ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

INFLUENCE OF MINERAL FILLERS ON SHORT TERM AGEING CHARACTERISTICS OF ASPHALT MASTICS

BY

HIZBAWI SISAY

A thesis submitted to the department of civil engineering for partial fulfillment of the requirements for the degree of masters of science in civil engineering

Advisor

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February 24, 2022

Addis Ababa

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ABSTRACT

Asphalt pavements’ deterioration due to asphalt binder ageing has been a subject of many researches. Different aspects of ageing, its causes and prevention mechanisms were the main focus in this researches and asphalt mixtures, mastics and neat binders have been in use for these purposes. Among these material mixtures, asphalt mastics were found advantageous for they resemble asphalt mixtures better than neat binders and relatively cost less during production than asphalt mixtures. One way to reduce effect of ageing with mastics is to use appropriate mineral fillers with chemical properties to reduce chemical products of ageing or have physically capability to adsorb the molecules formed during ageing. In order to address this issue in more feasible way, this paper presents experimental tests conducted to investigate the effect of using unconventional and abundant filler materials (OPC, PPC, red brick powder and wood ash) as a substitute to a conventional (limestone) filler on the industry to lessen the effect of short-term ageing. Chemical, microscopic, mechanical and rheological tests are conducted on a 60/70 bitumen, the conventional and unconventional fillers as well as on mastics produced from the combination of bitumen and different filler proportions. The results are presented in terms of FTIR spectrums, microscopic images and complex shear modulus (G*) master curves. Consequently, the results suggest that all the fillers have a mitigating effect towards short-term ageing as the offsets in master curves of aged and unaged mastics are less significant than the neat binder. Furthermore, some of the fillers (red brick powder in an excellent way, OPC and PPC in a medium manner) have the desired characteristics to effectively replace the conventional filler used as reference while wood ash filler has relatively the worst characteristics to serve as a replacement for limestone filler.

ACKNOWLEDGEMENT

I would like to thank my advisor Dr. Abubaker Ahmed for his kind comments and the time he had given me. I would also like to acknowledge Mr. Atnafu Admas for his continuous support throughout the research, the highway laboratory technicians in the university and my dear friends who have contributed to this work. Last but not least, I am grateful for my family for their unconditional support.

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CHAPTER 1

INTRODUCTION

1.1. Background

Asphalt has been a widely used construction material for long time especially from the start of asphaltic pavements. The material has been referred and is referred here as asphalt binder to signify its primary function in asphalt mixtures, which is binding other constituent materials of the mixture. The physical properties and, ultimately, performance of this material is determined by its chemistry or chemical composition. The chemical composition of asphalt primarily depends on its crude oil source and refinery process [1].

Throughout construction and use of asphalt pavements, asphalt binder goes through different processes. One of these processes, which has been a subject of many researches is ageing of asphalt binder. Ageing of asphalt binder is one of the reasons accountable for progressive deterioration of asphalt pavements through time. The process is usually accompanied by stiffening and embrittlement of the binder, which in turn makes hardening of asphalt mixture to take place. As a result, pavement life will be reduced due to pavement distresses associated with the hardening [1]. The most important modes of pavement failure or distresses that are significantly affected by aging are fatigue cracking and rutting induced by vehicular loading induced and thermally induced cracking, and raveling induced by moisture induced [2].

Aging of asphalt binders is induced by chemical or physical changes during the production of the pavement and throughout its service life. The physical changes are due to a reversible process called physical hardening that can be attributed to molecular restructuring. The most important mechanisms among those which cause chemical changes in the ageing process are oxidation and loss of volatile components [3]. In chemical terms, aging first leads to a decrease in aromatic content and subsequently to an increase in resin content, together with a higher asphaltene content [4].

The chemical and rheological changes associated with ageing are well understood for neat asphalt binders as the result of much research on the subject. However, testing of aged asphalt binder alone does not appear to be adequate for predicting mixture performance. This is because of the fact that asphalt binders exist together with aggregates and fillers in asphalt pavements, and these components may have mitigating or catalytic effect that on aging. As a result, ageing tests to mimic the actual ageing process should consider combination of asphalt mixture components. This is either considering the whole mix or its subsets (i.e. asphalt mortar or asphalt mastic).

Because of the fact that, oxidative aging produces substantial changes in the chemistry of the asphalt-aggregate interface, particularly with an asphalt-aggregate configuration that is susceptible to aging, the aging of asphalt-aggregate mixes is influenced by asphalt and aggregate. However, the majority of the asphalt aggregate interface area corresponds to the fine aggregates and the filler, since these fractions possess a significantly higher specific surface area compared with coarse aggregates. Hence, testing of asphalt binder and filler together is an efficient approach to predict the performance of asphalt mixture [5], [6]. In this study, the blend of asphalt binder and filler particles passing the No. 200 sieve (smaller than 0.075 mm) is referred to as asphalt mastic. It is the binding medium that holds the aggregates of an asphalt mixture together, and it plays an important role as the link between bitumen properties and mixture performance.

Ageing of asphalt mastics can be different in many ways from the ageing of neat asphalt binder. Primarily, because of a significant decrease in the exposure to oxygen, that depends on the film thickness, due to the more viscous nature of the mastic and second, the filler in asphalt mastic forms a geometrical barrier to oxygen diffusion. This was already recognized by researchers [7], and could also limit oxygen diffusion in ageing tests whose movement is governed by oxygen diffusion. The presence of high filler content in some mixes may also enhance the potential risk of binder absorption when the filler is porous [8]. Even though, all these conditions may seem to result inappropriate interpretation, they are the reasons why asphalt mastic is used for the ageing studies to demonstrate the actual ageing process of binder in asphalt pavements.

Despite the fact that asphalt mastic ageing is influenced by the characteristics of the asphalt binder and the mineral filler properties, the properties of the fillers in asphalt mastic dominate in terms of physicochemical interactions between the binder and the mineral surface, as the fines are embedded in the bitumen and, thus, the majority of the surface area is generated by the fine minerals [5]. So, the contribution of the mineral fillers in the process of ageing is worth a thorough study.

Several physical and chemical processes are thought to govern the effect of mineral fillers during the aging process of asphalt mixtures. Some mineral components on the surface of fillers may catalyze bitumen oxidation [9]. The adsorption of polar asphalt compounds (i.e., asphaltenes) onto fillers is much larger than for other, less polar (i.e., resins) or nonpolar (i.e., aromatics and saturates) compounds [9], [10]. This phenomenon, in turn, makes the asphalt less oxidizable. Asphalt absorbed within the pore space of the fillers may have differing chemical and physical properties compared with bulk asphalt [11].

The effect of conventional mineral fillers such as hydrated lime has been studied previously and they were found to have an effect on the ageing process. But, the fillers in consideration were small in scope as they were mostly comprised of commercially available fillers. The fillers suggested other researchers for the sake of economy were not considered. These other fillers are those referred here as non-conventional mineral fillers. They are products of a wide range of locally available materials and thus have different physical and chemical characteristics. Hence, their effect on ageing of bitumen and the distresses associated with it will be different.

As a result, the purpose of this study is to develop a better understanding on the use of non-conventional mineral fillers and different conventional fillers in asphalt pavements in terms of their contribution to asphalt mastic ageing. Therefore, a short-term ageing study on bitumen-filler mastics involving Dynamic Shear Rheometer (DSR) and Fourier Transform Infrared (FTIR) spectrometry will be carried out and the chemical as well as physical changes involved under different mineral fillers will be compared.

1.2. Statement of Problem

Ageing is one of the reasons for the failure of asphalt wearing courses. The consequences of this process are a decrease in a level of comfort and safety which force pavement maintenance and rehabilitation activities. Beside the damage to lives and property, the pavement maintenance and rehabilitation works require a significant amount of budget for man power, machinery and construction material. The problem with construction materials is twofold. First, the process and the energy wasted in manufacturing makes pavement materials relatively costly which will make the rehabilitation process difficult especially for developing countries like Ethiopia. Second, most of the constituent materials to asphalt pavements are non-renewable and usually do not fit for reuse. As a result, studies concerned with cost reduction and environmental protection through the use of economic, reusable and renewable materials in addition to development of effective mixture designs are of paramount importance. Concerning the economics in asphalt materials, the mineral fillers in asphalt mixture (or asphalt mastic to be specific) could be a good area of research among other things. Waste materials such as stone dust and ash have been a subject of some studies and have been proved to enhance mixture properties. The studies were generally concerned with comparing the characteristics of these fillers with that of conventional ones and were not addressed to specific problems such as ageing. Besides, there is not much information on the impact of different types of conventional fillers that could be used in asphalt mixtures such as Portland cement. Consequently, a research on the impact of some fillers on crucial processes such as ageing to promote economical and environmentally friendly practices is worth considering. Such studies in combination with other material, processing and safety studies will result effective and efficient ways to construction and rehabilitation of asphalt pavements.

1.3. Objective

1.3.1. General objective

The main objective of this study is to examine the effect of some Portland cements (i.e. OPC & PPC), and some non-conventional fillers (brick dust and wood ash) as a replacement for limestone filler to mitigate the negative impacts of short-term ageing in asphalt mastics.

1.3.2. Specific objective

More specifically, the analysis is carried out for the following reasons:

- To present an ideal filler bitumen ratio for optimum performance of the stated filler types through critical concentration tests.
- To find out the effect of non-conventional fillers (i.e. brick dust and wood ash) on short term ageing properties of asphalt mastic when used as a replacement for conventional limestone filler and
- To determine the effect of different types of Portland cement (OPC & PPC) on short term ageing characteristic of asphalt mastic as a replacement for conventional limestone filler.

1.4. Research Questions

The following questions are answered in the thesis:

- Do the fillers have microscopic characteristics resembling the control limestone filler?
- Do the fillers have chemical characteristics favorable to mitigate short-term ageing in asphalt mastics?
- Do rheological tests on mastics incorporating these fillers justify the results from microscopic and chemical tests?

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

Bitumen is no more understood as a simple water proofing and sticky material. With continuous effort of researchers in different fields, it is now possible to chemically define its constituent parts and understand their interaction with other substances at microscopic level. The chemical and associated mechanical changes within bituminous mixes during application and life span of asphalt pavements are also fairly understood. Consequently, this chapter goes beyond the common definition to shade a light on the different chemical and physical properties that constitute its pro-founding function from different researches. It's characteristics and proportioning when in use with other materials (mineral fillers in mastic and aggregates in mixtures) are also presented. As the main aim of this thesis is to access effect of mineral fillers towards retarding the oxidative ageing of bituminous binders, previous researches on mechanism of ageing, it's simulation and effect on performance, and methods to retard ageing are reviewed and summarized.

2.2. Bituminous Binders and Mixes

Bitumen, a term used in Europe and in this paper interchangeably with the American term asphalt cement or simply asphalt, is a usually naturally extracted construction material in use for hundreds of years for its waterproofing and sticking properties. However, it was not until the synthesis of artificial bitumen from crude oils it finds its way in to modern construction industry especially in pavements. In present day terminology, bitumen is defined as a "virtually involatile, adhesive and waterproofing material derived from crude petroleum, or present in natural asphalt, which is completely and nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperature [12]."

Until modern refining technologies became available at the turn of the 20th century, bitumen has seldom been produced artificially [13]. The technology has progressed and currently almost all of the bitumen for pavement applications is obtained artificially by distillation of crude oil [14]. This, however, does not completely halted the market for natural bitumen as it is still in use in the paving industry as an additive for straight-run bitumen. Regarding artificial bitumen, its chemical composition and proportion may vary with the crude source and refinery process used [13].

In chemical terms, bitumen is mainly composed of carbon and hydrogen atoms. In addition, heteroatoms such as sulfur, nitrogen and oxygen with some traces of metals such as vanadium and nickel are also found. However, to understand the properties of bitumen sufficiently, it is usually characterized chemically as a composition of four fractions namely saturates, asphaltenes, resins and aromatics or usually in short as SARA [15].

Asphaltenes represent generally 5-20 wt.% of a paving grade bitumen [16] and are by far the more studied bitumen fractions because of their viscosity building role [15]. Asphaltenes now are defined as the insoluble part of a bitumen (or a crude oil) in n-heptane but soluble in toluene. Asphaltenes form a black powder at room temperature [16] and are largely responsible for the black color of the bitumen. They are also the most polarized molecules in the complex [13].

The other three fractions are collectively referred as maltenes which represent the soluble part of the bitumen in n-heptane. Saturates are responsible for forming a lightly colored or colorless liquid at room temperature while covering 5–15 wt.% of a paving grade bitumen [16]. They are the least polarized molecules after aromatics and resins.

Aromatics, also called naphthene aromatics, are the most abundant constituents of a bitumen together with the resins, since they amount for 30–45 wt.% of the total bitumen [16]. They form a yellow to red liquid at room temperature [16] and are somewhat more viscous than the saturates at the same temperature [17].

Resins, also called polar aromatics, also cover about 30–45 wt.% of the total bitumen [16]. Depending on the solvent used, they can out number aromatics. If saturates and aromatics are oily liquids at room temperature, resins form a black solid at room temperature [16].

The effect of the relative amount of these fractions on mechanical, rheological and physical characteristics of binders was a subject of several researches. In this regard, the fractions of bitumen are usually categorized as either polar or non-polar fractions. It has been reported that polar fractions are the ones responsible for the elastic behavior while the non-polar parts are the ones which provide the viscous behavior [18].

