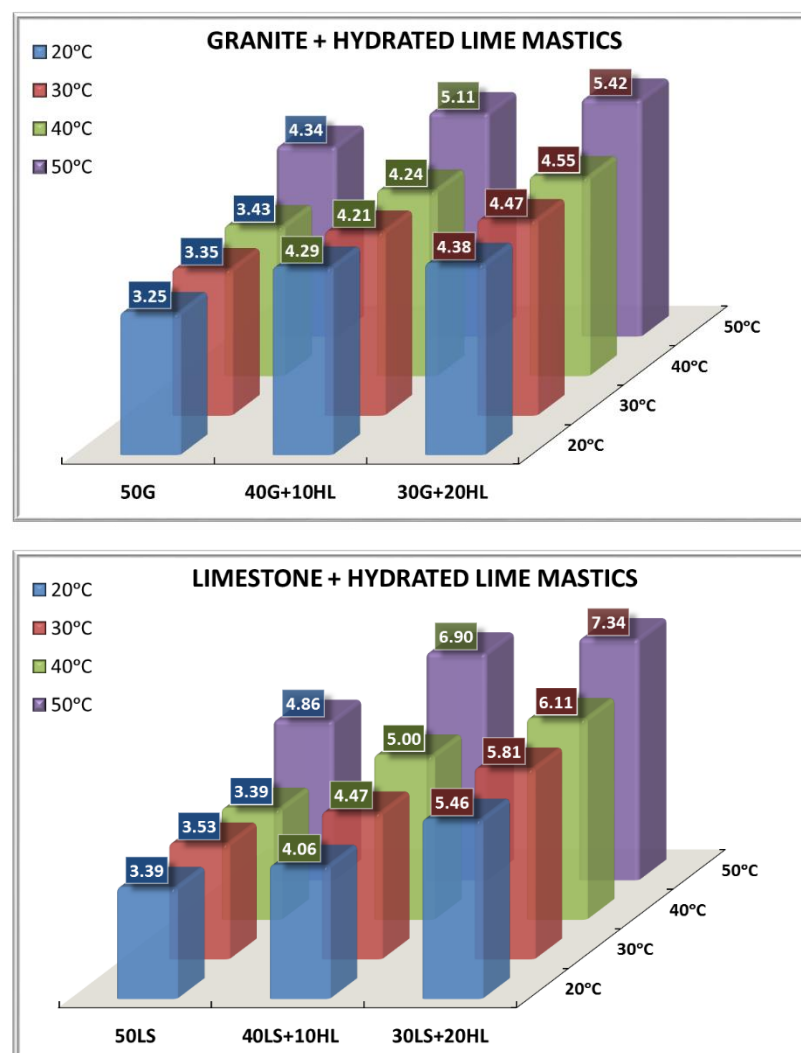


Figure 5-6 Complex modulus (G^*) stiffening ratios of different mastics

The results reveal that the stiffening effect of filler on bitumen at higher temperatures is more pronounced than that at lower temperatures. This is due to the difference of the modulus between bitumen and fillers becoming larger at

higher temperatures, since the bitumen shows increasing viscous flow at higher temperatures while the filler is still in its rigid state. This will be discussed in more detail in this chapter. Furthermore, the effect of fillers on mastic ageing rheological properties was evaluated using the dynamic shear rheometer (DSR) and the resultant complex modulus master curves are presented in Figure 5-7 and Figure 5-8.

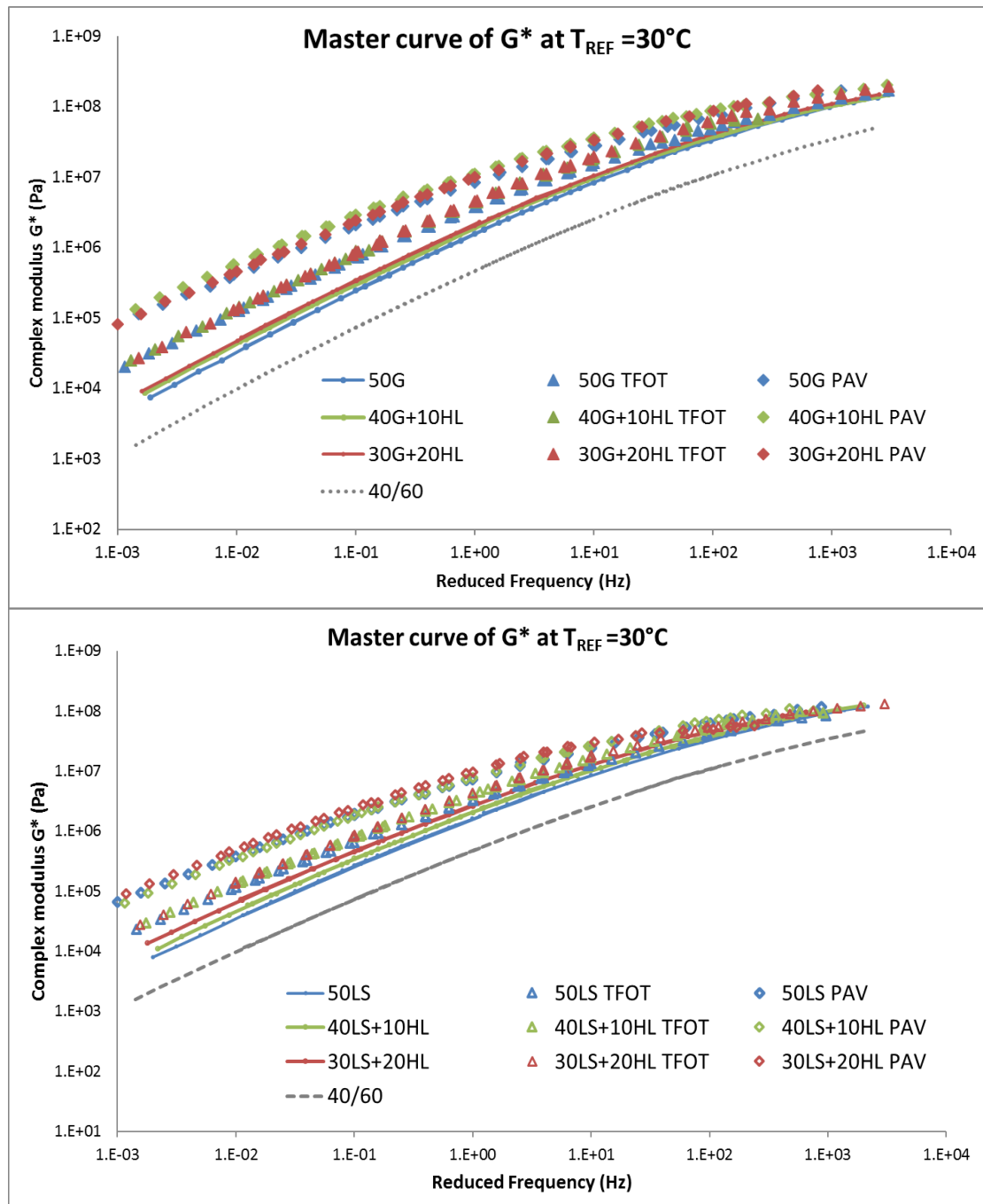


Figure 5-7 Complex modulus master curves for G+HL and LS+HL bitumen-filler mastics at different ageing stages

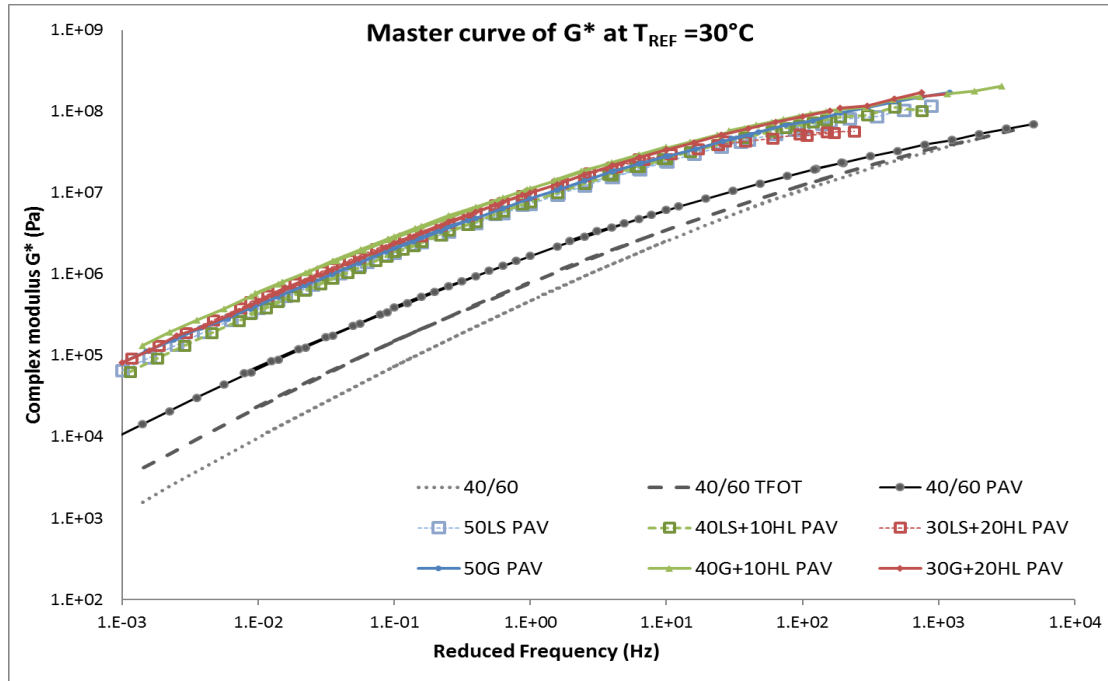


Figure 5-8 Complex modulus master curves for base bitumen, G+HL and LS+HL mastics at different ageing stages

Master curves with WLF shifting have been constructed at a reference temperature of 30°C for the base bitumen and the bitumen filler mastics. In Figure 5-7 and Figure 5-8, the master curves after short and long-term ageing are shown. It is clear from the figures that the effect of ageing is significant on the rheological behaviour of the mastics and base bitumen. It can be noticed that the effect of ageing on the complex modulus (G^*) master curves are associated with an increase in G^* . This is more pronounced at low frequencies (high temperatures). The change in G^* after PAV ageing is considerably greater than after TFOT ageing due to the severe ageing conditions in the PAV. The results also show that even if there was a slight difference in G^* for different mastics, this difference almost disappears after ageing. This means that the rate of change of mastic ageing is different for each filler combination. As can be seen from the G^* master curves, the effect of different filler combinations on stiffening and ageing of mastics is not clear from the master curves. Thus, in order to make the comparison more quantitative, the complex modulus (G^*) values at 20°C, 0.4 Hz for the 8 mm testing geometry were selected for ageing index calculations.

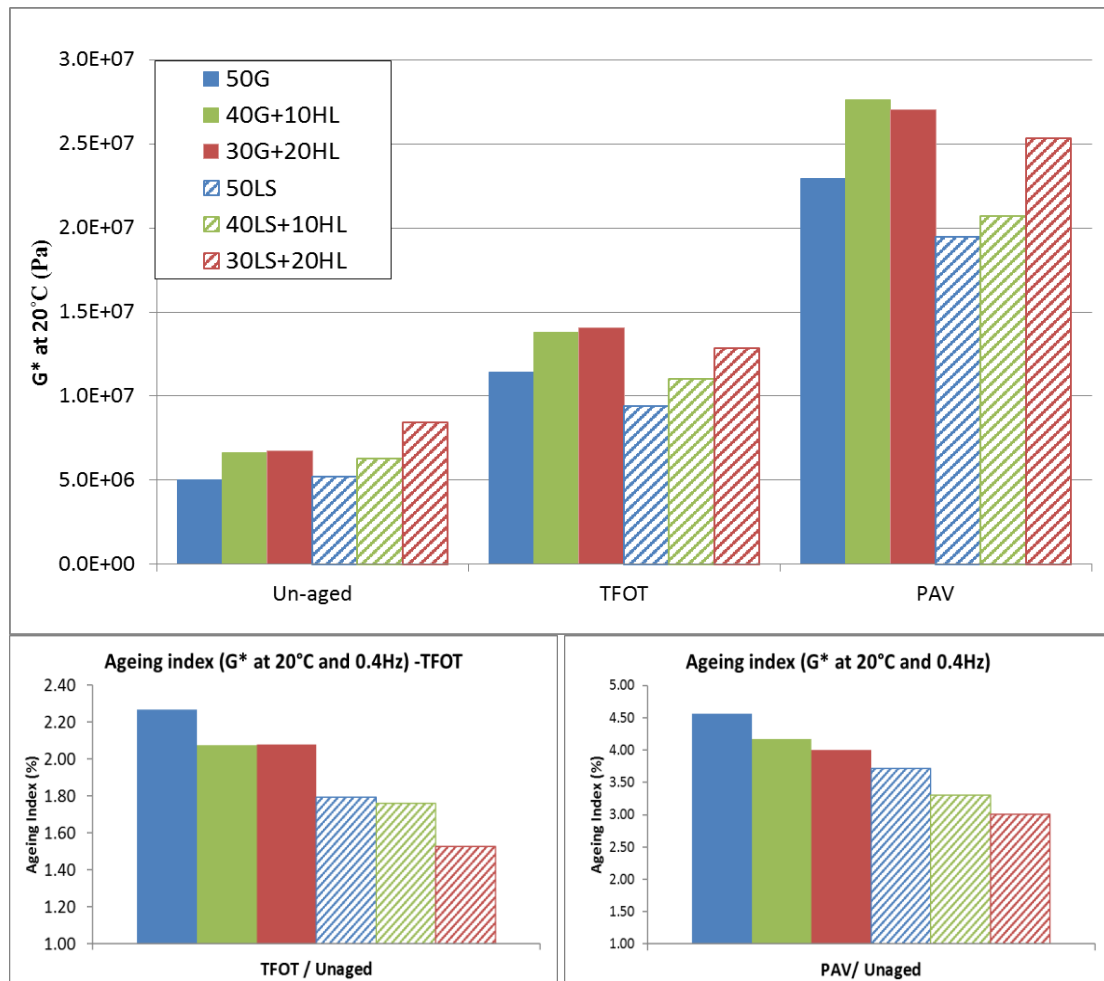


Figure 5-9 Mastics stiffness (G^*) and Complex modulus ageing index of mastics after short and long-term ageing

It can be seen in Figure 5-9 that all mastic complex modulus values increase with ageing. In all cases after ageing, mastics containing granite and hydrated lime filler are stiffer than those containing limestone and hydrated lime filler with the same percentages. It could also be noticed from the calculated ageing indices that replacing 20% of hydrated lime does not make a significant additional effect compared to the 10% of hydrated lime with granite filler. Furthermore, the results confirm that the combination of 30%LS+20%HL was a stiffer mastic before ageing; however, after short-term and long-term ageing, the mastics with LS+HL was softer than mastics with G+HL fillers. This means the LS+HL combination reduces the rate of ageing and oxidation within the mastics more than that of G+HL for the combinations and ageing conditions used in this study.

These results from the G^* ageing index correlate with these discussed earlier from the viscosity and softening point.

5.3.6.2 Phase Angle Master Curve

Phase angle master curves for the base bitumen mastics were constructed at a reference temperature of 30°C. Figure 5-10 compares the phase angle master curves for the base bitumen and the bitumen filler mastics with different combinations. Figure 5-11 shows the ageing effect on phase angle master curves.

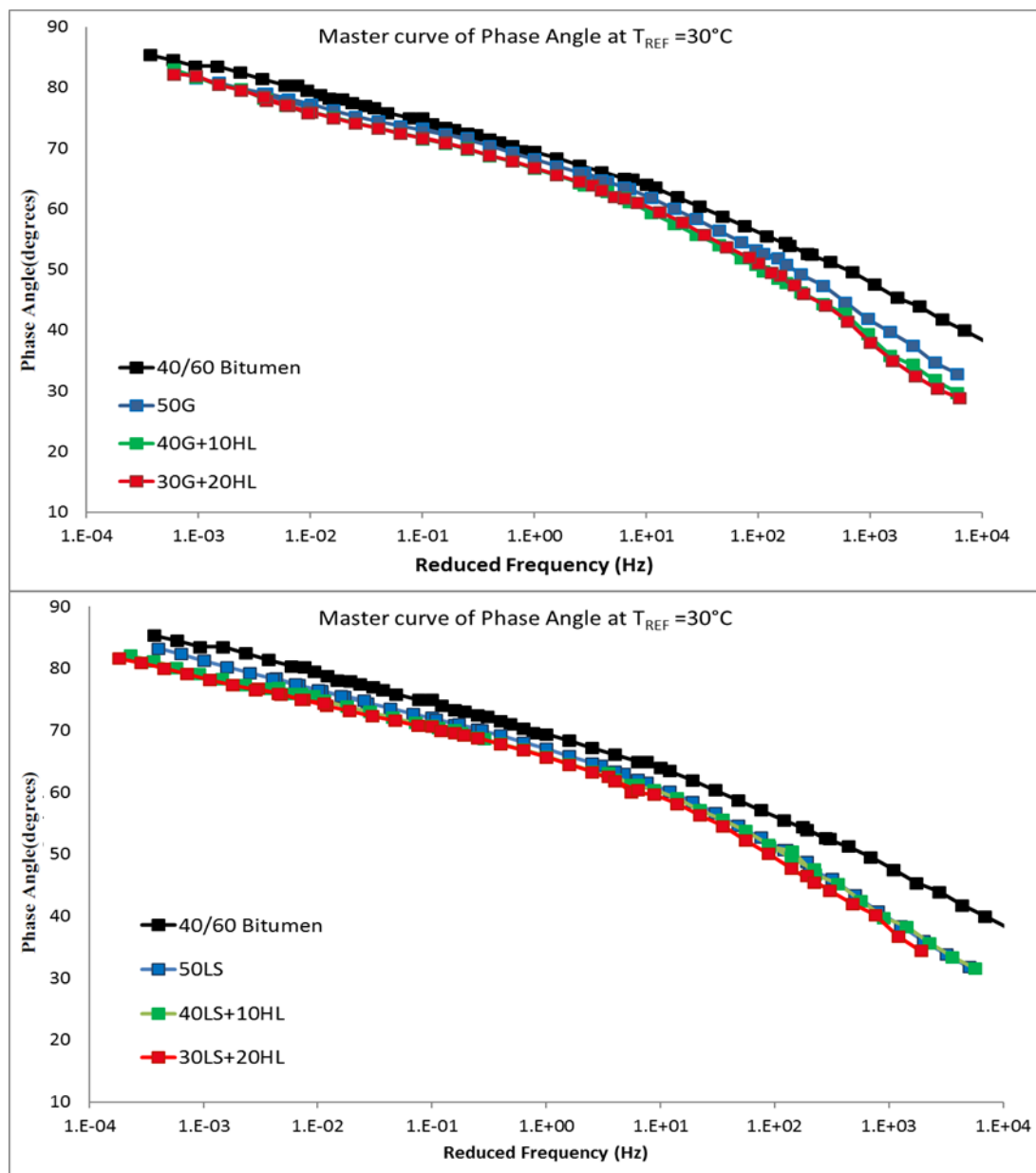


Figure 5-10 Phase angle master curves for unaged bitumen and mastics

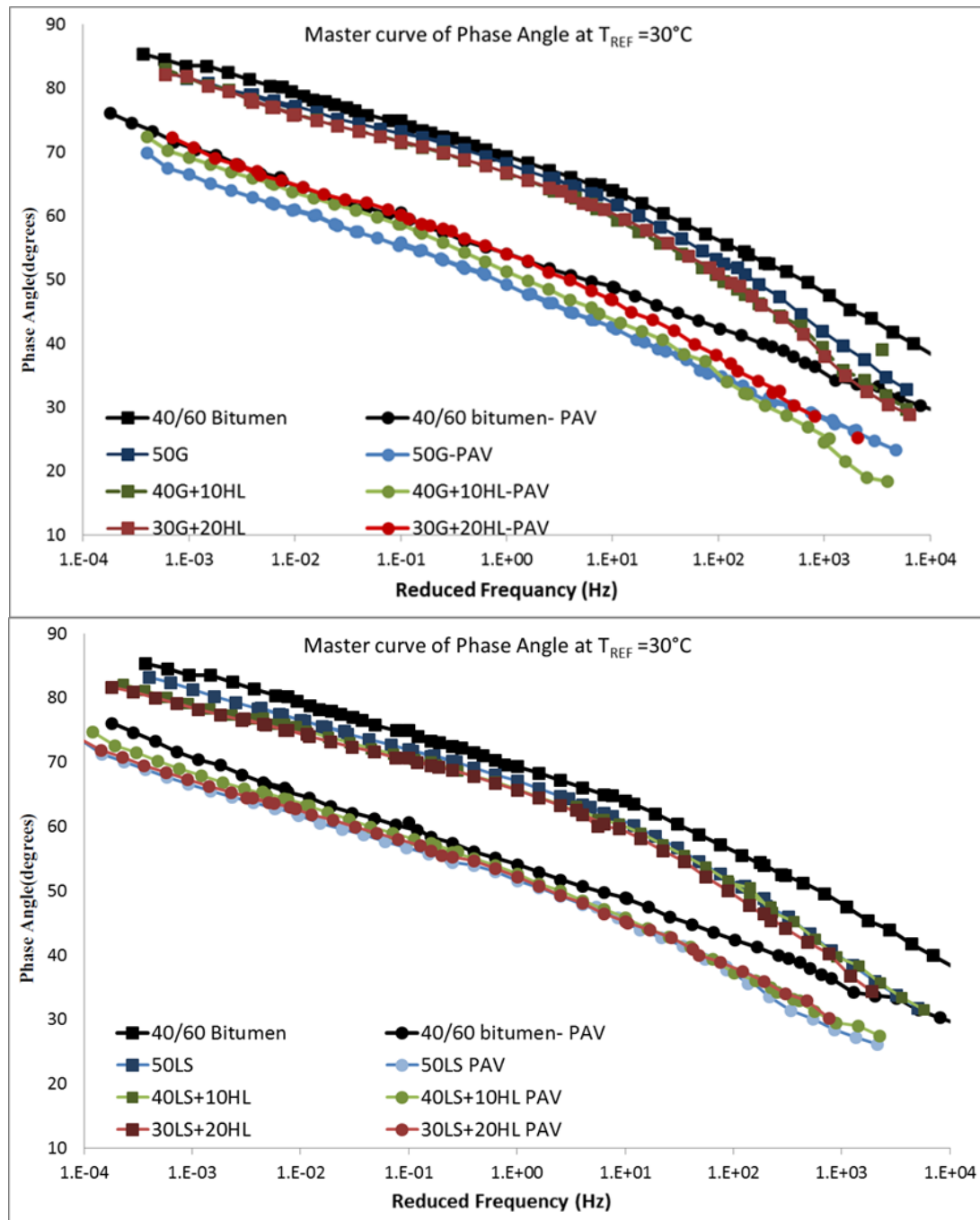


Figure 5-11 Phase angle master curves for base bitumen and mastics before and after PAV ageing

Figure 5-10 shows that the phase angle master curves for bitumen-filler-mastics at high frequencies significantly tend towards the lower phase angle values compared to the base bitumen. This indicates a more elastic response of the mastics at high frequencies. Over the central and low-frequency regions, the phase angle master curves of the bitumen and mastics are only slightly different.

Comparing the phase angle master curves of the mastics with different combinations, it can be noticed that all mastic combinations tend towards the same phase angle versus frequency relationship. However, there is a slight reduction in phase angle for mastics with HL replacement.

The master curves of phase angle for base bitumen and mastics before and after PAV ageing are shown in Figure 5-11. It is clear that the addition of the mineral fillers to bitumen decreases the phase angle in all cases. However, after PAV ageing the effect of hydrated lime replacement is clear. It reduces the change in phase angle over the range of tested frequencies. This indicates that the mastics containing HL tend to have a higher phase angle compared to mastics without HL. The effect of hydrated lime on the phase angle was more significant with the granite mastics than the mastics with limestone. This is a relative measure of the ability of mastics with hydrated lime to dissipate energy. The higher phase angle of hydrated lime containing mastics should be beneficial in reducing cracks in aged pavements.

5.3.6.3 FTIR analysis

In this study, the FTIR test was performed on the recovered bitumen from mastics before and after ageing. The Carbonyl C=O ageing index was used to evaluate the effect of ageing on different mastics and it was calculated as follows:

Carbonyl index (C=O): $A_{1700}/\Sigma A$

The sum of the area ΣA represents: $A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}$

The infrared absorption spectrum between 500cm^{-1} and 4000 cm^{-1} has been recorded for bitumen recovered from granite mastics. The absorption bands belonging to bitumen functional groups that are affected by ageing, such as carboxylic acids (C=O) were used to evaluate the increase in oxidative ageing products, which can be determined through FTIR, utilising a very strong band around 1700cm^{-1} . Figure 5-12 shows the FTIR spectrum for the recovered binder

from mastics before and after different ageing stages. It can be noticed that the carbonyl area increases with the ageing of the mastics.

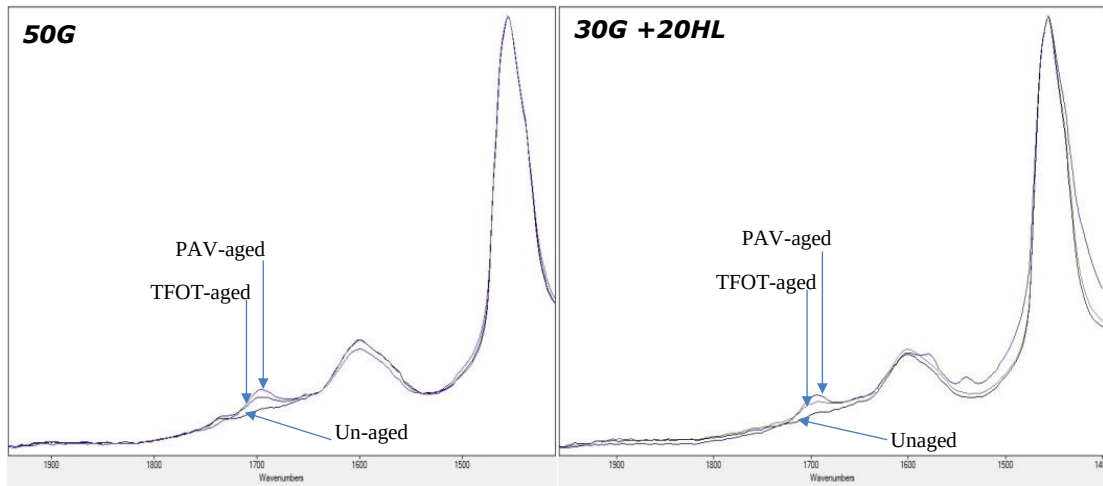


Figure 5-12 FTIR spectrum for recovered bitumen of granite mastics

In addition, according to this scan result, the carbonyl index was calculated and is presented in Figure 5-13. It can be seen that the binder recovered from the mastic of hydrated lime with granite contains less oxygenated products after both short- and long-term ageing. This indicates that less ageing occurred in the mastics with HL. These results can explain the lower ageing index for mastics including hydrated lime, which means a slower rate of increase of the heavier oxygenated products in mastics containing hydrated lime with ageing.

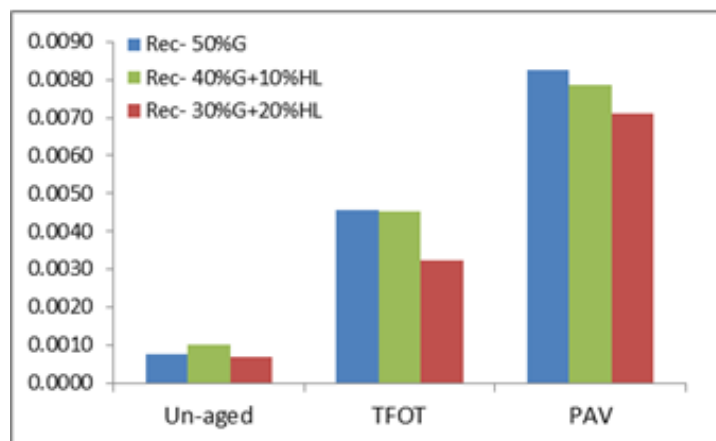


Figure 5-13 Carbonyl index of recovered binder from mastics after TFOT and PAV ageing

5.3.6.4 Ageing Time Study for mastics with different fillers

The intensity of the influence of the mineral fillers on ageing keeps changing as the ageing simulation continues due to the changes in their adsorbing and catalysing abilities. Therefore, mastics containing different filler combinations were further studied in order to show the effect of hydrated lime on the rate of stiffening of the mastics.

The mastics were aged in the TFOT oven at 163°C and a thickness of 2.2mm for different ageing times (2, 5, 10 and 20 hours). The empirical tests including the viscosity at 135°C and the softening point were carried out after each ageing level and the ageing index was calculated using both tests. The results are shown in Figure 5-14 and Figure 5-15.

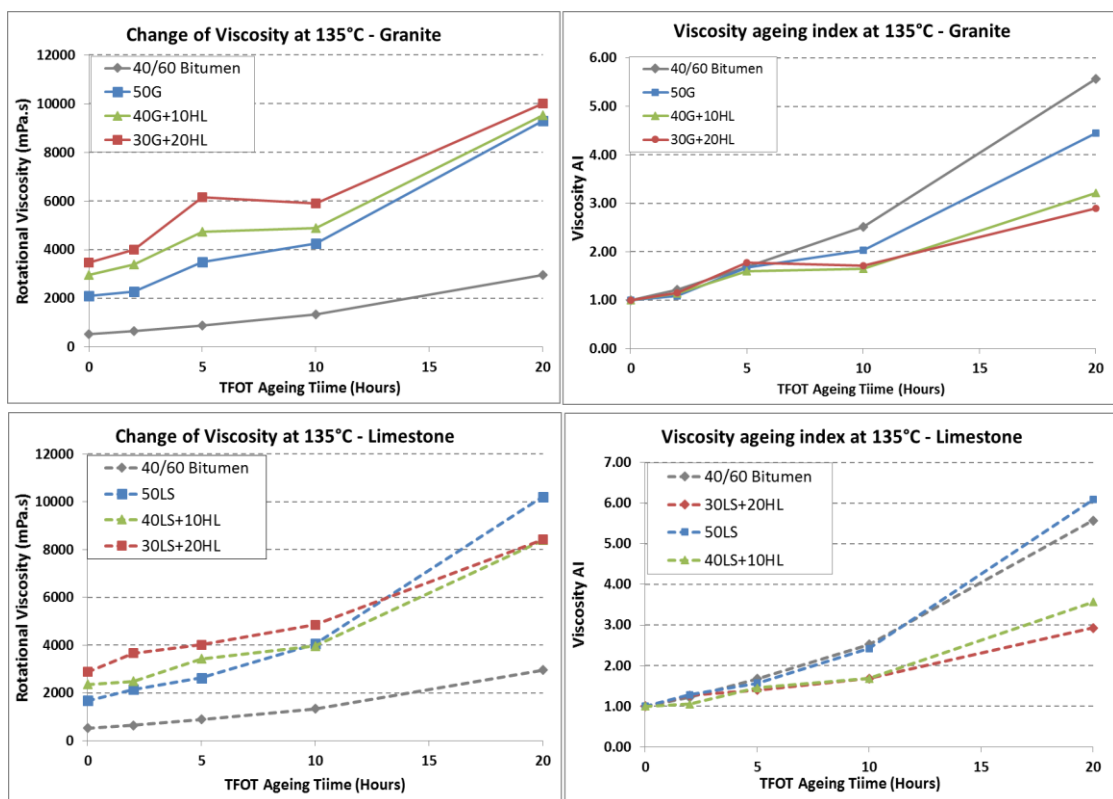


Figure 5-14 Ageing index calculated from viscosity at 135°C for mastics with different TFOT ageing times

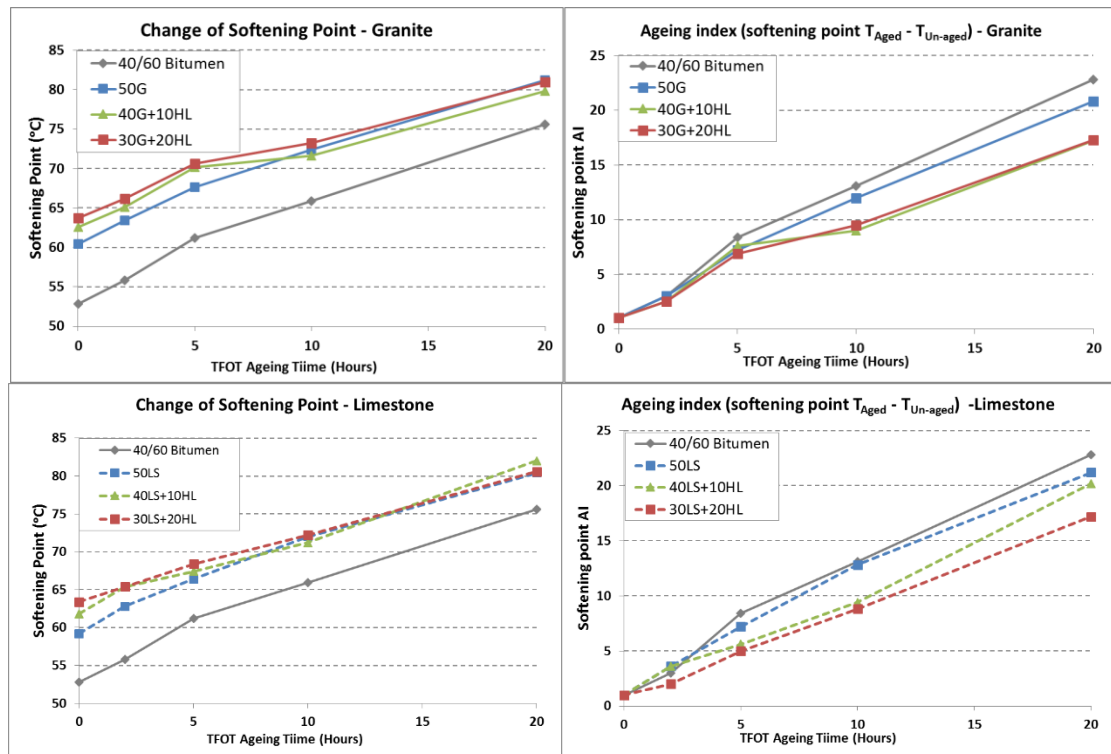


Figure 5-15 Ageing index calculated from Softening point for mastics with different TFOT ageing times

From the results, it can be seen that mastics containing hydrated lime are initially stiffer than the granite or limestone only mastics. However, with ageing, the rate of increase in stiffness for the mastics without HL is higher than for mastics with hydrated lime. After 20 hours ageing in the TFOT, the mastics containing hydrated lime remain almost the same as or softer than the mastics with only granite or limestone fillers.

The ageing indices calculated from the viscosity and softening point show that the mastics containing hydrated lime always have a lower ageing index. The rate of increase in the ageing index for mastics containing HL is always lower. It can also be noticed that the effect of HL becomes more pronounced for the longer ageing times (especially after 5 hours TFOT ageing). Furthermore, the results reveal that replacing fillers with 20% hydrated lime does not make an additional significant effect on the ageing index compared to the 10% hydrated lime replacement. In addition, it is clear that replacing 10% or 20% of fillers by hydrated lime can reduce the ageing index by up to 50% compared to the neat bitumen. The rheological properties of mastics aged at different ageing times in the TFOT were measured

using the DSR and the resultant complex modulus master curves are presented in Figure 5-16. The G^* master curves for the mastics after different ageing times show that these curves are smooth and continuous. The effect of ageing is clear, the complex modulus increases as the ageing time increases. The ageing effects seem to be different for mastics with different filler composition. So in order to make it clear, the ageing index from the complex modulus change with ageing times was calculated and the results are presented in Figure 5-17.

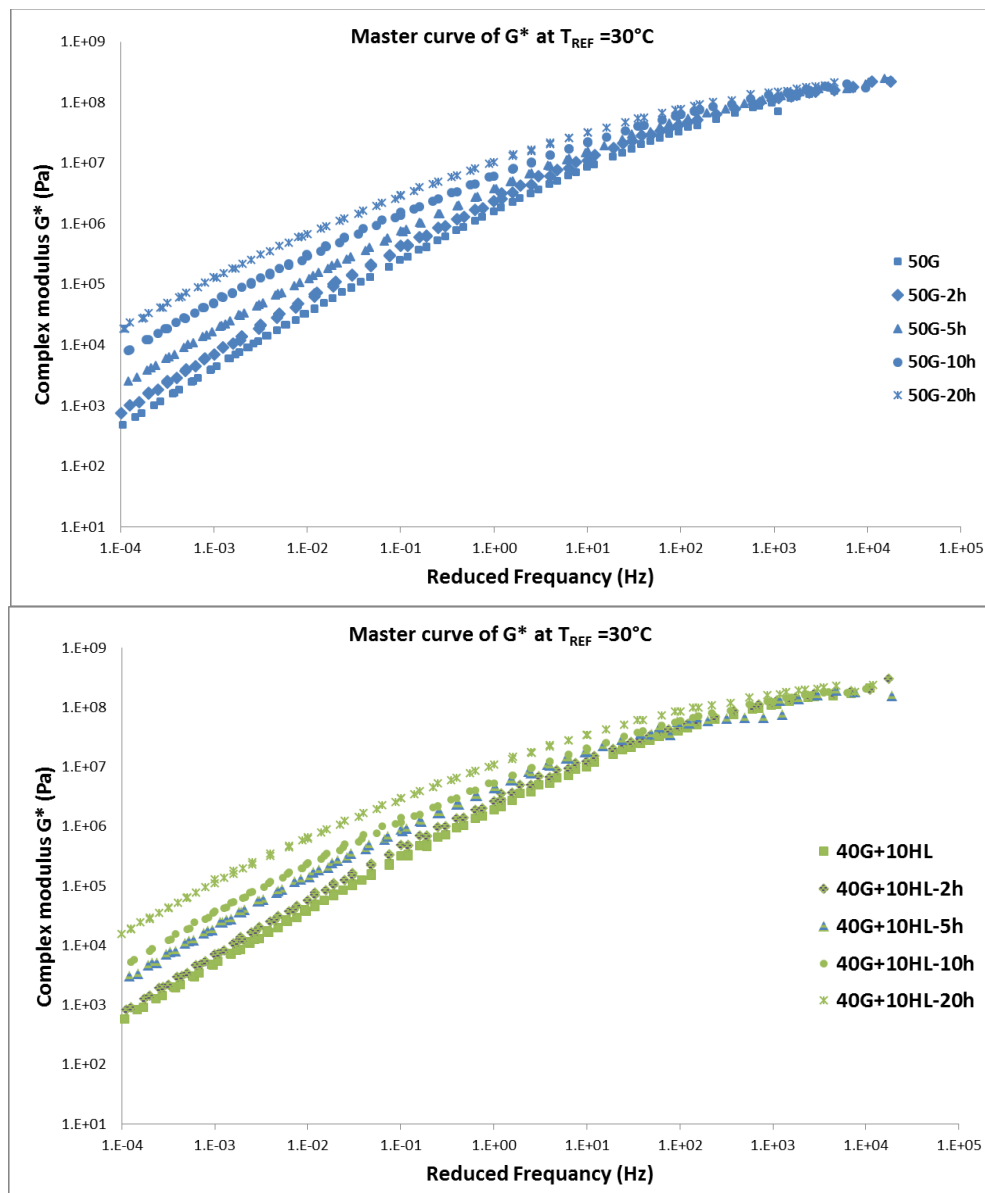


Figure 5-16 continues ...

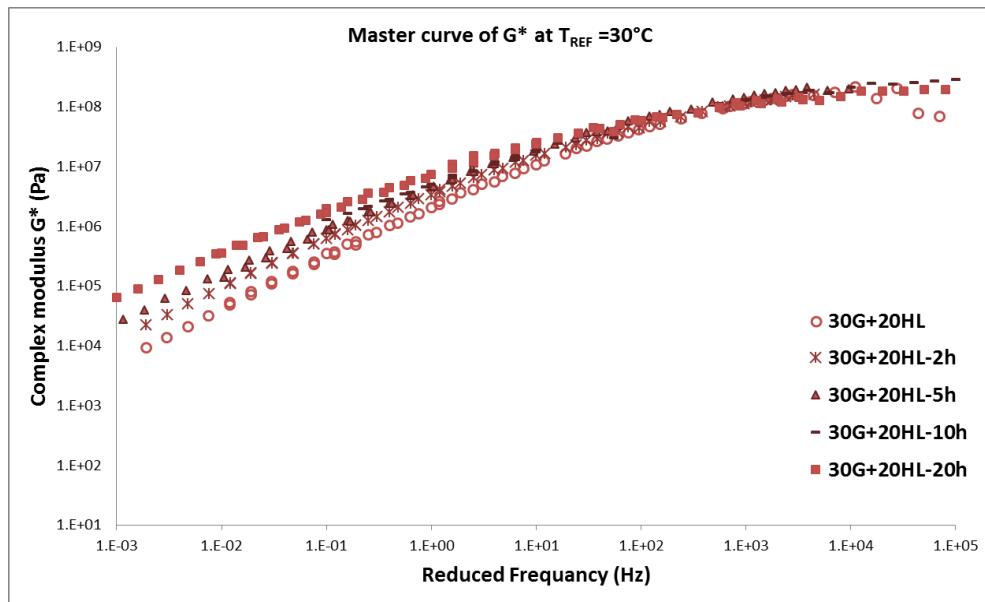


Figure 5-16 Complex modulus master curves for mastics aged for different times in TFOT

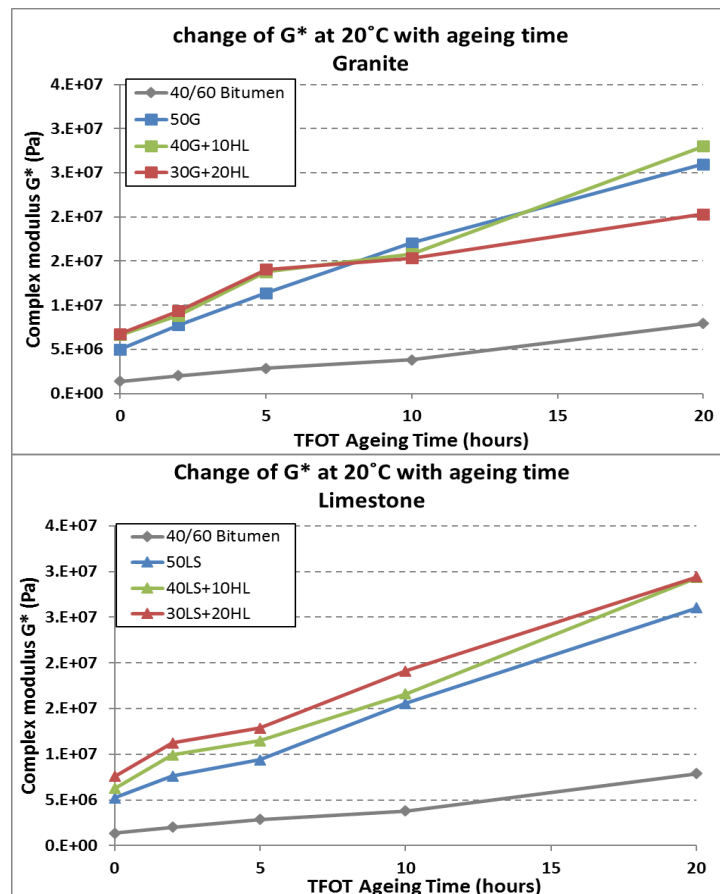


Figure 5-17 continues ...

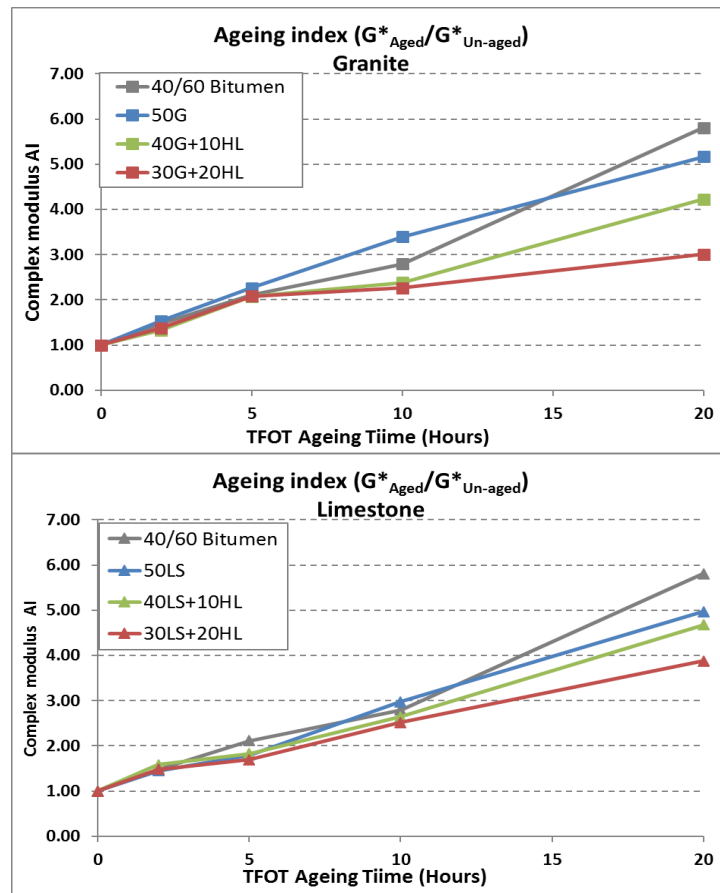


Figure 5-17 Ageing index calculated from complex modulus for mastics with different TFOT ageing times

The results show that the complex modulus of different mastics and the bitumen are increasing with the ageing time in the TFOT oven. In addition, they show that the rate of increase in the complex modulus for the mastics containing hydrated lime is slower than mastics without hydrated lime. This beneficial effect of hydrated lime was confirmed by the calculated ageing indices, they show that the mastics with hydrated lime always have a smaller ageing index compared to the original mastics and to the neat bitumen.

5.4 Effects of bitumen-filler interactions on mastic ageing

The bituminous binder is always in contact with mineral fillers in asphalt mixtures, thus the mechanisms of oxidative ageing of binders are influenced by the physical and chemical interaction between fillers and the bitumen. This study attempts to investigate the factors that affect the ageing process of binders. The effect of granite fillers and hydrated lime with two different bitumen binders on mastic ageing was investigated in this study.

5.4.1 Materials

In this study, mastics were produced using two types of bitumen and two different fillers. The two binders used were a 40/60 Pen binder (B1) and another softer 100/150 pen bitumen (B2). The properties of the binders are presented in Table 5.4. It is worth to note that the 100/150 (B2) is the same bitumen denoted as B4 in Chapter four earlier.

Table 5.4 Bitumen properties

Bitumen		Specific gravity	Penetration (dmm)	R&B SP (°C)
B1	40/60	1.03	44.8	52.7
B2	100/150	1.03	119	44.8

The two fillers used in this study were granite filler (G) and hydrated lime (HL). All fillers used in this study were substantially finer than 63µm in particle size.

Table 5.5 shows the results of the property characterisation of the fillers used in this study.

Table 5.5 Summary of filler properties

Filler Type	Specific Gravity	Rigden Voids (%)	Surface area (m ² /g)	Grading		
				D10	D50	D90
Granite	2.66	47.15	1.26	1.705	14.58	55.10
Hydrated Lime	2.22	61.62	2.24	1.509	7.137	20.27

5.4.2 Mastic preparation and testing programme

Mastic samples have been made by mixing the granite filler with bitumen B1 and B2 to produce mastics of 50% filler by mass. Then the granite was replaced by hydrated lime at percentages of 10% and 20% by mass to produce a total of six different mastics. Thus the mastics produced with the 40/60 pen bitumen B1, were labelled as B1+50G, B1+40G+10HL and B1+30G+20HL for mastics with only 50% granite by mass, 10% HL replacement and 20% HL replacement respectively. Similarly, the mastics produced with the 100/150 pen bitumen B2 were labelled as B2+50G, B2+40G+10HL and B2+30G+20HL. All mastic mixing was done manually following the procedures mentioned previously in Section 5.3.2.

The testing programme in this study was divided into two stages: in the first stage, the mastics were subjected to short-term ageing in the TFOT oven and long-term ageing in the PAV oven. For the short-term ageing, the samples were heated in the TFOT oven for 5 hours at 163°C and with a film thickness of 2.2mm. For the long-term ageing, mastics were aged in the PAV oven at 90°C and under a pressure of 2.1MPa for 20 hours after the short-term ageing in the TFOT.

In the second stage, in order to investigate how the type of bitumen affects the ageing properties with time, an ageing study with time was carried out. In this stage the mastics with soft and hard bitumen and different proportions of fillers were aged for different times: 2, 5, 10 and 20 hours in the TFOT oven at 163°C with a bitumen film thickness of 2.2mm.

At each level of ageing in both stages, the mastic properties were tested and the ageing index was calculated from different tests carried out on the mastics.

The empirical tests carried out are the rotational viscosity at 135°C using a Brookfield rotational viscometer according to [BS EN 13302:2010](#) and the ring and ball softening point (R&B) according to [BS EN 1427:2015](#). The change in the rheological properties of the mastics after ageing was tested using the dynamic

shear rheometer (DSR). The DSR measurements were carried out with a Bohlin Gemeni model DSR under the following test conditions:

- Mode of loading: Controlled-strain,
- Temperatures: 0 to 50°C (10 °C intervals),
- Frequencies: 0.1 to 10 Hz

Figure 5-18 illustrates the testing programme used in this study.

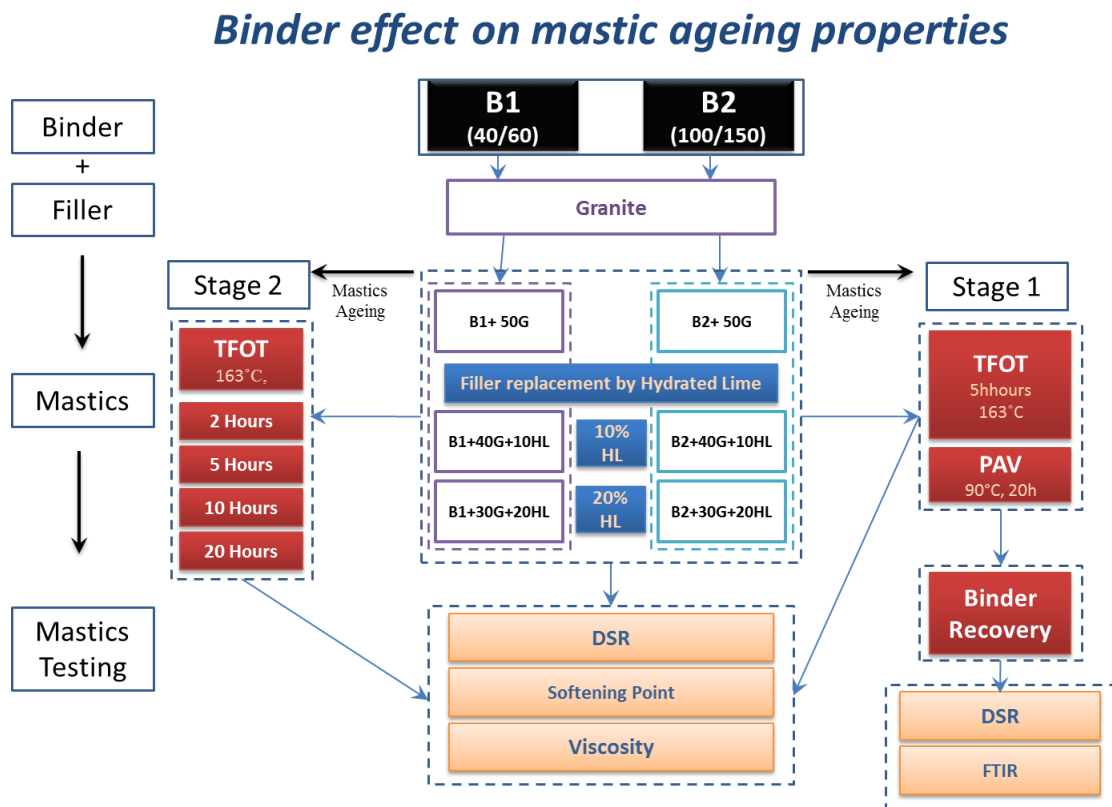


Figure 5-18 Binder effect on mastic ageing testing programme

5.4.3 Results and discussion

5.4.3.1 Ageing Index after short- and long-term ageing

The indices after TFOT short-term ageing and long-term ageing after the PAV ageing procedures were calculated. The ageing indices were calculated from the results of viscosity, softening point, and the complex modulus of the mastics and are presented in Table 5.6.

Table 5.6 Properties of unaged, TFOT and PAV aged mastics

Mastic ID	Viscosity (mPa.s)	G* (Pa)	S.P (°C)	Viscosity AI	G* AI	S.P AI
B1+50G	2090	5.03×10^6	60.6			
B1+50G TFOT	3506	1.14×10^7	66.8	1.68	2.27	6.2
B1+50G PAV	8314	2.29×10^7	77.4	3.98	4.56	16.8
B1+40G+10HL	2970	6.63×10^6	62.3			
B1+40G+10HL TFOT	4739	1.38×10^7	70.2	1.60	2.08	7.9
B1+40G+10HL PAV	6803	2.76×10^7	76	2.29	4.17	13.7
B1+30G+20HL	3465	6.76×10^6	64			
B1+30G+20HL TFOT	6143	1.41×10^7	70.9	1.77	2.08	6.9
B1+30G+20HL PAV	8614	2.70×10^7	78	2.49	4.00	14
B2+50G	853	1.74×10^6	51.8			
B2+50G TFOT	1842	2.89×10^6	57.4	2.16	1.66	5.6
B2+50G PAV	2185	6.48×10^6	63.8	2.56	3.72	12
B2+40G+10HL	1294	1.38×10^6	53.2			
B2+40G+10HL TFOT	1540	2.79×10^6	58.4	1.19	2.03	5.2
B2+40G+10HL PAV	2394	6.51×10^6	62.8	1.85	4.73	9.6
B2+30G+20HL	1644	1.61×10^6	55.8			
B2+30G+20HL TFOT	2573	3.00×10^6	59.2	1.57	1.86	3.4
B2+30G+20HL PAV	2924	6.12×10^6	63.8	1.78	3.81	8

It can be noticed from Table 5.6, that the mastics containing hydrated lime are initially stiffer than the mastics without hydrated lime as can be seen from the initial viscosity, softening points and complex modulus values before TFOT and PAV ageing. This higher initial stiffening effect of the hydrated lime on the mastic was expected as the hydrated lime filler has more surface area and higher Rigden voids, which is well known in the rheology of suspensions. The stiffening ratio of the fillers was calculated to compare the effect of fillers on the mastics prepared with different binders and to show the effect of the hydrated lime on mastic stiffening. The stiffening ratio of viscosity and complex modulus was calculated by dividing the values of viscosity or complex modulus of mastics by the values of the base bitumen used for preparing the mastic. For the softening point, the stiffening ratio was calculated as the difference in softening point values between the mastic and the base bitumen. The stiffening ratio results are shown in Figure 5-19. It is obvious that the mastics prepared with the 40/60 (B2) bitumen have a higher stiffening ratio at all filler compositions. It can also be noticed that the effect of the hydrated

lime replacement on the mastic stiffening is different between the two binders used in this study. These results indicate that the hydrated lime interacts with the bitumen and this interaction depends on the bitumen composition and source.

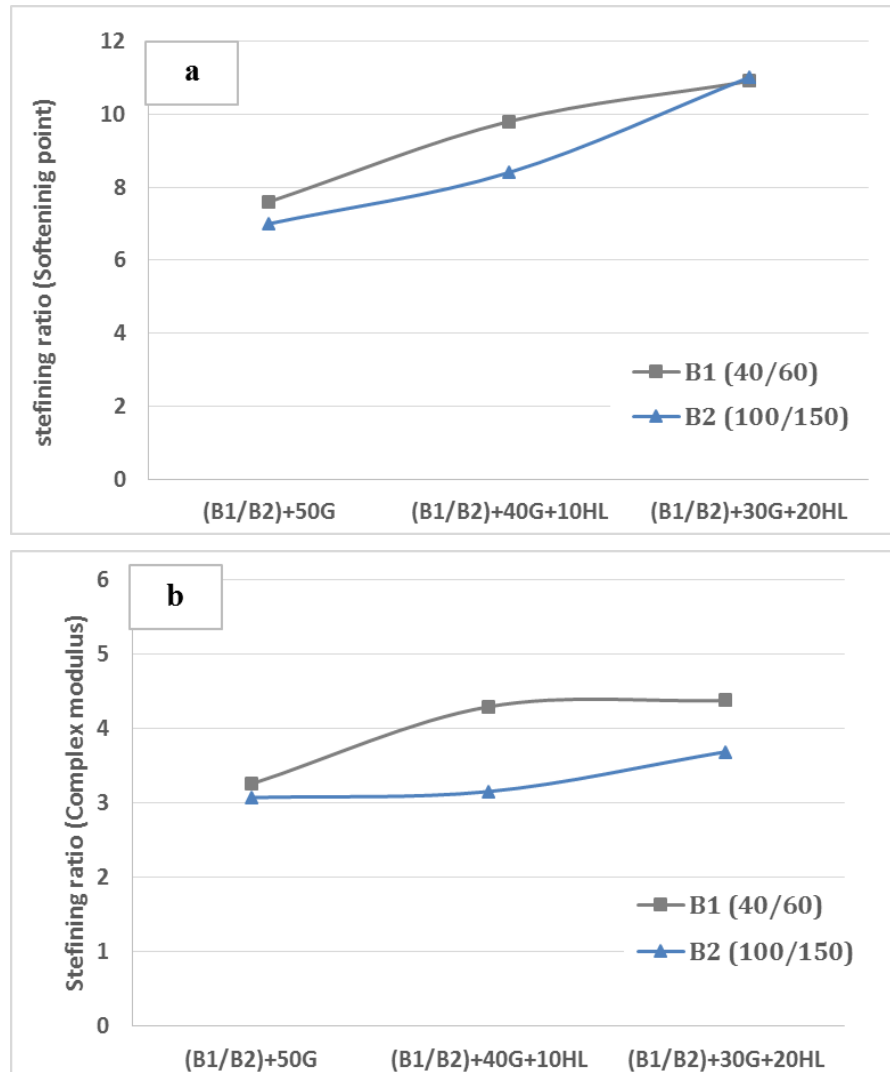


Figure 5-19 Stiffening ratio of fillers on mastics a) Softening point b) complex modulus

The higher stiffening ratio of mastics containing hydrated lime can be related to the higher specific surface area of hydrated lime filler as well as the granular type particles of hydrated lime, which have a very rough texture as seen from the microscopic morphology SEM imaging in Chapter Three. However, granite fillers have mostly angular type particles with smooth to slightly rough texture.

Regarding the ageing effect, it is clear that all the different ageing indices for the tested mastics increase with the ageing process. That means the mastics become

stiffer with ageing. In addition, the effect of hydrated lime on the ageing behaviour of the mastics is clear. The mastics containing hydrated lime have lower ageing indices for most of the samples tested. It could also be noticed, that replacing granite filler with 20% hydrated lime does not make a significant additional effect compared to the 10% hydrated lime replacement.

In addition, from Table 5.6, the effect of the hydrated lime on the ageing indices of mastics prepared with the two different binders can be compared. It is clear that the mastics prepared with the soft bitumen (B2) have lower ageing indices in most of the tested mastics. However, it is important to mention that the bitumen B2 itself has a higher ageing index compared to bitumen B1 in all tests used in this study. This indicates that an interaction between the fillers and bitumen could happen and this depends on the chemical composition of the bitumen and the filler type and concentration. Furthermore, it can be seen that the ageing indices calculated from different tests rank the mastics ageing behaviour differently; however, as a general trend, the mastics containing hydrated lime always have a lower ageing index. A correlation between these ageing indices has been made and the results show that they correlate well. The results of viscosity and softening point were better correlated to each other than they are correlated with the complex modulus.

5.4.3.2 Ageing time study of mastics

In order to compare the effect of hydrated lime and the bitumen type on the rate of mastic ageing, the mastics were aged in the TFOT oven for different ageing times up to 20 hours. The ageing indices were calculated as mentioned earlier. The results are presented in Figure 5-20. The results show that as mentioned earlier, the ageing indices of the mastics with soft binder 100/150 (B2) are lower than the mastics prepared with the 40/60 bitumen (B1). This is more obvious with the mastics containing hydrated lime.

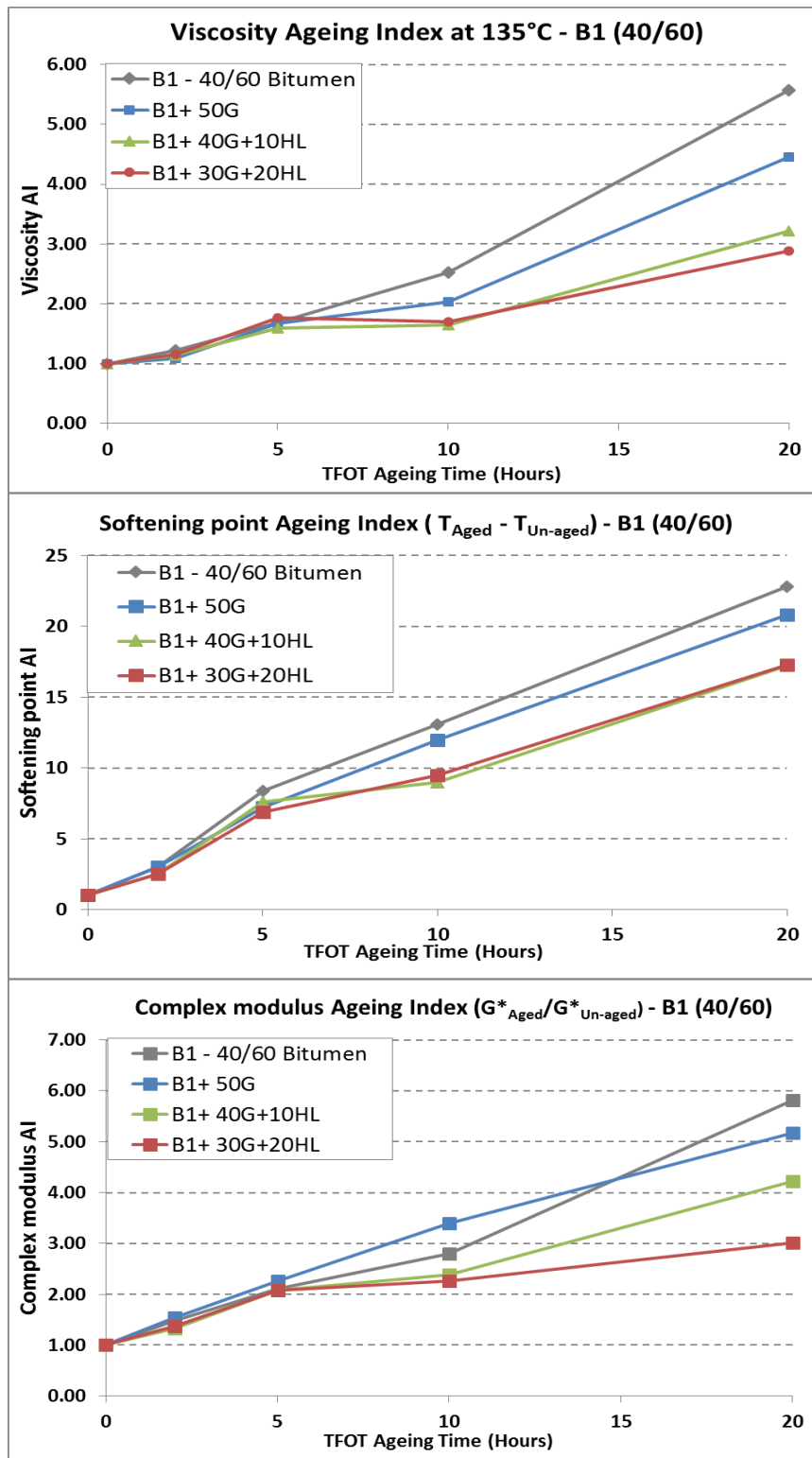


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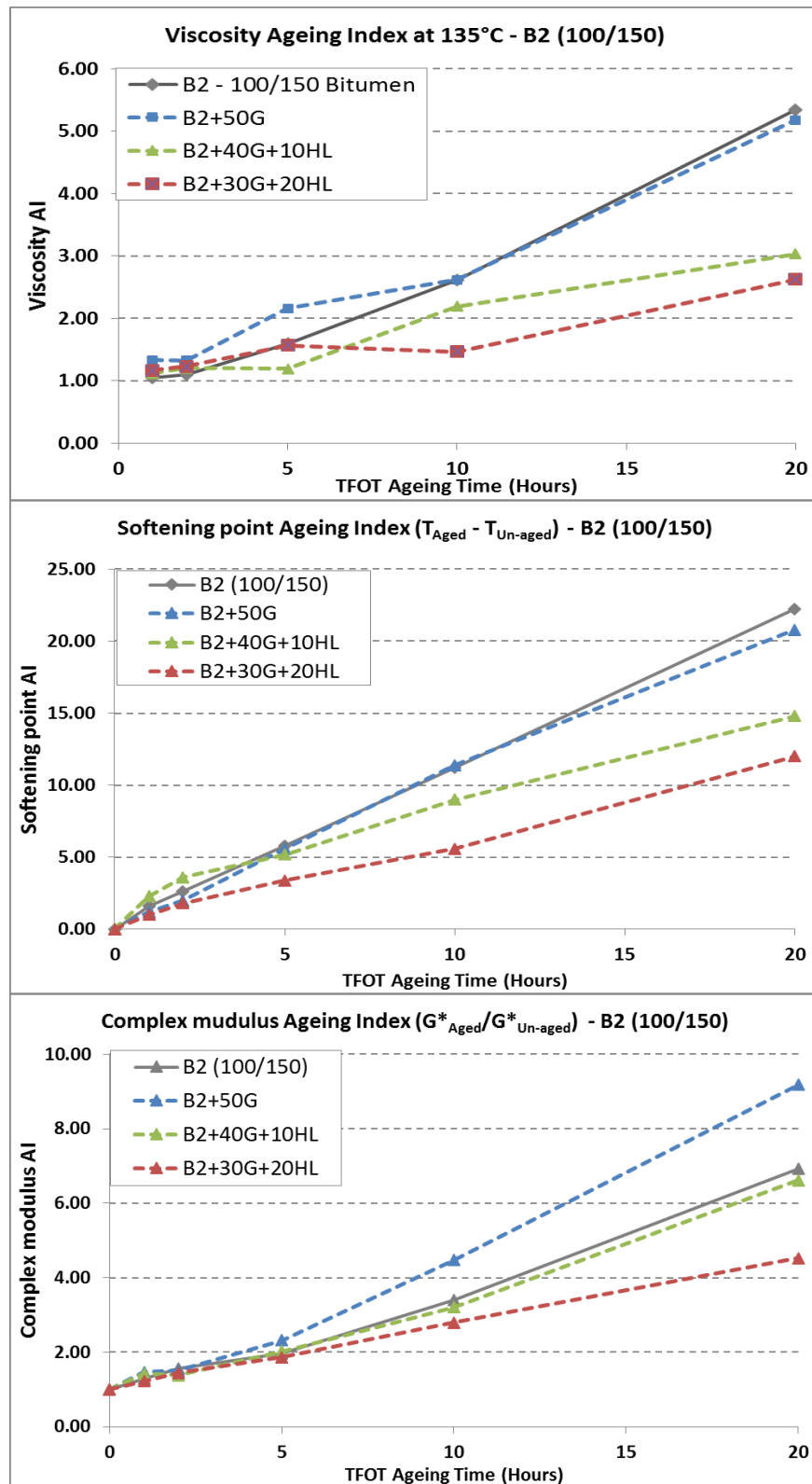


Figure 5-20 Ageing indices of the mastics with different time TFOT ageing

These results indicate that hydrated lime changes the ageing susceptibility of the mastics. It also indicates that an interaction between hydrated lime and bitumen could be happening which is not the case with granite.

In addition, the effect of hydrated lime on slowing down the ageing rate is clear; the ageing indices of the mastics containing hydrated lime are always lower than for mastics with only granite fillers with both bitumen binders used in this study.