The difference in properties of the component fractions and the difference in relative amount from sample to sample, has made it difficult to obtain a bitumen that would work under all possible climates and conditions. In an effort to address such problems, pavement engineers grade them for use in a certain environmental condition or performance related criteria. Generally, they are graded either as a soft or hard binder; the softer binder being generally suitable for cold climates and the harder for hotter regions. Different physical tests are conducted to conform a bitumen to its desired grade.

Other specific grading mechanisms formulated by different national authorities are also available. Among them, penetration grading using a standard needle at room temperature is common despite being empirical and having some disadvantages. Thus, the name penetration grade bitumen. Penetration grading's basic assumption is that the less viscous the asphalt, the deeper a needle will penetrate [19]. Penetration depth is empirically correlated with asphalt binder performance. Therefore, asphalt binders with high penetration numbers are used for cold climates while asphalt binders with low penetration numbers are used for warm climates. However, it is the 60/70 penetration grade bitumen with penetration value of 50 ± 10 which is the most commonly used in most countries including Ethiopia. Even though, there are 80/100 and 40/50 grades which are used at times for some climatic conditions in different parts of the country [20].

Despite playing the major role in water proofing and binding, bitumen is not used alone in building a durable road surface. In fact, a road surface mixture is composed of coarse and fine aggregates, mineral filler and comparatively small amount of bitumen. The mix can be fashioned in several ways to make a pavement conform to a certain condition or climate but the mostly used mixes are hot mix asphalt (HMA) and warm mix asphalt (WMA). The main difference between the two is the temperature in which they are mixed and applied which is lower for WMA [21].

All the efforts applied to produce different mixes are to construct a durable and strong pavement which is at the same time environmentally friendly and economical. The durability of asphaltic concrete is greatly influenced by the environmental changes during the year between hot and cold temperatures and between day and night. High temperatures can soften the bitumen and consequently reduce the stiffness of asphaltic concrete making the mix more susceptible to rutting. On the other hand, low temperature can increase the stiffness of bitumen and reduce the flexibility of the asphaltic concrete, hence, inducing fatigue failure. As a result, cracking of the pavement surface may develop which adversely affects the performance of the asphaltic concrete. Thus, high temperature stiffness and low temperature flexibility are important properties in bituminous mixtures respectively to avert rutting and cracking [22].

A pavement design usually begins by determining the properties of available materials, environmental conditions and vehicular loads. Then a prediction of long-term and short-term performance will follow allowing engineers to make changes to their designs for better performance. The performance prediction has been made from mathematical models formulated from experimental tests on either binders and their mixes. There is no doubt that studies on mixes containing all the basic components will give the most accurate prediction. However, they are usually expensive and time consuming. Consequently, the focus is shifting on to binders and mastics characterization and extending the results to mixes. Asphalt or bitumen mastic is a combination of binder and mineral filler which is the actual binding agent between aggregates of a mix. In other words, it is an intermediate material that is closer to the asphalt mixture than the binder alone. The correlation between rheology of base bitumen and bituminous mixes has been found to be a positive one since effective models have been developed to predict even complex modulus of a mix [23]–[26]. Provided that the same domain of behavior, small strain or failure, is considered some studies have also mentioned that low temperature parameters of a bitumen can predict similar parameters on a mix [27], [28] . Regarding asphalt mastics, the fillers in mastic have larger surface area to bind with bitumen than aggregates in a mix. This makes mastic more representative of the actual reaction a bitumen will go through service life of a pavement. On the other hand, it is more realistic to consider mastic to predict rheology or other parameters of mixes since at least there is a reaction between a solid and a viscous material than there in in pure bitumen [29].

However, the problems involving asphalt pavements are not quite solved due to the number of variables involved. A complete solution should consider all possible properties of component parts, their interaction with each other, proportioning of parts and the reaction to different climatic and loading condition by each part or as a whole. As for the properties of the parts, both the chemical and physical properties need to be considered for they are responsible for the effectiveness of the interaction between parts and added change in behavior due to interconversion of different chemical compounds [30].

To accurately capture the intended properties, proportioning of component parts in asphalt mixes or mastic is of paramount importance. Earlier studies have been blending the parts on weight basis. The mechanisms are usually a fixed filler/bitumen ratio in mastics and fixed bitumen/aggregate and filler/aggregate ratios in asphalt mixtures. However, since different fillers and binders have different densities, conventional weight proportioning may give rise to excess or inadequate quantity of filler in the mix. Hence, volume proportioning has been used in some researches. The volume proportioning can be of some volume of binder or filler to a certain amount in weight of an aggregate or of a method to get an optimum mixture. The latter method stands on the notion that despite the advantages, filler addition must be rationally controlled because filler type and content should be determined according to the desired volumetric and physical-mechanical properties [31]. In previous studies, Ridgen [32] and Ruiz [33] recommended that a filler volume in a filler-bitumen matrix should be limited volumetrically to avoid over stiffening.

Later on, practical methods such as ‘‘Universal Caracterizacio´n de Ligantes’’ (Universal Binder Characterization) or shortly the UCL method were developed to characterize filler-bitumen matrix and coined the term critical concentration which in turn depends on the type of filler and binder used. Filler critical concentration is reached when a mastic starts to stiffen. The critical concentration corresponds to a dispersion of filler particles in the bitumen moving as freely as possible but in contact with each other. In other words, the critical concentration is attained when the applied stress is consumed in the viscous deformation of the continuous bituminous medium and frictional resistance between particles is at a minimum. Such a packing is expected in the sediment obtained by simple settling of filler dispersion in a fluid medium chemically related to binder, like kerosene. It was suggested that it is advantageous to use fillers in mastics even to retard ageing as long as their content is not beyond the critical concentration [34].

The critical concentration of a filler can be found from a test proposed by Ruiz [33] and later got into Argentinean standard IRAM 1542.

$$C_c = \frac{P}{VG_f} \qquad 2.1$$

where C_c is the critical concentration, P is the filler dry weight, V is the volume of filler settled in kerosene for 24 hours and G_f is the filler specific weight.

When filler is added to mixes, bituminous mastic viscosity increases gradually with increasing the volumetric concentration:

$$C_v = \frac{Filler\ volume}{Filler\ volume + Bitumen\ Volume} = \frac{\frac{P_f}{G_f}}{\frac{P_f}{G_f} + \frac{P_b}{G_b}} \qquad 2.2$$

where P_f is the filler weight percentage, P_b is the bitumen weight percentage, G_f is the filler specific weight and G_b is the bitumen specific weight.

So, it is the ratio C_c/C_v which is usually maintained to get the intended purpose out of a certain filler. It is usually between 0.9-1.1 for most fillers.

Once the property of component materials and their relative amount is addressed vehicular loads and processes from environmental conditions need to be accounted in pavement design. One of such processes is bitumen ageing.

2.3. Ageing of Bituminous Binders

As known to many, bitumen is easily exposed to the actions of natural heat, light and oxygen since it is usually used as a finishing material in construction industry, mostly in pavement engineering industry. The exposure will tend to degrade the bitumen to some level by certain processes shortening life of an asphalt pavement [35]. One of such processes is bitumen ageing. Bitumen ageing is primarily associated with the loss of volatile components, the introduction of polar oxygen-containing chemical functionalities on asphalt molecules causing increased molecular interactions and aromatization, and ultraviolet radiation during asphalt mixture construction (short-term ageing) and service (long-term ageing) [36].

2.3.1. Mechanism of ageing and its simulation

Based on reviewed literature, the major processes that cause asphalt binder aging are oxidation, volatilization, and UV radiation [37]. Among these, oxidation was found to be the main cause of bitumen ageing and ageing driven by the other processes is negligible [38], [39]. This is only considering the overall bitumen matrix in a pavement structure for it is UV radiation which causes severe damage if surface bitumen alone is considered [40]. As a result it is oxidative ageing which is mostly covered in literature even though some suggest multi-factor coupling ageing test should be considered since it is closer to the actual service conditions of bitumen [41]. With oxidation, a bituminous binder ages when highly polar molecules such as polar aromatics interact with oxygen and the state of molecular dispersion within the binder is altered producing new polar molecules with oxygen-containing chemical functional groups. This in increase polar functional groups reduces molecular flow and kinetics. The material becomes stiffer with increased viscosity, reduced phase angle, and resulting a material susceptible to various stresses. Moreover, the process gets intensified with time as more polar molecules are produced. On the other hand, less reactive molecules with low polarity or nonpolar elements suffer less aging or no aging (oxidation) [42].

Much effort has been made to obtain information on the organic molecular groups in pure and aged binders in which new functional groups are formed. Among the groups, the heterogeneous functional groups in binders have been identified to have the largest impact on changes in property since they are highly polar and relatively more interacting groups. They are made up mainly of large organic molecules such as carboxylic acids, anhydrides, ketones and sulfoxides [43].

To summarize, in chemical terms ageing causes

- a reduction of the maltene fraction and an increase of asphaltenes and resins;
- aromatics transform into resins, which in turn transform into asphaltenes;
- polar functional groups increase (mainly the carbonyl and sulfoxide groups), as well as the asphalt's molecular weight [37].

Following the chemical changes, the physical changes during ageing are

- increase in binder viscosity and stiffness;
- behavior change from ductile to brittle;
- loss of cohesion and adhesion with aggregates and
- reduction in resistance to fatigue, moisture damage, low temperature cracking and tire wear resistance [37].

Thus, type of bitumen crude source and its production process are the major parameters for base bitumen which dictate its performance under aging [44]. Along with these, it has been also reported that, the chemical bonds that surround the aggregate or fillers, as well as their type, have an influence on the bitumen ageing process [37]. Degree of exposure and time are other things that need to be considered in aging studies as damage due to ageing increases with these parameters [40].

The ageing process observed in field is simulated in laboratory with two distinct steps. Short-term ageing of bituminous binders is a well-accepted concept that represents ageing of binders during plant mixing, production, transportation and construction. Simulation of this ageing is carried out in controlled laboratory conditions and these aged binders are used to predict binder rutting performance. Similarly, the simulation of long-term ageing of binder accounts to ageing of the binder during service life of the pavements and these binders are used to characterize the binder response to fatigue performance in the SUPERPAVE test protocol. Two well-established laboratory test methods are generally practiced for evaluating the short-term ageing of bitumen binders: the thin film oven (TFO) test method where a pan filled with bitumen is placed on a rotating pan on the horizontal plane and the rolling TFO (RTFO) method that uses cylindrical glass bottles filled with bitumen which are rolled in the vertical plane. It was reported that ageing susceptibility of binders may be ranked differently when different evaluation methods are used. However, regardless of the type of parameters measured, a strong correlation was observed between TFO and RTFO, and the two ageing procedures show similar severity [36].

In the case of long-term ageing, although developing a single test method to characterize aging sensitivity seems impossible due to the many variables involved, the mostly practiced method is simulation in a pressurized ageing vessel (PAV) under constant conditioning of pressure and temperature. The use of same conditioning in characterizing materials for pavement construction and research will facilitate the exchange of data and enable faster developments [45]. The RTFO and PAV are the part of the test protocol of the mechanical SUPERPAVE specifications [46].

The reliability of the laboratory processes can be checked through comparison of changes in chemical properties and the rheological response of aged bitumen with the one obtained from field. The chemical changes can be quantified from methods like Fourier-transform infrared (FTIR) spectroscopy while the rheological changes can be captured from dynamic shear rheometer (DSR) tests. In terms of chemistry from FTIR tests it was reported that bitumen under ageing shows a high variability of the carbonyl and sulfoxide functional groups. Furthermore, it was confirmed that two distinct phases of ageing, with an initial increase of sulfoxides and a second phase in which carbonyls formation occurs [47].

These changes in chemical composition do increase viscosity of bitumen and consequently cause asphalt hardening [1], [22]. It is this hardening or embrittlement of bitumen which makes ageing one of the most important factors for pavement distress types, resulting in changes to desirable physical properties. In the past, researchers have been trying to correlate the physical changes through changes such as penetration and ductility [48]. However, it was later suggested that these empirical properties do not sufficiently describe the changes with ageing and expressing the changes in terms of performance based rheological parameter changes with temperature and frequency is better [7]. The rheological parameters are usually complex modulus (G*) and phase angle (δ) and researchers have been doing so in recent decades. In the shear mode under dynamic testing, G* represents the total resistance to deformation, while δ represents the magnitude of deformation [7]. Moreover, analysis of rheological properties showed that the effect of ageing can be observed from a shift of the black space diagram curves towards lower phase angles; moreover the shape of the curves changes to a straight line and the curvature reduces [47].

2.3.2. Effect of ageing on pavement performance

Ageing is one of the major factors to development of pavement distresses. Researches have been conducted through the years to thoroughly understand the way ageing affects performance of pavement surface and the effect of different parameters on the whole ageing-performance dilemma. The studies have been using a virgin bitumen or a one extracted from pavement surfaces while others use mastic or the whole mixture.

Research [36] has shown that ageing influences bitumen chemistry and rheology significantly. Chemical changes include the formation of carbonyl compounds and sulfoxides, transformation of generic fractions, and increases in number of large molecules or molecular association and molecular weight. Hence, the mechanical properties of aged bitumen become more solid-like, as indicated by increased complex modulus and decreased phase angle. The increase in viscosity and consequent hardening is positively related to pavement age [49].