In order to compare the different ageing indices, a correlation has been made between the different ageing indices after the TFOT ageing for different times. The results of this correlations are presented in Figure 5-21. The results show that there is a good correlation between these ageing indices with a correlation coefficient $R^2 = 0.86 - 0.87$. A statistical analysis has been carried out and the correlation coefficients were calculated and checked, the results indicated that the correlation is significant at the 0.05 level

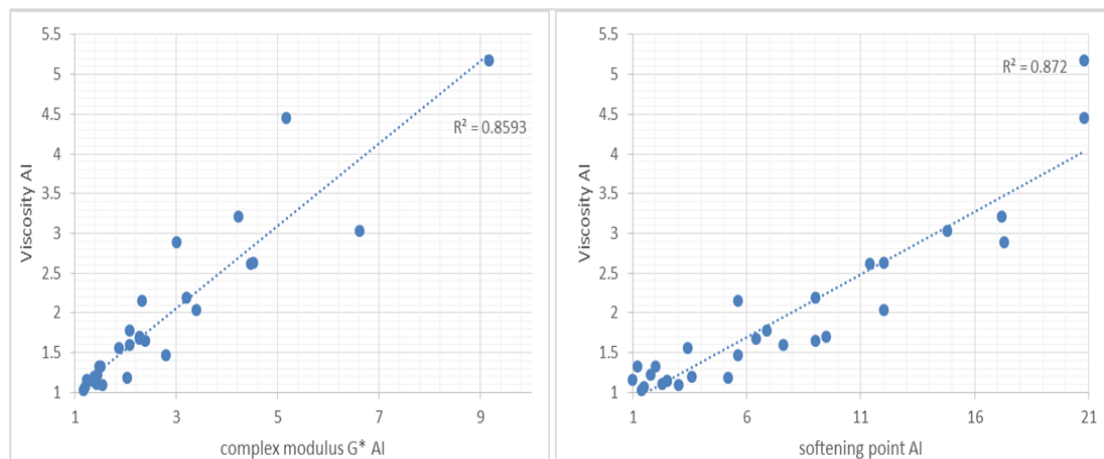


Figure 5-21 Correlation between different ageing indices after TFOT ageing

5.5 Chapter Summary

The main aim of this chapter was to investigate the effect of different fillers on bitumen-filler mastics ageing. Particular attention was paid to study the benefits of using hydrated lime on mitigating the ageing effect in the mastic phase. The ageing was quantified after different ageing stages and the effect of fillers was compared. Furthermore, the effect of physical and chemical interaction between fillers and bitumen was studied. The effect of hydrated lime with two different bitumen binders on mastic ageing was investigated in this study as well. Different ageing indices were used for quantifying the ageing effect on mastics. On the basis of the laboratory test results on the mastics and recovered bitumens, the following conclusions were derived:

- The effect of the filler on mastics as measured by the increases in the viscosity and softening point show that for the same filler concentrations granite tends to stiffen the mastics more than limestone filler. Furthermore, hydrated lime replacement of filler at 10 and 20% increases the stiffening effect on the mastic.
- Mastics containing 10 or 20% hydrated lime show a lower ageing index compared to the original mastics and to the neat bitumen as well. This effect is more pronounced after long-term ageing. It was noticed from the calculated ageing indices that replacing 20% of filler with hydrated lime does not make a significant additional effect on reducing ageing compared to 10% of hydrated lime.
- The mastics with LS+HL are softer than mastics with G+HL fillers after ageing even when they were stiffer before ageing. That means the LS+HL combination reduces the rate of ageing and oxidation within the mastics

more than that for G+HL combinations for the ageing conditions used in this study.

- From FTIR analysis it was concluded that the binder recovered from the mastic of hydrated lime with granite contains less oxygenated products after both short- and long-term ageing. This indicates that less ageing and stiffening occurred in the mastics with HL. These results can explain the lower ageing index for mastics including hydrated lime, which means a slower rate of increase of the heavier oxygenated products in mastics containing hydrated lime with ageing.
- From the ageing time study on the mastics, it was concluded that the rate of increase in the complex modulus, viscosity and softening point for the mastics containing hydrated lime was slower than for mastics without hydrated lime. This beneficial effect of hydrated lime was confirmed by the calculated ageing indices, as they show that the mastics with hydrated lime always have a lower ageing index compared to the original mastics and to the neat bitumen.
- The effect of the hydrated lime replacement on mastic stiffening with different binders is different. These results could indicate that the hydrated lime interacts with the bitumen and this interaction is different with different binders and depends on the bitumen composition and source.
- The results in this chapter indicate that hydrated lime slows down the ageing rate compared to the other fillers and it could interact differently with different bitumen binders, thus a more detailed investigation is needed to understand the mechanism and interaction between fillers and bitumen during ageing. This will be discussed in Chapter Seven.

Chapter 6: Ageing of Asphalt mixture: Mechanical properties

6.1 Introduction

The differences in rankings based on either short-term or long-term ageing for asphalt mixtures and pure bitumen or bitumen mastics (bitumen and filler) indicate the need for testing to evaluate the ageing susceptibility of a mixture. Clearly, the ageing of bitumen alone or in mastics with the fillers could not indicate how a mix will age at the larger scales with mixtures and in the field. Thus, testing is needed to determine the influence of the different factors on mixture ageing. This influence appears to be related to the chemical interaction of the aggregate and fillers with the bitumen binder, which may be related to adhesion, where the greater the adhesion, the greater the mitigation of ageing ([Bell et al.,1994b](#)).

In order to investigate the influence of aggregate type and the effect of the fillers and the hydrated lime replacement of the original fillers on bitumen and mixture ageing, a typical acidic aggregate (granite) and a typical basic aggregate (limestone) were used in this study. These two types of aggregates were used for producing 0/14mm close graded dense asphalt mixtures specimens with different percentages of hydrated lime replacement of the original fillers. The specimens were artificially aged using the SHRP long-term ageing ([Scholz,1995](#)). The ageing properties of both the mixture specimens and the recovered binders were tested at different ageing stages.

6.2 Materials

In this study, one type of bitumen was used, a 40/60 bitumen, and a typical 'basic' aggregate of crushed limestone, which was obtained from Tunstead Quarry, Derbyshire, UK. Another typical 'acidic' aggregate of granite from Bardon Hill Quarry was used in this study as well. The characterisation of limestone and granite aggregates was presented in Chapter Three. In terms of the fillers used with each aggregate type, the same natural filler types were used. So with granite aggregates, granite filler was used and with the limestone aggregates, limestone filler was used to prepare the asphalt mixture. However, in order to see the effect of hydrated lime on the ageing of asphalt mixtures, a replacement of the fillers by hydrated lime at 1% and 2% of the total aggregate weight was utilised. In all cases, the total filler content in the mixture was kept the same at 5% of the total aggregate weight.

In terms of the mixtures, one bitumen content was used to produce all the different mixture combinations. The binder content adopted in this study was 5%, in order to keep the same percentages as used in the mastics study (50% bitumen: 50% filler content).

The final gradations of the aggregates used in this study are presented in Figure 6-1, where the gradation of both granite and limestone aggregates can be seen. The composition of aggregates was designed ensuring that the gradation of the aggregate fell into the recommended grading envelope for 0/14 mm size close graded surface course. In addition, the properties of the bitumen used are shown in Table 6.1. However, the properties of the fillers and hydrated lime, they are the same as discussed earlier in Chapter Three.

Table 6.1 Bitumen basic properties

Bitumen	Penetration (dmm)	Softening point (°C)	Viscosity at 135 °C (mPa.s)
40/60 bitumen	46	51.60	445

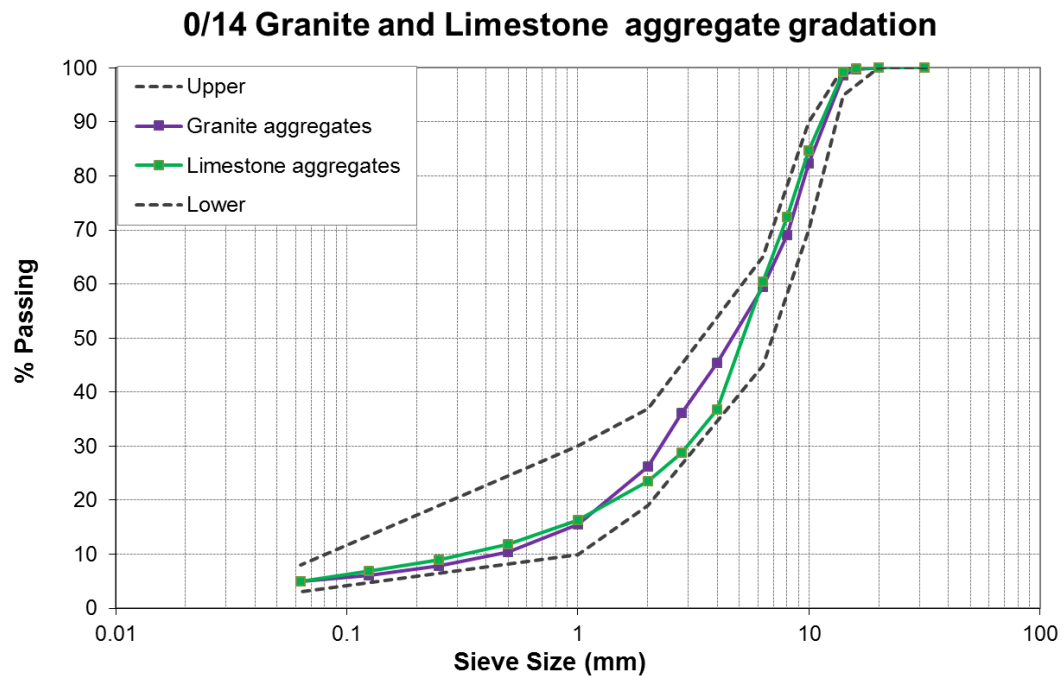


Figure 6-1 Granite and limestone aggregate gradations

6.3 Testing Programme

In order to achieve the aims and objectives of this study, and to study the effect of hydrated lime on the ageing of asphalt mixtures the following testing programme was utilised in this study.

- Two types of mixtures were designed according to the gradings shown above in Figure 6-1. An attempt was made to keep both the granite and limestone with similar gradations so the mixture volumetric properties could be similar and the effect of fillers and aggregates on the ageing of asphalt mixtures could be investigated more clearly.
- The total filler content of each mixture was kept at 5% by weight of aggregates. Mixtures were also prepared where 1% and 2% of the original fillers (granite or limestone) was replaced by hydrated lime.
- As the ageing of bitumen requires the presence of sufficient oxygen, so a relatively high air void content of 10% was targeted for asphalt specimens in this study.

- The asphalt mixtures were mixed in an asphalt mixer and compacted using a roller compactor. The mixtures were compacted into slabs of size: 305×305×100 mm immediately after mixing.
- After that, different specimens were cored from each slab and were trimmed into cylinders with a diameter of 100 mm and a height of 50 mm to be tested for ITSM and ITS tests. However, other 150mm cores were also scored from different slabs for the semi-circular bending (SCB) test.
- The samples were tested for their different mechanical properties such as ITSM, ITS and their fracture properties using SCB test.
- The specimens were then subjected to the SHRP long-term oven ageing protocol (at 85°C for 5 days), followed by a further testing for their mechanical properties after long-term ageing. Finally, the ageing effect of different mixtures was quantified using different ageing indices and analysis approaches.
- The binder of the aged specimens was recovered and the effect of ageing on the binders recovered from different samples was investigated by rheological and chemical means using the DSR and FTIR spectroscopy respectively.

A summary of the testing programme is shown in Figure 6-2.

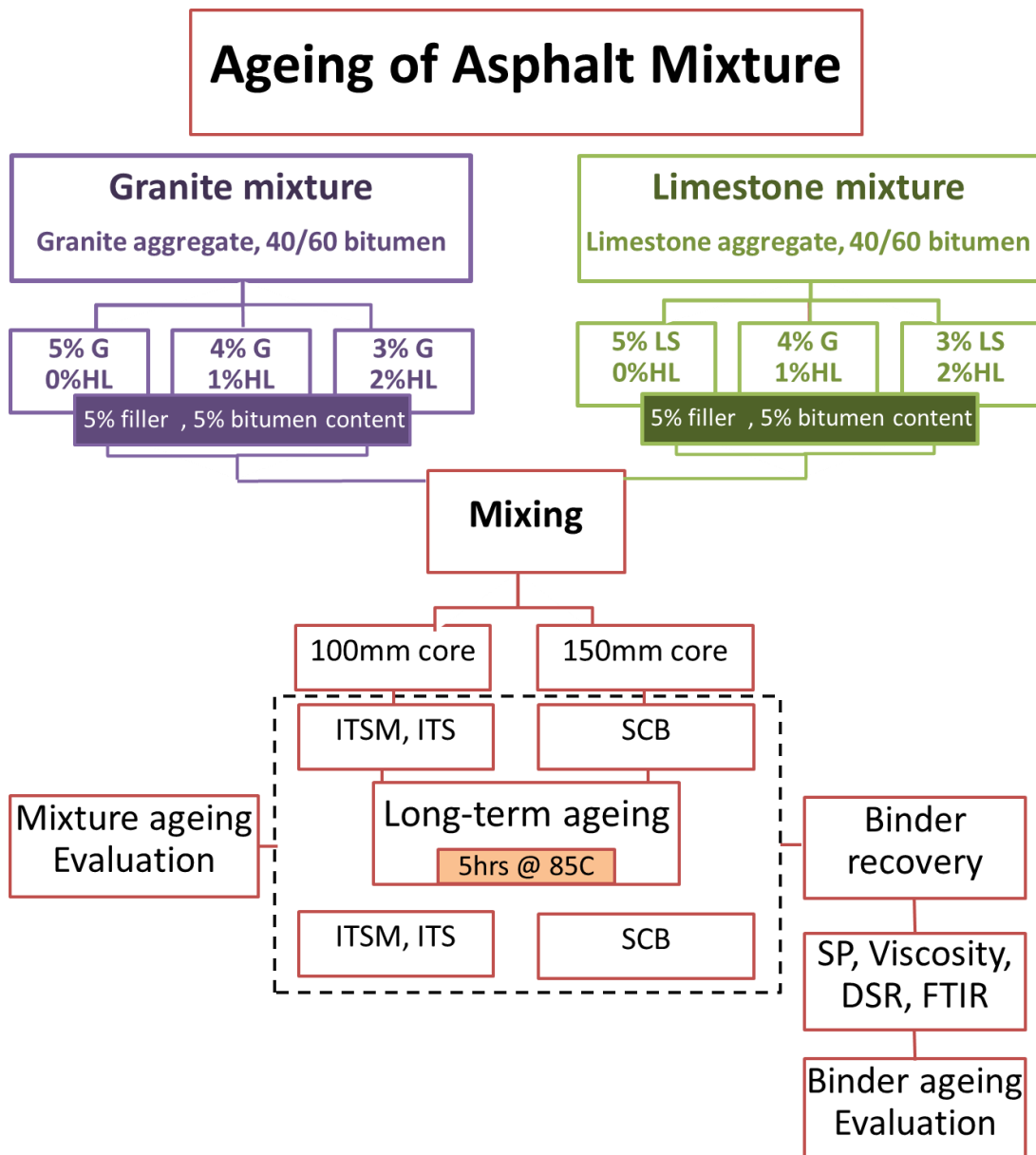


Figure 6-2 Experimental programme

6.3.1 Ageing simulation

Ageing of asphalt binders and mixtures is mainly due to oxidation and volatilisation of specific components of the bitumen. Oxidation is the chemical reaction that happens between oxygen in the air and the bitumen binder. Ageing usually takes place in two stages. The first stage is during plant mixing, transportation and placement at high temperature. The second stage is during in-place service of the pavement during its lifetime, which will happen due to exposure to the environment.

The effect of laboratory ageing depends on the procedure used and the factors used in this simulation such as ageing time and temperature, and if the mixture is in a loose or compacted state.

Two laboratory ageing procedures are used for simulating the ageing of asphalt mixtures. The short-term ageing procedure (STOA) according to (AASHTO PP2) is designed to simulate the ageing that a mixture will undergo during plant mixing and construction. The long-term ageing procedure (LTOA) (AASHTO PP2) is designed to simulate the total ageing the compacted mixture will undergo during about 7 to 10 years service life. For the long-term ageing LTOA procedure, a compacted mixture is aged in a forced draft oven for 5 days at 85°C.

In this study, the effect of long-term ageing was studied. The specimens after being cored from the slabs were tested for their initial properties such as ITSM and then were aged in the forced draft oven for 5 days at 85°C. Afterwards, the same testing was carried out for the aged samples.

In order to keep the sample geometries unchanged with ageing, the samples were encapsulated in a steel cage (Figure 6-3), so the air could penetrate them, but the dimensions would remain the same during the ageing process, so the testing results will not be affected.



Figure 6-3 Sample ageing procedure involving encapsulating in steel cages.

6.4 Results and discussion

6.4.1 Sample description

Samples were prepared with different combinations of granite or limestone mixtures with and without hydrated lime and aged with the long-term ageing procedure. The air void content for each specimen was determined using the sealed specimen method according to the British standard. As the maximum density of asphalt mixture is required in the final calculation of air voids, this was determined according to [BS EN 12697-5:2009](#), then the air voids for all the specimens were calculated.

The average air voids for the cored samples was determined. The average air void content for the granite mixture was 10.6%, with a maximum of 11.7% and a minimum of 9.3%. For the limestone mixture, the average air void content was 9.6% with a maximum of 10.4% and a minimum of 9.0%. These results show that the air voids for each mixture are in a small range, thus, the effect of different air void contents on ageing will be minimised and the different fillers and aggregates would be the main factors affecting the ageing.

The experimental programme mainly involved assessment of the hydrated lime's effect on the performance of the mixtures. Firstly, the mechanical properties were evaluated before and after ageing. Then work was also extended to test the effect of the long-term ageing process on the recovered binder. Table 6.2 summarises the experimental testing programme. The results of these tests are covered in the following sections.

Table 6.2 Testing procedure summary

Test	Standards	Tested samples
Mechanical properties		
Indirect tensile stiffness modulus (ITSM)	BS EN 12697-26	Unaged, LTOA
Indirect tensile strength (ITS)	BS EN 12697-23	Unaged, LTOA
Semi-circular bending test (SCB)	BS EN 12697-44	Unaged, LTOA
Testing of recovered Binder		
Dynamic Shear Rheometer (DSR)		LTOA
Fourier transform infrared (FTIR)		LTOA

6.4.2 Indirect tensile stiffness modulus (ITSM)

The indirect Tensile Stiffness Modulus Test (ITSM) is a simple and rapid test method for measuring stiffness modulus of asphalt mixtures, which is the most important input for pavement design to predict the structural behaviour in the road. Stiffness modulus is dependent on a number of factors such as asphalt mixture composition, binder grade and level of compaction as well as test conditions such as the temperature and loading frequency ([Read and Whiteoak,2003](#)). The ITSM test was used since it is inexpensive, simple and can be quickly conducted. In addition, ITSM was performed in order to allow repeat tests on the same specimens at different ageing stages and conditions to nullify variability in the mixtures and to derive reliable results for stiffness.

Test configuration

The test was conducted according to the European standard [BS EN 12697-26](#) using the NAT equipment. The principle of the ITSM test is that a cylindrical specimen is exposed to repeated sinusoidal compressive loads through the vertical diameter plane, which develops a relatively uniform tensile stress perpendicular to the direction of the applied load and along the vertical diametral plane. The resulting horizontal deformation of the specimen is measured and an assumed Poisson's ratio is used to calculate the tensile strain at the centre of the specimen. The test is normally carried out on 100mm or 150mm diameter samples with a thickness

between 30mm and 75mm. In this study, the test was carried out on specimens with 100mm diameter and samples were trimmed to 50mm thickness. According to BS EN 12697-26, an impulsive load was applied with a rise-time of 124 ± 4 ms, to achieve a target horizontal deformation of 5 ± 2 μ m. Ten conditioning pulses were applied to the specimens followed by five test pulses. Figure 6.4 and Table 6.3 summarise the test configuration and testing conditions used in this study.

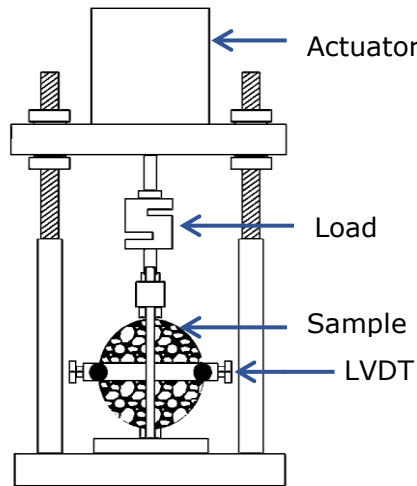


Figure 6.4 ITSM test configuration

Testing conditions for all samples were according to the BS standard for testing at different temperatures: 0°C 10°C and 20°C. The samples were tested in two directions without a relaxation time between testing. The two tested diameters were perpendicular to each other and the mean value of the stiffness for the second diameter's test should be within the specified limits of EN 12697 part 26, which are +10% and -20%. Automatically, the test load and horizontal strain were measured and stored, and the stiffness modulus was calculated by Equation 6-1.

$$S_m = \frac{F \times (v + 0.27)}{(z \times h)} \quad \text{Equation 6-1}$$

Where:

- S_m Stiffness modulus (MPa)
- F ; Applied vertical load (N)
- v : Poisson's ratio (0.35 assumed)
- z Amplitude of horizontal deformation (mm)
- h Thickness of the sample (mm)

Table 6.3 ITSM testing parameters

Item	Range
Specimen diameter	100 mm
Transient peak horizontal deformation	5 μm
Rise time	124 ms
Poisson's ratio (assumed)	0.35
Test temperature	0, 10, 20°C
Specimen thickness	50 mm

6.4.2.1 Results and discussion

The ITSM was performed at different temperatures on the same specimens. Three specimens per mix were tested under the same conditions. The tests were performed at 0, 10 and 20°C, both before and after the samples were aged using the LTOA procedure. The average results for ITSM at these testing temperatures are shown in Figure 6.5.

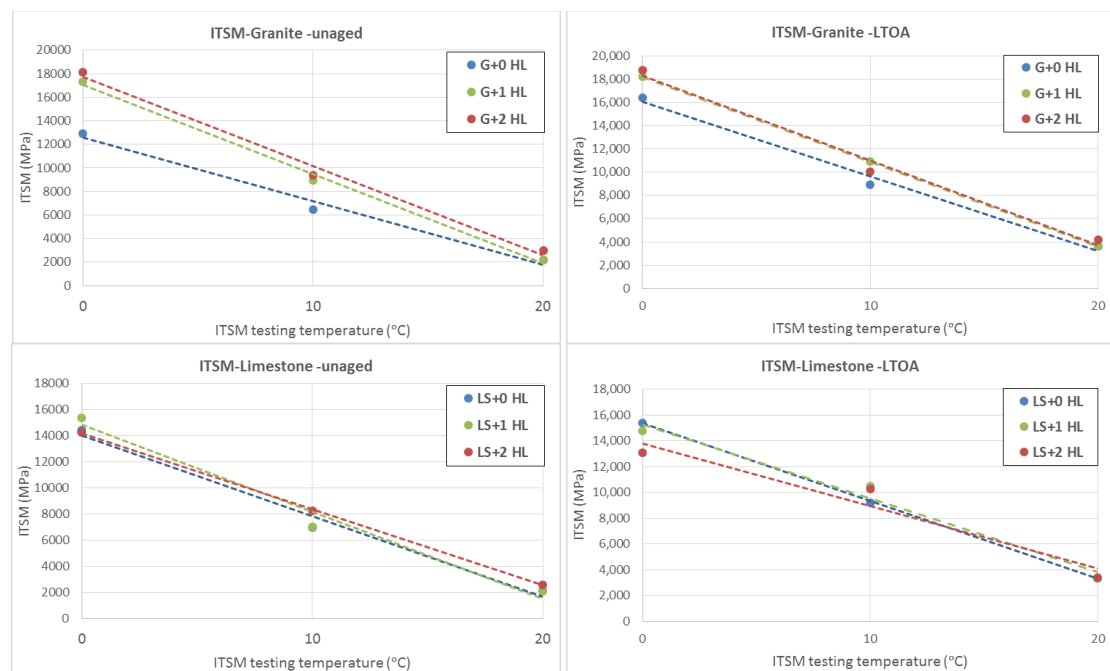


Figure 6.5 ITSM Values at different testing temperatures before and after LTOA ageing

From the results above, it can be seen that the ITSM values decrease with increased temperature. This trend is evident in both mixtures and it varies with different filler combinations. In addition, it is clear that before ageing, the samples containing hydrated lime and granite fillers have higher values than the mixture without

hydrated lime before ageing, especially at the lower temperature of 0°C. However, the effect is less pronounced for the limestone mixtures.

The increase in the ITSM values for the mixtures after ageing is less for the mixtures containing hydrated lime, makes the values at lower temperatures appear to be in a closer range. To show this change in the ITSM values at different temperatures before and after ageing, the ageing index, which is calculated by dividing the values of ITSM of aged mixtures by the unaged values of the same sample. The calculated ageing indices at different temperatures are presented in Figure 6.6.

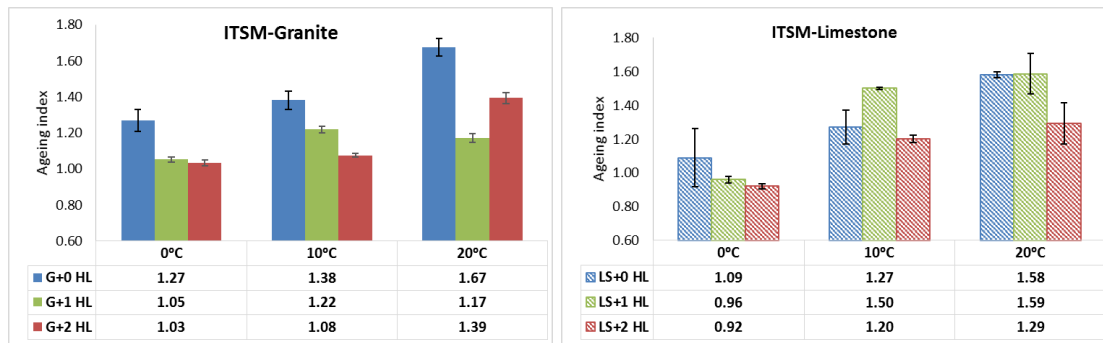


Figure 6.6 ITSM Ageing index (AI) at different testing temperatures (with standard error bars)

From calculated ageing indices, it can be noted that the ageing indices from ITSM generally increased with temperature increase. Furthermore, the ageing indices for the limestone mixtures are smaller than for the granite mixtures. In addition, the effect of hydrated lime replacement is clear, especially with granite mixtures where it can be seen to reduce the effect of aging as the ITSM increase in stiffness for a mixture containing hydrated lime is less than for mixtures without hydrated lime. To show this effect more clearly, the ITSM values before and after ageing and the ageing index at 20°C are presented in Figure 6.7.

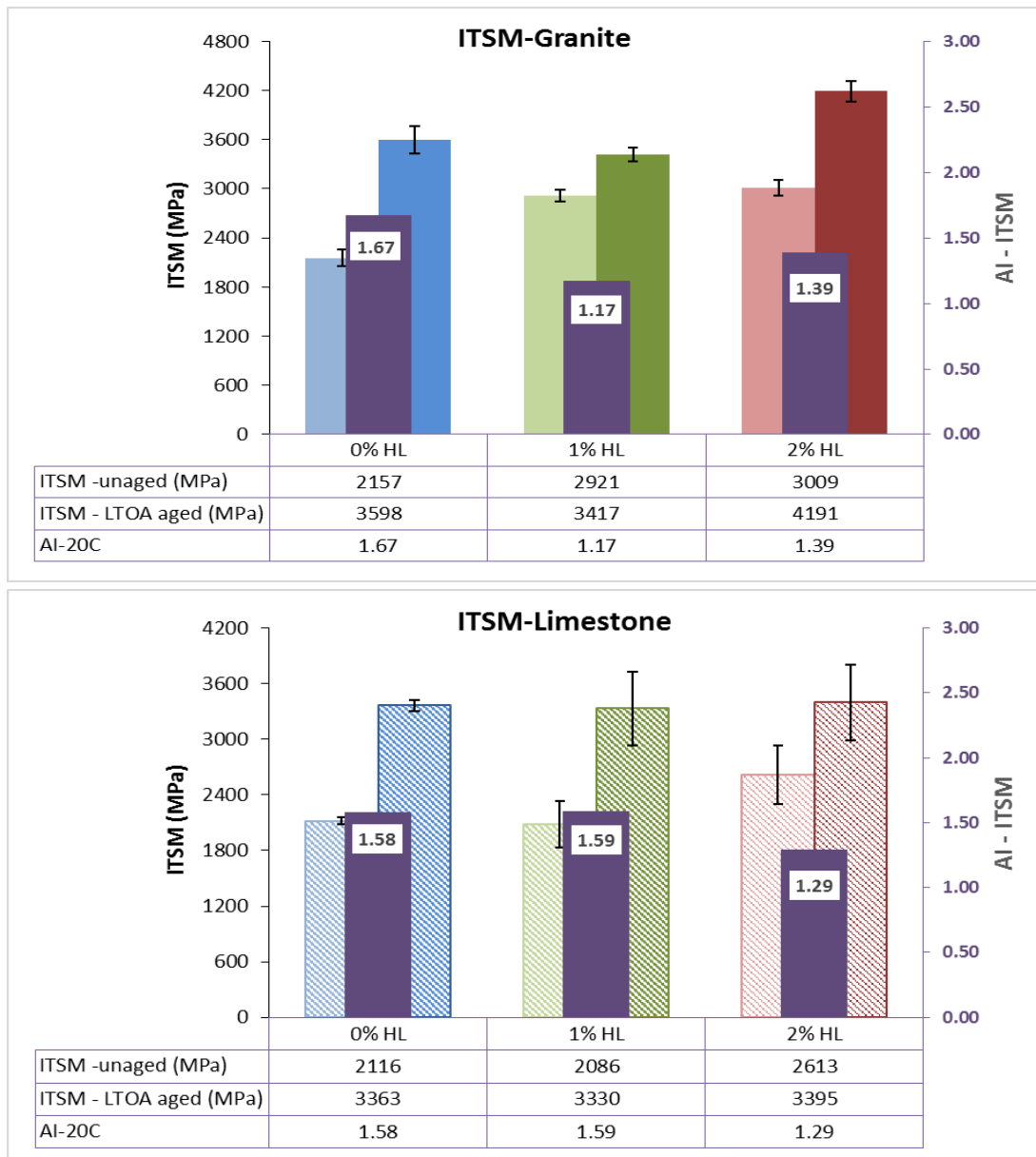


Figure 6.7 ITSM before and after ageing and Aging index (AI) at 20°C

The results show that the effect of hydrated lime on stiffening the mixture is more pronounced in the granite mixture. The stiffness increased by replacing 1 and 2% of the filler with hydrated lime by up to 35 and 40% respectively. However, the limestone mixtures were less affected by the hydrated lime replacement. The stiffness was almost unchanged after 1% replacement of the filler and increased by up to 20% when 2% of limestone filler was replaced by hydrated lime.

From the results of the ITSM testing of the mixtures, it can be seen that the effect of hydrated lime replacement of the fillers on the ageing of the asphalt mixtures is clear and it can reduce the ageing as seen from the ageing indices. However, this effect is different between the granite and limestone mixtures. The behaviour when the base filler is replaced at different percentages in the different mixtures differs. As a result, more investigation about the factors and mechanisms of modification may be needed.

6.4.3 Indirect tensile strength (ITS)

The ITS test was applied to assess the tensile strength of the different mixtures with varying percentages of hydrated lime. The ITS test involved applying a diametric compressive load with a constant deformation rate of 50 ± 2 mm/min on the samples between two uniform loading strips. This enables tensile stresses to develop along the diametric vertical plane to cause a splitting failure. The ITS was obtained for each specimen according to Equation 6-2.

$$ITS = \frac{2P}{(\pi \times D \times H)} \times 1000 \quad \text{Equation 6-2}$$

Where

ITS: is the indirect tensile strength, expressed in kilopascals (kPa)

P: Vertical load (N); D: Diameter of specimen (mm); H: Height of specimen (mm);

The test was conducted at 20°C using an INSTRON loading frame in accordance with [BS EN 12697-23](#). After the ITSM of different samples was measured as described earlier, the ITS test was carried out on the same specimens. This procedure is possible since the ITSM test is non-destructive. The ITS results for different mixture combinations are presented in Figure 6.8.

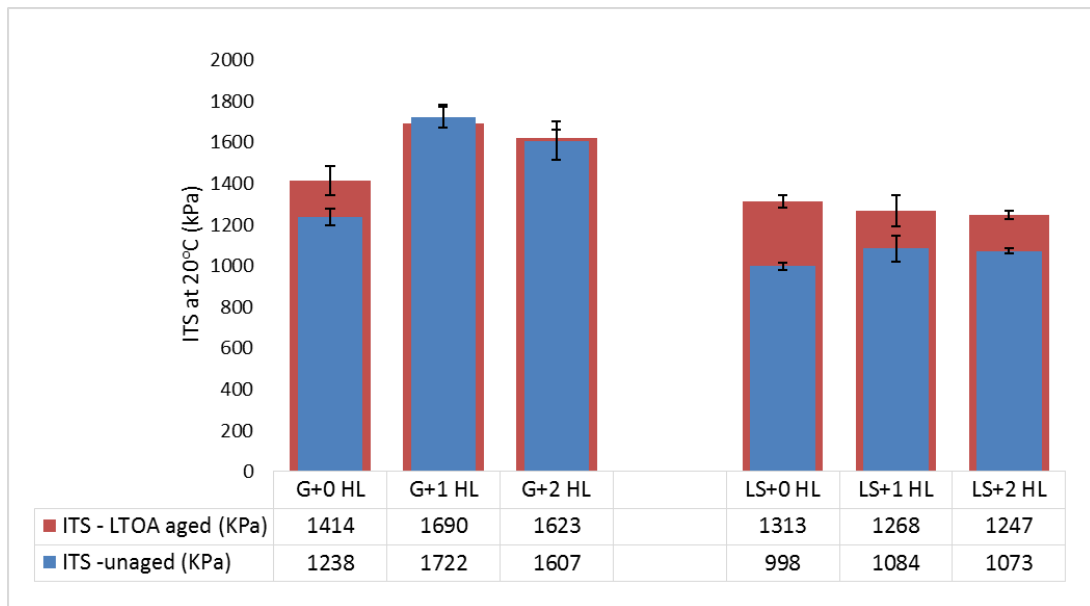


Figure 6.8 ITS of mixtures before and after LTOA ageing

The results show that granite mixtures have higher ITS values than limestone mixtures. Also, it can be noticed that with hydrated lime replacement, the ITS for both the granite and limestone mixtures increases. However, the increase in granite mixtures is more pronounced than in the limestone mixtures. Moreover, it can be seen that using 2% hydrated lime in the mixture does not give any significant increase in ITS values compared to 1% hydrated lime in the mixture for the unaged mixtures.

The results also reveal that the increase in the ITS for granite mixtures after ageing is lower than that of limestone mixtures. In addition, for the mixtures containing hydrated lime the increase in ITS after ageing is less than that for the mixtures without hydrated lime. The increase in ITS values before and after ageing was calculated as an ageing index by dividing the aged ITS by the unaged values. The results for the ITS ageing indices for different samples are shown in Figure 6.9.