Some studies have demonstrated the effect of ageing on pavement's fatigue performance regardless of its type (oxidation during manufacture or during the service life). Miró and others had considered the relationship between temprature and ageing with fatigue performance in modified and neat binders. They have reported that ageing irrespective of binder type increase the risk of fatigue cracking. However, after ageing it was the modified binders which were found to be equally suspectible to fatigue failure than the neat binders eventhough the modification was primarily done to lower fatigue suspectibility [50]. This can be extended to bituminous mortars containing bitumen, filler and fine aggregates [51]. Testing temprature was also noted to cause a misjudgement on the effect of ageing at times since at certain tempratures, the modified binders may be suspectible to some visco-elastic phenomena (plastic flow, thixotropy, etc.) that co-exist with fatigue damage [50]. The relative contribution of ageing on fatigue damage with temperature and binder type has also been recognized in [52]. With a new evaluation method using DSR, a negative relationship between fatigue properties and laboratory ageing of asphalt mastic was reported by Van den Bergh and Van de Ven [53]. Their conclusion was based on the fact at an equal stress level, the number of loading cycles to failure for aged samples is higher than that of unaged samples. It has been also reported that ageing has a greater effect in mastic rheology than filler particle size [54]. The trend was complemented by López-Montero and Miró as they, from their mixture study, have similarly reported that aged mixtutres show a sharp decrease in initial modulus in fatigue tests while initial modulus of unaged mixture decreases progressively with the number of fatigue cycles. Consequently, failure strain of aged samples was lesser. They further reported that the effect of water to either stiffness degradation or failure strain is rlatively small compared to ageing although they have used dense mixtures difficult for water immrsion [55]. The negative impact of binder ageing on mixture fatigue resistance and the fact that it becomes notable with temperature increase was reported in [56].

Bitumen ageing could also have significant effect on rutting performance of pavements. The topic has been a focus for some researchers. Among them, Singh and Kumar [57] from their Linear amplitude sweep (LAS) and Multiple stress creep recovery (MSCR) tests conclusively shown that ageing improves the stress susceptibility of the asphalt binders with respect to rutting parameters. The effect can be directly related to bitumen chemical composition and it was suggested that some ratio indicating the relative proportion of component parts can be put to a limit to improve rutting performance after ageing [58]. In case of binders rejuvenated with chemicals like waste engine oil, ageing will make them more susceptible to rutting than virgin binders [59]. On the other hand, some additions like Nano silica have a positive effect towards providing aged pavements adequate rutting resistance [60].

As for mastics, it was found that different fillers will result in different degree of rutting resistance and it is the specific surface area of the fillers which has a significant effect among the properties [61]. Different binders from different sources whether they have similar grade or not will also result different rutting performance on ageing [62].

Regarding studies with mixtures, Radziszewski have concluded that rutting performance is depndent on the type of mix used i.e. Superpave mix, porous asphalt mix, stone mastic asphalt or other, and on the type of modification used on a neat binder. Superpave mix and modification using fine rubber were found to be more resistant to rutting [63]. Moreover, WMA mixes generally provide lesser performance to rutting at higher temperatures than HMA mixtures while wax based mixes perform better than chemical based ones within the WMA groups [64]. A definitive trend cannot be suggested however when considering other WMA technologies [65].

With respect to low temperature performance, it has been confirmed through bending beam rheometer tests that ageing deteriorates the low temperature cracking resistance of asphalt binder and the trend can be also positively correlated with asphalt mixtures [66]. In addition, properties of base bitumen or any other modifier should be rationally selected since they have significant impact [67] and some suggested that rheological properties of binders from conventional tests could indicate low temperature cracking resistance behavior [68]. With low-temperature bending and splitting tensile tests it was found that amount of mineral filler should be controlled not to exceed some amount as it will embrittle asphalt mixtures during long-term aging, thereby deteriorating the tensile properties [69]. Quite a few studies have been conducted on mixtures. Among them, a study by Wu and colleagues [70] concluded that short term ageing condition in laboratory has the major effect on low temperature cracking resistance of polyester fiber asphalt mixture.

To conclude, beside the study of asphalt binders and mixtures as specimens there is also a large portion of literature on asphalt mastic to predict pavement performance. Asphalt mastic is asphalt mixture without the mineral aggregates. It is usually used as a substitute for asphalt mixtures in pavement performance studies for it is the one which actually affect bitumen behavior in asphalt pavements. This notion is from the fact that it is the mineral fillers which provide most of the surface area for the binder to stick on and affect its interactions. Thus, it is largely their property which affects the properties of the mix and ultimately pavement performance.

The research on asphalt mastic is large involving from studies on its constituent parts to the effect of additional materials on mastic properties. They area even gets bigger considering the micro-mechanical and numerical modeling studies to predict mastic behavior [71]. As for the additional materials, different fibers including basalt, diatomite, polyester and glass in addition to SBS and others have been proved to improve mechanical properties of asphalt mastic with conventional fillers at different temperature ranges [72]–[74]. However, the large portion of these studies have been on effect and improvement methods of bitumen and mineral filler properties as constituent asphalt mastic materials. Among them, Chao Li et. al. from their study on different steel slag fillers and limestone have concluded that addition of such mineral fillers in to bituminous materials will enable the bitumen-filler complex to own a better high-temperature deformation resistance. They have also indicated that it is the steel slag containing mastic which perform better than the limestone containing ones due to the stable mastic structure provided by the steel slag filler [75].

Regarding low-temperature cracking resistance, Qiushi Li and his colleagues have established that mineral fillers (steel slag powder and limestone powder) have a positive effect. It is again the steel slag powder containing mastic which have higher resistance though it was mentioned that the resulted should be confirmed by further tests on asphalt concrete mixtures [76].

2.4. Anti-ageing in Bituminous Binders

On the basis of previous literature, it was shown that ageing is one of the major processes that shorten pavement life. However, earlier studies were limited to studying the ageing process without improving the ageing resistance [22]. Hence, in order to prolong the life of asphalt pavement, mechanisms to reverse binder ageing have been one of the hot topics in bitumen researches contemporarily [35]. Anti-ageing can be done either by modifying the binder to improve its properties or protecting it from the mechanisms that cause ageing. The latter is almost impossible. As for the first option, an internal report of the Asphalt Institute identified 48 types of bitumen modifiers comprising of 13 polymers, 10 hydrocarbons, 6 mineral fillers, 6 antioxidants, 6 anti-stripping additives, 4 fibers, 2 extenders, and 1 oxidant [77]. An ideal modifier should be able to control age hardening and be compatible with any type of bitumen [22]. Although many different modifiers have been used in bitumen modification, over 90% of modification goes to polymer modification or addition [78].

2.4.1. Polymer Modification of Bitumen

Generally, the polymer modified binders tend to have high viscosities at high temperatures posing workability difficulties during the production of asphalt mixtures [78]. Despite that, polymers can impart desirable physical properties to the base bitumen through forming a 3D cross-linking network. It is evident that the identification of chemical composition and reactions of base asphalt during hardening from aging can help in its modification to produce longer-lasting asphalt pavements [79]. Again, the property of resultant polymer modified binders was reported vary depending on the type of modifier, modifier content, mixing conditions (temperature, mixing time, shear intensity) [78].

Various elastomer and plastomer modifiers have been sought to address this problem. Polymer modifiers vary in function and effectiveness, and development of modified bituminous material to improve the overall performance of pavements has been the focus of research for the past few decades [22]. Consequently, it was suggested that the degree of modification or effectiveness should be judged based on resistance of binders to certain distresses like fatigue and rutting damage [78].

Various polymer antioxidants provided by natural resources such as phospholipids, ascorbic acid as well as lignin from rice husk where also subject of research in order to reduce age hardening in asphalt binders and it was reported that phospholipids-treated binder exhibited the highest resistance to oxidation and the lowest age-hardening effect compared to the other tested anti-oxidants [80]. In addition, epoxy polymers have been reported to result in reduced sulfoxide in asphalt mastic indicating their use to limit oxidation of asphalt binder [81]. The work on polymer modification is rather big and since it is the main subject of this thesis interested reader is referred to read [79], [82]–[84].

2.4.2. Mineral Filler Modification of Bitumen

Asphalt binder can be also modified by mineral fillers to resist ageing. Asphalt binder and filler blend to form asphalt mastic which constitutes the effective adhesive film in asphalt concrete. An asphalt mastic imparts most of its characteristics to the asphalt concrete mixture and also dictates several forms of distresses in asphalt mixtures and pavements [29]. So, pavement performance can be improved through better engineering of the mastic which requires a fundamental understanding of the binder properties, filler properties and physico-chemical interaction between asphalt and filler.

The modification by fillers can be clearly seen from bitumen and mastic tests under aging, as it is the mastic which will be stiffened less under ageing [85]. The less stiffening is a result of prior stiffening of bitumen by mineral fillers. Though there are different mechanisms towards the stiffening action in of fillers, the one from just rigid nature of the fillers (volume filling) and micro scale physico-chemical interaction between asphalt and fillers take the most part [86]. Physico–chemical interactions result in adsorption of polar fractions of the asphalt onto filler surfaces leading to the formation of an interphase layer on the surface of particles and modifying the asphalt binder matrix [87]. A greater stiffening effect is observed for fillers which induce greatest microstructural changes as a result of physico– chemical interaction which is mostly affected by filler specific surface area. Physio–chemical interaction is anticipated to lead to a softening or decrease in complex modulus of the effective asphalt binder matrix and increase in complex modulus of the adsorbed or fixed asphalt since polar components adsorb to the surface of the filler [29]. Thus, results suggest the formation of adsorbed interphase layer plays a more critical role in determining macroscopic rheology of mastics than softening of the binder matrix [87]. Furthermore, it was reported that the effected thickness of binder–filler interaction was nanoscale [88] which becomes thicker with the increasing of filler volume fraction[89]. Within this specific thickness, the ‘‘bee’’ structure of asphalt surface disappears gradually, and the modulus increases significantly when the tested samples are closer to the aggregate surface [88]. The interaction increases with aging degree [90].

In chemical terms, some results show that a higher content of alkaline mineral filler within the critical volume fraction range produced a greater interaction ability between the asphalt and filler which intern affects the aging performance [30]. Moreover, in comparison to inert fillers like basalt, active fillers like hydrated lime perform better to improve performance of asphalt binders under ageing [91] . However, the interaction is more of physical [30] and the finer the filler is the stronger the interface interaction is [23], [89]. In light of this, Buttlar and his colleagues showed that hydrated lime improves stiffness of asphalt mastic through physiochemical reinforcement beside its basic volume filling reinforcement. They have also showed that hydrated lime provides better results than baghouse fillers in this aspect [86].

The effect that microstructure of mineral fillers play was also studied by researchers among others by Liu and his coworkers. They have concluded that volcanic ash fine filler improves viscoelastic properties of Styrene-Butadiene-Styrene (SBS) modified asphalt mastic. It was shown that it has "bumpy" morphology and Nano-porous structure allowing it to have more areas to interact with SBS and bitumen. Besides, it provides more chances for the SBS modifier to play a major role in improving mastic properties through its elasticity forming a crosslink network [72]. Other property which need to be taken in account is specific surface area (SSA) of mineral fillers. It is reported that among other properties like density and hydrophilic property it is this property which plays a great role in stiffening and retard ageing of bitumen. Cheng et al. have reported that diatomite filler which provides more specific surface area improves middle and high temperature properties of asphalt mastic better than hydrated lime, limestone or fly-ash while having lower hydrophilic properties [74]. However, conclusions based only on SSA should not be final as it was reported that some fillers would stiffen the mix less because of their round shape grains even though they have higher surface area [92]. The effect of other filler morphological characteristics was also confirmed by other researchers and they have concluded that different performances are not affected by similar properties. For example, it was shown that fatigue behavior is more sensitive to angularity index, average diameter, aspect ratio and fractal dimension while rutting is not [93].

Das and Singh conducted tests on hydrated lime and basalt containing asphalt mastics to access their ageing, rutting, thermal cracking and fracture potential. It was found that beside the low temperature cracking and improved rutting performance, hydrated lime can significantly decrease the ageing potential of asphalt mastic. Increasing the proportion of hydrated lime up to 20% will get a proportional improvement to ageing with quantity of filler [91]. In agreement with this, D. Lesueur et al. using a new method to replace RTFO and PAV have put forward that hydrated lime slows down ageing more than other active fillers like Portland cement and that mineral fillers from crushed limestone or granitic aggregate have no effect on bitumen ageing [94].

Xing and others have devised a new method to study the long-term aging properties of SBS modified bitumen. It was found out that, with a method maintaining filler/bitumen ratio before and after ageing, mineral fillers (limestone and ash) will slow down the ageing of base bitumen. They will also further affect the degradation of SBS modifiers due to ageing with ash having the greater effect in contrast to limestone. [95]. Beside the ash used here, larger particle steel slag powder was also reported to decrease the degree of bitumen ageing better than limestone filler due to the fact that it contains higher CaO content than limestone filler, have rougher surface texture and higher specific surface area. From chemical point of view, the presence of CaO will enable the steel slag powder to absorb more polar components (asphaltene) of the bitumen with help of the mentioned physical properties [76]. Limestone filler however was found to have a lower effect to improve temperature sensitivity of asphalt mastic than some fillers such as granite and andesite [89]. In another research, it was mentioned that it is the basic nature of limestone filler which plays a crucial role in its interaction role. The material has a stronger adsorption capability and catalyzes the oxidation of bitumen more than acidic fillers such as gritstone [96]. Besides, it the mostly used filler type in different parts of the world [97]. The reason for its wide use needs another research since some suggest other mineral fillers perform better in some conditions. For example, granite and marble fillers were reported to result in better rutting performance than limestone filler in mixtures [98].