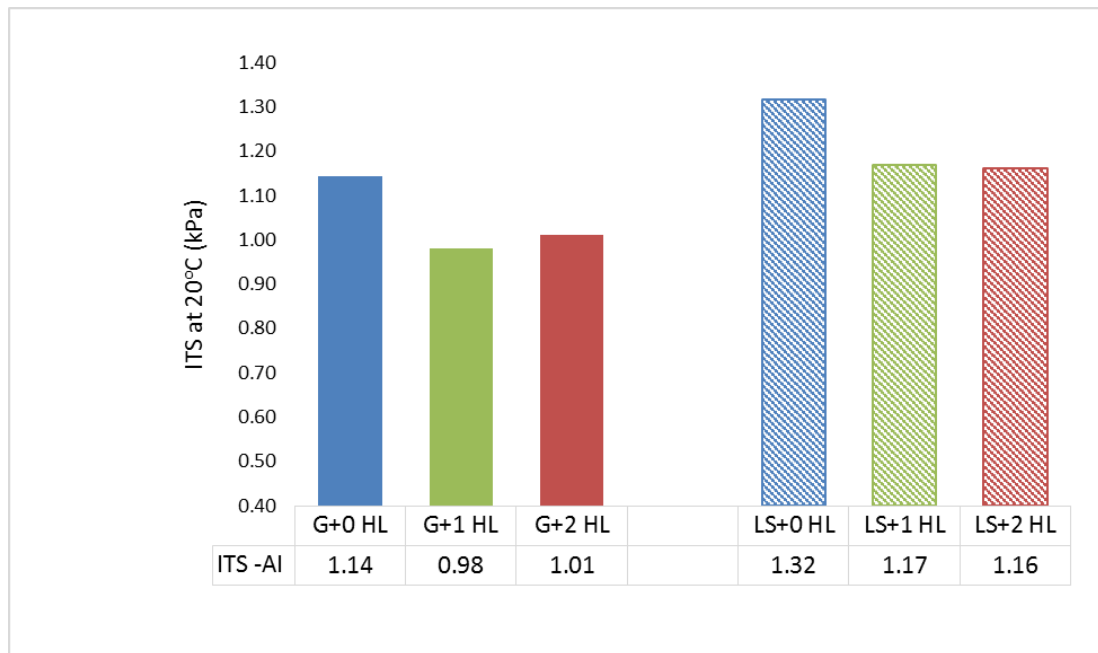


Figure 6.9 ITS ageing indices for different mixtures

The results show the beneficial effect of hydrated lime on the ageing of the asphalt mixture by reducing the increase of ITS after ageing. This effect of hydrated lime is clear for both mixtures. However, it can be noticed that 1% and 2% hydrated lime replacement in the mixture have almost the same effect on ageing indices. The samples containing hydrated lime have lower ageing indices than the original samples without hydrated lime.

6.4.4 Semi-circular bending (SCB) test

The semi-circular bending (SCB) test was used to evaluate the tensile strength or fracture toughness of different mixtures used in this study for the assessment of the potential for crack propagation. Figure 6.10 presents the SCB test configuration. The test was conducted in accordance with [BS EN 12697-44](#). The specimen consists of a 150 mm diameter half cylinder containing a notch (crack) of 10 mm depth from the centre of its bottom edge as shown in Figure 6.10. A standard three-point load is applied to fracture the specimen. The maximum load that the specimen can resist before failure is recorded. During the test, the

deformation increases at a constant rate of 5 mm/min. As per [BS EN 12697-44](#) the maximum stress at failure, σ_{max} (N/mm²) and the fracture toughness K_{Ic} (N/mm^{3/2}) have been calculated in accordance with Equation 6-3 and Equation 6-4, respectively.

$$\sigma_{max} = \frac{4.263 \times F_{max}}{D \times t} \quad \text{Equation 6-3}$$

where

D : Diameter of the specimen (mm); t : Thickness of specimen (mm); F_{max} : the Maximum force applied to the specimen (N).

$$K_{Ic} = \sigma_{max} \times f\left(\frac{a}{W}\right) \quad \text{Equation 6-4}$$

where:

W : Height of specimen (mm); a : Notch depth of specimen (mm); σ_{max} : Stress at failure of specimen (N/mm²); $f\left(\frac{a}{W}\right)$: Geometric factor of specimen; for $9 < a < 11$ mm and $70 < W < 75$ mm, then $f\left(\frac{a}{W}\right) = 5.956$.

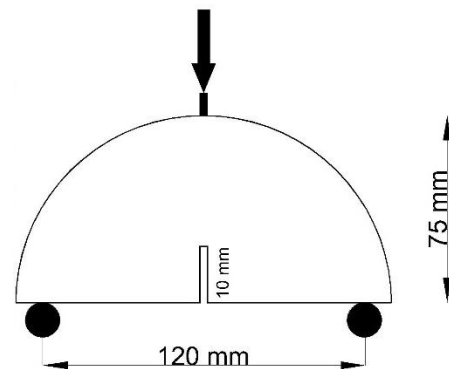


Figure 6.10 SCB configuration test

The evaluation of fracture was performed at 0 and 20°C. The cracking propagation at low temperature was evaluated at 0°C as recommended by the [European](#)

[Committee for Standardization\(2010\)](#), while 20°C was selected to be similar to previous evaluation in the ITS test. The fracture toughness K_{Ic} of different mixtures tested at 0°C and 20°C is presented in Figure 6.11 and Figure 6.12 respectively.

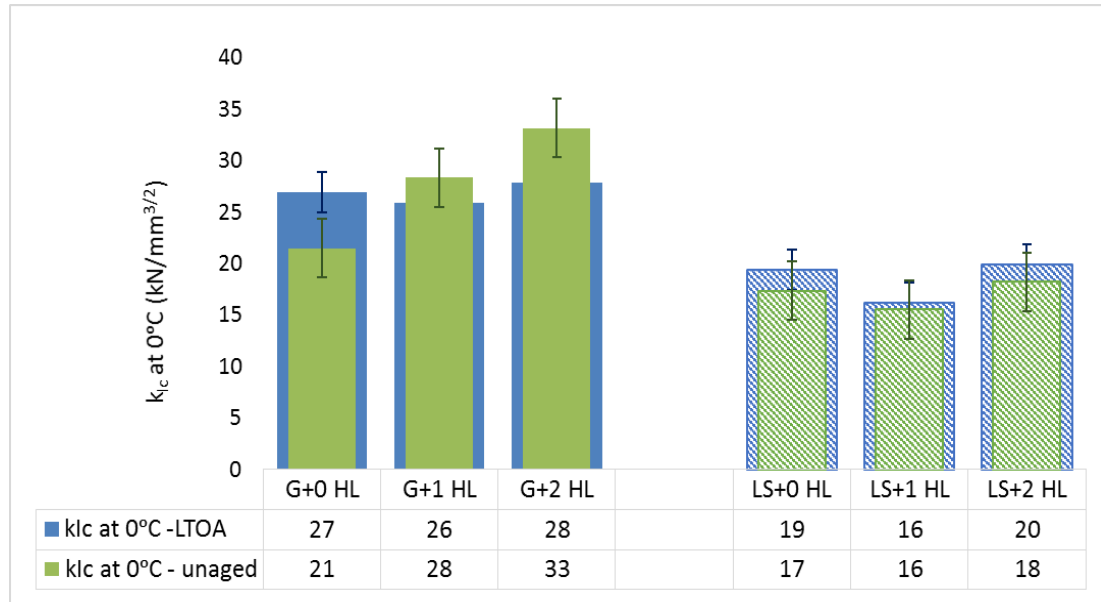


Figure 6.11 Fracture toughness at 0°C before and after LTOA

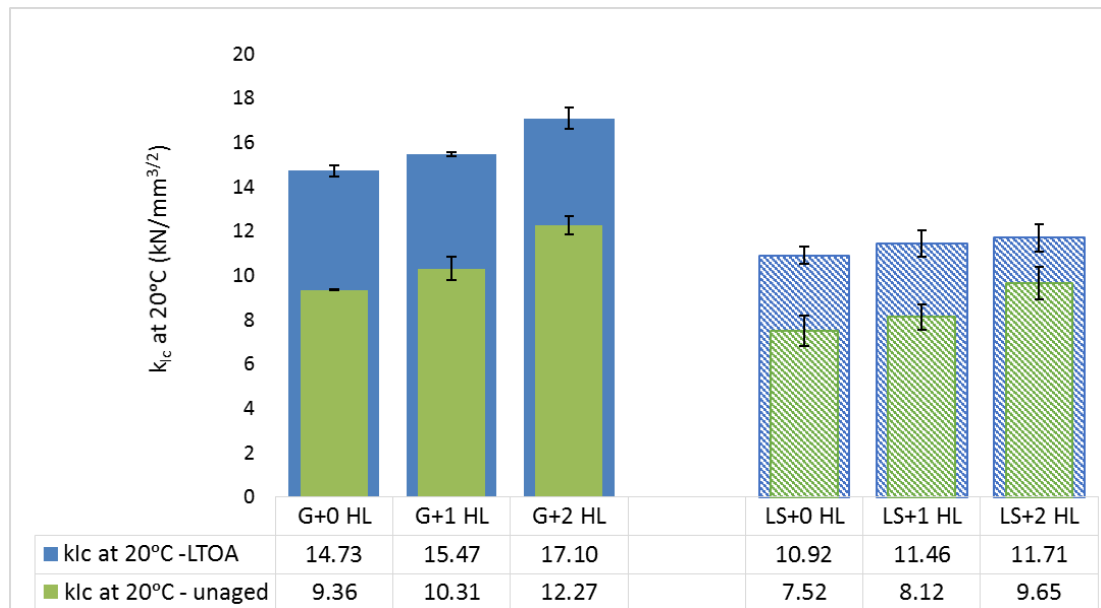


Figure 6.12 Fracture toughness at 20°C before and after LTOA

From the results above, it can be seen that the fracture toughness for the granite mixtures is higher than for the limestone mixtures at both temperatures. The effect of hydrated lime on the fracture toughness before ageing is not clear at the lower temperature at 0°C. However, at 20°C there is a slight increase in fracture toughness.

If we consider the effect of ageing on the fracture toughness, it can be seen that at low-temperature (0°C) this effect is minimal and is not clear with the granite mixtures. However, at the higher temperature of 20°C, the ageing effect is more pronounced and it is clear that the fracture toughness increases after ageing. Moreover, it can be noticed that the mixtures containing the hydrated lime replacement have higher fracture toughness than the original mixtures. The change in fracture toughness was calculated as an index and the results are presented in Figure 6.13.

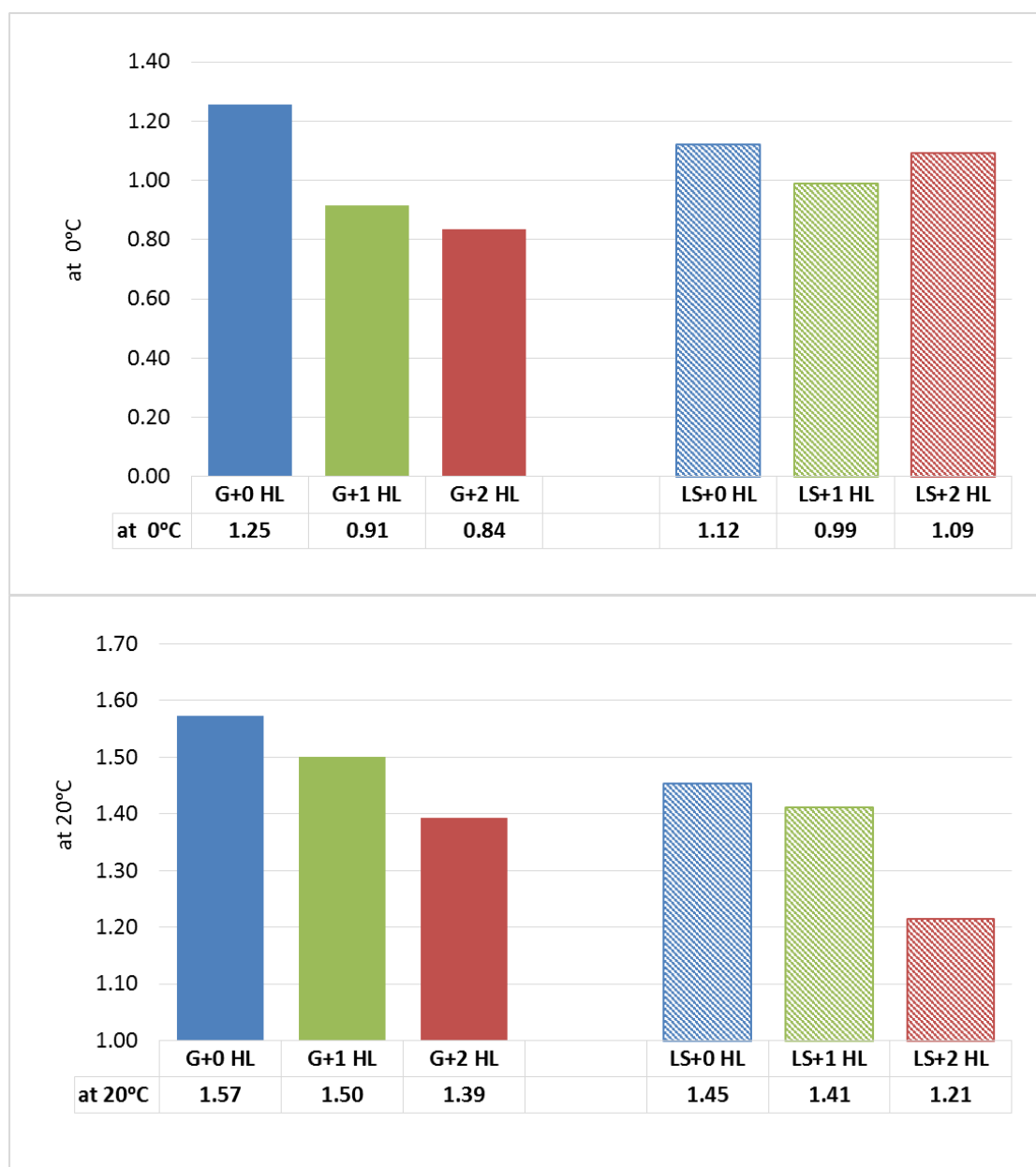


Figure 6.13 Fracture toughness index at 0°C and 20°C

Overall, it can be concluded that hydrated lime replacement of the natural granite and limestone fillers caused a reduction in the increase of the fracture toughness after LTOA. A bigger increase in fracture toughness after ageing at 0°C could mean that the fracture becomes more brittle. Thus, the beneficial effect of hydrated lime to reduce this effect is clear. Therefore, it is worth suggesting future research to cover this area in order to understand fully the fracture mechanism and the real effect of hydrated lime on fracture energy.

6.4.5 Binder recovery

In order to investigate the effect of mixture ageing on the bitumen ageing, bitumen from the LOTA mixtures after testing were recovered and their properties were tested. The effect of ageing on bitumen stiffening was measured by the increase in the softening points and viscosity of the recovered binders. In addition, the rheological properties of the recovered binders were tested using the dynamic shear rheometer (DSR). Finally, the effect of the mixture ageing on the bitumen chemical evolution was evaluated using the FTIR. As mentioned earlier, the results for the binder tests are averages of three replicates for viscosity and FTIR and two replicates for softening point and complex modulus, and the results were repeatable. The percentage deviation with respect to the mean value representing all the replicates tested was less than 10%.

6.4.5.1 DSR analysis

The master curves for the complex modulus of the recovered bitumen from the mixtures after LTOA are presented in Figure 6.14 and Figure 6.15 for binders recovered from granite and limestone mixtures respectively. From the master curves, it can be seen that the recovered binders of different mixtures after LTOA are almost the same. Moreover, it can be noticed that the long-term ageing protocol

used in this study for the mixtures gives almost the same severity of ageing found for the PAV for the pure bitumen ageing.

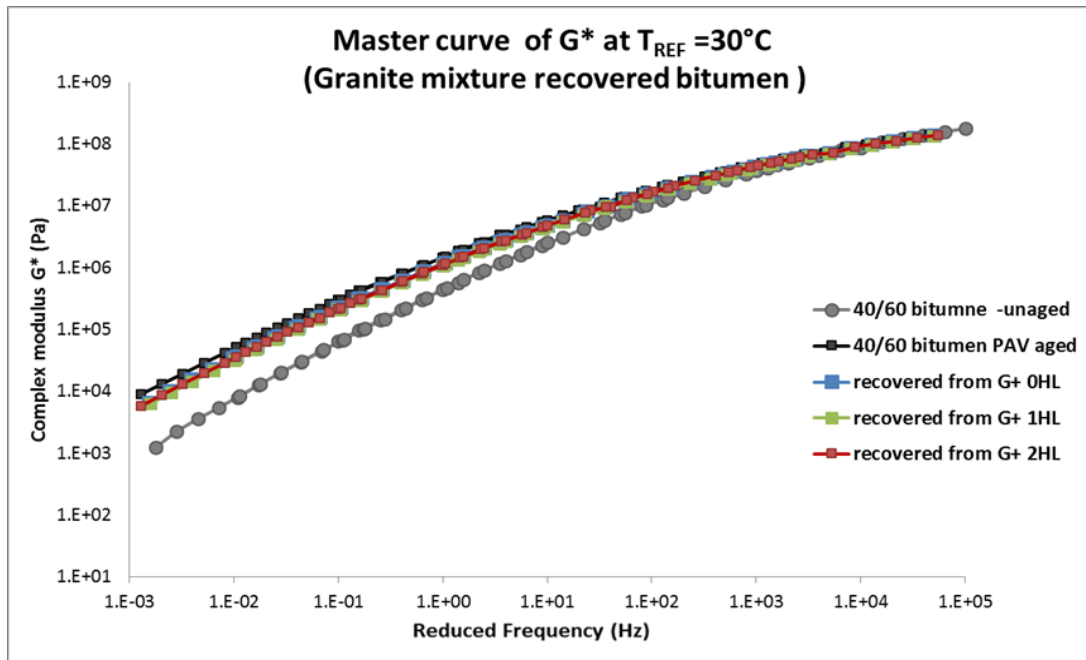


Figure 6.14 Complex modulus of recovered bitumen from granite mixtures

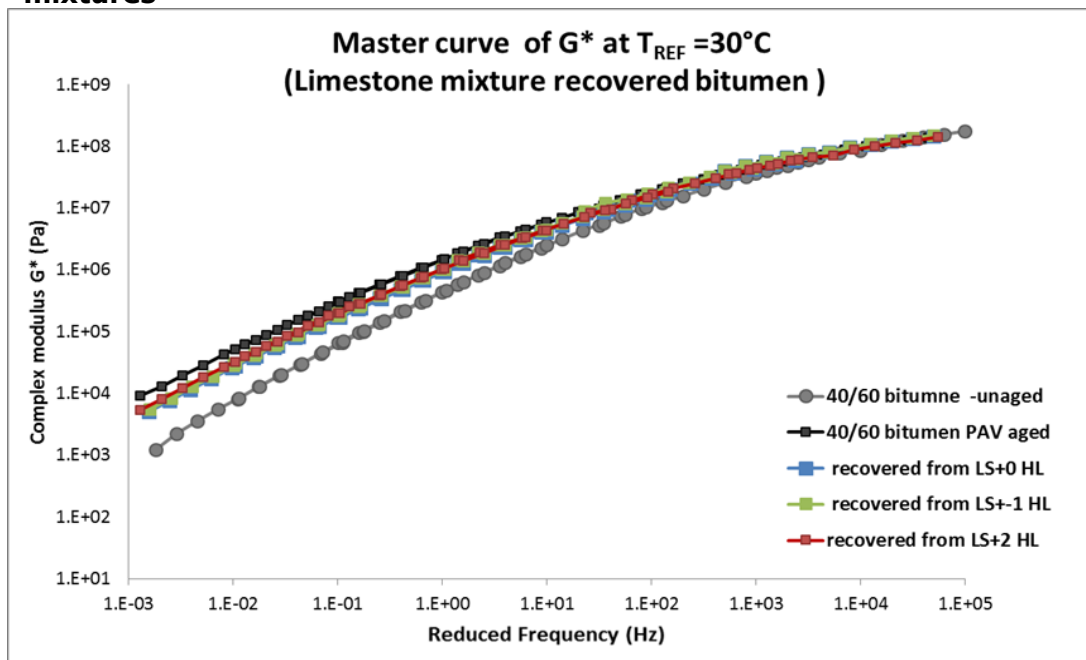


Figure 6.15 Complex modulus of recovered bitumen from limestone mixtures

In order to quantitatively illustrate the effects of mixture ageing on the age hardening of bitumen binder within the asphalt mixture, the complex modulus (G^*) ageing indices at different temperatures and 0.4 Hz were calculated and the results are presented in Figure 6.16 and Figure 6.17 for granite and limestone mixtures.

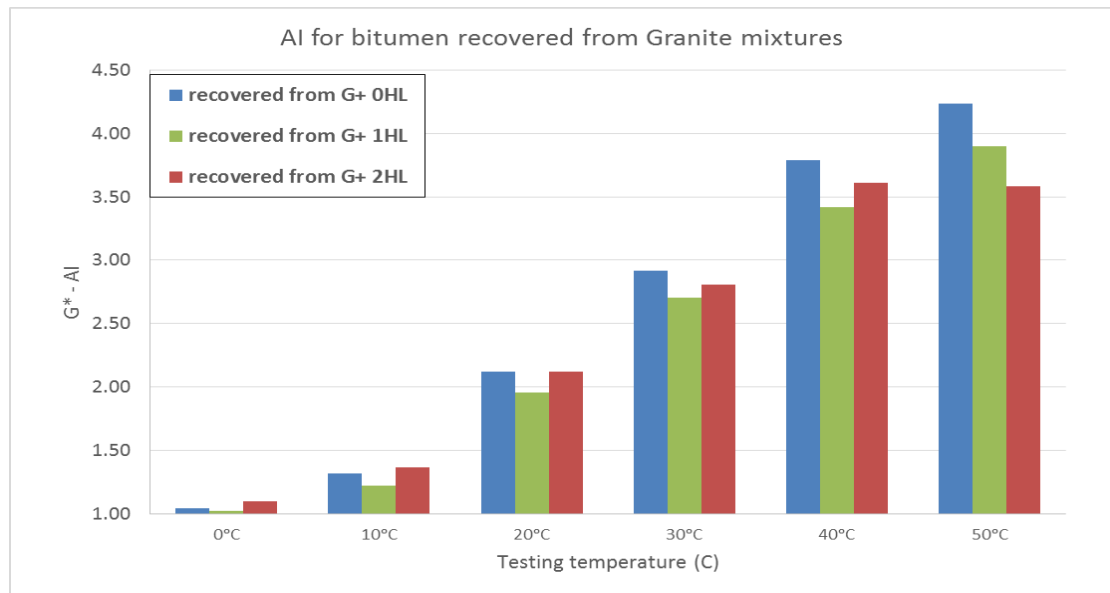


Figure 6.16 Complex modulus AI of recovered bitumen from granite mixtures

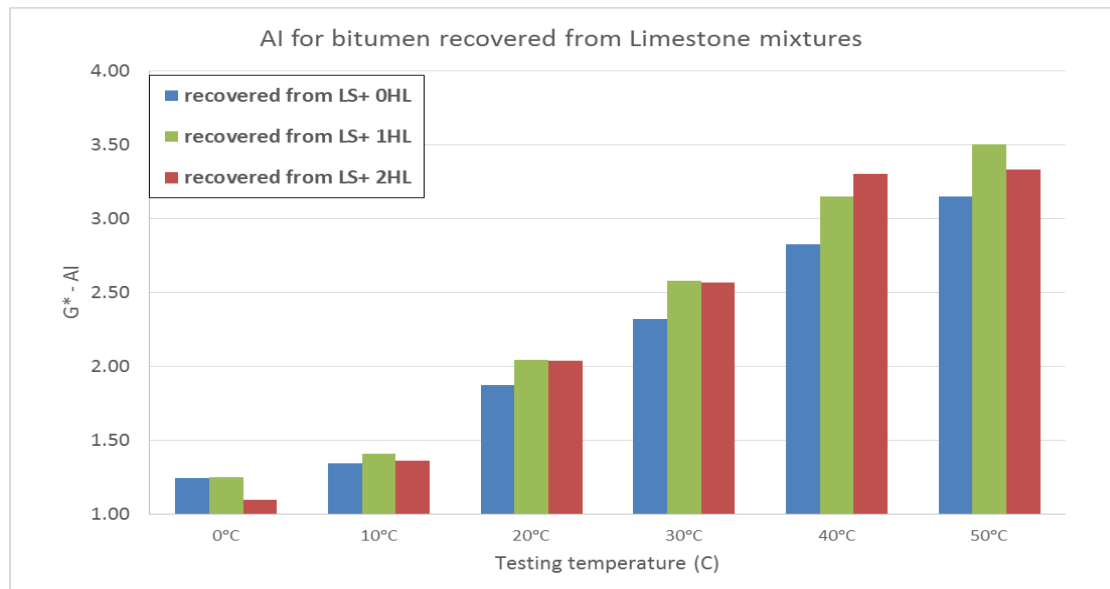


Figure 6.17 Complex modulus AI of recovered bitumen from limestone mixtures

It can be seen that in general, the ageing indices for the binders mixed with granite are much higher than those for the binders mixed with limestone, which could mean that a stronger age hardening has happened to the binders in the granite mixtures. In addition, it is interesting to see that the ageing indices for the bitumen recovered from limestone mixtures with hydrated lime were slightly higher than without HL. This is in contrast to the results for the granite mixtures where the binders recovered from the mixtures containing hydrated lime have slightly lower ageing indices compared to the granite only mixtures.

6.4.5.2 Softening point and Viscosity

As mentioned earlier, the effect of ageing of asphalt mixtures on the recovered bitumen was measured by the increase in the softening point and the change in rotational viscosity at 135°C. Similarly, the ageing indices for the recovered bitumen were compared to the initial values of the softening point and viscosity of the binder before mixing. The results of these ageing indices are shown in Figure 6.18.

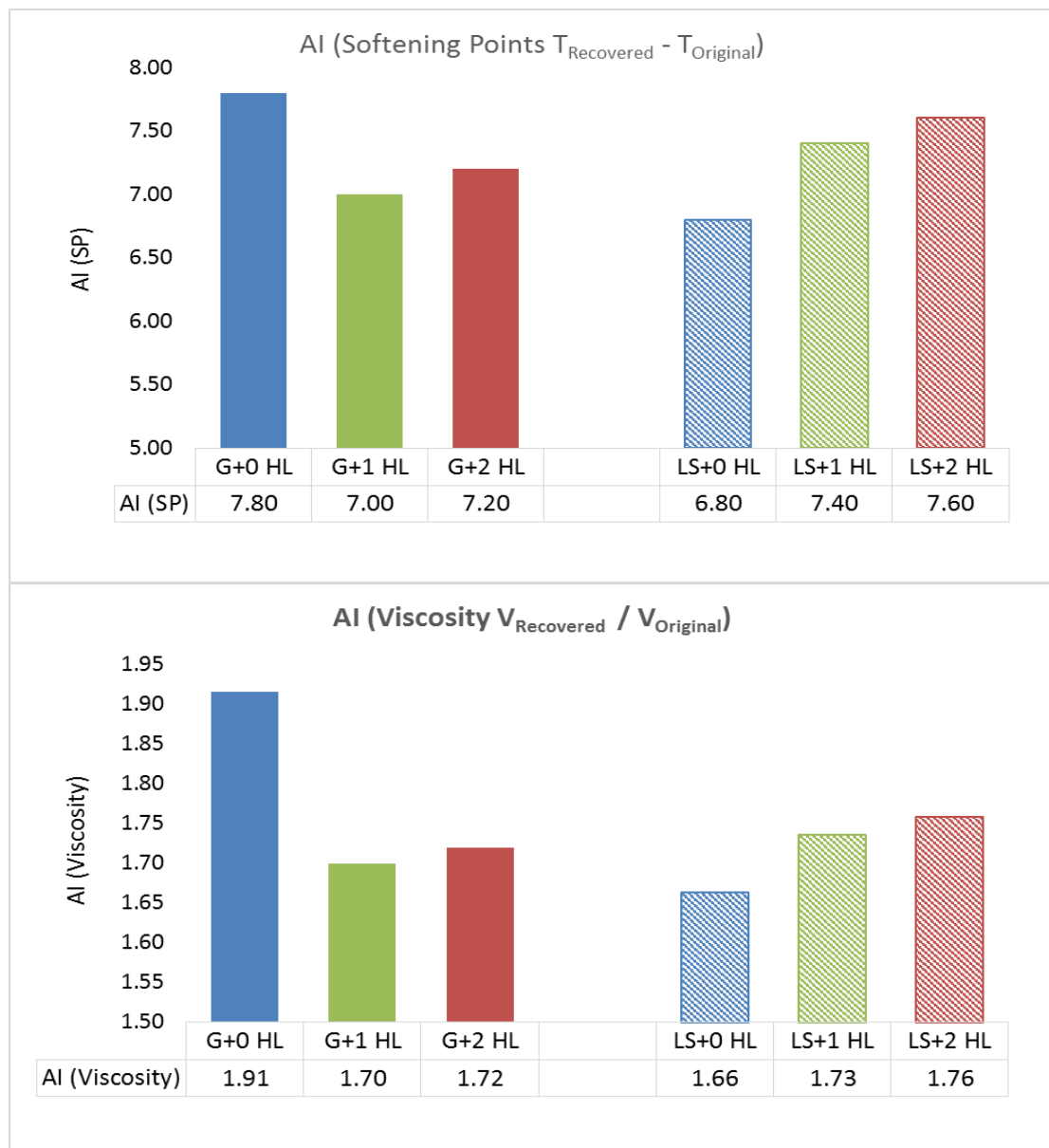


Figure 6.18 Softening point and viscosity AI of recovered bitumen

The results from the ageing indices of the softening point and the rotational viscosities show the same conclusion as derived from the rheological properties from the DSR complex modulus ageing indices. They shows that the ageing indices for granite mixtures are higher than these for the limestone mixtures. The effect of hydrated lime with the granite mixture is more pronounced, meaning that it can reduce the effect of ageing on the bitumen. However, this effect in the limestone mixture is not clear.

6.4.5.3 FTIR analysis

The recovered binder of the mixture was tested with FTIR spectroscopy to investigate the chemical changes in the bitumen and to check for the evolution of oxidative products in the bitumen after the LTOA of the mixture. The spectra of the recovered bitumen from the granite mixtures are shown in Figure 6.19 and the calculated carbonyl and sulfoxide indices and the sum of both indices are presented in Figure 6.20

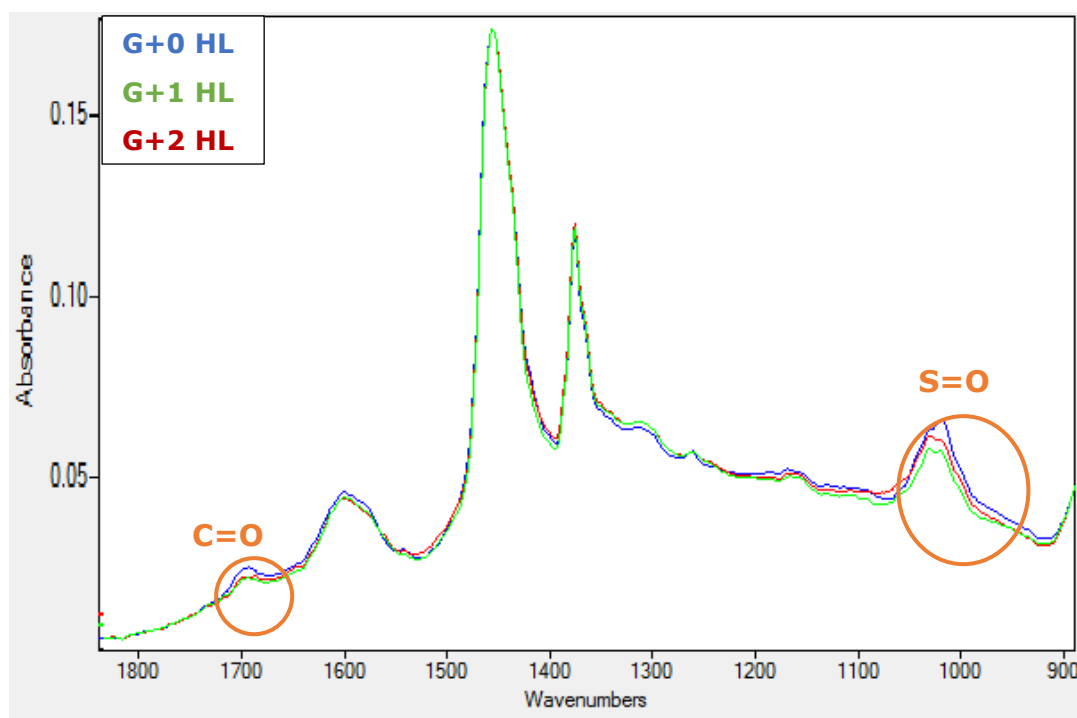


Figure 6.19 FTIR spectra of the bitumen recovered from Granite mixtures

The results of the calculated ageing indices confirm the other results from the recovered binders. They show that the binder recovered from the granite mixture has higher carbonyl and sulfoxide indices, which makes it a harder binder and means more ageing happened in the granite mixture. However, with the hydrated lime replacement, it reduces these aging indices, which shows the protective effect of hydrated lime with the granite mixtures to reduce the ageing. Moreover, the change in FTIR ageing indices for the limestone mixture is less pronounced and these results are in agreement with other results on the recovered binders.

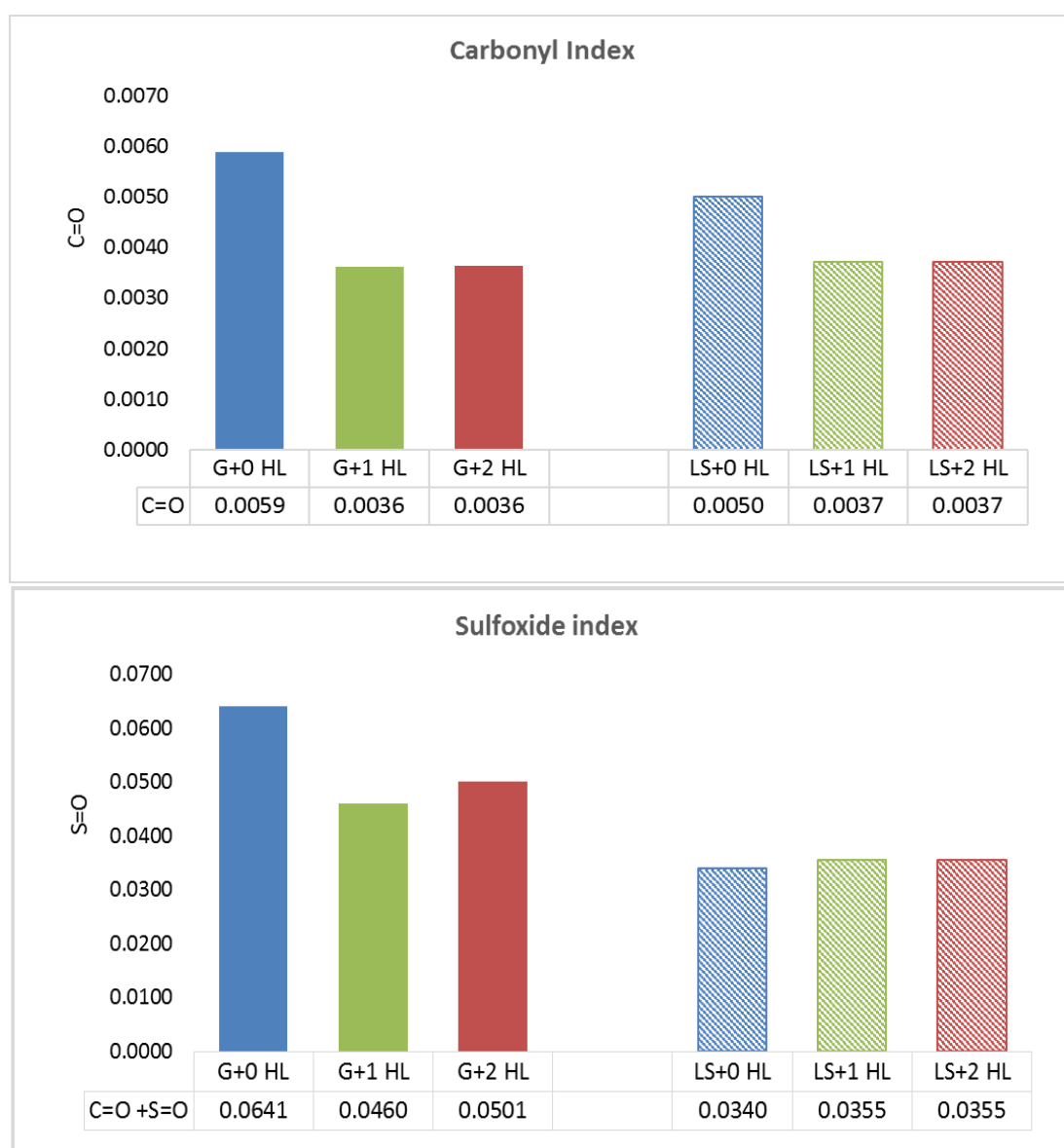


Figure 6.20 FTIR carbonyl and sulfoxide ageing indices

6.5 Chapter summary and conclusions

In this study, asphalt concrete samples were prepared with granite and limestone aggregates with and without hydrated lime and subjected to long-term ageing.

The effect of hydrated lime replacement of the natural aggregate fillers at 1 and 2 % by mass of aggregates on the ageing properties of asphalt was investigated.

This effect on the mixtures was investigated by different tests on their mechanical properties, indirect tensile stiffness modulus (ITSM), indirect tensile strength (ITS), and their fracture properties using the semi-circular bending (SCB) test.

Furthermore, the bitumen binder of the aged specimens was recovered. The effect of ageing on the recovered binders from different samples was investigated by rheological and chemical means using the Dynamic Shear Rheometer (DSR) and Fourier Transform Infra-Red (FTIR) spectroscopy.

The main conclusions derived from this study are summarised as follows:

- The ageing indices calculated from the ITSM tests generally increased with temperature increase. Furthermore, the ageing indices of the limestone mixtures were lower than those of the granite mixtures.
- The results show that the effect of hydrated lime on stiffening the mixture is more pronounced with granite mixture.
- From the results of the ITSM testing of the mixtures, it can be concluded that the effect of hydrated lime replacement of the fillers on the ageing of the asphalt mixtures is clear. It has been shown that hydrated lime replacement can reduce the ageing as seen from the ageing indices. However, this effect is different between the granite and limestone mixtures.

- The results of the ITS test show the beneficial effect of hydrated lime on reducing the ageing of the asphalt mixture by reducing the increase of ITS after ageing. This effect of hydrated lime is clear for both mixtures. However, 1% and 2% of hydrated lime replacement have almost the same effect on the ageing indices. The samples containing hydrated lime always have lower ageing indices than the original samples without hydrated lime.
- From the SCB test, it could be concluded that hydrated lime replacement of the granite and limestone fillers caused a reduction in the increase of the fracture toughness after long-term ageing at 0°C. More increase in fracture toughness after ageing at 0°C could mean that the development of fracture was becoming more brittle. Thus, the beneficial effect of hydrated lime to reduce this effect is clear from the SCB.
- The tests for evaluating the recovered bitumen binders from the different mixtures with and without hydrated lime show that the bitumen binder recovered from the granite mixture containing hydrated lime is always softer than the recovered binder with only granite filler. In addition, the FTIR test shows that hydrated lime reduces the ageing and hardening by reducing the production of oxidation products such as carbonyl and sulfoxide.

Chapter 7: Effect of Hydrated Lime on Ageing: Detailed investigation

7.1 Introduction

Hydrated lime is one of many potential additives used in bitumen to improve the properties and the performance of asphalt mixtures. Hydrated lime in hot mix asphalt (HMA) creates multiple benefits. A considerable amount of information exists in the literature on hydrated lime's ability to control water sensitivity and its well-accepted ability as an anti-stripping agent to inhibit moisture damage. However, recent studies demonstrate that lime also generates other effects in asphalt mixtures. Specifically, hydrated lime acts as an active filler that has anti-oxidant effects. These properties create multiple benefits for pavements.

Hydrated lime has been used as an additive for asphalt mixtures for a considerable time. However, its impacts are not fully recognised. With the unique properties, hydrated lime may prove to be an additive with a special impact on the rheology and damage mechanics of asphalt mastics.

The need still exists for developing more effective treatments or additives for controlling oxidative hardening and ageing in asphalt pavements. In order to do so, a comprehensive study is needed to develop a better understanding of the ageing mechanisms, factors affecting bitumen ageing in the presence of different fillers and especially hydrated lime. Thus, understanding the impact of hydrated

lime and the effect of different fillers on asphalt mixture ageing is therefore of great interest.

In order to investigate the effect of hydrated lime on the stiffening and ageing of mastics, a detailed study was proposed. In this study, mastics with different percentages of hydrated lime were compared to mastics made with other fillers (granite and limestone). The effect of hydrated lime on stiffening and ageing mitigation was evaluated by different means. (1) Basic properties: penetration, softening point and rotational viscosity, (2) Mechanical and rheological behaviour using dynamic shear rheometer (DSR), and (3) a Chemical approach with Fourier transform infrared (FTIR) spectroscopy. The evaluation testing aimed to understand the mechanisms hydrated lime employs for ageing mitigation. In addition, this study focuses on interactions between hydrated lime and the bitumen that affect and reduce the ageing in bitumen mastics and mixtures.

7.2 Materials and testing programme

7.2.1 Materials

Three types of fillers were used in this study, granite filler (G), limestone filler (LS), and hydrated lime (HL). The properties of the fillers are as summarised earlier in Chapter Three, see Table 3.8.

One type of bitumen; a 40/60 Pen bitumen with a penetration of 45dmm and a softening point of 50°C was used to prepare the mastics. The mastics were manually prepared as discussed in Section 5.3.2.

7.2.2 Testing programme

The aim of this study was to individually evaluate the effect of each of the three fillers on the ageing properties of the mastics. In order to understand the mechanisms of these fillers, especially the hydrated lime to mitigate the ageing,

this study was performed in two parts. The first part of this research study was to investigate the hydrated lime effect on mastic stiffening and in addition, to understand the reasons and factors behind this phenomenon. The second part of this study was to investigate the effect of hydrated lime on ageing mitigation and the factors that affect ageing at the mastic level. Furthermore, this part attempts to address how hydrated lime affects the mechanisms of ageing of bitumen mastics. In order to achieve these objectives, the ageing study was performed in two stages. The first stage was by ageing the different mastics using standard TFOT short-term ageing and then the standard long-term PAV ageing. The second stage, called the ageing time study, where the mastics were aged in the TFOT oven for extended times of 2, 5, 10, and 15 hours. The stiffening effect was evaluated after mixing the fillers with the bitumen, using the softening point and rotational viscosity. In addition, the Dynamic Shear Rheometer (DSR) was used to study the rheological effect of different fillers on the mastics and to quantify the ageing and stiffening effect of the fillers.

The mastics were prepared at three levels of filler volume concentration (filler volume in the mastic to the total volume of the mastic). The filler percentages selected were 5, 15 and 30-vol% of filler in the mastics.

In addition to the evaluation of the ageing of the mastics, the binders and the fillers were recovered from the mastics and the change in their properties was investigated using Fourier transform infrared (FTIR) spectroscopy. In addition to this testing programme, the ageing time study was performed in the TFOT in order to evaluate the effect of each filler on the ageing rate of the bitumen mastics and to understand the behaviour of these mastics after being subjected to extended ageing. The testing programme is illustrated in the schematic diagram in Figure 7-1.

The results for the tests involved in this study are the average of three replicates for viscosity and FTIR ageing indices and two replicates for softening point and

complex modulus, and the results were repeatable. The percentage deviation with respect to the mean value representing all the replicates tested was less than 15%.

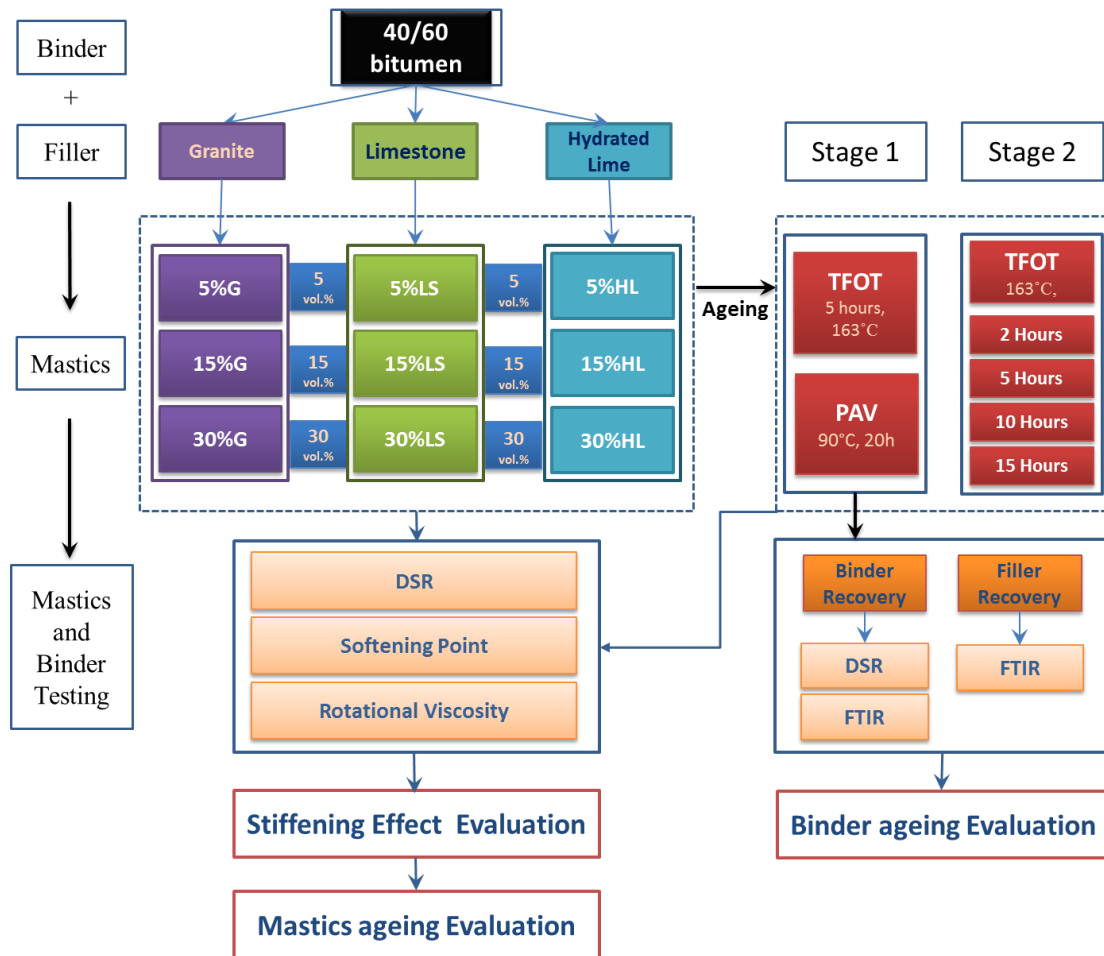


Figure 7-1 The testing programme of the detailed mastic study

7.3 Stiffening effect of Hydrated Lime

The stiffening effect of mineral fillers in the bitumen mastics and mixtures has been studied by several researchers ([Lesueur et al.,2017](#); [Hesami et al.,2012](#); [Abbas et al.,2005](#); [Heukelom and Wijga,1971](#)). The researchers evaluated the stiffening effect by looking at stiffening indicators such as the increase in the softening point and viscosity in addition to using modern rheological techniques.

Heukelom and Wijga stated that the volume fraction of the filler is the key parameter that controls the stiffening of the mastics ([Heukelom and Wijga,1971](#)).

In practice, the filler to binder ratio in a mastic can be controlled based on either weight or volumetric concentrations. Moreover, many studies have shown that in addition to volumetric concentration, the interactions between the filler and the bitumen binders have an important role affecting the performance of the mastic and consequently the mixture performance. Researchers have proposed that in order to better understand the influence of the fillers on the mastic performance, it is important to carefully study the effects of the physicochemical interactions happening between fillers and bitumen ([Petersen et al.,1987](#)).

In order to investigate the stiffening effect of the hydrated lime on the mastics, different volume percentages of fillers (HL, G, LS) were mixed with the (40/60) bitumen and the relation between the increase in stiffening and volume percentages is presented in Figure 7-2.

Clearly, the stiffening effect of hydrated lime is greater compared to the other fillers. This effect is more pronounced at higher concentrations. However, it can be noticed that the stiffening effect of both granite and limestone fillers are almost the same as can be observed from the indicators used (softening point, viscosity and complex modulus).

Some researchers have indicated that the stiffening effect of hydrated lime is more pronounced at higher temperatures. However, in this study, it can be noticed that this stiffening effect of the hydrated lime can be seen at different temperatures as these tests were performed at different testing temperatures. It is also worth noting that the stiffening effect of hydrated lime on the complex modulus of the mastics was investigated by the DSR frequency sweep test at different temperatures and similar results were observed at all tested temperatures.

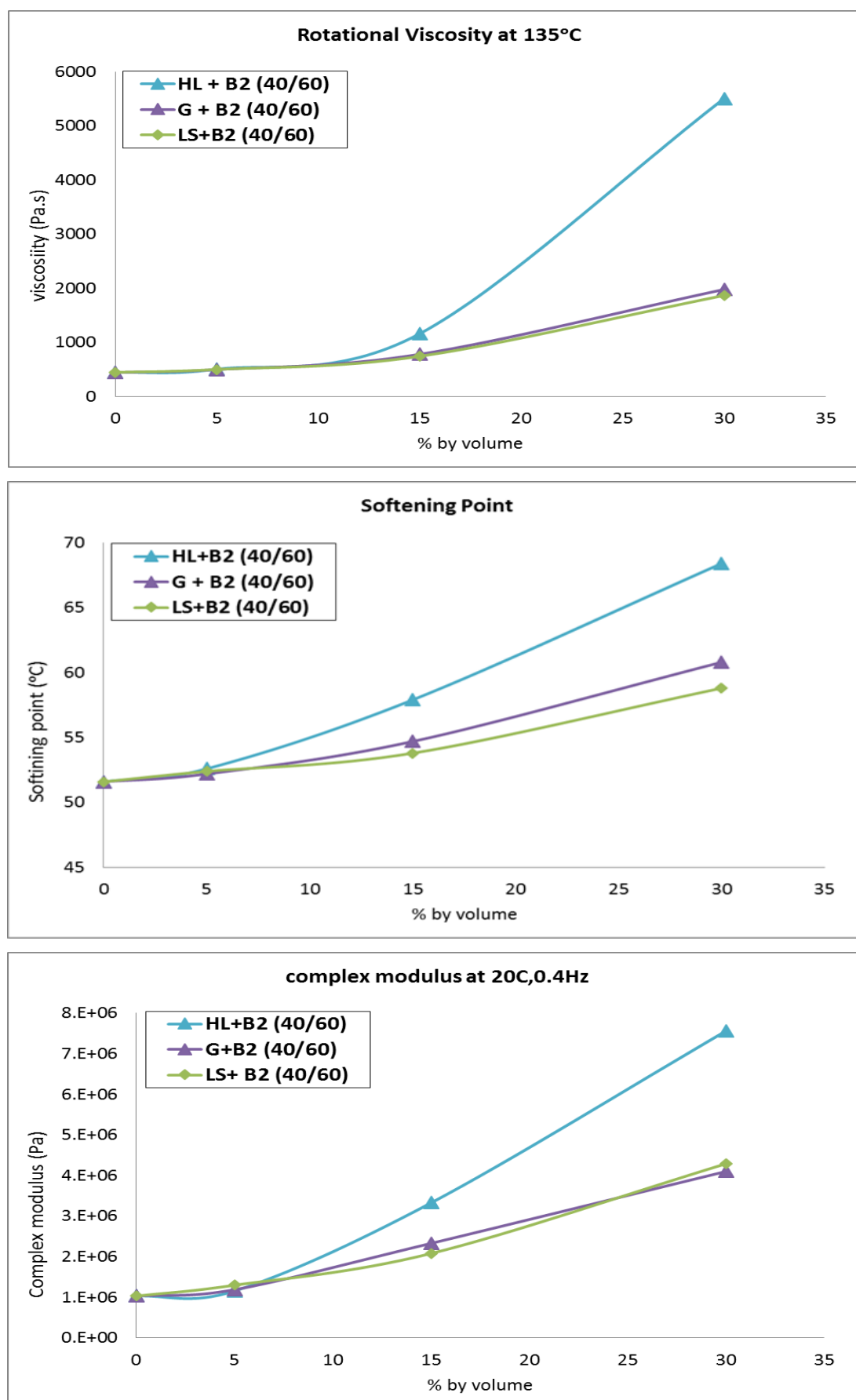


Figure 7-2 Stiffening effect of hydrated lime on viscosity, softening point and the complex modulus for mastics with 40/60 bitumen

Furthermore, in addition to the B2 (40/60) bitumen mastics, mastics with two other bitumen binders were used to further investigate this stiffening effect of the hydrated lime with different binders. Mastics with B3 (50/70) bitumen and B4 (100/150) bitumen were prepared with different filler percentages. The stiffening effect was evaluated as discussed before. The results for the stiffening effect with these binders are shown in Figure 7-3.

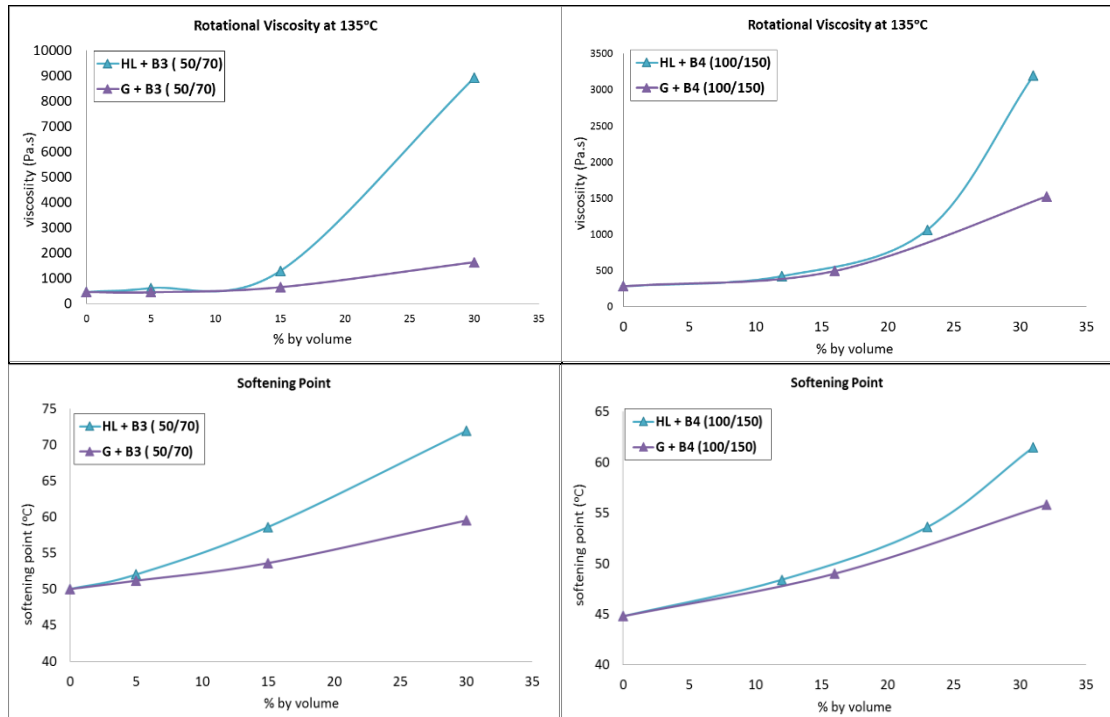


Figure 7-3 Stiffening effect of hydrated lime on viscosity and softening points for mastics with different binders

The results above show that similar to the 40/60 bitumen, hydrated lime has a higher stiffening effect than the granite filler. This effect seems to be bitumen specific. In order to show this effect more clearly the stiffening ratios were calculated for each bitumen mastic as follows:

$$\text{viscosity stiffening ratio} = \frac{\text{Viscosity of mastics}}{\text{viscosity of base bitumen}} \quad \text{Equation 7-1}$$

$$\text{Softening point stiffening ratio} = \text{SP of mastic} - \text{SP of bitumen} \quad \text{Equation 7-2}$$

The results for the stiffening ratios of softening point and viscosity for the mastics with different binders are shown in Figure 7-4. It can be noticed from the results that the granite fillers have almost the same stiffening effect with the three different bitumen binders used in preparing the mastics in this study. However, this effect is different for the hydrated lime. It can be seen that similar hydrated lime concentrations can result in significantly different stiffening ratios with different binders.

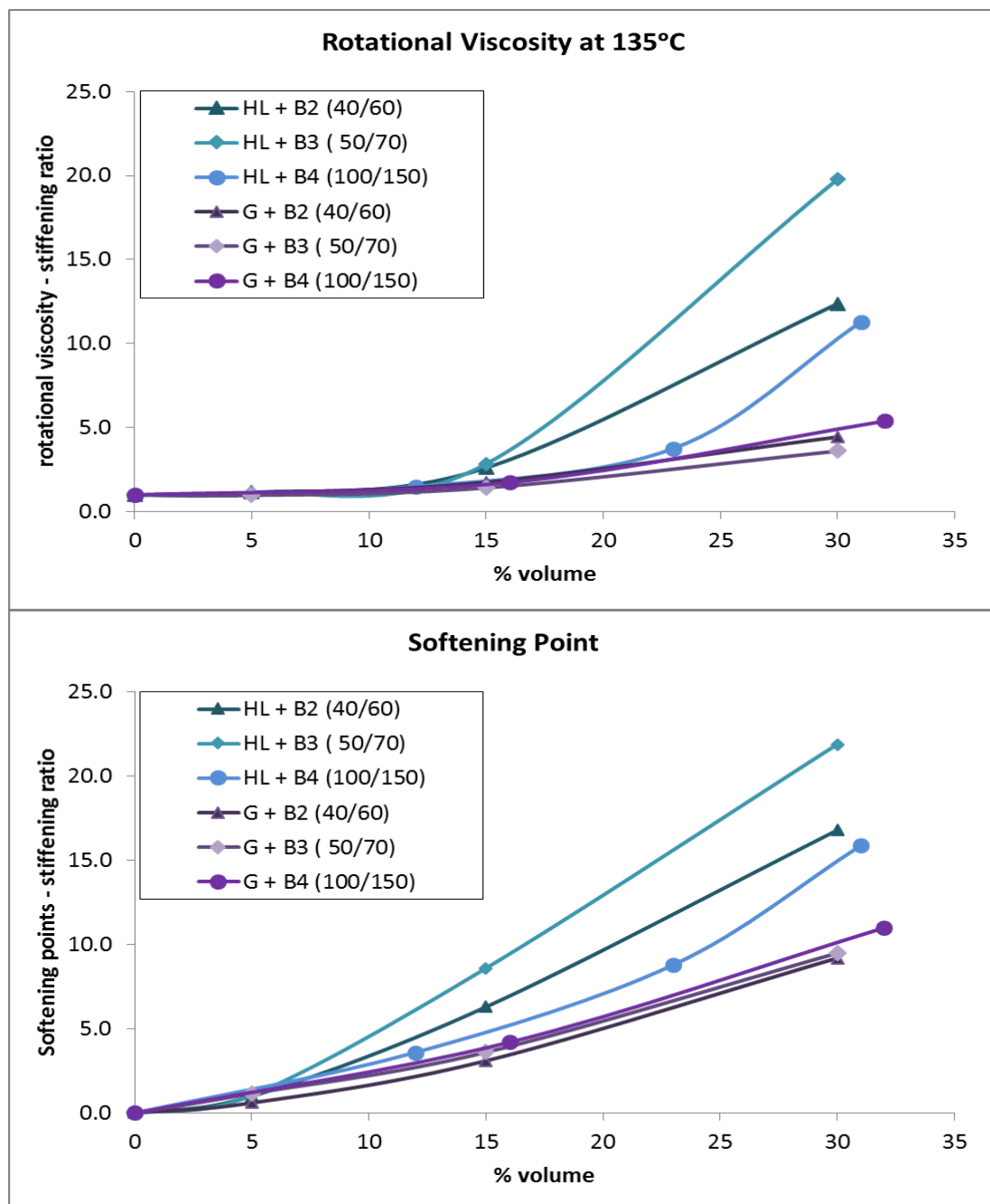


Figure 7-4 Stiffening ratio of fillers in different bitumen mastics

These properties of the hydrated lime on mastic stiffening effect could indicate that there is a significant interactive effect between the bitumen used and hydrated lime. These properties can affect ageing as well as the rheological properties of the mastics and asphalt mixture as concluded in previous studies by ([Petersen et al.,1987](#)). Furthermore, ([Kim et al.,2003](#)) suggested that, since the behaviour of bitumen mastics with hydrated lime is highly binder dependent then this could indicate that the effectiveness of hydrated lime in a mastic is controlled by physiochemical interaction.

Moreover, an investigation by ([Wang et al.,2011a](#)) on the effect of mineral filler characteristics on the stiffening of mastics and mixtures, found that the Rigden voids (RV) in the filler, fineness modulus and possibly the CaO content are the most significant properties to affect mastic performance. This effect was varied based on the type of bitumen binder, and they refer to the possibility of bitumen-filler interactions.

From the results presented in Figure 7-2 to Figure 7-4, it can be concluded that the effectiveness of hydrated lime on mastic stiffness is different from limestone and granite fillers and it is highly bitumen dependent. Hydrated lime was more effective than granite and limestone filler, which implies that mechanisms other than a volume filling effect could be occurring. Therefore, further investigation into this phenomenon is needed to understand the mechanisms and the factors affecting this behaviour of mastics containing hydrated lime.

In order to understand the effect of hydrated lime on mastics and to compare with the behaviour of granite filler, the bitumen was recovered from mastics just after mixing and a DSR frequency sweep was performed on the recovered bitumen in order to evaluate the stiffening of the recovered bitumen using the dynamic complex modulus. To make a comparison between mastics containing hydrated lime and granite fillers, complex moduli for the mastics and the recovered binders tested at 20°C and 0.4 Hz are shown in Figure 7-5.

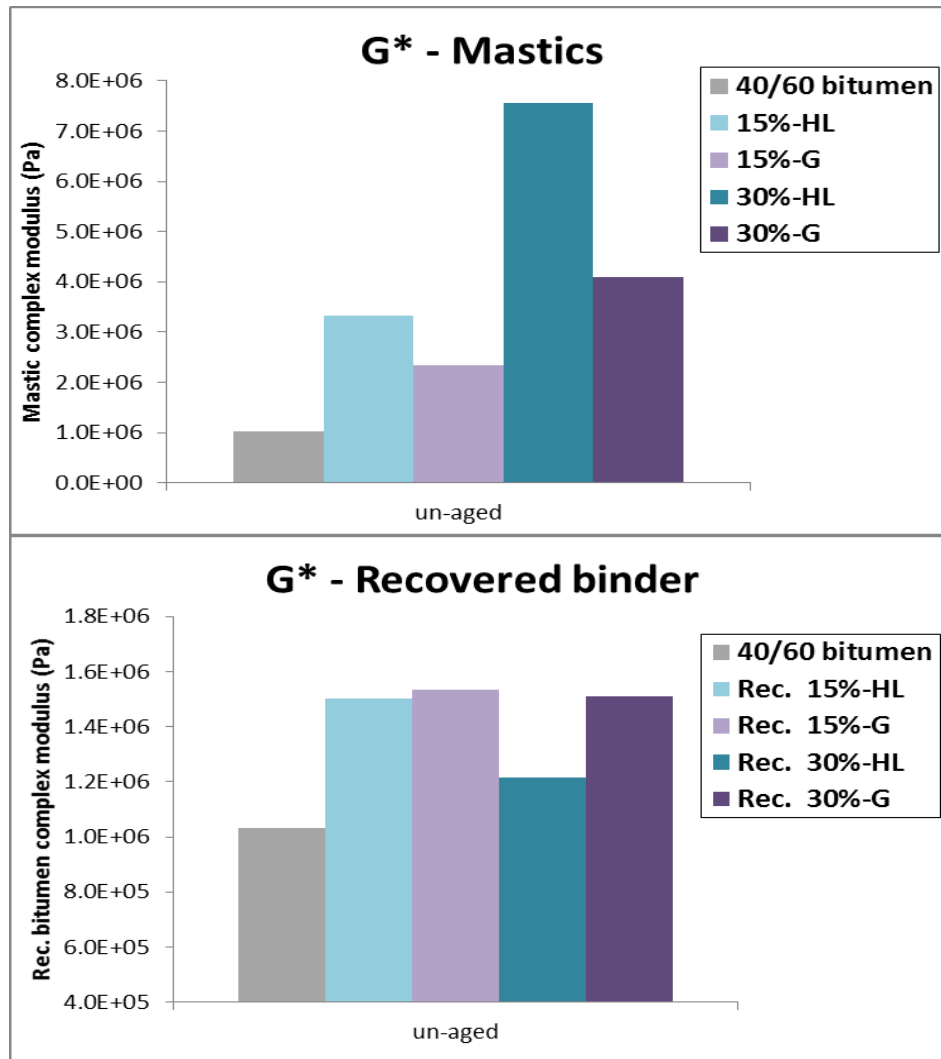


Figure 7-5 complex moduli of mastics and recovered bitumen for granite and hydrated lime mastics

The results in Figure 7-5 show that the complex modulus of the hydrated lime mastics is much higher than those for granite mastics. This effect is more pronounced at the higher filler concentration of 30% by volume. In contrast, the recovered bitumen from hydrated lime mastics is softer than the bitumen recovered from granite mastics. This effect is more obvious at the higher concentration of 30% filler by volume as well. These results indicate that there could be an interaction between bitumen and hydrated lime and this does not happen with the granite fillers. This effect will be further investigated in the following sections with the ageing results.

7.4 Stage 1: Long and short-term ageing of mastics

The effect of hydrated lime on ageing mitigation was studied. Two ageing simulation tests were used in this stage: TFOT ageing for short-term simulation and the PAV was used to simulate the long-term ageing. The tests were conducted according to the British Standards as mentioned earlier. Different ageing indicators, namely viscosity, softening point and the dynamic complex modulus were used to evaluate the effect of ageing on mastics. The ageing index (AI) was calculated for each mastic after ageing by dividing the aged property values by the unaged values for the same mastic. The results of the mastic stiffening ratios are presented in Figure 7-6. The effects of TFOT and PAV ageing on mastics are shown in Figure 7-7 and Figure 7-8 respectively.

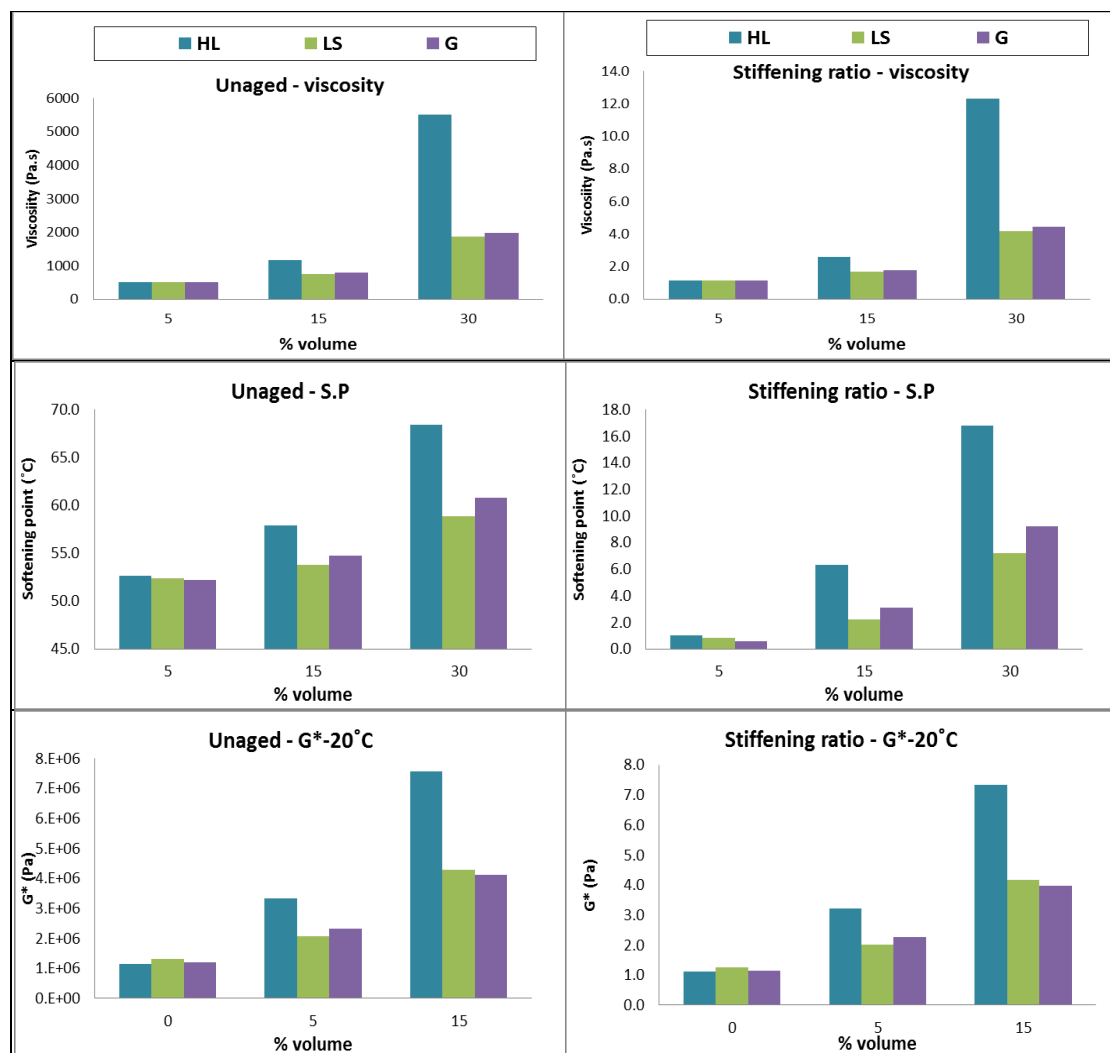


Figure 7-6 Unaged mastic properties and filler stiffening ratios

From the results presented in Figure 7-6, it can be noticed that the stiffening effect of hydrated lime is much larger compared to granite and limestone fillers for all the evaluating indicators (viscosity, softening point and the complex modulus). The stiffening effect of hydrated lime is almost three times that of the limestone and granite at 30% volume of filler in the mastics. In addition, it can be noticed that the stiffening effect of both limestone and granite fillers are similar. At the lower filler concentration, the stiffening effect of all fillers is almost the same in all the mastics. However, even though these tests were performed at different testing temperatures, the stiffening effect of hydrated lime is clear and pronounced in all these tests.