All things considered, the proportion of fillers in asphalt mastic should also be of major concern [3], [99]. X. Zhu et al. in their study regarding the effect of filler content on different properties of asphalt mastic using a molecular dynamic simulation have mentioned that increasing content of silica particles in bitumen -silica matrix will decrease interaction between bitumen particles while increasing the free volume in the mix. This in turn will make the mastic prone to diffused gas and age easily [100]. In terms of performance, it was stated that putting amorphous Carbon powder beyond a certain ratio in a mastic may even have a detrimental effect on rutting and fatigue resistance [101]. The impact of filler volume is not as easy it seems for it could have much more effect than bitumen or filler type [90]. Filler volume in asphalt-filler matrix could even the linear viscoelastic range for LVE decreases with increase in filler volume [102] even though the degree depends on the type of filler used [103].

Property of asphalt binders should be also accounted since aging may affect the interaction between filler and asphalt through the asphalt’s active components. It was reported that a bitumen with more asphaltenes and resins will have a stronger interaction ability [104]. Bitumen modification may also alter the effect of fillers on ageing related stiffness. Another research showed that in mastics with coal combustion byproducts as a filler and with unmodified binders no determinate effect on aging related stiffness was observed while for those with polymer modified binder, the fillers happen to enhance its properties as noticed by a significant retardation in aging related stiffness [105]. As a result a certain filler/polymer combination will result an absolutely different result from the other [106].

In contrary to the method followed here, some suggest that studies on contribution of individual component properties are not enough to characterize the asphalt filler system as a whole and the process it goes through. In order to address the issue, they tried to capture changes of some parameters which are functions of component properties such as average particle size, gradation, particle shape, presence of agglomerates, degree of dispersion, and the asphalt-filler interface with ageing and concluded that it is a better way of characterizing than previous methods which largely on component property like Rigden's fractional voids approach which is based on the properties of fillers alone [107]. However, the approach is cumbersome and not suitable to suggest modification on specific properties to improve pavement performance.

Finally, beside their contribution to enhance aging performance filler and binders also need to provide low cost and good environmental impacts. In this regard, wastes such as fly ash, stone dust and brick dust are good candidates [108]. Other "un-conventional" fillers such as ash with brick dust may also be considered after a thorough analysis. For a start, they do provide good stability and deformation characteristics to mixes [109].

2.5. Summary

In summary, a review of previous literature reveals that aging of bituminous binders is one of the major processes that could alter performance of asphalt pavements. Besides, it leads to the following conclusions and requirements for aging studies:

- Aging of bitumen is primarily caused by oxidation of its molecules during mixing, laying or service life of pavements. Aging will cause increase in certain chemical groups such as sulfoxides and carbonyls consequently resulting in hardening or embrittlement of the bitumen.
- The process can be effectively simulated in laboratory through RTFO and PAV tests while results or chemical and physical changes are best quantified with mechanisms such as FTIR and DSR respectively.

- Samples laboratory aging or the performance tests can be base binders, binders extracted from asphalt mixtures or asphalt mastics. A good (but not perfect) correlation among the performance of these sample types under similar ageing conditions was observed and using mastics is a twofer, the material being a good representative of actual asphalt mixture and give ease to perform the described tests on.
- Performance changes in mastic aging are expected to not only be influenced by the characteristics of asphalt binder but also by the properties of the mineral filler, as well as the molecular interaction between the two components. Among others, the quantity of polar components in bitumen, specific surface area of filler and filler chemical composition are the major parameters identified to affect mastic properties with aging.
- Relative amount of bitumen and mineral fillers in a mastic also have a major impact and it is volume proportioning advised to be followed for mastic and mixture tests since a weight basis approach could result under/over stiffening and
- Beside their main purpose in controlling age hardening, mineral filler use needs to serve the purpose of environmental conservation as well as economy.

Taking all conclusions in to consideration, analysis of the effect of some conventional and unconventional fillers on aging performance of asphalt mastic was featured in this thesis with a careful proportioning of component parts to result an optimized mix.

CHAPTER 3

METHODOLOGY

3.1. Introduction

This chapter will report the process followed to do the research along with the materials and equipment used. On account of the objectives and recommendations from literature materials were characterized both chemically and physically. A method of proportioning to obtain an optimum use of mineral fillers in mastics is described. Finally, the methods used to describe mastic behavior with DSR and analysis methods are outlined.

3.2. Materials

The raw materials used are nothing but the basic asphalt mastic ingredients, mineral filler and bitumen which form asphalt mastic in different proportions and combinations.

3.2.1. Bitumen

The bitumen (B) used in this study is a binder having penetration grade of 60/70 which is suitable for Ethiopia's climatic condition and used widely throughout the country. The sample was obtained from Ethiopian Construction Design and Supervision Works Corporation (ECDSWCO) material laboratory. It was latter tested to check if it conforms with the limits outlined in national manual. The pavement design manual of Ethiopian Road Authority (ERA) on Table 8.3 in Volume-I of its module lists three types of penetration grade binders (40/50, 60/70 and 80/100) for use in Ethiopia along with the limits to different empirical performance variables. Standard test methods and limits for 60/70 are tabulated here for easy reference.

Furthermore, additional physical properties such as specific gravity were also determined in order to calculate critical concentration of filler in a mastic. Besides, the bitumen was characterized chemically with FTIR to trace the changes with aging.

Table 3-1: Requirements for penetration grade bitumen

Test		Corresponding ASTM test standard	Limits for 60/70 bitumen
Based on original bitumen			
a) Penetration at 25 °C		D5	60-70
b) Softening point (°C)		D 36	46-56
c) Flash point (°C)	min	D 92	232
d) Solubility in trichloroethylene (%)	min	D 2042	99
After TFOT heating for 5h at 163 °C (D 1754)			
a) Loss by mass (%)	max		0.5
b) penetration (% of original)	min	D 5	54
c) Ductility at 25 °C	min	D 113	50

3.2.2. Mineral Fillers

Five types of mineral fillers are used to be mixed with the aforementioned bitumen sample. The first of these is a hydrated lime (L) which has been proved to have a significant impact on mastic ageing properties and used Worldwide as a conventional mineral filler. Hence, it is used as a control mineral filler in this thesis. The other four are used to test their effect as on ageing as waste and readily available materials. The first two are Portland cements which are readily available and manufactured with in the country. They are designated here using the first two letters from their usual acronyms. Ordinary Portland Cement will be referred henceforth as OP and Pozzolana Portland Cement as PP. Fillers obtained from waste red bricks and wood ash are also used here to study their use as a substitute material for the standard mineral filler. The filler obtained from the red bricks is designated here as RB while A is used for the ash obtained from logs of Eucalyptus tree previously used for formwork purposes.

The fillers are characterized by their specific weight and further through their critical concentration. In addition, the morphological characteristics of the fillers was determined through scanning electron microscopy (SEM). Chemically, they were subjected to FTIR tests to determine their original functional groups.

3.2.3. Asphalt Mastics

Four groups of asphalt mastics each with different filler types and proportions by percent volume were prepared. Mastic samples were made first by mixing L filler with B proportioning filler and bitumen to result optimum performance using filler critical concentrations. Then the L will be replaced by the other four filler at percentages of 25%, 50 %, 75 % and 100% by volume to produce a total of 17 different mastics. The samples with their names and proportions are listed in the following table.

Table 3-2: Laboratory produced mastic samples

Groups	**Naming**				
	Control	**OPC**	**PPC**	**Red brick**	**Ash**
100% of each filler	**B+L**	B+O	B+P	B+R	B+A
75%L+25% other fillers	-	B+75L25O	B+75L25P	B+75L25R	B+75L25A
50%L+50% other fillers	-	B+50L50O	B+50L50P	B+50L50R	B+50L50A
25%L+75% other fillers	-	B+25L75O	B+25L75P	B+25L75R	B+25L75A

The proportioning was performed converting the percentage volumes in to proportional weights using specific gravities of fillers and bitumen. The volume proportions are however initially calculated from specific gravities and critical concentrations of fillers determined using IRAM Standard 1542 – Argentina described briefly later in this chapter. Sample calculations showing the proportioning procedure are given here for B+L and B+50L50O.

With L specific weight (G_f) = 2.70 g/cm^3, L critical concentration (C_c) = 0.33, bitumen specific weight (G_f) = 1.02 g/cm^3, assumed bitumen weight (P_b) = 45.0 g and assumed ratio $C_v/C_c = 1$, equation 2.2 will result

$$C_c = C_v = \frac{\text{Filler volume}}{\text{Filler volume} + \text{Bitumen Volume}} = \frac{\frac{P_f}{G_f}}{\frac{P_f}{G_f} + \frac{P_b}{G_b}}$$

$$\Rightarrow P_f = \frac{C_v * G_f * P_b}{G_b * (1 - C_v)} = \frac{0.33 * 2.70 * 45}{1.02 * (1 - 0.33)} = 59.4 \text{ g}$$

$$\Rightarrow \text{filler/bitumen ratio} \, (P_f/P_b) = \frac{59.4}{45.0} = 1.32 \text{ (in weight).}$$

If a total of 35 g mastic is required e.g. for RTFO sample, $\mathrm{P_f = (59.4/(45 + 59.4)) \times 35 = 19.9\ g\ and\ P_b = 15.1\ g}$ are required.

Similarly, for 50L50O filler with $G_f = 2.91\ g/cm^3$ and $G_{OPC}=3.13\ g/cm^3$

$$\mathrm{P_f = \frac{C_v * G_f * P_b}{G_b * (1 - C_v)} = \frac{0.28 * 2.91 * 45}{1.02 * (1 - 0.28)} = 48.3\ g}$$

$$\Rightarrow \mathrm{filler/bitumen\ ratio\ (P_f/P_b) = \frac{48.3}{45.0} = 1.07\ (in\ weight).}$$

If a total of 35 g mastic is required e.g. for RTFO sample, $\mathrm{P_f = 48.3/45 + 48.3 = 18.1\ g\ and\ P_b = 16.9\ g}$ will be needed. In order to calculate the proportion of a 75% L and 25% O by volume, P_f is converted to volume and each will take their part. Thus,

$V_{HL} = 0.75 * \mathrm{P_f/G}_f = 0.75 * 18.1/2.91 = 4.8\ cm^3\ and\ V_{OPC} = 0.25 * 18.1/2.91 = 1.6\ cm^3$ will be needed. Again, for ease of measurement the volumes will be converted in to weights with specific gravity of each filler type. As a result, in order to obtain a 35 g mastic sample of B+75L25O $\mathrm{P_{HL} = V_{HL} * G_{HL} = 13.1\ g,\ P_{OPC} = V_{OPC} * G_{OPC} = 5.0\ g\ and\ P_b = 16.9\ g}$ is needed.

All mastic mixing was done manually. The bitumen was stirred by hand and the accurate mass of filler was added slowly while the stirring was continued. The mastic will be continuously stirred as it cools down until the temperature become low enough to prevent the filler from settling. The mastics were then poured into small vessels for later testing. Before each test, each mastic was heated until it becomes liquid enough to pour and stirred to ensure homogeneity.

3.3. Methods

3.3.1. Bitumen tests

The tests on the base bitumen are of two types. The first group of tests include those conventional tests used primarily to conform its property with the limits put down by national standard. The second group of tests, including DSR and FTIR tests, are not unique for the base bitumen and are performed in order to compare the base bitumen properties with properties of the different mastic samples prepared from the virgin bitumen. They are to trace the effect of mineral fillers from base bitumen perspective. Since they are not exclusive to base bitumen, description of the tests is provided in later sections of this chapter.

The first group of tests are those described in Table 3-2 along with specific gravity test. The tests are standardized and a brief description can be referred from a standard document. However, a small description is made here for easy reference.

3.3.1.1. Specific gravity of bitumen

The quantity was determined with the pycnometer method according to ASTM D 70-03 or AASHTO T 209. Specific gravity of the sample was calculated from its mass and the mass of water displaced by the sample in the filled pycnometer from the following equation.

$$Specific\ gravity, G_b = \frac{C - A}{(B - A) - (D - C)} \tag{3.1}$$

where A = mass of pycnometer (plus stopper), B = mass of pycnometer filled with water, C = mass of pycnometer partially filled with asphalt, and D = mass of pycnometer plus asphalt plus water.

3.3.1.2. Penetration Test

In order to measure the consistency (hardness or softness) of the asphalt binder, the penetration test was conducted using a penetrometer following a standard test method for penetration of bituminous materials described under ASTM D5 or AASHTO T 49. As described before, higher values of penetration indicate a soft bitumen and the lower the value the harder the bitumen gets.

3.3.1.3. Softening Point

The standard method stated in ASTM D 36 or AASHTO T 53 was followed to determine softening point (the temperature at which a material attains a particular degree of softening) of the bitumen using a ball and ring apparatus shown in Figure 3.1.

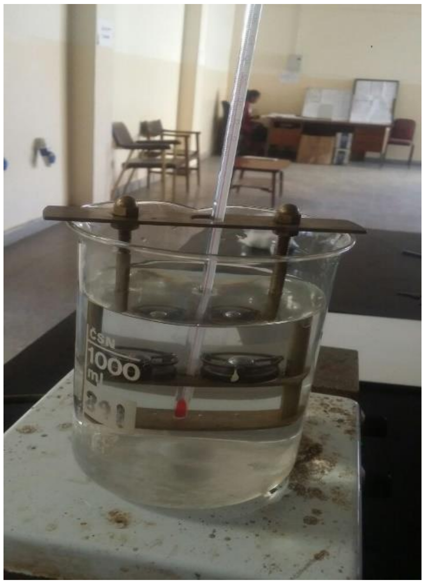


Figure 3.1. Ball and ring apparatus

3.3.1.4. Flashing point test

For the purpose of this study, an Open Cup flash point tester shown in Figure 3.2 was used according to ASTM D 92 or AASHTO T 48.