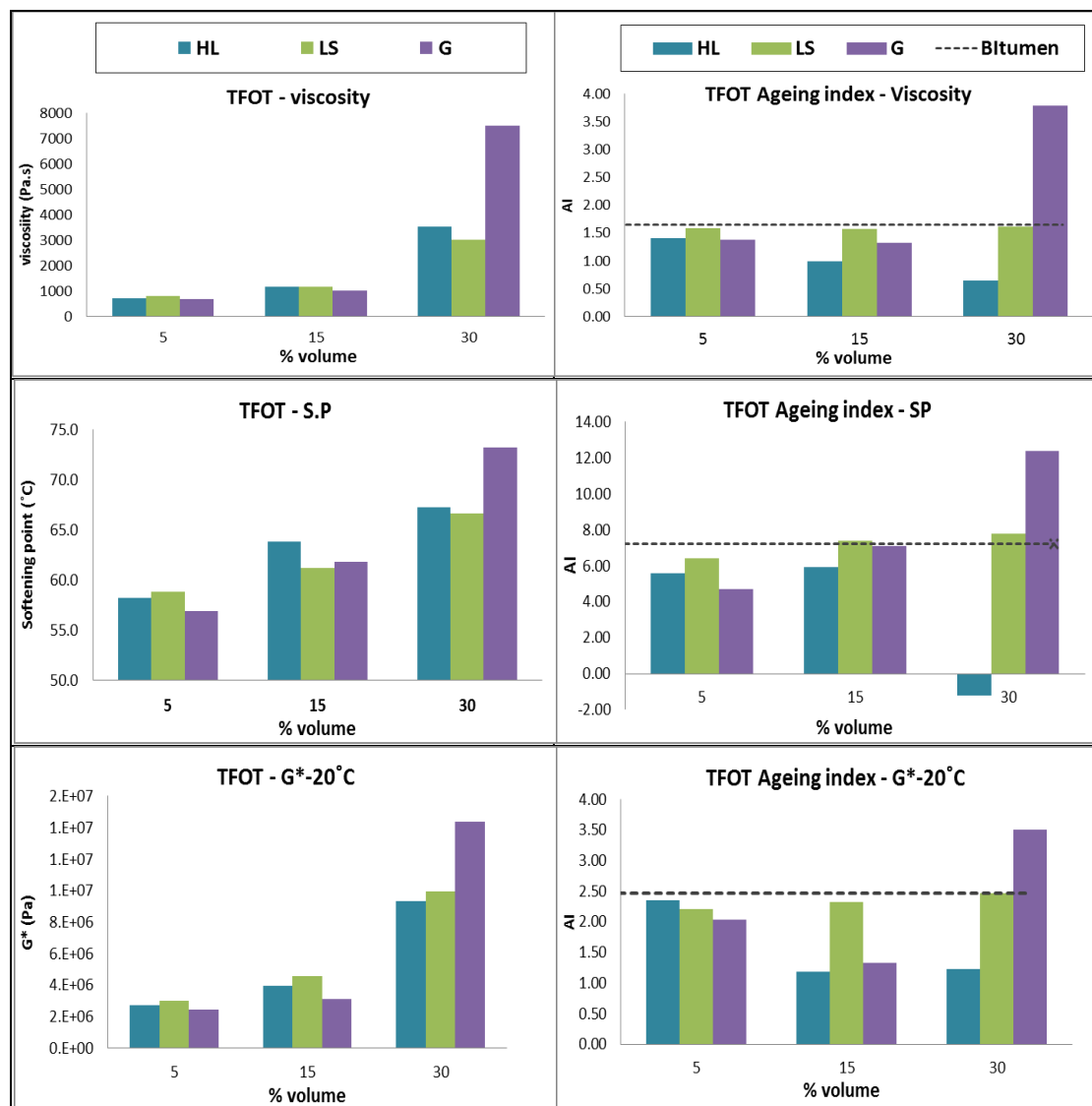


Figure 7-7 mastics ageing indices after TFOT ageing

From the results in Figure 7-7 it can be observed that although, before TFOT ageing, the hydrated lime mastics were much stiffer than the granite and limestone mastics, after TFOT ageing they are either softer or the same stiffness as other mastics, especially at higher concentrations. This means that the hydrated lime mastics exhibit the lowest ageing increase rates.

The calculated ageing indices after TFOT ageing show that hydrated lime always has the lowest ageing indices compared to the other mastics. Moreover, when the concentration of hydrated lime in the mastics is increased, the ageing index after TFOT decreases.

Furthermore, the ageing indices for granite mastics are the highest at higher filler concentrations. It can be noticed that the ageing indices for 30%vol. granite mastics are higher than the pure bitumen ageing index, which means that the addition of this percentage of granite increases the ageing. In contrast, the hydrated lime at 30% vol. concentration reduces the mastic stiffness from what it was before the TFOT ageing. As can be seen, the ageing indices are lower for the viscosity and negative for the softening point. The softening point decreases by about two degrees after TFOT ageing and the viscosity dropped to 64% of the unaged mastic viscosity.

The strange effect of the granite filler at higher volume concentrations needs more investigation to understand the factors and the reasons for this behaviour.

In order to establish the causes for these interesting results, the bitumen binder was recovered from the mastics and the chemical changes in the bitumen during ageing were investigated using FTIR. In addition, the rheological changes of the recovered binder were tested using the DSR. The results and discussion of these tests will be presented later in this chapter.

However, the results for the long-term ageing in the PAV will be discussed and presented first. Figure 7-8 shows the mastic ageing indices after the PAV ageing.

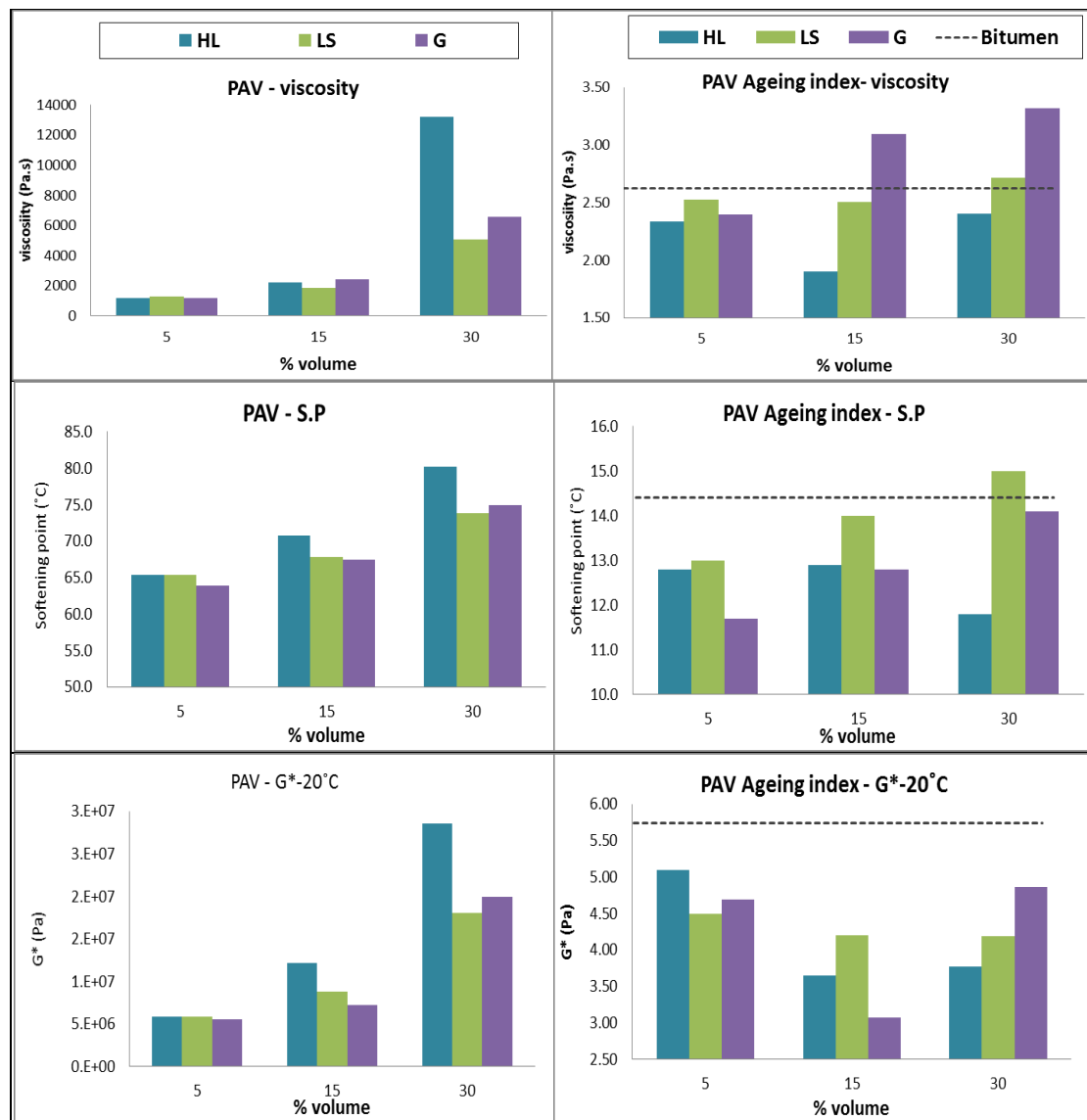


Figure 7-8 Mastic ageing indices after PAV ageing

These results show that despite the hydrated lime mastics being softer than the granite mastics after TFOT, they became stiffer than the granite mastics after PAV ageing.

According to the ageing indices after PAV, it can be noticed that hydrated lime has lower ageing indices than granite and limestone at 30% vol. concentration. However, at lower filler concentrations, it can be seen that the ageing indices are not consistent in ranking the mastic ageing.

In general, from both the short-term and long-term ageing results, it can be concluded that the ageing indices are affected by the concentration of the filler, especially at higher concentrations. In addition to that, the filler type had a very

significant effect on the ageing indices, as it was seen that hydrated lime decreased the ageing indices more than the other fillers. Furthermore, the ageing evaluation indicators used can in some cases rank the mastics differently; this effect was more pronounced after PAV ageing than after the TFOT ageing.

From the results above, it was also observed that increasing the granite filler concentration in the mastics resulted in increasing the ageing rather than reducing it. In contrast, generally, increasing the concentration of hydrated lime in the mastics decreases the ageing. These findings indicate that for each filler there will be a different optimum filler concentration that will result in the best stiffening effect on the mastics, as well as better ageing mitigation. This optimum depends on the filler properties and the possible interaction between the filler and the bitumen.

In a study done by ([Wu,2009](#)), mastics made with 40 vol.% of mineral filler (limestone and gritstone) after TFOT ageing were tested. The result showed that the ageing index of the mastics after 1 hour ageing was lower than that of the neat bitumen. Their findings were explained by the combination of the adsorption of the lighter fractions of the bitumen on the surface of the fillers and the catalytic effect of the mineral fillers. This corresponded to an increase in polar components after bitumen was recovered and tested by FTIR. The study suggested that the adsorption action of the acidic gritstone did not last as long as that of the basic limestone. This is why the ageing indices of limestone mastics were lower than those of gritstone.

7.4.1 Recovered bitumen - DSR analysis

In order to investigate the adsorption and catalytic effect of fillers on the bitumen mastics, the fillers and the bitumen were recovered after different ageing stages. They were tested for their changes in their chemical and rheological properties using FTIR and the DSR respectively.

In order to investigate the effect of the fillers on the rheological properties of the recovered bitumen, the results from the DSR are presented in the form of isochronal plots for the complex modulus and the phase angle. The isochronal plots were used to compare the effect of ageing for the recovered bitumen from the hydrated lime mastics and the granite mastics. The isochronal plots presented in Figure 7-9 show the complex modulus and the phase angle of the recovered bitumen at different testing temperatures up to 50°C

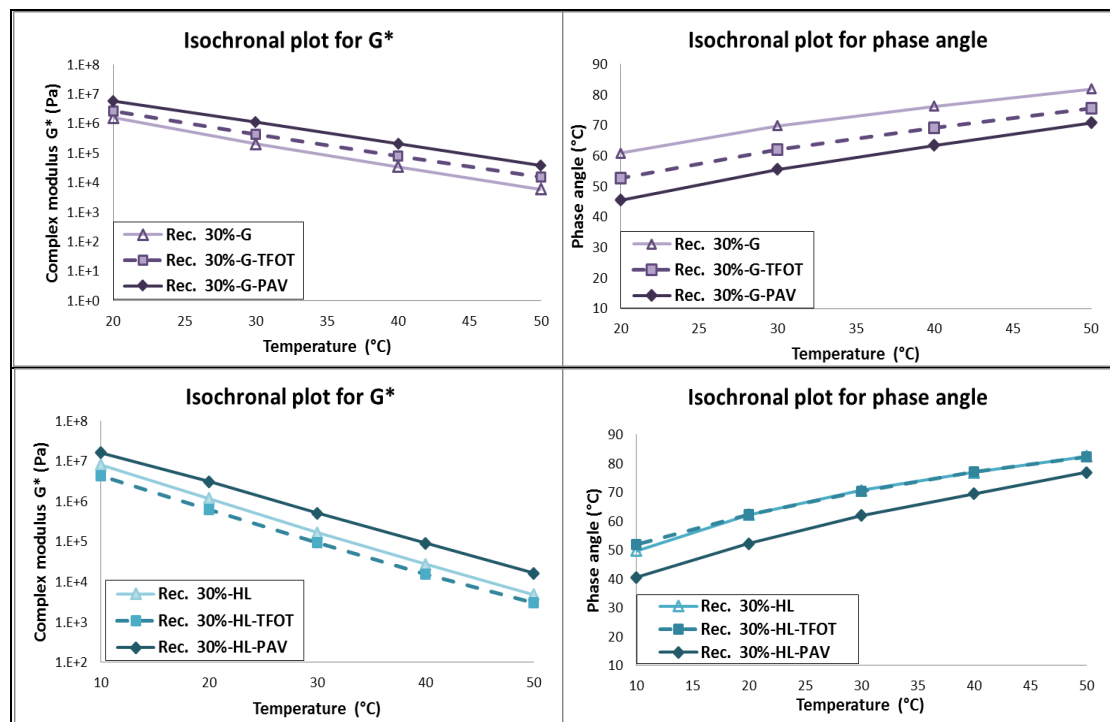


Figure 7-9 Isochronal plots for G^* and δ of the recovered bitumen from granite and hydrated lime mastics after different ageing stages.

The resulting isochronal plots show that, at all testing temperatures, for granite mastics, the complex modulus increases and the phase angle decreases as the ageing proceeds from TFOT and PAV. In contrast, for the bitumen recovered from hydrated lime mastics, it shows that after TFOT it has a lower complex modulus than the bitumen recovered from the unaged mastics. Similarly, the phase angle for the bitumen recovered from the TFOT aged hydrated lime mastics does not show any drop at all tested temperatures. It has phase angles similar to those recovered from the unaged hydrated lime mastics. For further investigation and to make the results more comparable, the complex moduli of the recovered bitumen were compared to the mastic complex moduli after different ageing stages. The mastics and recovered bitumen complex moduli at 20°C and 0.4Hz were chosen for this comparison. The results are presented in Figure 7-10.

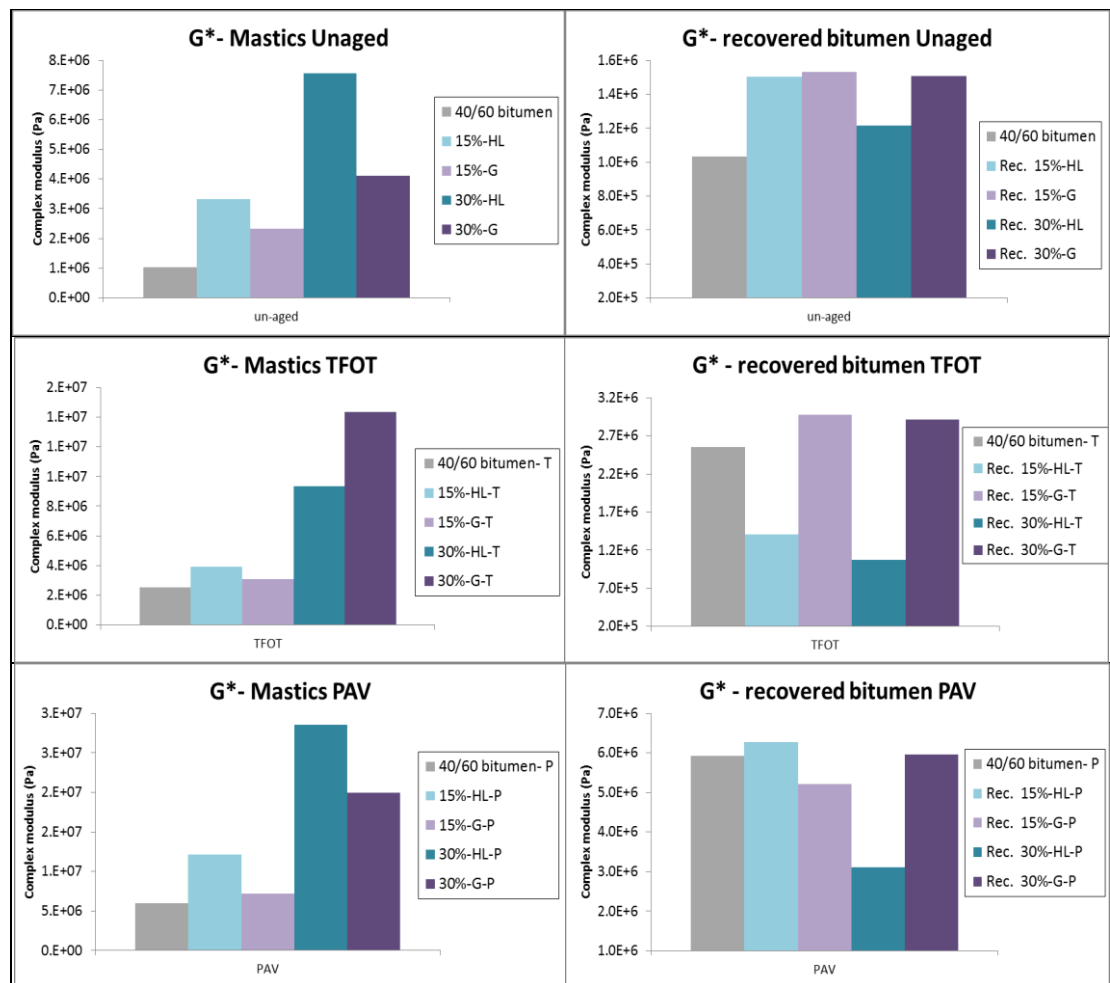


Figure 7-10 Mastics and recovered bitumen complex modulus at different ageing stages.

Comparing the complex modulus for the recovered bitumen and the mastics it can be noticed that, for the unaged mastics at the same filler concentrations, the mastics with hydrated lime have higher complex modulus than the granite mastics. However, the recovered bitumen from the hydrated lime mastics is softer than that recovered from the granite mastics. After TFOT, the hydrated lime mastics became softer than granite mastics and, similarly, the recovered bitumen was still much softer than bitumen recovered from granite mastics. Similarly, after PAV, the recovered binder from the hydrated lime mastics is always softer than that recovered from the granite mastics. In general, after TFOT and PAV ageing, the recovered bitumen from hydrated lime mastics is the softest and is softer than the aged bitumen at the same ageing stage. The effect of the fillers on the rheological properties of the mastics and the recovered bitumen was further studied. The phase angle for both the mastics and recovered bitumen are shown in Figure 7-11.

The results show that, as expected, the phase angle decreases as ageing proceeds. For the mastics, adding filler to the bitumen slightly decreases the phase angle, which indicates a more elastic behaviour. It is clear that the addition of the mineral fillers to bitumen decreases the phase angle in all cases. With ageing, the phase angle of the mastics decreases more. However, for the recovered bitumen, the bitumen recovered from hydrated lime mastics shows significantly higher phase angle than bitumen recovered from granite mastics. Furthermore, this recovered bitumen from hydrated lime mastics has a higher phase angle than that of the pure bitumen at the same ageing stage. This significantly higher phase angle (δ) for the recovered bitumen from hydrated lime mastics, could be a relative measure of the ability of asphalt to dissipate energy, in aged HL-treated pavements, which should be beneficial in reducing cracking in aged pavements ([Little and Petersen, 2005](#)).

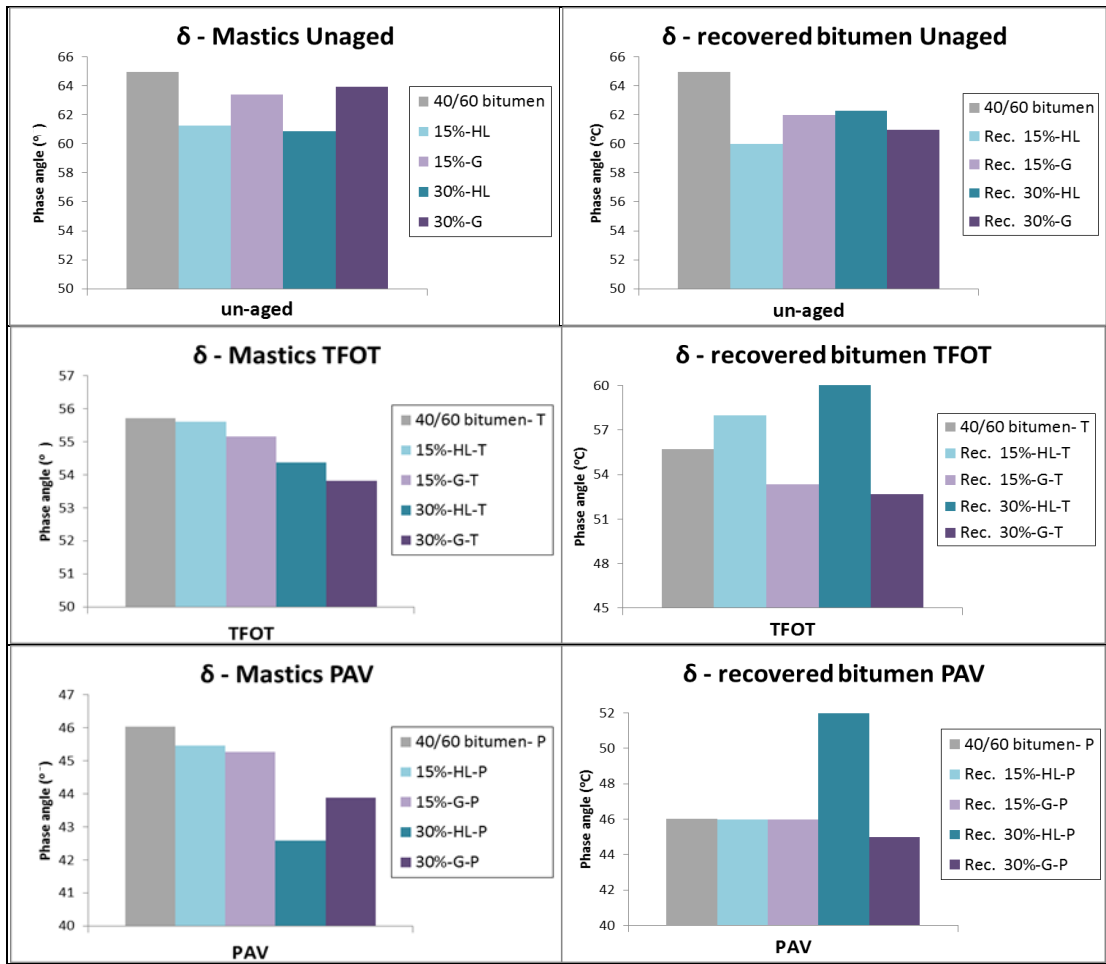


Figure 7-11 Mastics and recovered bitumen phase angle at different ageing stages.

In order to compare the results quantitatively, the ageing indices for both the mastics and recovered bitumen were calculated. The ageing indices for mastics and the recovered bitumen were calculated according to the following equations, respectively.

$$\text{Aging index of mastic} = \frac{G * \text{of aged mastic}}{G * \text{of un aged mastics}} \quad \text{Equation 7-3}$$

$$\text{Aging index of recovered bitumen} = \frac{G * \text{of Recovered bitumen}}{G * \text{of base bitumen} - \text{unaged}} \quad \text{Equation 7-4}$$

The results for the calculated ageing indices for the granite and hydrated lime mastics and their recovered bitumen after different ageing stages are presented in Figure 7-12.

The results show that, among the recovered binders, the bitumen recovered from hydrated lime 30% vol. concentration always has the lowest ageing index at different ageing stages. It can be noticed that the bitumen recovered from these mastics has significantly lower ageing than that recovered from granite mastics with the reduction in aging index being almost 50%.

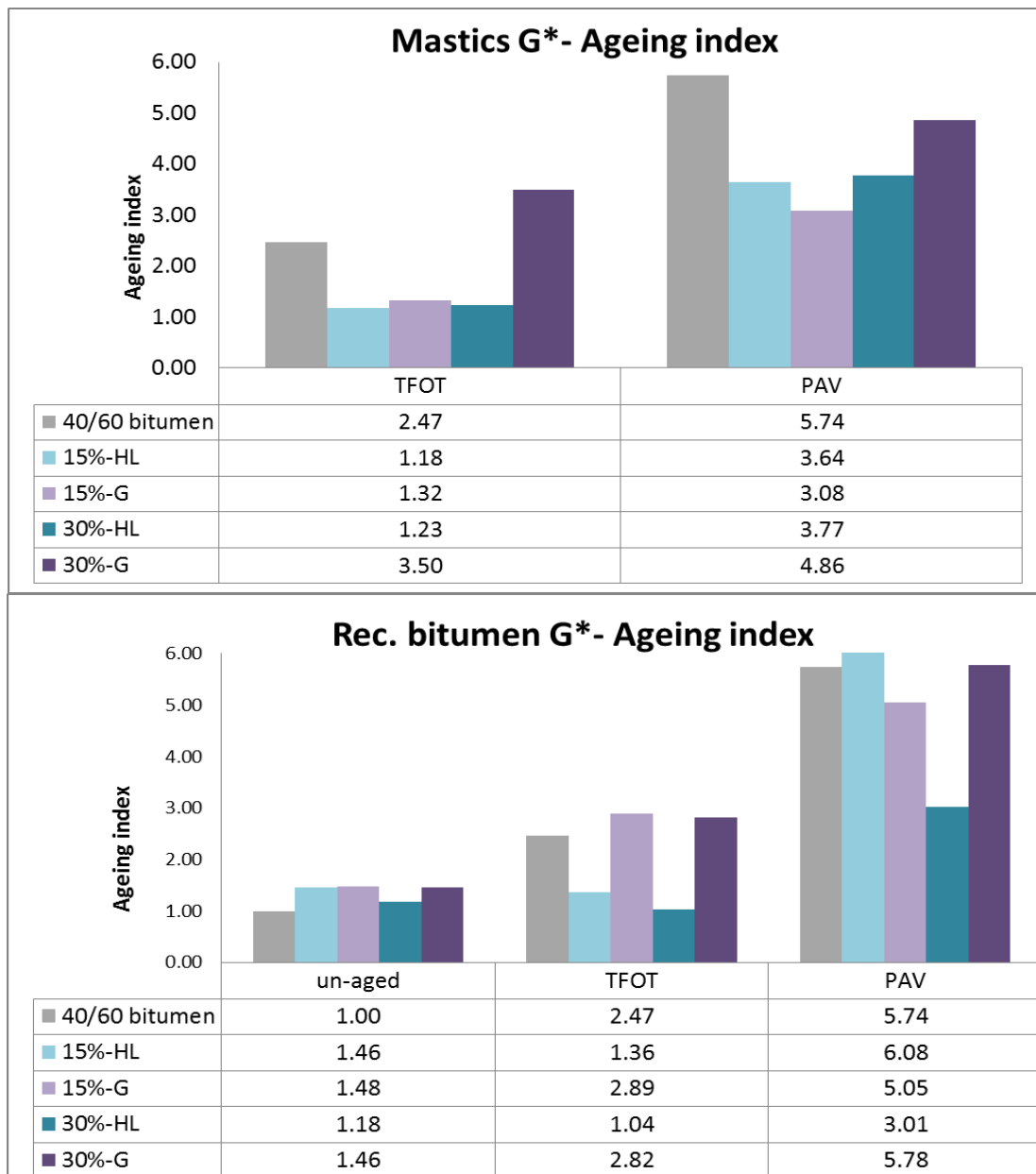


Figure 7-12 Complex modulus ageing indices for mastics and the recovered bitumen after different ageing stages

These results show that there is a similar ranking for the mastic hardening and the recovered bitumen.

For the recovered bitumen, the results revealed that after TFOT the recovered bitumen from 30% vol. HL was softer than that recovered from the unaged mastic. Furthermore, the results indicate that filler type can significantly influence the ageing properties of the bitumen in contact with them, which could prove that some filler types may interact with the bitumen more than others. Hydrated lime has been considered as an active filler, which has the potential to interact with different bitumen binders. Some studies have related this effect to the adsorption of polar components from bitumen ([Wu,2009](#); [Anderson et al.,1994](#)).

For the higher aging indices, even higher than for pure bitumen, the reason could be due to these fillers exhibiting some catalytic effect which increases the aging. Thus, in order to investigate the adsorption/ absorption effects of the fillers, the chemical changes in the recovered bitumen and the recovered fillers were studied using FTIR. The discussion is presented in the sections below.

7.4.2 Recovered bitumen- FTIR analysis

The FTIR analysis on the recovered bitumen evaluates the binder age hardening degree according to the carbonyl and sulfoxide formation as a result of bitumen oxidation.

Carbonyl and sulfoxide groups are the most important oxidation products. Both indices are identified as key parameters when studying bitumen ageing. As known, bitumen oxidation causes the formation of functional groups, which are characterised by the growth of groups in the bands at 1700 cm⁻¹ and 1030 cm⁻¹, which represent carbonyl formation (C=O) and sulfoxide formation (S=O), respectively. The carbonyl and sulfoxide ageing indices were calculated for the recovered bitumen after different ageing stages. A comparison of the recovered bitumen ageing indices with those of the pure bitumen where made.

The carbonyl and sulfoxide ageing indices were calculated as follows:

$$\text{Carbonyl index (C=O)} = A_{1700}/\Sigma A,$$

$$\text{Sulfoxide index (S=O)} = A_{1030}/\Sigma A$$

Where:

The sum of the area ΣA represents: $A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}$.

Examples of the results for FTIR spectra are presented in Figure 7-13, while the resultant chemical ageing indices for the recovered bitumen are presented in Figure 7-14.

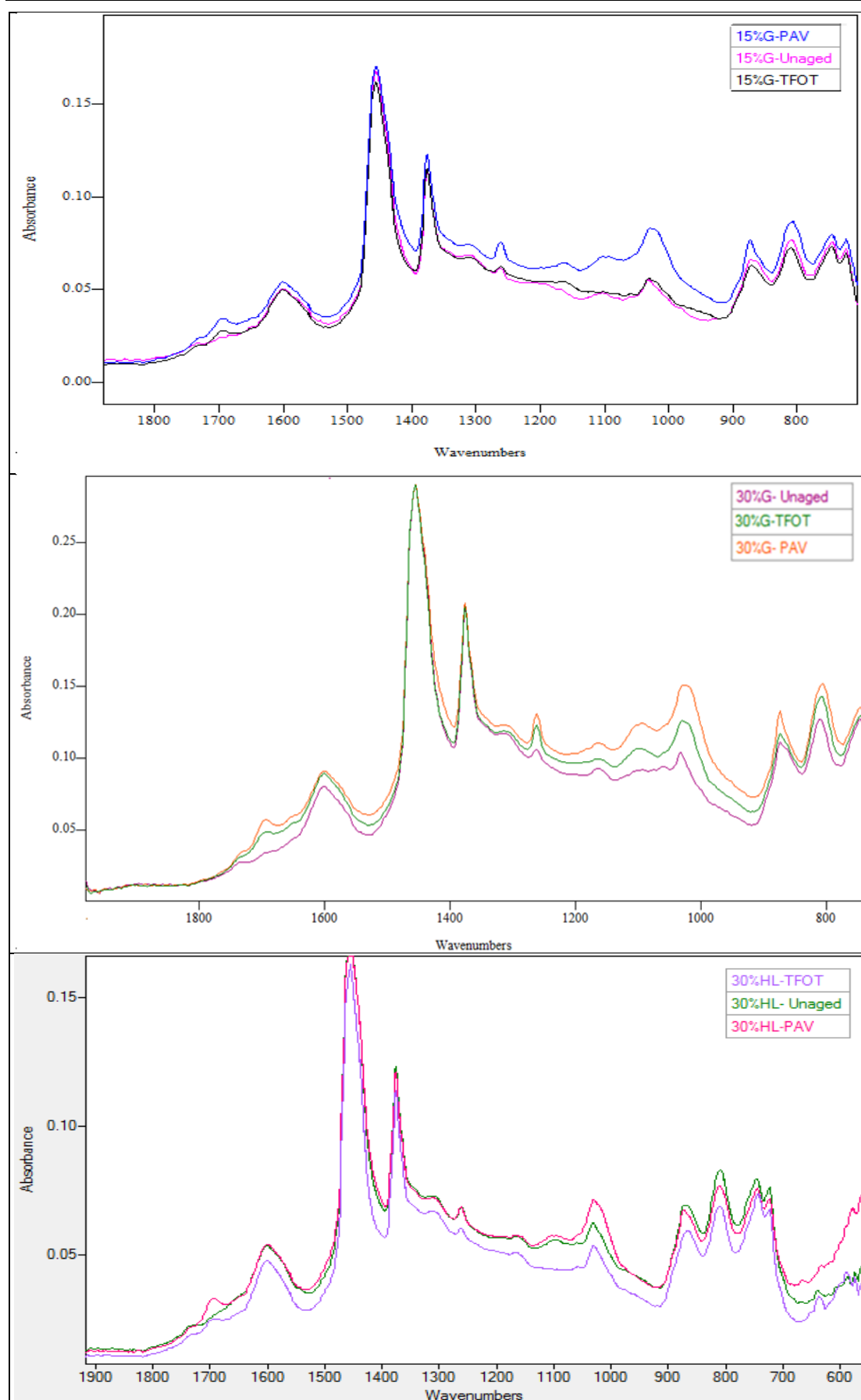


Figure 7-13 FTIR spectrums for the bitumen recovered from the mastics after different ageing stages.