Figure 3.2. Cleveland open cup tester

3.3.1.5. Solubility in trichloroethylene

A procedure described in ASTM D 2042 or AASHTO T 44 was followed to determine the bitumen solubility in organic solvent. A measure of how much bitumen dissolves in the solvent was reported as bitumen solubility.

$$\% \text{ Soluble} = \left(\frac{\text{mass of original bitmn} - \text{mass of insoluble bitmn}}{\text{mass of original bitmn}}\right) \times 100 \qquad 3.2$$

3.3.1.6. Ductility

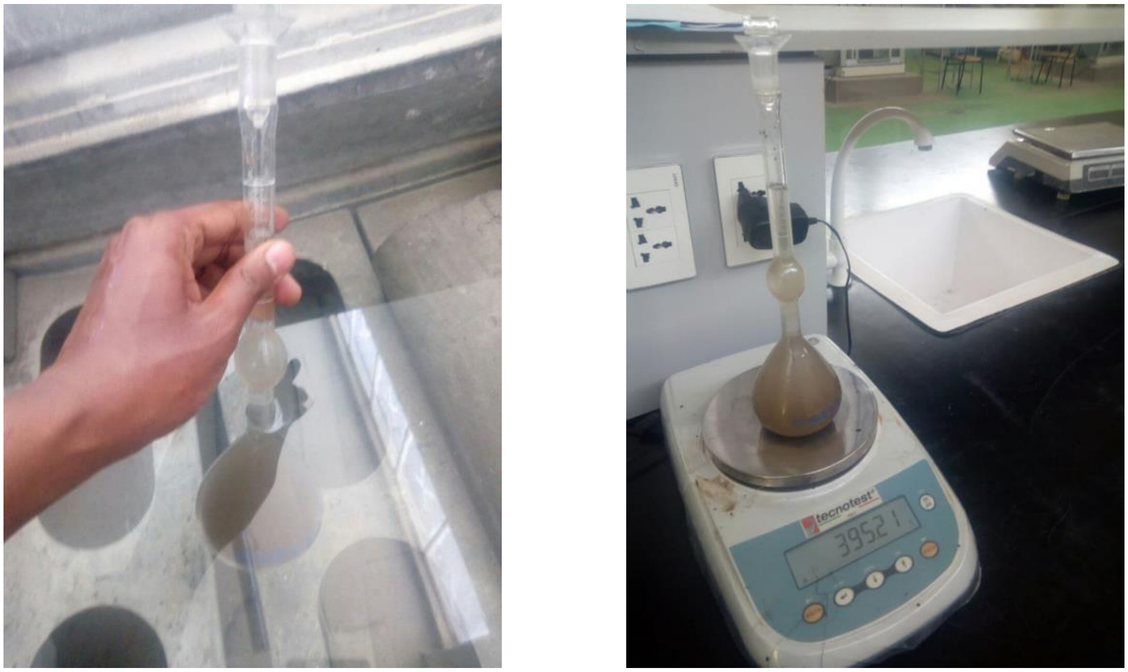
Ductility test of bitumen is a measure of its elasticity or adhesiveness. The test was conducted according to ASTM D113 or AASHTO T 51.

3.3.2. Filler Tests

The mineral fillers were subjected to FTIR spectrometry similar to the virgin binder and mastics. In addition, they were subjects of specific gravity, critical concentration and morphological tests.

3.3.2.1. Specific gravity

The specific gravity of fillers (the original five) was determined according ASTM C 188 or AASHTO T 133 using standard Le-Chatelier Flask. The process begun with filling the flask with kerosene (for OPC and PPC) or ethanol (for L, red brick and ash) to a certain level and taking initial reading (Figure 3.3 (a)). Later, a specified weight (64 g for Portland cements and 50 g for the other three types) of mineral filler was added while maintaining the flask at constant temperature and final reading of the liquid was taken ((Figure 3.3 (b)).).



(a) (b)

Figure 3.3. Density determination of mineral fillers

Finally, the density of the fillers was calculated as follows:

$$\rho(\mathrm{g/cm^3}) = \frac{\text{mass of filler (g)}}{\text{displaced volume (cm}^3\text{)}} = \frac{\text{mass of filler (g)}}{(\text{final reading} - \text{initial reading})(\mathrm{cm^3})} \qquad 3.3$$

The specific gravities were calculated from the densities as follows:

$$G_f = \text{ filler density/water density at 4°C (1 g/cm}^3\text{)} \qquad 3.4$$

Specific gravity for the other 12 filler combinations was determined using the specific gravities of the component parts and their respective volume fractions.

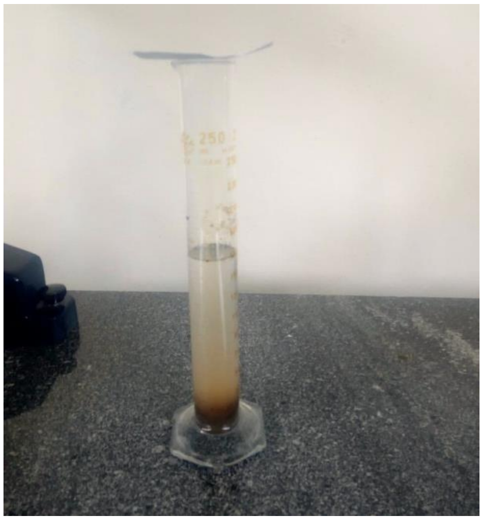
$$G_f = \left(\frac{\text{Volume fraction of filler 1}}{100} * G_{f1}\right) + \left(\frac{\text{Volume fraction of filler 2}}{100} * G_{f2}\right) \qquad 3.5$$

3.3.2.2. Critical concentration

Critical Concentration corresponds to a dispersion of the particles of the filler in the bitumen in the loosest possible state but with contact between them, when the applied stress is consumed in the viscous deformation of the continuous bitumen medium and the frictional resistance between the particles of filler tend to a minimum.

To determinate the Critical Concentration the fillers according to IRAM Standard 1542, Argentina, a known mass of dry filler was added to 20 cm^3 of dry kerosene, contained in a test tube graduated at 0.1 cm^3 of 25 cm^3. The test tube was then immersed in a boiling water bath (Figure 3.4 (a)) and the content was shaken with a fine wire until the air was completely eliminated (Figure 3.4 (b)). Once it is free of air, it was removed and allowed to settle in complete rest for 24 hours (Figure 3.4 (c)). Then the sediment volume was read which should be between 8 and 12 cm^3 at the end of the test.

(a) (b)



(c)

Figure 3.4. Procedure for determination of critical concentration

The critical sediment concentration (Cc) was calculated finally using equation 2.1 as

$$C_c = \frac{P}{\left(V \times G_f\right)}$$

where P is the filler mass in g, V is the sediment volume in cm^3 and G_f the dry filler density g/cm^3.

The critical concentration was determined for each filler and filler combinations described in Table 3-2. Filler samples other than the first five combinations were proportioned volumetrically with given percent of constituent and thoroughly mixed to uniformity before they were mixed with kerosene.

3.3.2.3. Morphology

Filler morphology was determined using images obtained from scanning electron microscopy (SEM) which is the most important technique for the analysis of morphological characteristics like size, shape, topography, and surface composition [110]. An image of the SEM used in this thesis is shown in Figure 3.5. In general, it produces magnified images of a sample by scanning it with a beam of electrons.

Figure 3.5. Scanning electron microscope (SEM)

The SEM image was produced only the base fillers as analysis regarding morphology of other filler combinations can be deduced from their morphology and volumetric proportion in a certain filler combination. The images were analysed qualitatively to identify particle shape while a software is used to measure particle sizes.

3.3.3. Mastic tests

The tests conducted on the mastic described in Table 3-2 were of two types. The first one is involves conditioning the samples to simulate short term ageing in RTFO. The second group include chemical tests with FTIR and rheological tests with DSR. The latter tests are to compare the properties of the mastics before and after ageing, and with each other. Again, they were also performed for base bitumen to access the improvement provided by mastic.

3.3.3.1. Short term ageing

Short term ageing is a conditioning step that simulates aging of asphalt binders during construction. The rolling thin film oven (RTFO) has been used here for the conditioning according to the steps outlined in AASHTO T 240. Ageing was carried out for the neat binder and 17 mastic samples.

3.3.3.2. Chemistry

The chemical changes during aging were discovered through FTIR spectrometry on neat bitumen and mastic samples. Infrared absorption spectroscopy is the method which scientists use to determine the structures of molecules with the molecules' characteristic absorption of infrared radiation. Therefore, IR spectroscopy can result in a positive identification (qualitative analysis) of every kind of material. In addition, the size of a peak in the spectrum is a direct indication of the amount of material present [111].

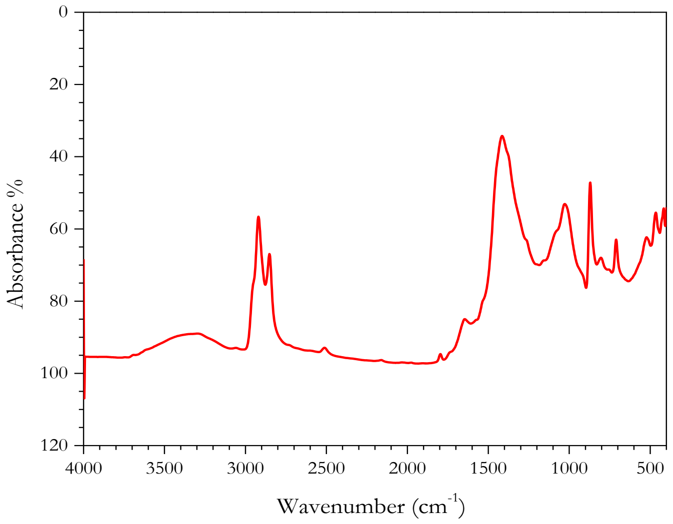


Figure 3.6. Example FTIR spectra

A qualitative analysis of FTIR was done here in this research to identify functional groups before and after ageing of the bitumen or mastic samples. Because of complex interactions of the atoms within a molecule, the IR absorption of the functional groups may vary over a wide range. However, many functional groups give a characteristic IR absorption at specific, narrow frequency ranges regardless of their relationship with the rest of the molecule and it is these ranges of frequencies/wavelengths from literature which were used to identify specific functional groups.

3.3.3.3. Rheology

Several fundamental and research-based binder tests can be carried out using dynamic shear rheometer (DSR). From those different tests for the purpose of this study amplitude sweep test (AST) and frequency sweep test (FST) have been performed.

I. Testing mechanism

The Standard test method for described in AASHTO T 315-10 was followed to determine rheological properties of neat bitumen/mastics using DSR shown in Figure 3.7.

Figure 3.7. Dynamic shear rheometer

As for test temperatures, three of the MEPDG standard temperatures, 21.1 °C, 37.8 °C and 54.4 °C, were used for AS and FS tests.

II. Linear amplitude sweep test

The amplitude sweep test was carried out following the test standard AASHTO T 315 at a constant frequency of 10 rad/sec at specific test temperatures (21.1 °C, 37.8 °C and 54.4 °C). The test can be performed in controlled shear or strain mode. The shear stress control mode was chosen here with minimum shear stress 100 pa and maximum shear stress 90000 pa in order to obtain the limiting value in terms of strain.

Amplitude sweep is an oscillatory DSR test with variable stress or strain amplitude at constant frequency. The main or the sole purpose of this test is to determine the Linear Viscoelastic (LVE) range of a viscoelastic material which is the region where the applied oscillation is non-destructive. It was determined here from log-log graph of complex shear modulus (G*) on y-axis and strain (γ) in the x-axis and shear modulus in the y-axis.

Although there is an option of automatic analysis, a manual (visual) analysis using a graphing software was used to determine the limiting strain. The process is simple, using the data table of the test protocol, the last γ-value of the LVE range is determined at which the G* values are just beginning to show a noticeable deviation from the previously constant values. This measuring point is taken as the limiting value. A 5% tolerance was allowed which means all those G* values which are below 95% of the plateau value were considered to be outside of the LVE range.

III. Frequency sweep test

Frequency sweeps are oscillatory tests performed at variable frequencies, keeping the amplitude at a constant value. The frequency sweep test was conducted in a strain-controlled mode varying from 0.1Hz to 25 Hz. In order to ease the test process, a single strain value corresponding to minimum strain of the LVE range of all the samples from the amplitude sweep test. From the tests it was found out that the minimum was 2%. Accounting for errors in test process and the method used to obtain the strain values, a 1% strain was chosen to examine the binder well within linear viscoelastic range for FST.

IV. Method of analysis

The rheological tests in this research are all oscillatory where only two independent raw data are measured. When performing oscillatory tests, a rheometer measures not more than two raw data can be presented: stress and δ when pre-setting the strain, or strain and δ when pre-setting the stress, respectively. From these two independent variables are determined the viscous (e.g. as G'') and the elastic portion (e.g. as G') of the viscoelastic behaviour. If further parameters (e.g. $|G^*| = \sqrt{(G')^2 + (G'')^2}$) are presented they should be regarded only as another possibility to show the obtained test results.