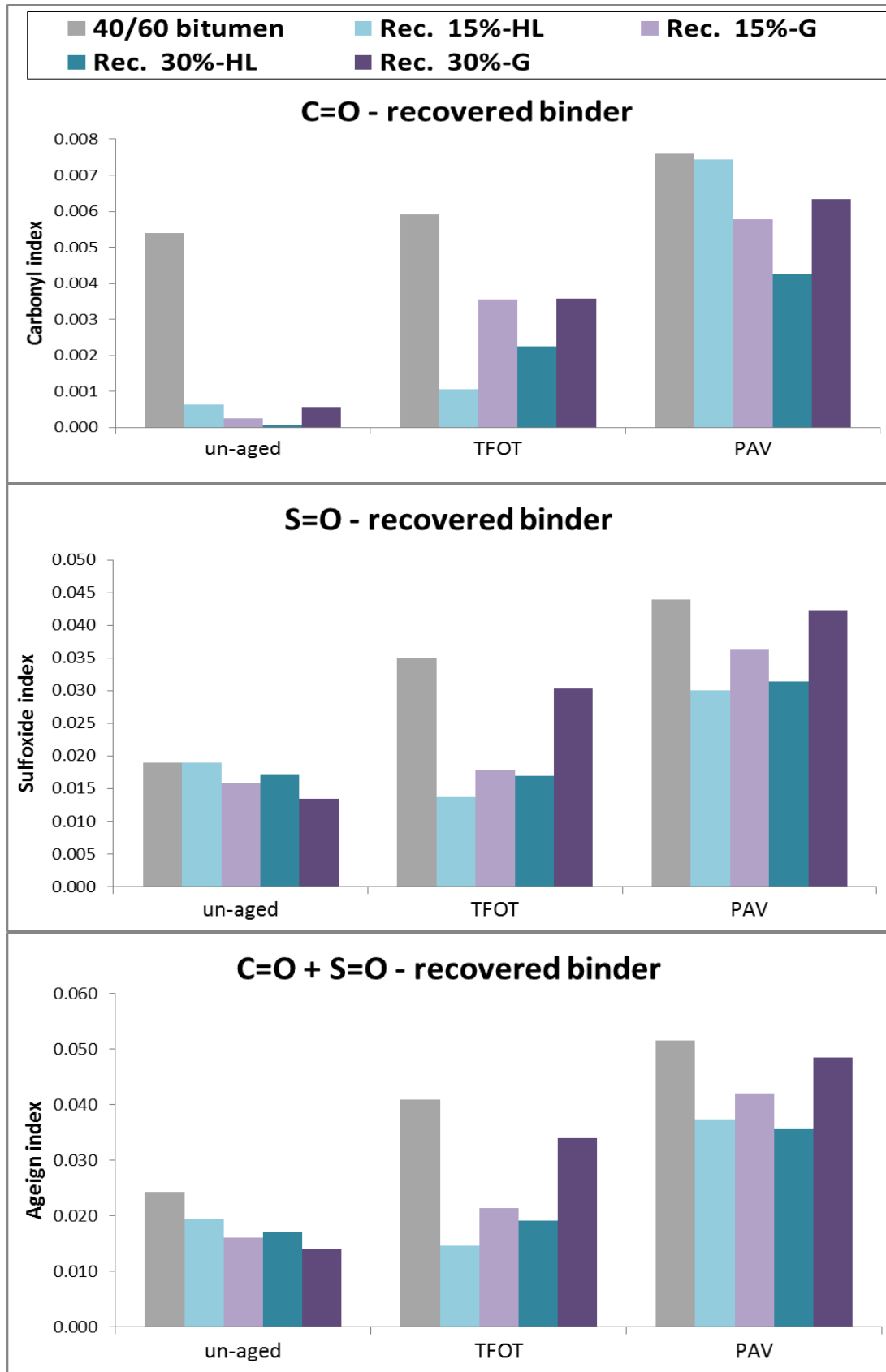


Figure 7-14 Chemical ageing indices for the recovered bitumen after different ageing stages.

The results from the FTIR test reveal that the carbonyl C=O index was significantly affected by the fillers mixing with the bitumen. It can be noticed that the recovered bitumen from the unaged mastics has very low C=O index compared to the unaged bitumen. The C=O index for the recovered bitumen from different mastics is about 85% less than that of the unaged 40/60 pen bitumen used to prepare the mastics. As ageing proceeds, it can be noticed that after TFOT, the bitumen recovered from the hydrated lime mastics is softer than the bitumen recovered from granite mastics of the same filler concentrations. However, all the recovered bitumens after TFOT still have lower C=O indices for the HL mastics. Furthermore, after PAV ageing, bitumen recovered from the 30% HL mastics has the lowest C=O index. These results for the carbonyl C=O indices are in agreement with the previous results from the complex modulus evaluation. This shows that the recovered bitumen from hydrated lime mastic has a lower complex modulus (i.e. it is a softer binder). Similarly, the lower carbonyl index means less oxidation products generated during ageing, which means less ageing for the hydrated lime mastics. These results are in agreement with previous studies ([Wang et al.,1993](#); [Glover et al.,2005](#); [Lu et al.,2008](#)).

On the other hand, the effect of filler on the sulfoxide index (S=O) is different from the carbonyl (C=O) index. It was observed for the bitumen recovered from the unaged mastics, that the S=O index is not significantly affected by the filler mixing with the bitumen. However, it can be seen that almost all the recovered bitumen and the unaged pure bitumen have lower S=O indices than that of the pure bitumen. After TFOT ageing, it can be noticed that the S=O index of the pure bitumen shows the highest increase. The other recovered bitumen from mastics after TFOT does not show a significant change from the unaged recovered bitumen except for the 30% granite fillers which shows a higher increase in S=O than other recovered binders. Moreover, after PAV ageing a further increase in S=O can be observed for all recovered binders and the pure bitumen. However, in all cases, the bitumen recovered from hydrated lime mastics shows the lowest S=O index.

Meanwhile, carbonyl and sulfoxides are the major oxidation products of the ageing process; their sum indicates the relative degree of oxidation in binders.

In general, the FTIR results for the recovered bitumen from mastics show the significant effect of fillers on the ageing of mastics. Furthermore, they indicate that different fillers can affect mastic ageing differently. The results also confirm the beneficial effect of hydrated lime to reduce the age hardening effect on the mastics by reducing the formation of the oxidation products such as carbonyls and sulfoxides as observed from the FTIR indices.

As the rheological and physical characteristics of the bitumen are strongly related to the chemical changes in the bitumen, fewer oxidation products reflect a lower stiffening and hardening in the mastics. Overall, bitumen stiffening and hardening, which was measured by an increase in complex modulus and a decrease in phase angle, was reflected in the growth of the carbonyl and sulfoxide chemical functional groups. These results are in agreement with previous studies, which have confirmed that an increase in viscosity, softening point and stiffening of aged binders is related to an increase in their carbonyl content, ([Glover et al.,2005](#); [Fernández-Gómez et al.,2013](#); [Petersen and Glaser,2011](#); [Yut and Zofka,2014](#); [Soenen et al.,2016](#)).

In addition to the FTIR test for the recovered bitumen, the asphaltenes content was used to evaluate the increase in stiffening due to the change in bitumen chemistry after ageing. Figure 7-15 presents the asphaltenes content for the recovered bitumen from the 30% vol. concentration mastics. The results for the asphaltene contents show that the bitumens recovered from the mastics have a lower asphaltenes content than the pure bitumen aged at the same ageing stage. Furthermore, the results show that the bitumens recovered from hydrated lime mastics has the lowest asphaltenes content at different stages.

The asphaltenes contents of the recovered bitumen are well correlated with the results of the carbonyl indices and show similar trends for the tested binders.

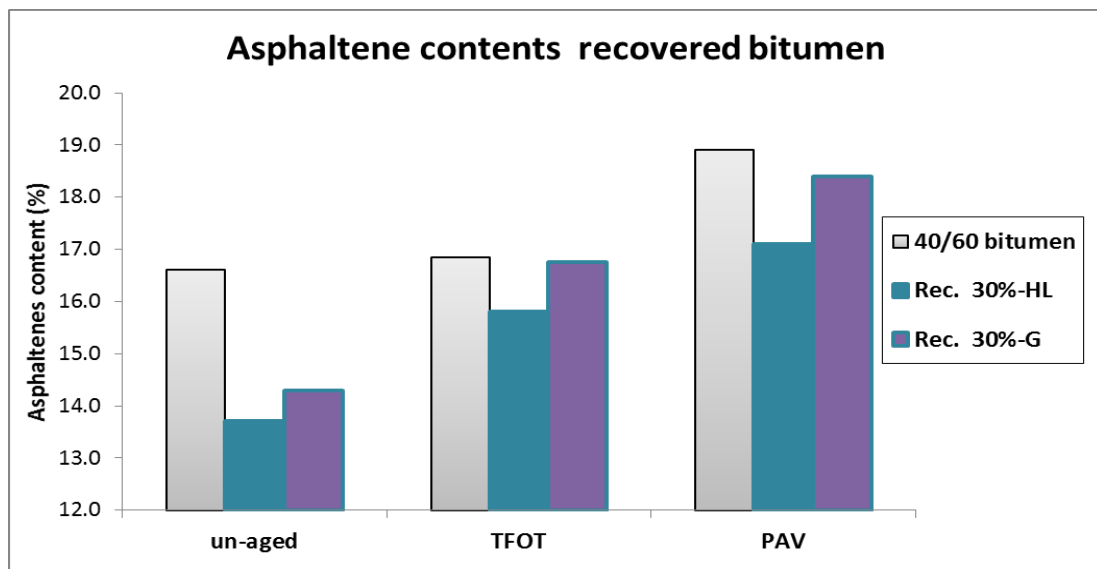


Figure 7-15 Asphaltene content of the recovered bitumen from the mastics after different ageing stages

The results of the carbonyl indices and the asphaltene content of the recovered bitumen show a lower carbonyl index and less asphaltene content for the bitumen recovered from the hydrated lime mastics. These could prove the ability of hydrated lime particles to adsorb polar components of bitumen. In addition, the results could imply that some interactions between the polar components of bitumen and the mineral surface of the fillers may be irreversible. Thus, in order to prove this concept, attempts were made to test the residual filler recovered from the mastics using the FTIR test and to compare the results with those of the original ones. The FTIR spectrum for the original hydrated lime particles and the granite fillers are presented in Figure 7-16.

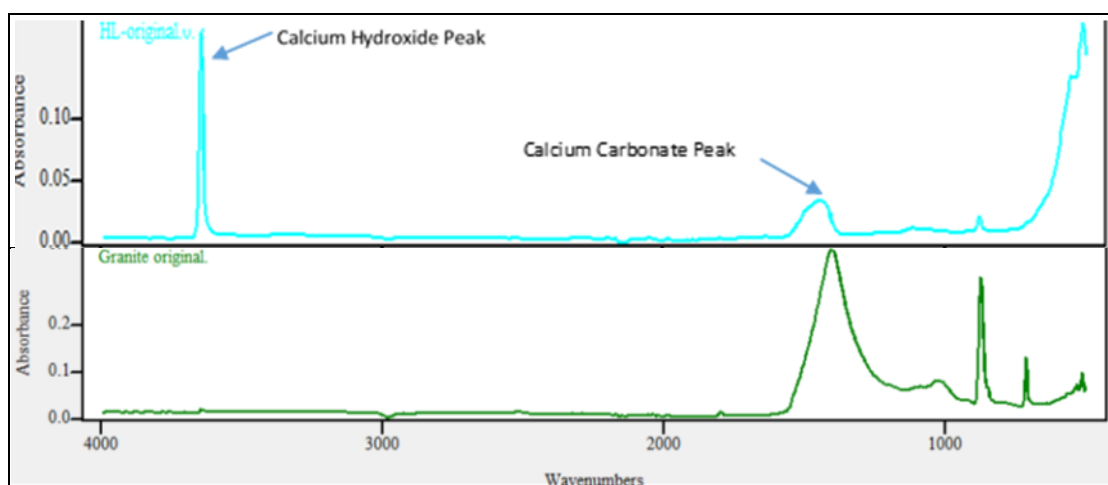


Figure 7-16 FTIR spectrum of the original hydrated lime and granite filler particles

It can be noticed that for the hydrated lime particles spectrum there are two main peaks representing the main composition of the hydrated lime, which are the Calcium Hydroxide peak $\text{Ca}(\text{OH})_2$ at 3640 cm^{-1} and the Calcium Carbonate peak CaCO_3 at 1390 cm^{-1} . These two main components of the hydrated lime comprise 96.00% and 2.77%, respectively, of the total chemical composition of the hydrated lime as provided by the supplier.

The changes in chemical composition of the fillers recovered from mastics after different ageing stages were also observed using the FTIR analysis. The spectrum of the recovered fillers from the unaged, TFOT and PAV aged hydrated lime mastics compared to the original HL particles are presented in Figure 7-17.

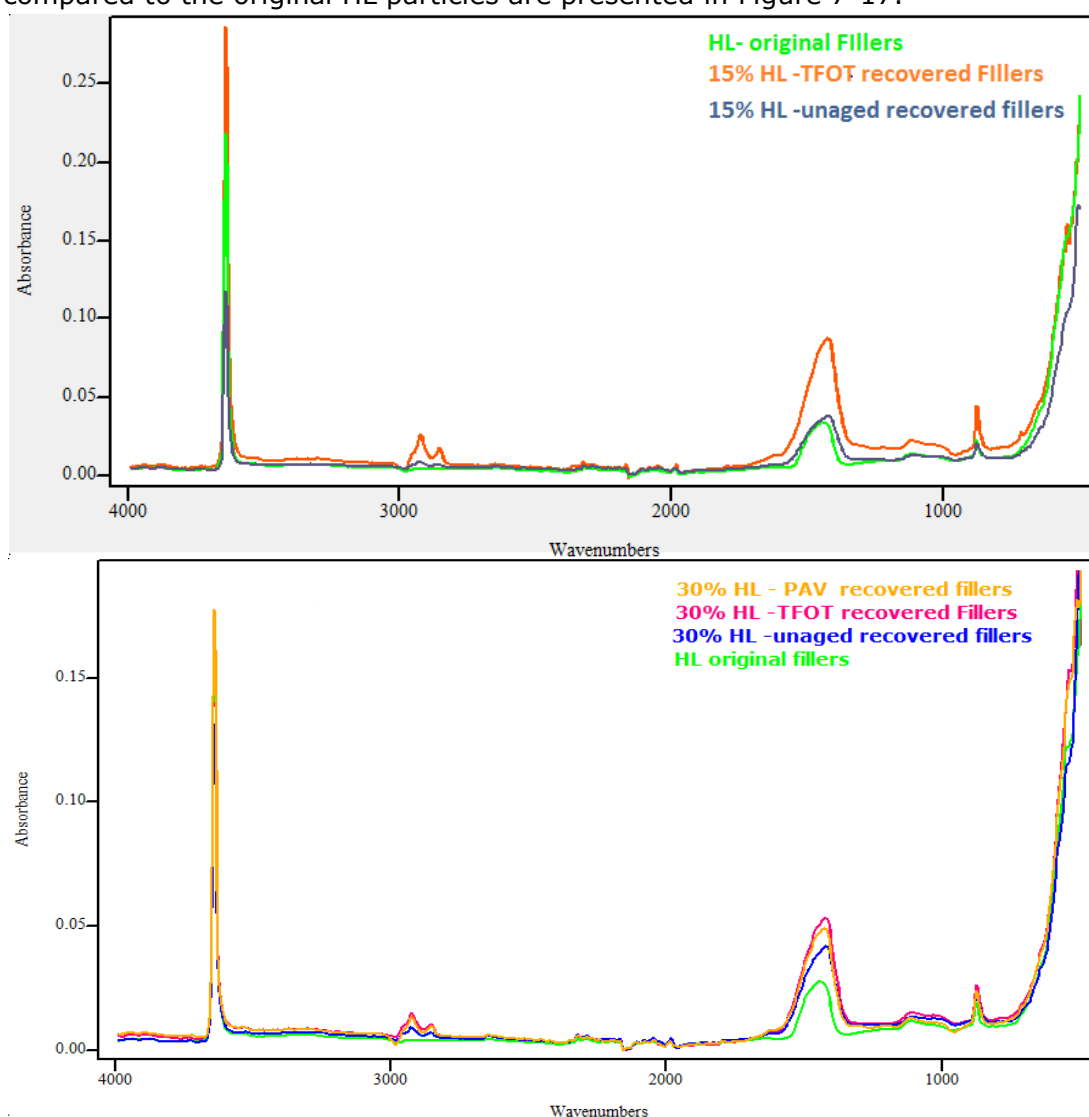


Figure 7-17 FTIR spectrum of the original hydrated lime and the recovered from mastics after different ageing stages

From the spectrum in Figure 7-17, it is observed that there are some main peaks affected by the ageing of the asphalt mastics. The intensity of these peaks increases with ageing. These peaks are observed around wavenumbers 1400, 2853, 2920, and 2950 cm^{-1} .

Similarly, the recovered fillers from the granite mastics were analysed and compared with the original granite mastics. The changes in the FTIR spectrum of the original granite fillers and the recovered fillers are presented in Figure 7-18. It can be observed that there is an increase in the intensity at the wavenumbers at peaks around 2850, 2920 and 2950 cm^{-1} , which increases as the ageing proceeds.

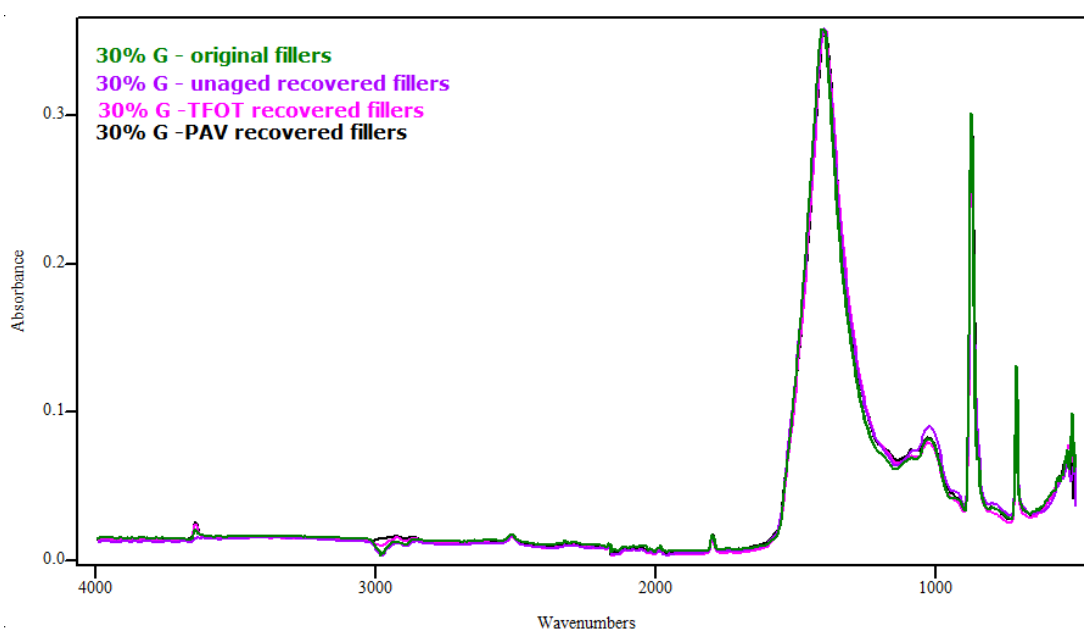


Figure 7-18 FTIR spectrum of the original granite and the recovered fillers from mastics after different ageing stages.

From the FTIR spectrum for both the hydrated lime and granite fillers, it can be noticed that both fillers share the same increase in the wavenumbers around 2853, 2920 and 2950 cm^{-1} . These changes could be referred to as interactions between the mineral filler surface and some components of the bitumen. This interaction could be irreversible, as it could be observed there still changes appearing in the recovered fillers after mixing with bitumen. These results could indicate that the fillers adsorbed some of the bitumen components at the corresponding wavenumbers where the changes were observed in the recovered filler spectra.

Thus, in order to further investigate this phenomenon, a quantitative analysis of the changes in the filler absorption at the corresponding wavenumbers was performed. Furthermore, the changes in the mastics and the recovered bitumen at these same wavenumbers were also investigated. The FTIR spectra for both recovered fillers and bitumen from the HL30% mastics are shown in Figure 7-19, while the FTIR spectra of the fillers and bitumen recovered from G30% are presented in Figure 7-20.

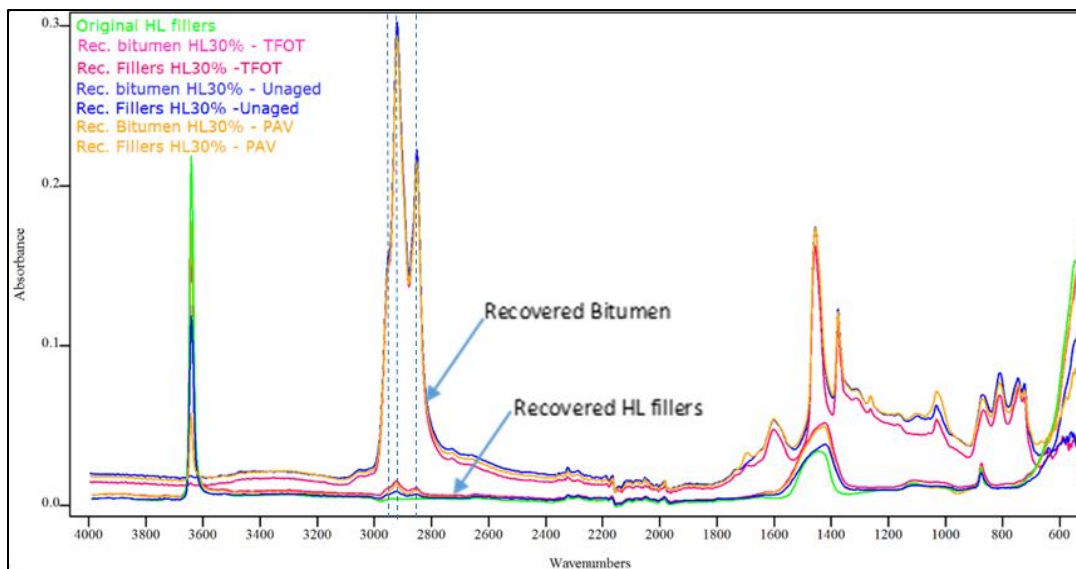


Figure 7-19 FTIR spectrum of the recovered bitumen and fillers from the 30%HL mastics after different ageing stages

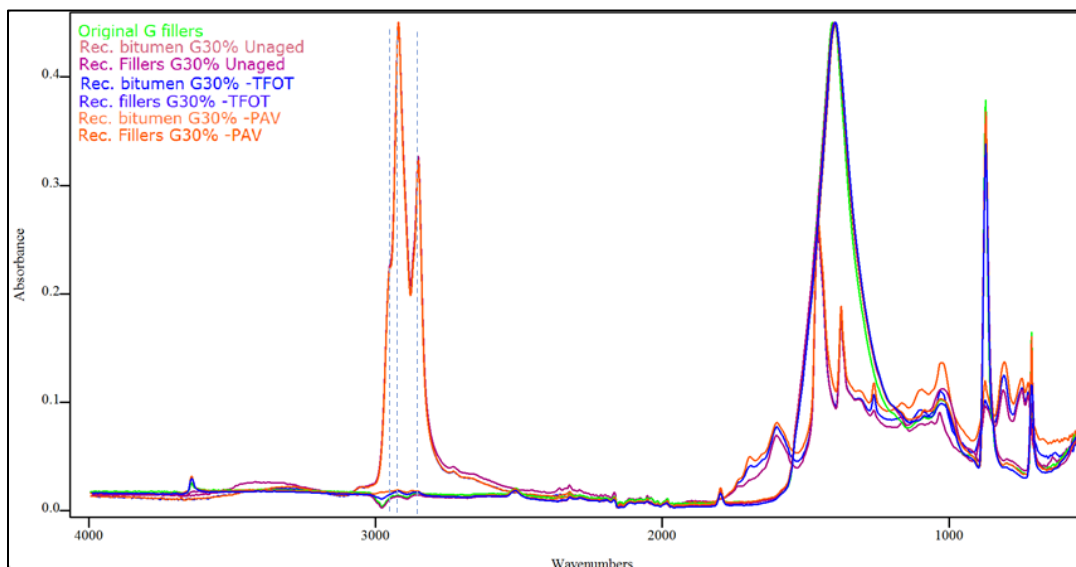


Figure 7-20 FTIR spectrum of the recovered bitumen and fillers from the 30%Granite mastics after different ageing stages

It can be observed from both Figure 7-19 and Figure 7-20 that the wavenumbers for the increased bands in the spectrum for the recovered fillers correspond to bitumen peaks. The peaks at these wavenumbers in the recovered bitumen are well defined. The four prominent peaks observed in the 3000–2800 cm^{-1} region correspond to the stretching vibration absorption bands of the alkyl (C-H) in CH_2 and CH_3 of asphalt binder ([Nivitha et al.,2015](#); [Cong et al.,2014](#)). This means in other words that these wide absorption peaks at 3000–2800 cm^{-1} correspond to the carboxylic acid of bitumen. Strong absorption peaks at 2920 and 2850 cm^{-1} corresponds to the stretching vibration of paraffin C-H and cycloparaffin C-H. The absorption peak at 2950 cm^{-1} corresponds to stretching vibration of $-\text{CH}_3$, while the absorption peak at 2920 and 2850 cm^{-1} correspond to $-\text{CH}_2$ ([Tan and Guo,2014](#)).

Therefore, in order to compare the adsorption of the two fillers, the increases in the area of the recovered fillers corresponding to the carboxylic acid were calculated. The results are presented as increasing percentages of the area calculated from the recovered fillers around the wavenumbers 2853, 2920 and 2950 cm^{-1} compared to the original fillers. The results are presented in Figure 7-21.

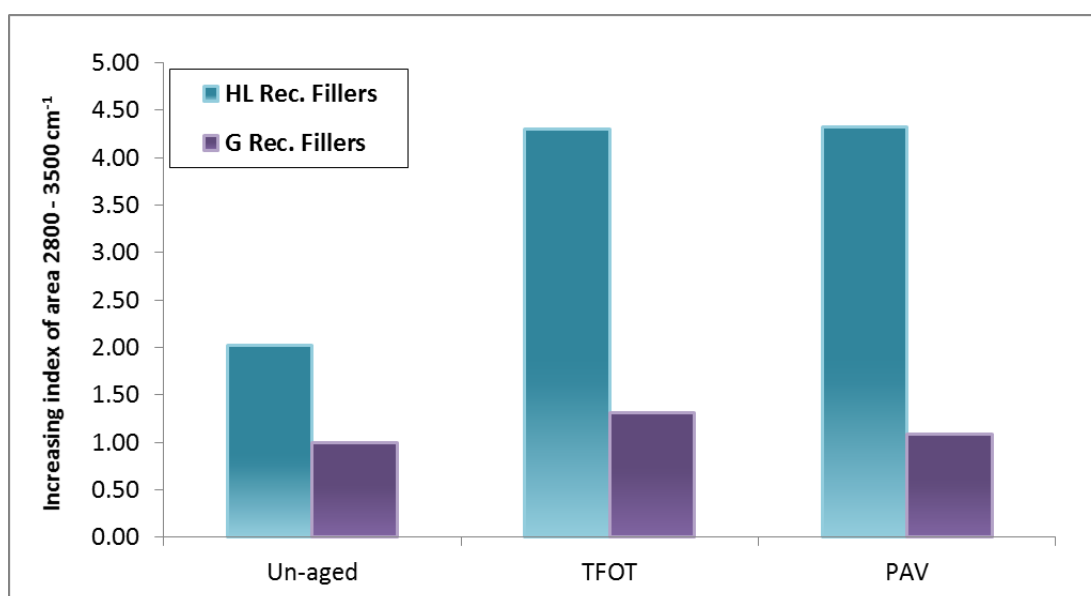


Figure 7-21 The increases in the absorbed area around 2853, 2920 and 2950 cm^{-1} for the recovered fillers from 30% vol. mastics.

The results in Figure 7-21 show that the adsorption on the hydrated lime fillers for the unaged mastics is higher than the carboxylic acid adsorbed on granite fillers.

Furthermore, the results show that the adsorption on the hydrated lime fillers increases as the ageing proceeds from TFOT to PAV. However, in contrast, the adsorption of the granite fillers for the calculated areas is almost the same with ageing and in all cases, it is lower than that of the hydrated lime.

These results confirm that the fillers can adsorb bitumen components on their surfaces and this interaction is irreversible, as it is not restored after the recovery of the fillers and the bitumen.

Moreover, the results above also confirm the results in Figure 7-14, which show that the carbonyl index of the bitumen recovered from hydrated lime mastics is lower than that recovered from the granite mastics. These results explain the mechanisms of how hydrated lime mitigates the ageing of asphalt mixtures and mastics. Therefore, this analysis of the results shows the beneficial effect of hydrated lime addition to the bitumen mastics and consequently to asphalt mixtures as discussed earlier in Chapter 6. Thus, the ability of hydrated lime to reduce the oxidative hardening could be explained by the following mechanism: Hydrated lime irreversibly adsorbs the reactive polar components on its surface and removes them from the bitumen. These adsorbed components are strongly interacting chemical functional groups, which are reactive to oxidation; thus, the removal of these components reduces the rate of formation of oxidation products such as asphaltenes and carbonyls.

Hydrated lime, as a chemically strong base, has the ability to react readily with acidic components of the bitumen such as carboxylic acids to form calcium salts such as calcium carbonate, which is insoluble. As a result, carboxylic acids and other related chemical functional groups in bitumen irreversibly react with hydrated lime; consequently removing these acidic components from the bitumen mastic reduces the ageing and hardening. The increase in the C-H of the carboxylic acid

on the recovered hydrated lime fillers is evidence of the adsorption ability of the hydrated lime particles compared to the granite filler particles as seen in Figure 7-21.

In addition, the results in Figure 7-17 and Figure 7-19 show the increase of the Calcium Carbonate peak (CaCO_3) for the recovered hydrated lime, especially from the TFOT aged mastics. This could prove the interaction of the acidic components of the bitumen with the hydrated lime forming calcium carbonate.

The results of this study confirm the previous observations by researchers about the ability of hydrated lime to irreversibly adsorb some components of the bitumen, which consequently reduces the rate of ageing ([Plancher et al.,1976](#); [Petersen et al.,1987](#); [Little and Petersen,2005](#); [Lesueur et al.,2013](#)).

Furthermore, to investigate the changes of the bitumen mastics with different filler percentages after ageing, the changes in the FTIR absorbed area of Carboxylic Acid O-H and C-H stretch, which can be characterised by the absorption observed in the area between 3000 - 2500 (broad, ν), was investigated.

The sums of the areas characterised by the peaks at 2853, 2920 and 2950 cm^{-1} for different mastics with different filler concentrations after PAV ageing were calculated and compared. The FTIR spectra for the wavenumbers of interest for different mastics with different fillers concentrations are presented in Figure 7-22 and Figure 7-23 for hydrated lime mastics and granite mastics respectively. The results of the calculated areas are shown in Figure 7-24.

From Figure 7-22, it can be observed that with the increasing of the hydrated lime fillers in the mastics, the intensity of the Calcium Hydroxide peak increases as observed at the wavenumber 3640 cm^{-1} . In addition it can be noticed that there is a decrease in the area between 3000-2800 cm^{-1} , which corresponds to the stretches of the carboxylic acids. This change was quantified and the areas of these peaks were calculated and compared.

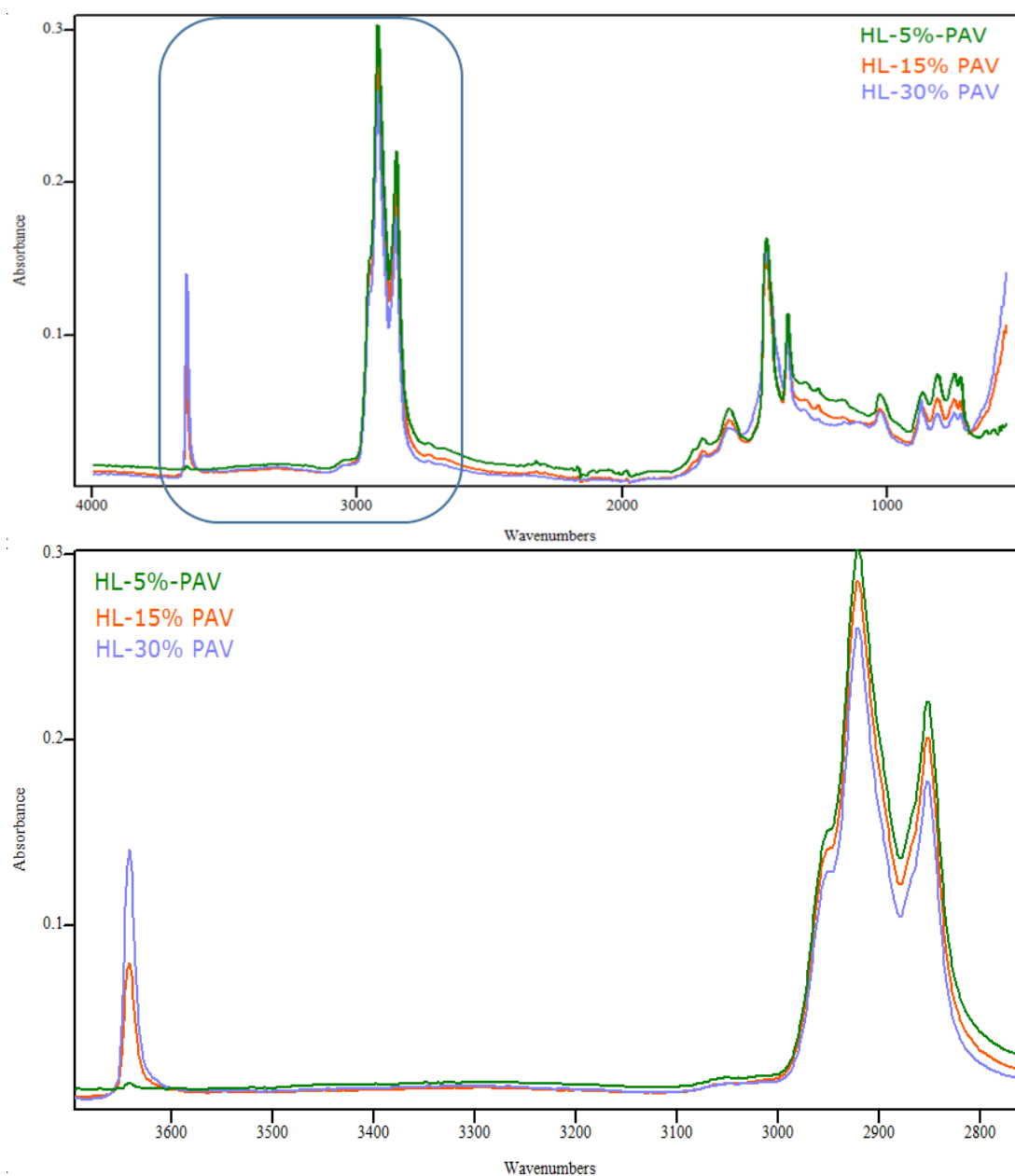


Figure 7-22 FTIR spectra of the hydrated lime mastics with different filler concentrations after PAV ageing

From Figure 7-23, it can be seen that at the same wavenumbers corresponding to the carboxylic acids of the bitumen there is only a decrease of the peaks at the higher granite filler contents in the mastic 30%G. Furthermore, the results from Figure 7-24 show that the decrease of the calculated area for hydrated lime mastics is more than that of the granite mastics. These results confirm the discussion above that hydrated lime has a higher ability to adsorb these bitumen components. Moreover, as can be seen by increasing the hydrated lime concentration in the mastics the adsorption increases (the calculated area decreases for the mastics).