Data obtained from DSR (rheological data) can be represented in different diagrams to ease analysis. The presentation of diagrams is recommended in any case on a double logarithmic scale, i.e. for amplitude sweeps as log G*(log γ) and frequency sweeps as log G*(log ω). For the FST tests, isothermal plots which are curves of complex modulus versus frequency at a constant temperature were used to represent behaviour of viscoelastic function at a constant temperature. The plots were later used to construct master curves.

The master curves were constructed using the principle of time temperature superposition. The master curve of an asphalt binder/mastic provides a relationship between the binder/mastic stiffness and reduced frequency over a range of temperatures and frequencies. Accordingly, the master curve makes it possible to predict viscoelastic properties over a wide frequency range and at any temperature.

To construct the master curves (of modulus), the stiffness of an asphalt binder/mastics at multiple temperatures and frequencies were measured. Then, |G*| data from three temperatures were plotted as a function of frequency on a log-log scale. These plots show data frequency sweeps at different temperatures (i.e. 21.1°C, 37.8 °C and 54.4 °C). A reference temperature of 20°C was chosen and the frequency sweep data at each temperature was shifted horizontally relatively to form a single curve showing |G*| as a function of reduced frequency. The shifting was done via shifting factors (a_T) which were calculated using the William-Landel-Ferry (WLF) empirical relationship [112] developed based on the time-temperature superposition.

$$\log \mathrm{a_T} = \frac{-\mathrm{C_1}(\mathrm{T} - \mathrm{T_{ref}})}{\mathrm{C_2} + (\mathrm{T} - \mathrm{T_{ref}})} \qquad 3.6$$

where $\mathrm{a_T}$ is shift factor, T is the temperature to be shifted, T_{ref} is the reference temperature, $C_1\ and\ C_2$ are constants equal to -19 and 92 respectively after [113].

The shifting factors relate frequency in experiment with the reduced frequency used in the master curves. Reduced frequency was calculated as

$$\log \mathrm{f_r} = \log \mathrm{f} + \log \mathrm{a_T} \qquad 3.7$$

The master curves were then fitted into a viscoelastic model until a smooth curve is generated. The smoothing was achieved using Microsoft excel solver to best fit the sigmoidal function for all asphalt binders. The sigmoid function to best fit the obtained G* data from the DSR is carried out with trial and error by changing the sigmoid constants and the shift factor. The sigmoid function to calculate the complex shear modulus is represented as

$$\log|G^*| = \delta + \frac{\alpha}{1 + e^{\beta + \gamma \log(f_r)}} \qquad 3.8$$

where $|G^*|$ is complex shear modulus, f_r is reduced frequency, and $\alpha, \beta, \gamma\ and\ \delta$ are sigmoidal constants calculated by trial and error.

Master curves allow the rheological data to be presented over a wide range of frequencies and temperatures in one plot. Therefore, to avoid presenting a large number of graphs, the results are mainly presented and analysed as master curves.

3.4. Experimental Program

The diagram below shows the process followed throughout the research. The materials (raw and mastics), the ageing process, tests conducted before and after ageing, and analysis methods are all there.

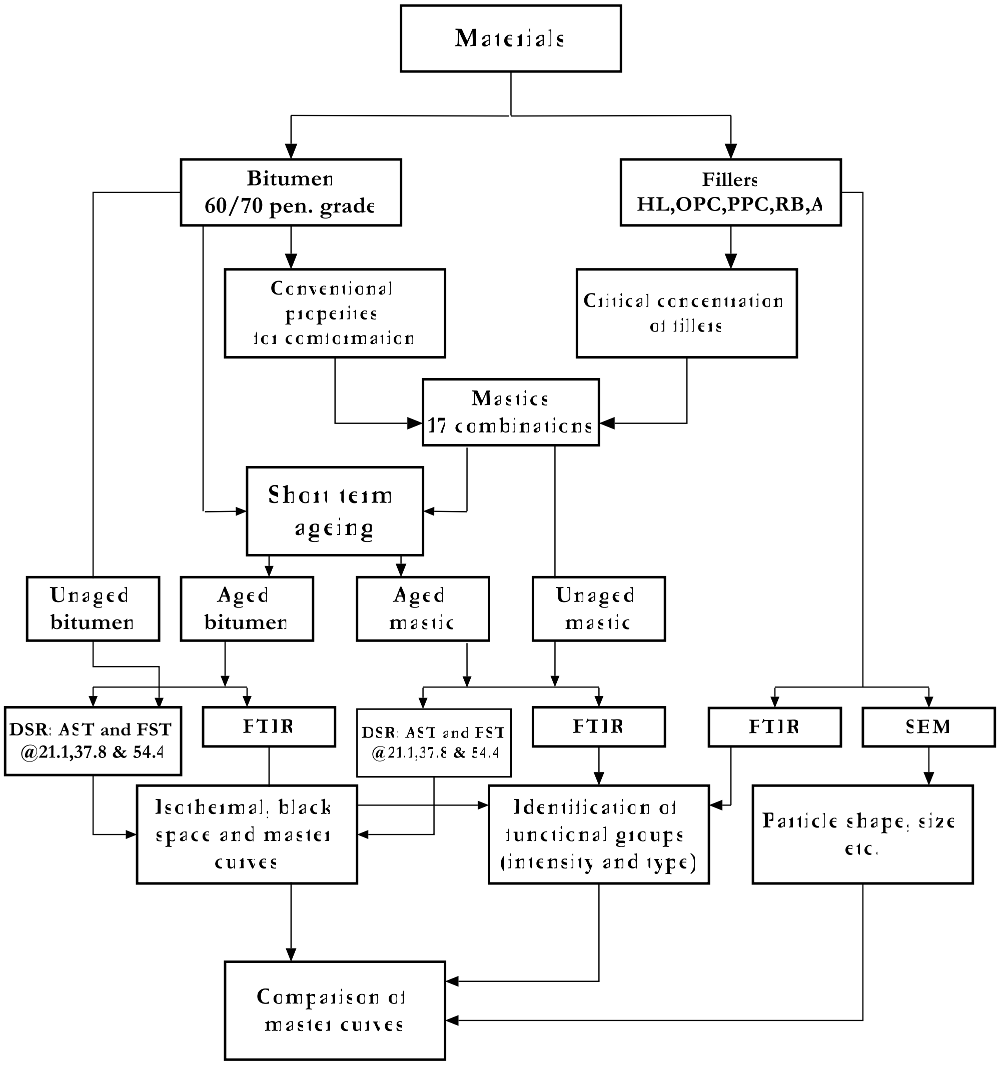


Figure 3.8. Research scheme

CHAPTER 4

RESULT AND DISCUSSION

4.1. Bitumen Properties

The bitumen was initially subjected to some conventional tests to conform it to be a 60/70 penetration grade bitumen according to ERA standards. Specific gravity and chemistry of the bitumen were also presented to access its contribution in filler-bitumen matrix.

4.1.1. Conventional properties

The conventional mechanical tests on bitumen indicated that the bitumen used in the study is indeed a 60/70 penetration grade bitumen as per ERA standard. The values of the tested parameters along with the limits for 60/70 bitumen are given in following table.

Table 4-1: Conventional test results for bitumen

Test		**Corresponding ASTM test standard**	**Test values**	**Limits for 60/70 bitumen**
Based on original bitumen				
Penetration at 25 ºC		D5	64	60-70
Softening point (ºC)		D 36	50	46-56
Flash point (ºC)	min	D 92	292	232
Ductility at 25 oC	min	D 113	100$^+$	100
Solubility in tri-cloro ethylene (%)	min	D 2042	99.45	99
After TFOT heating for 5h at 163ºC using D 1754				
Loss by mass (%)	max		0.014	0.5
Penetration (% of original)	min	D 5	85	54
Ductility at 25 oC	min	D 113	100$^+$	50

Moreover, the bitumen was found to have a density of 1.024 g/cm^3 after a pycnometer test according to ASTM D 70-03 with the procedure outlined in section 3.3.1.1. The value is of a typical bituminous binder which will have density values between 1.01 and 1.06 g/cm^3 [114], [115].

4.1.2. Chemistry

Once the bitumen was confirmed to be of 60/70 penetration grade, the original and RTFO aged binders were subjected to FTIR spectroscopy. The results are shown in the following figure as FTIR spectra.

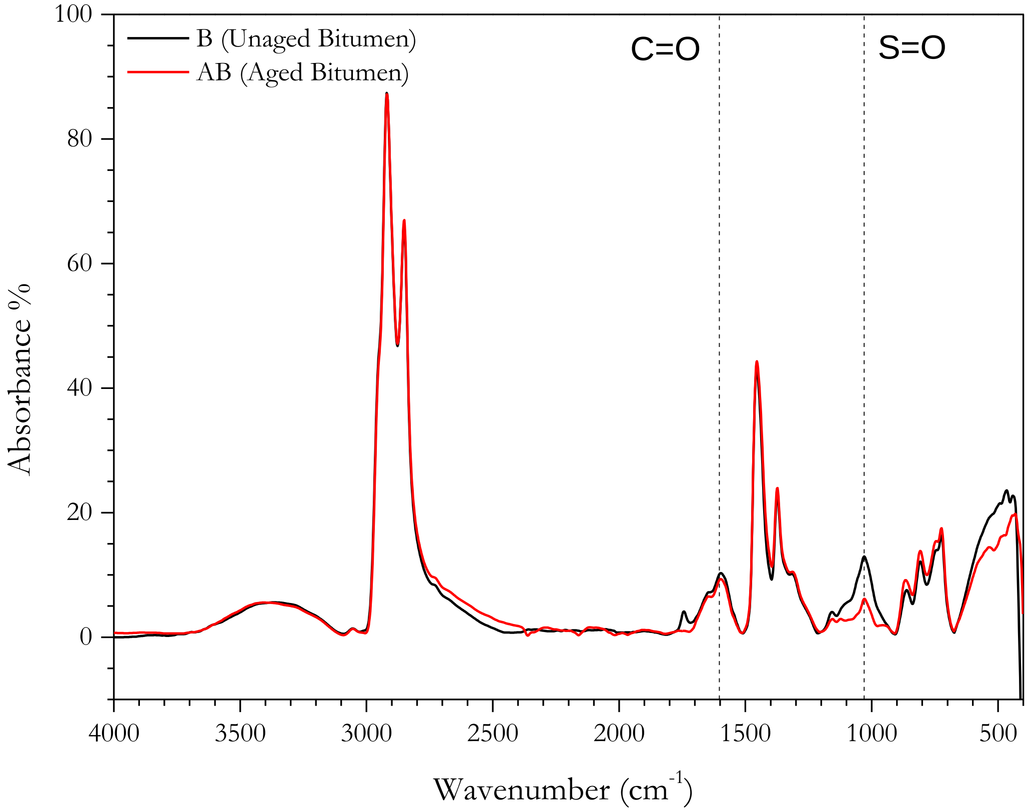


Figure 4.1. FTIR spectra for Aged and unaged bitumen

The spectrums indicate that there is not much difference between the samples. The peaks observed in the functional group region (<1500 cm-1) between 3000 and 2800 cm-1 indicate the presence of aliphatic hydrocarbons while those in the finger print area (>1500 cm-1) confirm the presence of aliphatic hydrocarbons and additional inorganic carbonates between 1500 and 1300 cm-1. In addition, less intense peaks between 3600 and 3200 cm-1 indicate that there are aliphatic alcohols and aliphatic amines in the samples. The similarity in aliphatic group ranges can be credited to the group's stable structure which makes them to being not affected by applied ageing procedures [116].

The spectra were investigated additionally to obtain information on changes in the chemical composition by oxidative ageing. Therefore, changes in the carbonyl (C=O) and sulfoxide (S=O) area were taken into consideration. The carbonyl area is commonly defined as the band around the 1680 cm−1 peak, whereas the sulfoxide area is the band around 1030 cm−1. The figure above shows stacked spectra from the unaged sample (black) and from the RTFO aged sample at 163 °C (red). Vertical marks in the diagrams indicate expected band maxima for carbonyl and sulfoxide bands. The spectrum does not show a distinct absorbance in the carbonyl area even in the unaged state. A little peak in carbonyl group range in unaged bitumen is most probably linked to the nature of the bitumen itself either from the origin of the crude oil or the refining process [117]. Absence of carbonyl group in unaged bitumen is acceptable since carbonyl peak is not an absolute indicator of oxidation but its increase is a relative indicator of oxidation [118]. As for the sulfoxide area, all bitumen samples show absorbance in this band even in the unaged state but the sulfoxide area tends to decrease upon RTFO ageing [118].

4.2. Filler Properties

4.2.1. Density and critical concentration

The fillers were initially subject of some basic tests to obtain a proportion that would result optimum performance of filler-bitumen matrix. Table 4-2 and Table 4-3 show the densities and corresponding critical concentration (C_c) values of the fillers and their combinations from the rests described in section 3.3.2.

Table 4-2: Density and critical concentration of original fillers

	Mass (g)	**Settled filler. Volume(cm^3)**	**Density (g/cm3)**	**Cc**
L	10	11.1	2.70	0.33
OPC	10	11.7	3.13	0.27
PPC	9	11.5	2.98	0.26
RB	7	9.3	2.61	0.29
A	4.1	11.2	2.57	0.14

The critical concentration of filler combinations was not referred from critical concentration of original fillers rather it was directly calculated using equation 2.1 after the densities were calculated from the densities of original fillers using equation 3.5.

Table 4-3: Density and critical concentration of filler combinations

Other fillers	Mass (g)	Settled filler volume(cm^3)	Density (g/cm3)	Cc
		75%L+25% Other fillers		
OPC	9	11.4	2.81	0.28
PPC	8.5	9.7	2.77	0.32
RB	9	10.3	2.68	0.33
A	6.5	10.2	2.67	0.24
		50%L+50% Other fillers		
OPC	9	11.3	2.91	0.27
PPC	9	10.8	2.84	0.29
RB	7.5	8.9	2.66	0.32
A	7.5	12	2.63	0.24
		25%L+75% Other fillers		
OPC	8.5	11.8	3.02	0.24
PPC	8.5	11	2.91	0.27
RB	9	11.8	2.64	0.29
A	5.5	11.75	2.60	0.18

The density values indicate that Portland cement fillers and combinations containing them are dense, the ones with OPC being even denser. The limestone filler was found to have a density value in the middle among the five fillers. The variation of density when the control L filler is replaced by other fillers is given in Figure 4.2. It can be seen that density increases as the quantity of OPC and PPC in a combination increase while it decreases with increasing quantity of RB and A fillers.

Regarding critical concentration, L was found to have the highest value among the fillers which means that more L mass is required to attain a condition where filler particles in the bitumen move as freely as possible but in contact with each other at the same time. It can be also concluded that addition of any other mineral filler to L generally decreases critical concentration and among the fillers it is RB which has highest C_c values while A has lowest ones (refer Figure 4.3). The difference in trend between density and critical concentration may be related to the chemistry and particle characteristics of the fillers which needs further tests.

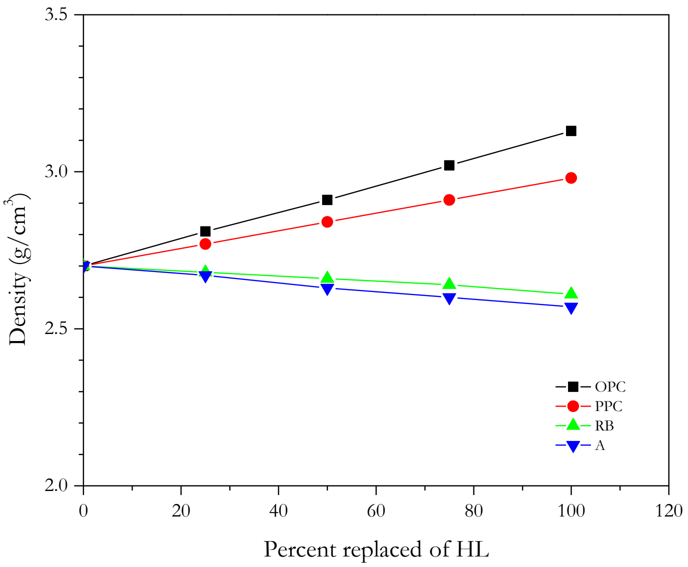


Figure 4.2. Variation of density with percent replaced

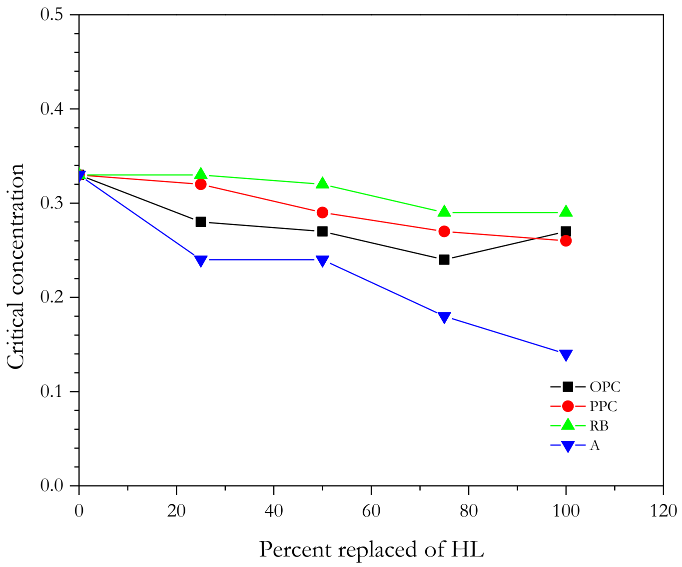
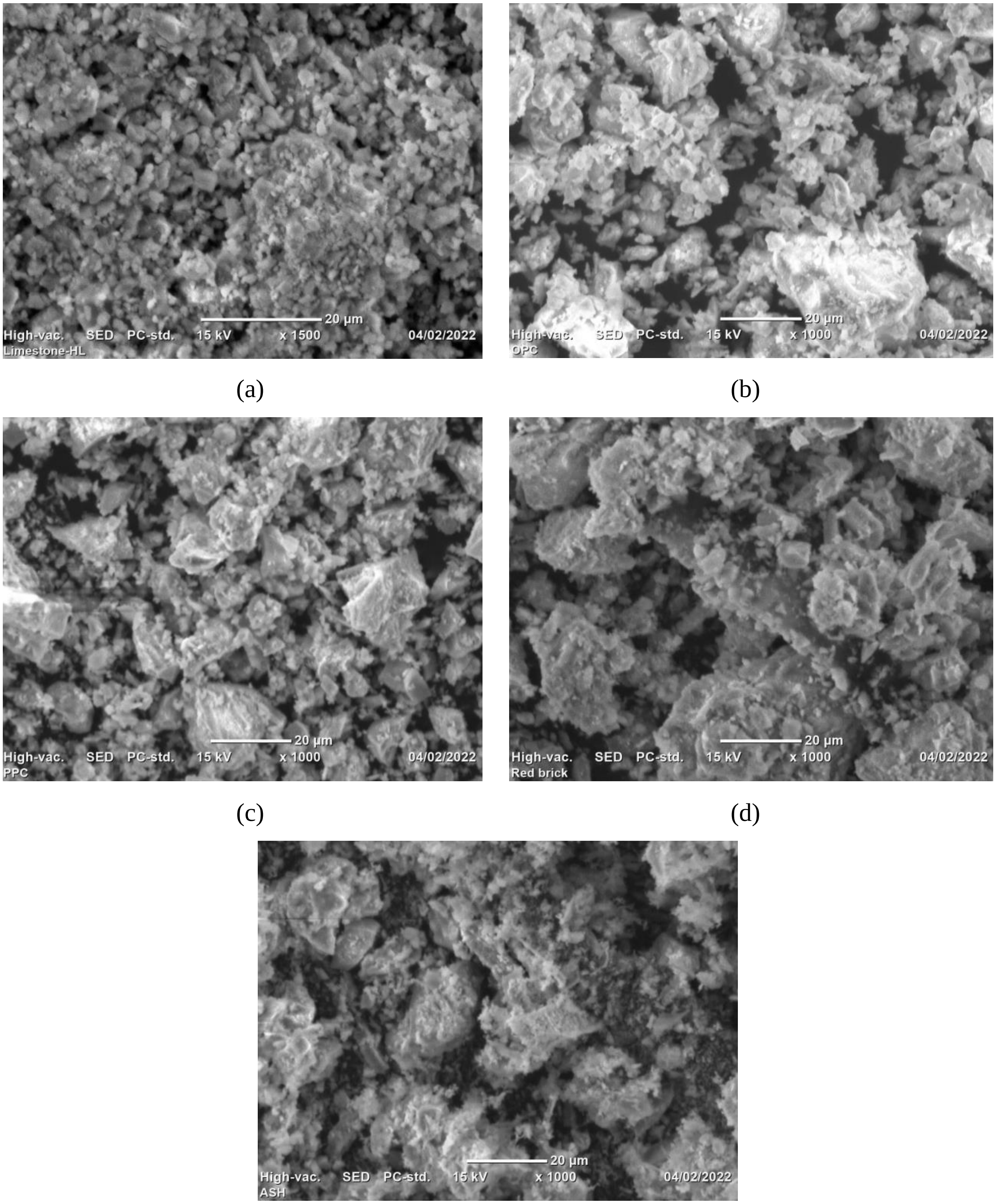


Figure 4.3. Variation of Cc with percent replaced

4.2.2. Particle morphology

Figure 4.4 shows the SEM image of all the fillers used in this research. As shown in the SEM images, the wood ash particles exhibited relatively even particle sizes; in contrast, limestone and red brick particles presented sizes that differed relatively significantly. The fine particles in these fillers can be found in large amount. The particles of OPC and PPC showed particle size distribution in the middle of the two groups.

Again, it can be seen that, OPC and RB fillers has mostly angular type particles with rough texture. Although PPC has similar angular particles, the surface of the particles has smooth to slightly rough texture. The limestone filler has got particles that are relatively rounded and granular. Wood ash fillers on the other hand a very rough (sharp) surface with angular and flaky particles.



(a) (b)

(c) (d)

(e)

Figure 4.4. SEM images of fillers (a) Limestone (b) OPC (c) PPC (d) Red brick filler (e) Wood ash

The SEM imaging results can be correlated with the other filler properties. It was stated that larger value of the specific surface area SSA and Ridgen voids are consistent with angular shape and rough texture of particles. In addition, it was shown that there is an increase of the SSA with the increase of the fine particle content [119]. Larger value SSA means there is chance of more bitumen being absorbed by the filler and a consequent increase of filler stiffening effect. In this respect, RB and OPC fillers would have a great chance of having larger SSA relative to the other fillers. The limestone will also be a good candidate since a large portion of the filler content is composed of fine particles in addition to the porous nature of the material.

4.2.3. Chemistry

The chemical composition of the fillers was also investigated by means of FTIR. Figure 4.5 shows a stacked spectrum of the fillers used without base line correction and in terms of transmittance. It can be seen that there is not significant difference in the spectrums above 1500 cm^{-1} (functional group region) and it is mostly of inorganic carbonates and aliphatic hydrocarbons.

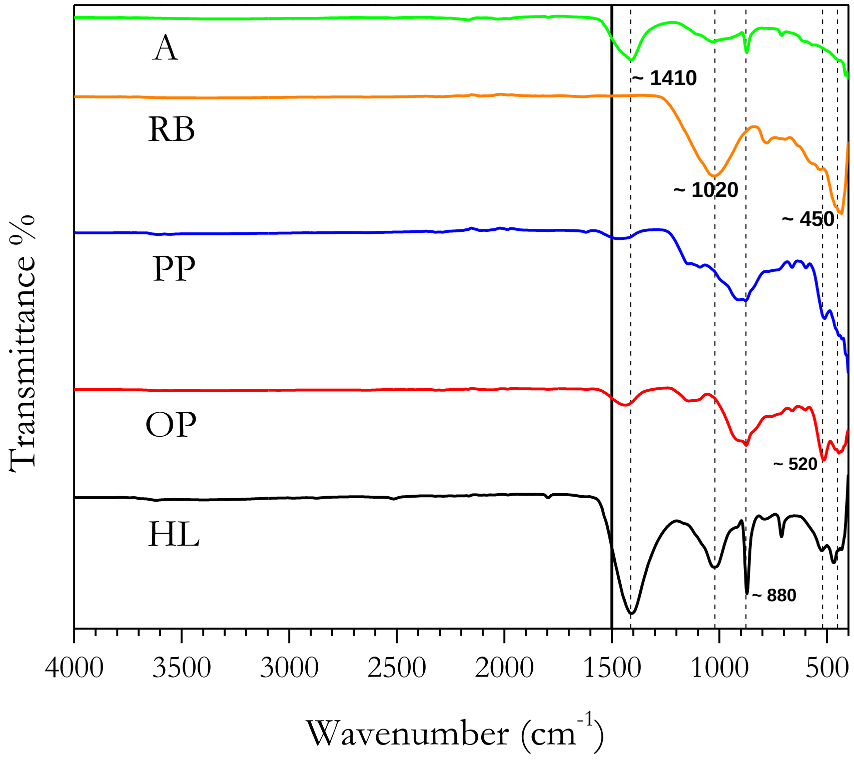


Figure 4.5. FTIR spectroscopy of original fillers

However, the patterns in the fingerprint region (< 1500 cm^{-1}) are slightly different and could therefore be used to identify differences among the fillers. The FTIR spectra of limestone (L) and wood ash (A) filler reveal the presence of some Ca, K and Mg carbonates with the peaks around 1410, 872 and 710 cm^{-1} are attributed respectively to the out of plane bending vibration, asymmetric stretching vibration, and the in-plane bending mode for powdered $CaCO_3$. In addition, L-filler has absorption peaks around 1020 cm^{-1} indicating the presence of sulfates. RB filler has resulted a bit different spectrum showing absorption peaks corresponding to quartz (~790 cm^{-1}) and the functional bond Si-O-Si (~1020 cm^{-1}). The Portland cements on the other hand, showed an almost similar spectrum showing the presence of C-O bonds assigned to carbonates around 1410 and 870 cm^{-1}.

4.3. Chemistry and Rheology of Mastics

4.3.1. Mastic chemistry

The figures from Figure 4.6 to Figure 4.10 show FTIR spectra of the aged mastics developed in the study. The spectrums are stacked together to show the relative difference a filler type and amount of replacement would result in terms of chemistry. In general, the spectrums are superposition of the neat binder spectrum and spectrum of fillers. In Figure 4.6 it can be seen that the aged mastics prepared with the fillers L, A, OPC and PPC all had higher or almost higher peaks in the carbonyl region than the aged bitumen, which indicates the catalysis of bitumen oxidation in these mastics.