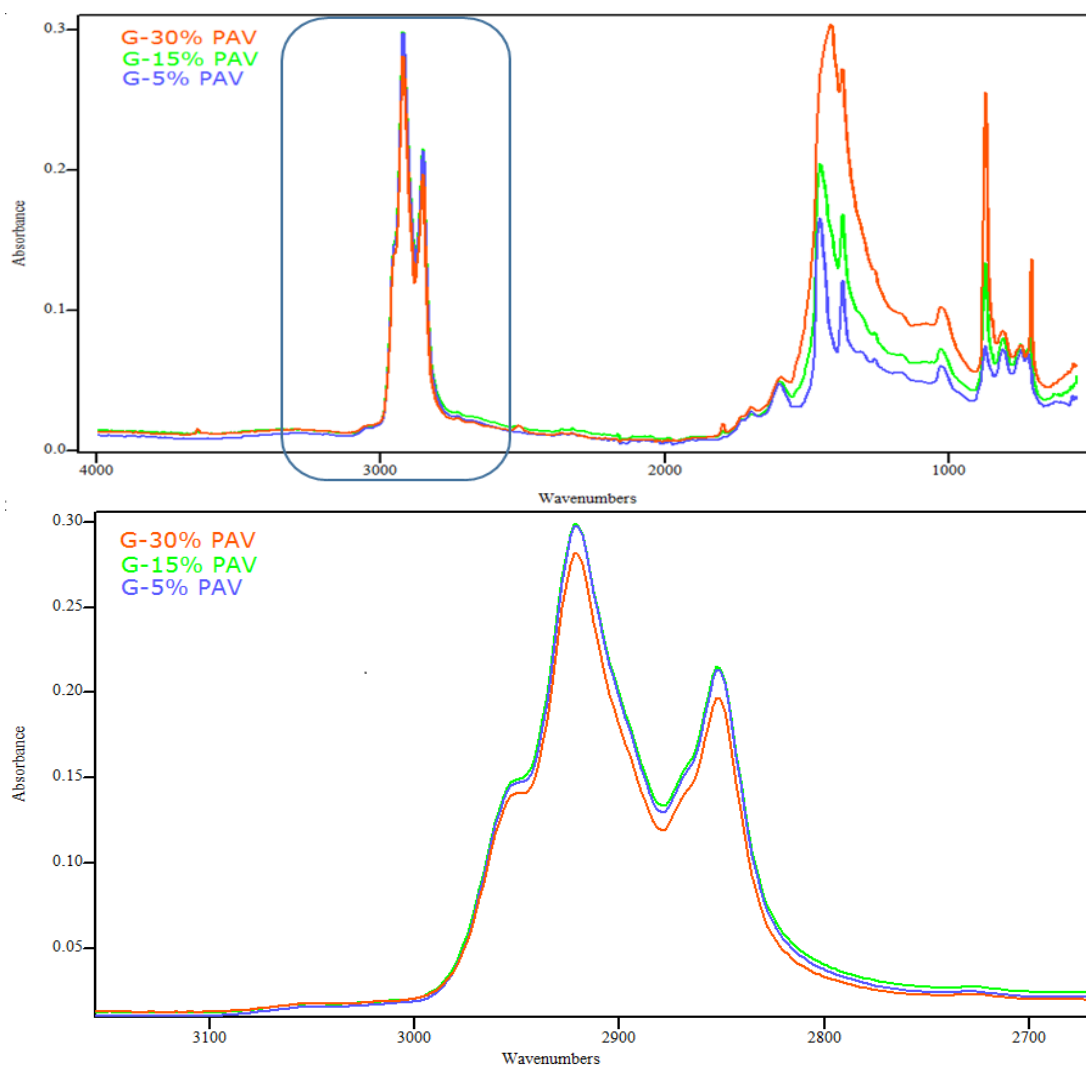


Figure 7-23 FTIR spectra for the granite mastics with different filler concentrations after PAV ageing

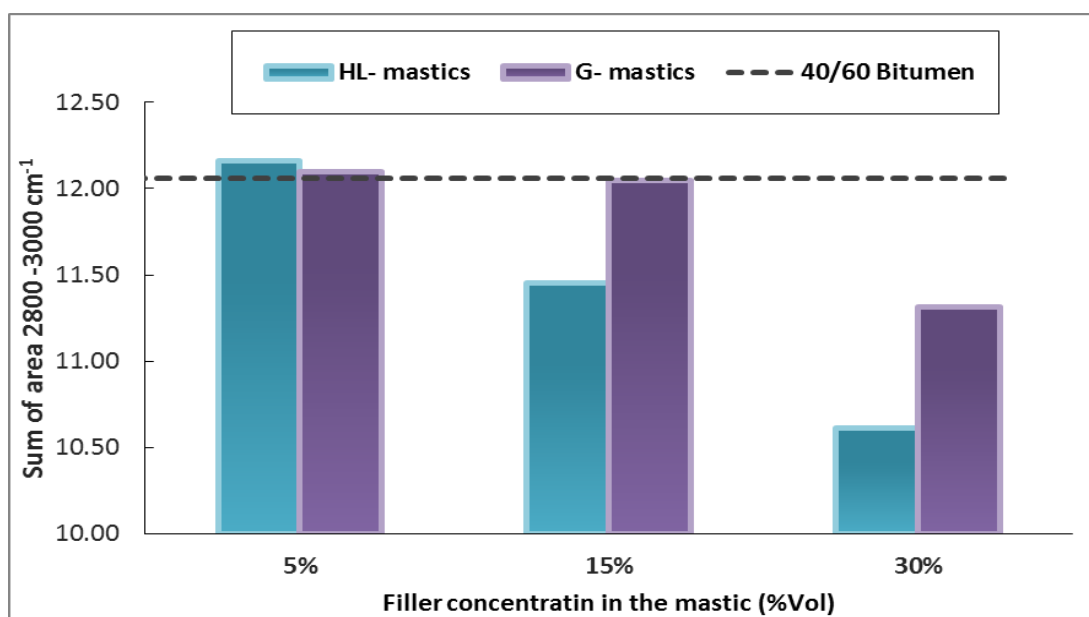


Figure 7-24 comparing the sum of the area 3000-2800cm⁻¹ of the granite and hydrated lime mastics FTIR spectra.

In concluding the testing performed in this stage and the results observed in this part of the study, the following remarks can be made:

- The ageing indices after TFOT and PAV ageing are significantly affected by the concentration of the filler, especially at higher concentrations.
- The effect of filler type and its properties significantly affect the ageing indices. Hydrated lime decreases the ageing indices more than the other fillers do after TFOT and PAV ageing.
- Increasing the concentration of hydrated lime in the mastics tends to decrease the ageing indices for the concentrations used in this study. However, increasing the granite filler concentration in the mastics resulted in increasing the ageing rather than reducing it.
- For the bitumen recovered from the mastics, the recovered binder from the hydrated lime mastics is always softer than that recovered from the granite mastics for the same ageing conditions. In addition, the bitumen recovered from the hydrated lime mastics shows significantly higher phase angles than bitumen recovered from the granite mastics.
- The chemical analysis of the changes on mastics, recovered fillers and bitumen, revealed that some interactions happened between the hydrated lime and some fractions of the bitumen. This effect is less pronounced in the case of granite fillers.
- The results from the FTIR test on the recovered bitumen from the mastics show that less carbonyls were produced after TFOT and PAV ageing for the hydrated lime mastics compared to the granite mastics, which shows the beneficial effect of hydrated lime on ageing.
- The results for the asphaltenes content test on the recovered bitumen show the same conclusion as the FTIR carbonyl index, which shows less ageing products present in the recovered bitumen from the hydrated lime mastics than in bitumen recovered from the granite mastics.

- The results from the FTIR tests on the recovered fillers prove the ability of hydrated lime to irreversibly adsorb some of the bitumen components (carboxylic acid products). This reduces the formation of the ageing products and consequently reduces age hardening. Unlike hydrated lime, the granite fillers do not exhibit this ability to react with bitumen.

Further investigation into the effect of fillers on the ageing rate of the mastics rather than using the standard ageing methods of TFOT and PAV, which can provide results only at two ageing stages, would be useful. Therefore, an ageing time study was proposed to investigate the ageing rate changes with different filler contents. The ageing time study will be discussed in the following section.

7.5 Stage 2: Aging time study

As discussed above, the mineral fillers can adsorb or catalyse the bitumen during ageing. The intensity of the influence of the mineral fillers on ageing keeps changing as the ageing continues, due to the changes in their adsorbing and catalysing abilities. Thus, it was felt that the ageing study with the standard TFOT and PAV ageing time is not enough to describe the whole situation about how the mineral fillers can affect the bitumen ageing. Therefore, mastics with different fillers at various percentages of filler volume concentration were further studied in order to show the effect of hydrated lime on the rate of stiffening and ageing of the mastics. The mastics were aged in the TFOT oven at 163°C at a thickness of 2.2mm for different ageing times (2, 5, 10 and 15 hours). The empirical tests including the viscosity at 135°C and the softening point were carried out at each ageing level. The ageing indices were calculated from these tests. In addition, the rheological changes were determined by the changes in the complex modulus with ageing. The effect of the TFOT ageing time on the properties such as viscosity, softening point and the complex modulus of the 15% vol. filler concentration mastics and the calculated ageing indices are presented in Figure 7-25.

The results of the mastic ageing show that the mastic and bitumen stiffening increases with the ageing time. The rate of mastic stiffening keeps changing as the time of the TFOT ageing proceeds.

It can be noticed from the results, that the rate of change in viscosity, softening point and the complex modulus for the pure bitumen is almost consistently increasing. However, the effect of the filler on ageing rate keep changing (increasing or decreasing the ageing rate) as the time in the TFOT proceeds. It can be noticed from Figure 7-25 that hydrated lime at 15% vol. concentration has the lowest ageing index compared to the other fillers. Moreover, the effect of hydrated lime to reduce the aging becomes clearer and more pronounced for the longer aging times.

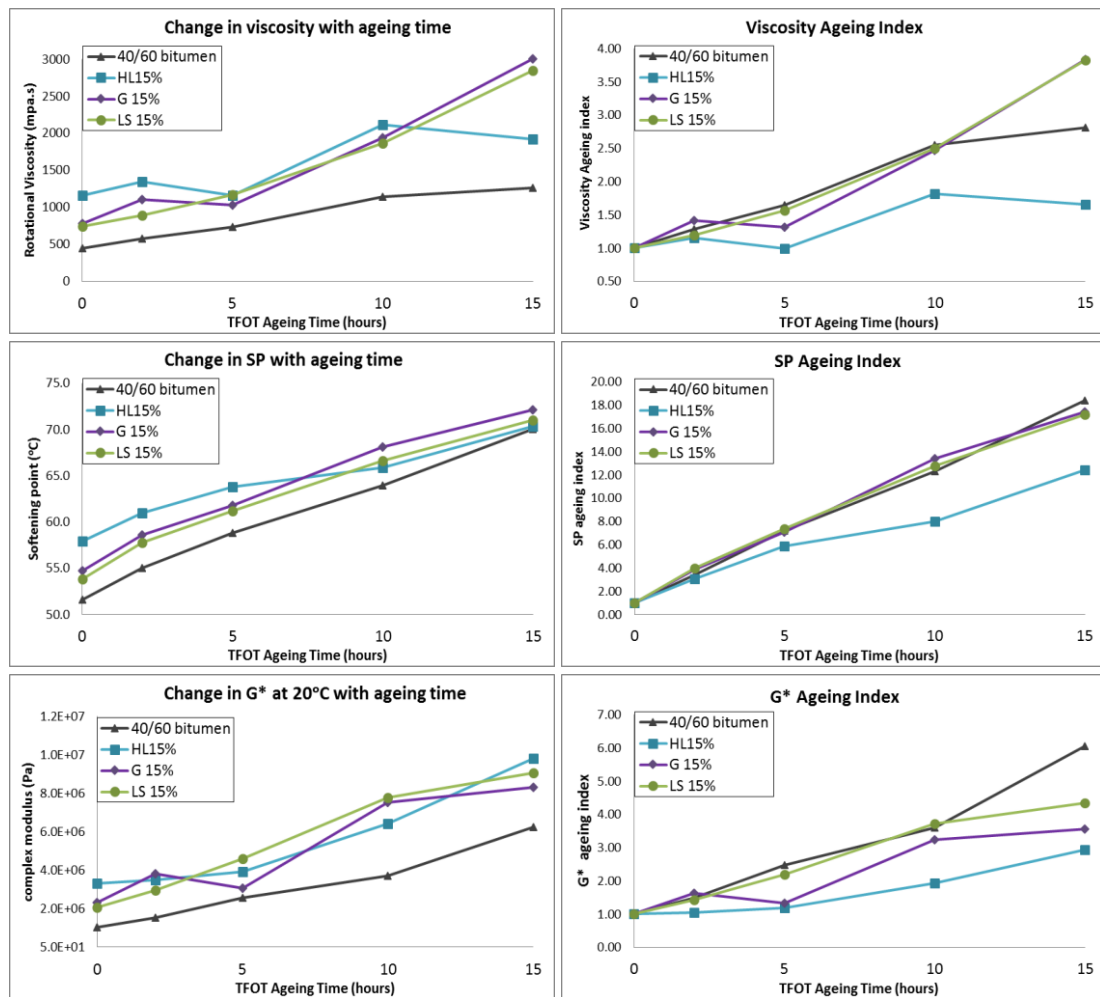


Figure 7-25 The effect of TFOT ageing time on the properties of the mastics of 15% vol. concentration and the ageing indices.

The comparison between the 30% vol. mastics aged in the TFOT oven at a thickness of 2.2mm after different ageing times is presented in Figure 7-26.

Comparing the ageing of the mastics of 15% vol. fillers to the 30% vol. filler mastics, it can be noticed that the concentration of fillers has an effect on the aging rate.

It is observed in Figure 7-26 that the rate of ageing experiences more changes at higher filler concentrations than observed for the 15% filler content. It can be noticed as well that the mastics exhibit different behaviours and rates of change with the ageing time for the different filler concentrations. This change is more pronounced for the granite mastics than the hydrated lime mastics.

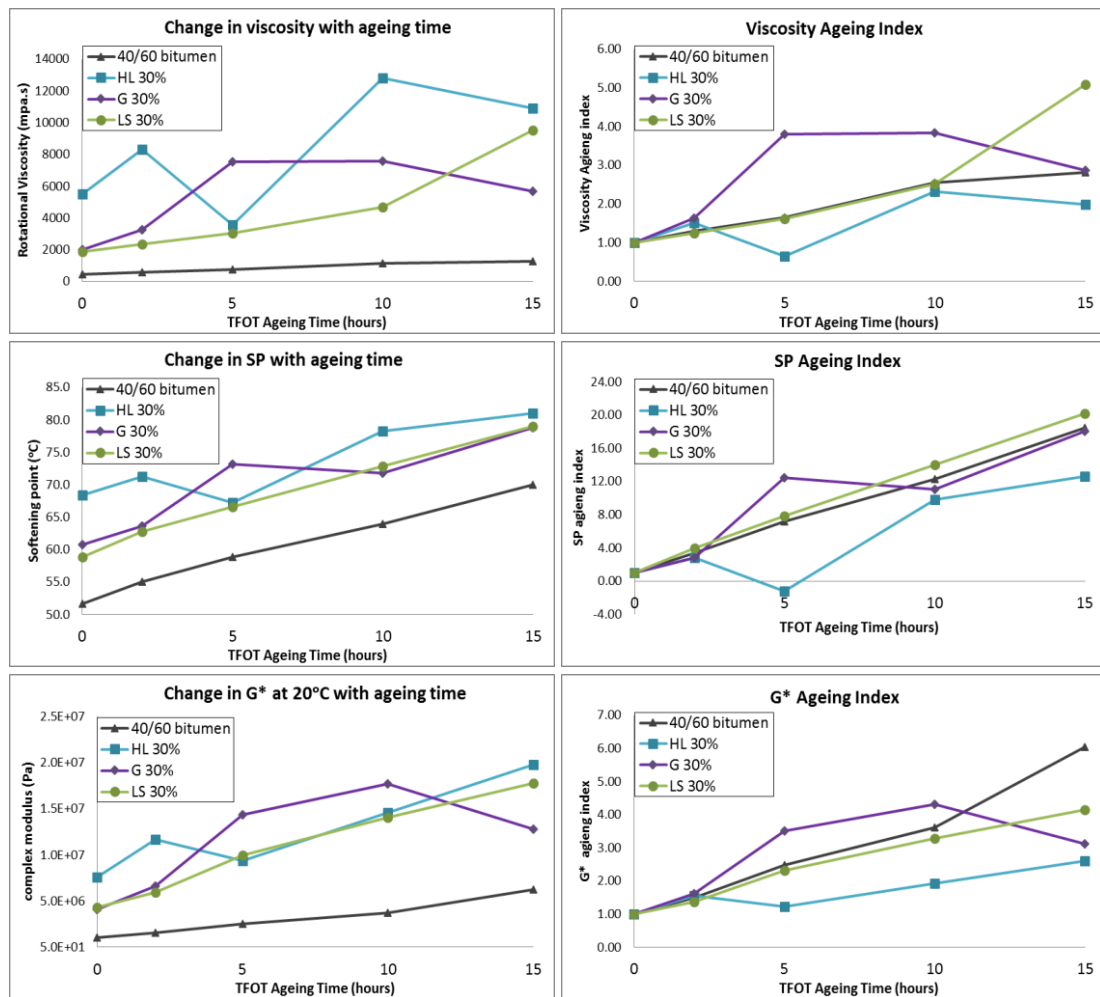


Figure 7-26 The effect of TFOT ageing time on the properties of the mastics of 30% vol. concentration and the ageing indices.

However, it can also be noticed that the ageing indices for the hydrated lime mastics are the lowest for all cases.

It is known that the effects of fillers on the asphalt mastics are directly related to their characteristics and the degree of concentration in the bitumen-filler system. There are diverse studies, which have assessed the effect of using mineral fillers on the ageing of the bitumen mastics and mixtures. The addition of filler can delay the ageing of bitumen as the filler particles are an obstacle to the diffusion of oxygen into the body of the bitumen thus, reducing the ageing oxidative products. As a consequence of this, the ageing of the mastics that contain fillers is expected to be less regardless of the filler nature or the physical and chemical properties.

However, the results show that the ageing indices for the granite mastics at 30% vol. concentration at some ageing stages is higher than that of the pure bitumen. This effect is not the same for the hydrated lime.

Significant differences were observed between the ageing rates of the mastics with different mineral fillers. The results show that the nature of the fillers (acidic or basic nature) can significantly affect the ageing rates. Granite fillers (acidic minerals) have the ability to catalyse bitumen oxidation, thus accelerating the bitumen ageing. In contrast, basic minerals, such as hydrated lime, show a greater ability to adsorb some components of the bitumen which can decelerate bitumen ageing. This is the reason the filler mastics exhibit these different effects.

([Anderson et al.,1994](#)), stated that aggregates with the least adsorption of highly polar fractions, such as granite, exhibit the highest catalytic effect in bitumen oxidation. In contrast, fillers showing the highest adsorption effect, such as the hydrated lime, exhibited the smallest catalytic effect.

The higher oxidative ageing of the granite mastics is related to the stronger catalytic ability of the granite fillers. However, the lower ageing indices for the hydrated lime mastics are related to the greater adsorption ability of hydrated lime. In general, it can be concluded that the ageing rate of the bitumen filler mastics depends on both the catalytic and adsorption effects. These two factors are changing with ageing time in the TFOT. This is clear for the granite mastics at 30% vol. concentration, where it can be observed that the ageing indices for the granite mastics keep increasing for the first few hours; however after some time they reduce and keep decreasing.

In addition, it can also be seen from the results above that the increase of the ageing index of hydrated lime mastics is not as severe as in the granite mastics. This indicates that the function of delaying age hardening by adsorption of polar components from bitumen to hydrated lime is relatively stable and continuous during the whole ageing programme.

7.6 Chapter Summary

This chapter has investigated the effect of hydrated lime and other fillers on mastic stiffening and ageing. In this detailed study on the mastics, the effect of hydrated lime on stiffening and ageing mitigation was evaluated by different means involving both physical and chemical properties. The evaluation testing was aimed at understanding the mechanisms of hydrated lime on ageing mitigation. Moreover, special attention was paid to the interactions between hydrated lime and bitumen, which affects the ageing of bitumen mastics.

From the discussion and the results from the stiffening and ageing tests performed, the following conclusions can be summarised:

- From the results of the stiffening effects of the fillers on bitumen mastics, it was observed that the granite fillers have almost the same stiffening effect with the different bitumen binders used in preparing the mastics. However, this is not the case for the hydrated lime. Furthermore, it was observed that the same hydrated lime concentrations in mastics can result in significantly different stiffening ratios with different binders.
- Comparing between mastics containing hydrated lime and granite fillers on the stiffening of the mastics and the recovered binders showed that the complex moduli of the hydrated lime mastics were much higher than those of granite mastics. This effect was more pronounced at higher filler concentration. In contrast, the recovered bitumen from hydrated lime mastics is softer than the bitumen recovered from granite mastics.
- In general, from both the short-term and long-term ageing, it was observed that the ageing indices are affected by the concentration of the filler, especially at higher concentrations. In addition to that, the effect of filler

type was very significant on the ageing indices as it was noticed that hydrated lime decreases the ageing indices more than the other fillers. Furthermore, the ageing evaluation indicators used can in some cases rank the mastics differently; this effect was more pronounced after PAV ageing compared to TFOT ageing.

- From the TFOT and PAV ageing simulations, it was observed that increasing granite filler concentration in the mastics resulted in increasing mastic ageing rather than reducing it. In contrast, generally, increasing the concentration of hydrated lime in the mastics decreases the ageing. These findings indicate that for each filler there will be a different optimum filler concentration that will result in the best stiffening effect on the mastics, as well as better ageing mitigation.
- The results from the FTIR test reveal that the carbonyl ($C=O$) was significantly affected by the fillers mixed with the bitumen. Furthermore, for the recovered bitumen, a lower carbonyl index and less asphaltenes content for the bitumen recovered from the hydrated lime mastics was observed. This could prove the ability of hydrated lime particles to adsorb polar components of bitumen. Furthermore, the asphaltenes content of the recovered bitumen is well correlated with the results of the carbonyl indices.
- The results from the FTIR tests on the recovered fillers prove the ability of hydrated lime to irreversibly adsorb some of the bitumen components (carboxylic acid products) and thus reduce the formation of ageing products and consequently reduce age hardening. Unlike hydrated lime, the granite fillers do not exhibit this ability to react and adsorb bitumen components.

- From the ageing time study, the results of the mastic ageing show that the mastic stiffening increases with the ageing time. The rate of mastic stiffening as evaluated by different ageing indices keeps changing as the time of the TFOT ageing proceeds. The fillers can increase or decrease the ageing of the mastics as the time in the TFOT proceeds.
- From the ageing time study, the higher oxidative ageing of the granite mastics is related to the stronger catalytic ability of the granite fillers. However, the lower ageing indices for the hydrated lime mastics is related to the greater adsorption ability of hydrated lime.

Chapter 8: Conclusions and Recommendations

8.1 Introduction

In this thesis, the main purpose was to develop a better and deeper understanding of asphalt ageing mechanisms and to evaluate the advantages of using hydrated lime to mitigate asphalt ageing during its long service life. With this purpose in mind, an initial investigation on pure bitumen was performed to be used as a base study to set up the parameters, tests and methods that were used in the subsequent stages. The effect of different ageing methods on bitumen properties was compared. Furthermore, the factors and parameters affecting bitumen ageing were investigated in Chapter 4.

The influence of different fillers on bitumen-filler mastics ageing was investigated. Furthermore, the effect of using hydrated lime as a replacement for these fillers was further studied in Chapter 5, and the effect of hydrated lime on mastic ageing further investigated with different binders for better understanding of the bitumen-filler interaction. In addition, Chapter 6 focused on the effect of using hydrated lime on the ageing of asphalt mixtures prepared with different aggregates and fillers. This was evaluated at the mixture level through different performance tests such as ITSM, ITS and semi-circular bending. Finally, an extensive study of mastic ageing was performed. This consisted of comprehensive detailed testing of mastics, conducted to better understand the interaction between bitumen and different fillers. In addition, investigations on the effect of hydrated lime on mastic ageing was further conducted to understand the mechanisms of hydrated lime on ageing mitigation.

Based on these, this chapter summarizes the main issues discussed in the previous chapters. The main conclusions are presented in Section 8.2, and then some recommendations for future research are also suggested in Section 8.3.

8.2 Conclusions

8.2.1 The main conclusions related to the pure bitumen ageing

A comparison between short and long-term ageing methods was performed on different bitumens; the effect of ageing on binders was quantified as Ageing Index (AI) for different properties, softening point, viscosity and complex modulus. In addition to the physical and rheological changes in the bitumen, the FTIR was used to study the chemical evolution in bitumen with ageing. The different ageing techniques and ageing indices were compared and the factors affecting these techniques and the ageing rates were evaluated. The main conclusions that were derived from this study can be summarized as follows:

- Comparing the effect of TFOT and RTFOT ageing methods on different binders, the short-term ageing methods were observed to be almost the same. This correlation between TFOT and RTFOT was observed to be strong using either chemical analyses or rheological measurements and the two methods show similar severity.
- For different bitumen binders tested in this study, the ageing indices calculated from different physical properties (viscosity and softening point) are well correlated and they reflect the change in rheological properties such as the complex modulus. The ageing indices calculated in this study all rank the bitumen ageing similarly.

- The complex modulus (G^*) ageing index calculated at different temperatures and frequencies in this study ranked the bitumen ageing similarly. However, the difference is larger at temperatures from 40-60°C and at lower frequencies. Furthermore, the change in phase angle (δ) is more pronounced at lower temperatures.
- The FTIR test on bitumen showed that the carbonyl index is correlated to the stiffness and hardening of the bitumen more than the sulfoxide index. Thus, the carbonyl index can be used as an ageing indicator rather than sulfoxide index.
- The results from ageing bitumen with different film thicknesses show that the ageing index decreases by increasing the bitumen film thickness. In addition, it shows that a power law describes the trend of ageing indices changes in film thickness. This conclusion applies to both ageing in the TFOT and the PAV.
- The ageing time study for different bitumens in the TFOT reveals that the effect of the extended time ageing in the TFOT oven on different bitumen binders does not change with the thickness. In addition, the relationship between the changes in different physical properties measured in this study remains the same with the two different thicknesses used in this study. However, the effect of a lower film thickness is more intense but with the same relation.
- The results of the ageing index relationship with the TFOT ageing time shows that the viscosity and complex modulus ageing indices as calculated in this study increase exponentially with TFOT ageing time.

8.2.2 The main conclusions related to the bitumen mastics ageing

The main aim of this study was to investigate the effect of different fillers on bitumen-filler mastic ageing. Particular attention was paid to study the benefits of using hydrated lime on the ageing of the mastics. Furthermore the effect of the physical and chemical interaction between fillers and the bitumen where studied. The effect of hydrated lime with two different bitumen binders on mastic ageing was investigated in this study as well. Based on the laboratory test results on the mastics and recovered bitumen, the following conclusions were derived:

- The stiffening effect of the filler on mastics as measured by the increases in the viscosity and softening point shows that for the same filler concentrations granite tends to stiffen the mastics more than limestone. Furthermore, hydrated lime replacement of the filler at 10 and 20% increases the stiffening effect on the mastic.
- The results of replacing the granite or limestone fillers in the mastics by 10 or 20% hydrated lime show a lower ageing index compared to the natural filler mastics and to the neat bitumen. This effect is more pronounced after the long-term ageing. In addition, it was observed from the calculated ageing indices, that replacing filler with 20% of hydrated lime does not make a significant additional effect on reducing ageing compared 10% replacement with hydrated lime.
- From the FTIR analysis, it was concluded that the binder recovered from the mastic of hydrated lime with granite contains less oxygenated products after both short- and long-term ageing. This indicates that less ageing and stiffening occurred in the mastics with hydrated lime.

- From the ageing time study on the mastics, it was concluded that the rate of the increase in the complex modulus, viscosity and softening point for the mastics containing hydrated lime was slower than mastics without hydrated lime.

8.2.3 The main conclusions related to mixture ageing

In this study, samples were prepared with granite or limestone aggregate mixtures with and without hydrated lime and then long-term aged.

The effect of hydrated lime replacement of the natural fillers at 1 and 2 % by weight of aggregate on the ageing properties of asphalt mixtures and the bitumen ageing were investigated. This effect at the mixture level was investigated using different mechanical property tests, indirect tensile stiffness modulus (ITSM), indirect tensile strength (ITS) and their fracture properties using the semi-circular bending (SCB) test. Furthermore, the bitumen binder of the aged specimens was recovered and the effect of ageing on the recovered binders from different samples was investigated by rheological and chemical means using the Dynamic Shear Rheometer (DSR) and Fourier Transform Infra-Red (FTIR) spectroscopy, respectively.

The main conclusions derived from this study are summarised as follows:

- The ageing indices as calculated from the ITSM tests generally increased with increased temperature. Furthermore, the ageing indices for the limestone mixtures are smaller than for the granite mixtures.
- The results show that the effect of hydrated lime on stiffening the mixture is more pronounced with the granite mixture; however, the limestone mixtures were less affected by the hydrated lime replacement.

- From the results of the ITSM testing of the mixtures, it can be concluded that the effect of hydrated lime replacement of the fillers on the ageing of the asphalt mixtures is clear and reduces the aging as seen from the aging indices. However, this effect is different between the granite and limestone mixtures.
- The results of the ITS test show the beneficial effect of hydrated lime on the ageing of the asphalt mixture as it reduces the increase of ITS after ageing. This effect of hydrated lime is clear for both mixtures. However, 1% and 2% of hydrated lime in the mixtures has almost the same effect on the ageing indices. The samples containing hydrated lime always have a lower ageing index than the natural mixture samples without hydrated lime.
- From the SCB test, it could be concluded that hydrated lime replacement of the granite and limestone fillers caused a reduction in the increase of the fracture toughness after long-term ageing at 0°C. A larger increase in fracture toughness after ageing at 0°C could mean the development of fracture becoming more brittle. Thus, the beneficial effect of hydrated lime to reduce this effect is clear from the SCB.
- The tests for evaluating the recovered bitumen binders from different mixtures with and without hydrated lime show that the bitumen binder recovered from the granite mixture containing hydrated lime is always softer than the recovered binders from the granite filler only mixtures. In addition, the FTIR test shows that the hydrated lime reduces the ageing and hardening by reducing the oxidation products such as carbonyls and sulfoxides.

8.2.4 The main conclusions related to detailed study on the effect of hydrated lime on ageing

In this study, mastics with different percentages of hydrated lime were compared to other fillers (granite and limestone fillers) with similar percentages. The effect of hydrated lime on stiffening and ageing mitigation was studied by different means; (1) Basic properties: penetration, softening point and rotational viscosity, (2) Mechanical and rheological behaviour using the dynamic shear rheometer (DSR), and (3) Chemical approach with Fourier transform infrared (FTIR) spectroscopy. The evaluation testing aimed to understand the mechanisms of hydrated lime on ageing mitigation. In addition, more attention was given to study the interactions between hydrated lime and the bitumen which affect the ageing in bitumen mastics and mixtures. In terms of the testing performed in this study, the following conclusions can be derived:

- The filler type and its properties significantly affects the ageing indices. Hydrated lime decreases the ageing indices more than the other fillers after TFOT and PAV ageing.
- Increasing the concentration of hydrated lime in the mastics tends to decrease the ageing indices for the concentrations used in this study. However, increasing the granite filler concentrations in the mastics resulted in increasing the ageing rather than reducing it.
- For the bitumen recovered from the mastics, the recovered binder from the hydrated lime mastics is always softer than that recovered from the granite mastics for the same ageing conditions. In addition, this bitumen recovered from hydrated lime mastics shows significantly higher phase angles than bitumen recovered from granite mastics.

- The chemical analysis of the changes in mastics, recovered fillers and bitumen revealed that some interactions happened between the hydrated lime and some fractions of the bitumen. These effects were less pronounced in the case of granite fillers.
- The results from the FTIR test on the recovered bitumen from the mastics showed that less carbonyls were produced after TFOT and PAV ageing for the hydrated lime mastics than for the granite mastics, which showed the beneficial effect of hydrated lime on ageing.
- The results for the asphaltenes content test on the recovered bitumen show the same conclusion as the FTIR carbonyl index, which shows less ageing products available in the recovered bitumen from the hydrated lime mastics than in that recovered from granite mastics.
- The results from the FTIR tests on the recovered fillers prove the ability of hydrated lime to irreversibly adsorb some of the bitumen components (carboxylic acid products). This reduces the formation of the ageing products and consequently reduces the age hardening. Unlike hydrated lime, the granite filler does not exhibit this ability to react with bitumen.

8.3 Recommendations

From the research done in this Thesis, some remaining questions have been identified which can be further investigated in future research efforts.

- In this study, the effect of HL was quantified by adding 10% or 20% HL as a mineral filler replacement in the bitumen to form a mastic and only 1% and 2% HL was used for mixture level testing. More concentrations of HL can be tried to find out if there is any change in the performance of aged mastics and mixtures with the use of a higher or lower concentration. Also, the interval between each concentration can be reduced to get a more precise optimum HL content.
- Only one type of HL was used in this study. A comparative study can be made to see if there is any change in the performance with the use of different HL types.
- There are limited studies talking about the cost benefits of the use of HL in asphalt mixtures depending on the ageing parameters evaluations. Thus, it could be beneficial to prepare a mathematical model to quantify the cost benefit with the change in each test parameter. If the cost is modelled with the output of each test result, it will be very easy to understand if a specific combination is beneficial or not.
- Although, the use of FTIR to study the chemical changes in the bitumen and recovered fillers was easy and it was able to quantify these changes in the bitumen and the fillers to explain the interactions between bitumen and fillers, other chemical means to quantify this effect and to confirm the results from this study could be beneficial.

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