The spectrums in the other fillers present a proportional decrease or increase in peaks of different spectral regions the mastics with L-filler only having higher peaks on C-O and carbonyl (C=O) regions. The peaks generally decrease with an increase of other filler contents.

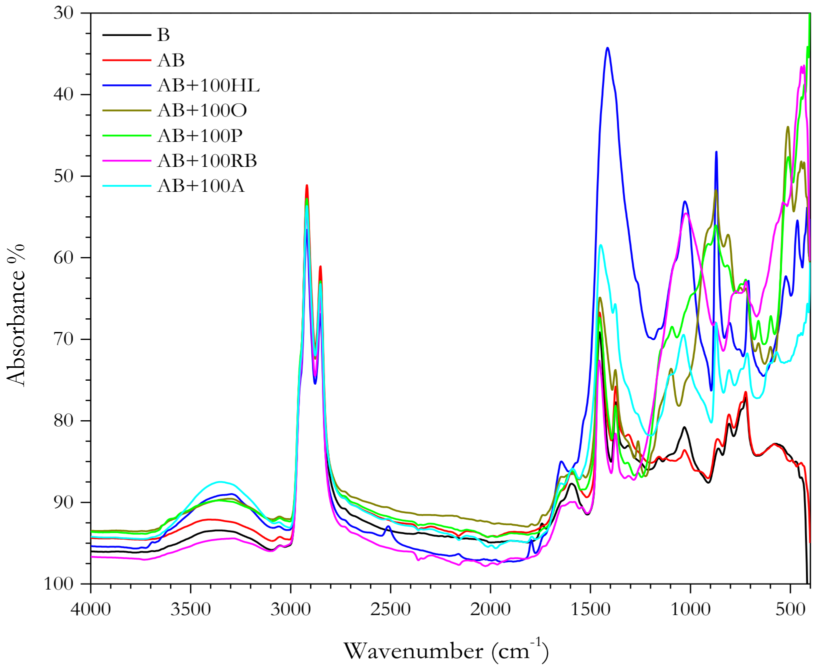


Figure 4.6. FTIR spectrum for neat binder and aged mastic with original fillers

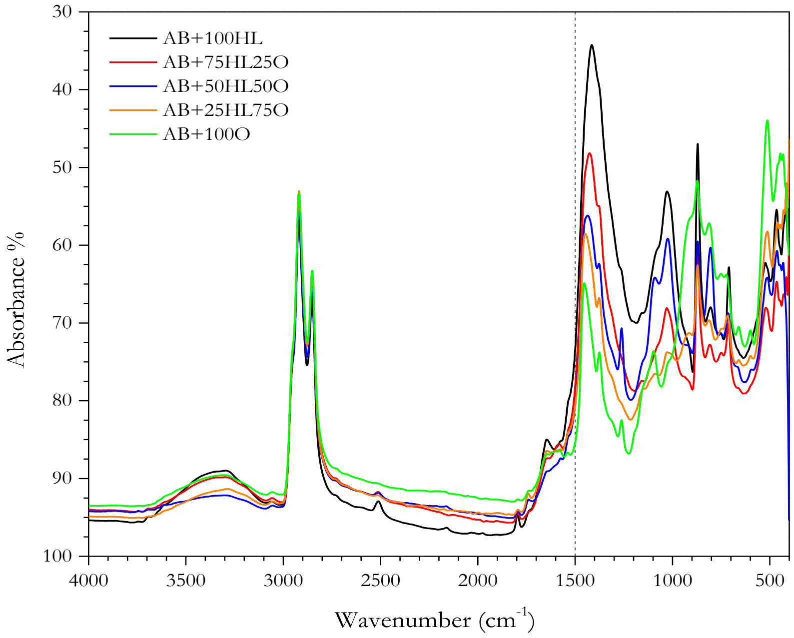


Figure 4.7. FTIR spectrum for aged mastics prepared by replacing L with OPC.

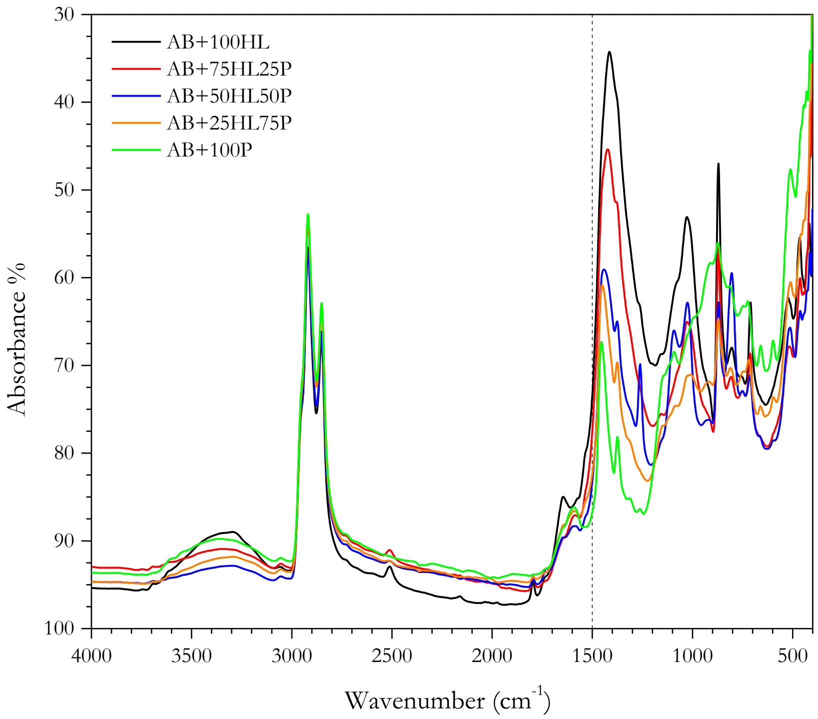


Figure 4.8. FTIR spectrum for aged mastics prepared by replacing L with PPC.

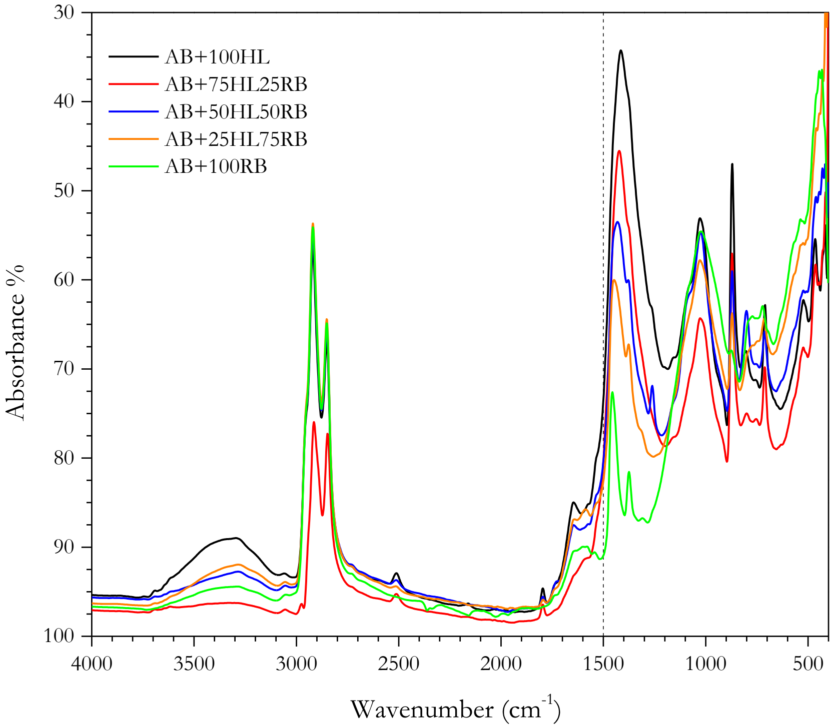


Figure 4.9. FTIR spectrum for aged mastics prepared by replacing L with RB filler.

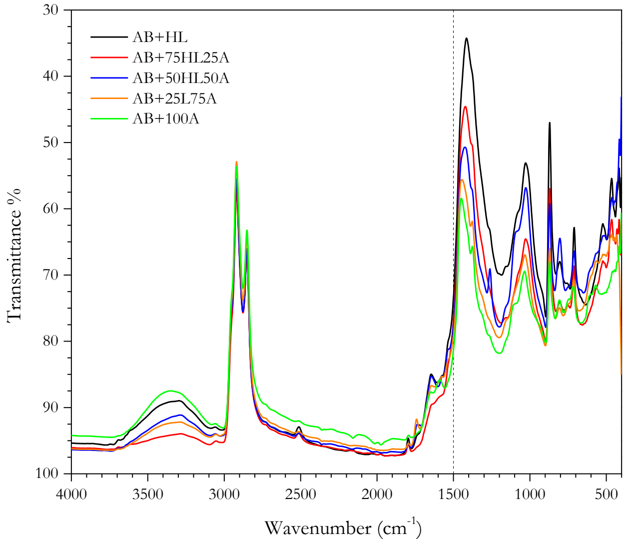


Figure 4.10. FTIR spectrum for aged mastics prepared by replacing L with A

4.3.2. Mastic rheology

4.3.2.1. Results of amplitude sweep tests

The AST results are represented here graphically with log-log scale of complex shear modulus (G*) in the y-axis and Strain in percent in the x-axis. As an example, Figure 4.11 below shows the amplitude sweep test result for base binder in aged and unaged states. Similar graphs for other mastic types are presented in Appendix.

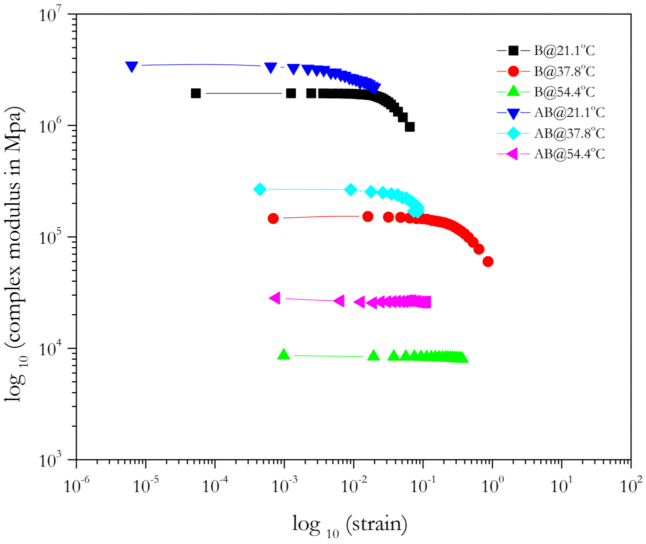


Figure 4.11. AST test results for base bitumen

The limiting strain values defining the linear viscoelastic region of mastics were analyzed considering the plateau strain values of each graph. The plateau modulus values are almost constant values of G* for different values of shear stress and shear strain before the graph declines as shown in Figure 4.11. Finally, for each and every curve of amplitude sweep results, a horizontal line along 0.95G* will be constructed to intersect the curve at a point. Then the corresponding strain value of that intersection point will be considered to be the limiting stain value. Limiting strain values calculated using these processes are presented below in Table 4-4, considering the effects of ageing, temperature and filler types.

Table 4-4: LVE limiting strains from AST

Ageing	**Unaged**			**Aged**		
Temperature	**21.1°C**	**37.8 °C**	**54.4 °C**	**21.1 °C**	**37.8 °C**	**54.4 °C**
Type	**Strain in %**					
B	1.997	15.761	19.01	1.17	5.64	9.64
100L	***1.09***	66.96	28.23	2.94	20.11	15.44
100OP	7.77	36.79	37.32	4.95	38.21	25.15
100PP	2.75	30.67	28.42	1.83	30.23	23.86
100RB	3.39	24.76	24.27	1.19	13.67	22.68
100A	6.81	48.08	47.83	1.69	27.19	38.27
25L+75OP	13.74	87.28	78.9	7.49	35.92	67.04
25L+75PP	12.94	83.02	54.43	10.9	65.14	51.35
25L+75RB	6.26	26.43	28.99	3.2	17.96	20.68
25L+75A	11.44	61.05	53.88	8.62	31.02	52.92
50L+50OP	1.337	13.45	46.67	7.63	32.84	17.74
50L+50PP	10.58	117.84	81.75	9	37.9	55.07
50L+50RB	4.57	36.09	39.98	3.23	20.43	30.84
50L+50A	11.45	56.51	80.62	5.92	20.77	35.7
75L+25OP	13.31	72.69	80.46	8.18	32.1	38.01
75L+25PP	11.07	60.42	61.02	7.36	30.94	34.13
75L+25RB	5.36	48.15	56.61	4.76	19.69	24.56
75L+25A	8.31	53.66	102.91	8.16	21.69	31.84

As a result, the minimum strain limit of 1% was chosen to conduct frequency sweep test and ensure the test would not be conducted outside of the materials' linear viscoelastic range. Besides that, this could be a good place to mention additional trends that have been observed during the test. Referring the graphs in Appendix and Table 4-4 it can be observed that

- At 21.1^{o}C temperature the limiting strain value for each sample is minimum and it increases with increasing temperature for all mastic samples for they will get less stiff
- There is not significant change in the limiting strains due to ageing or filler types though it was the unaged samples which were having higher values among unaged and aged samples while samples containing RB filler had lesser values among mastic filler types.

4.3.2.2. Results of frequency sweep tests

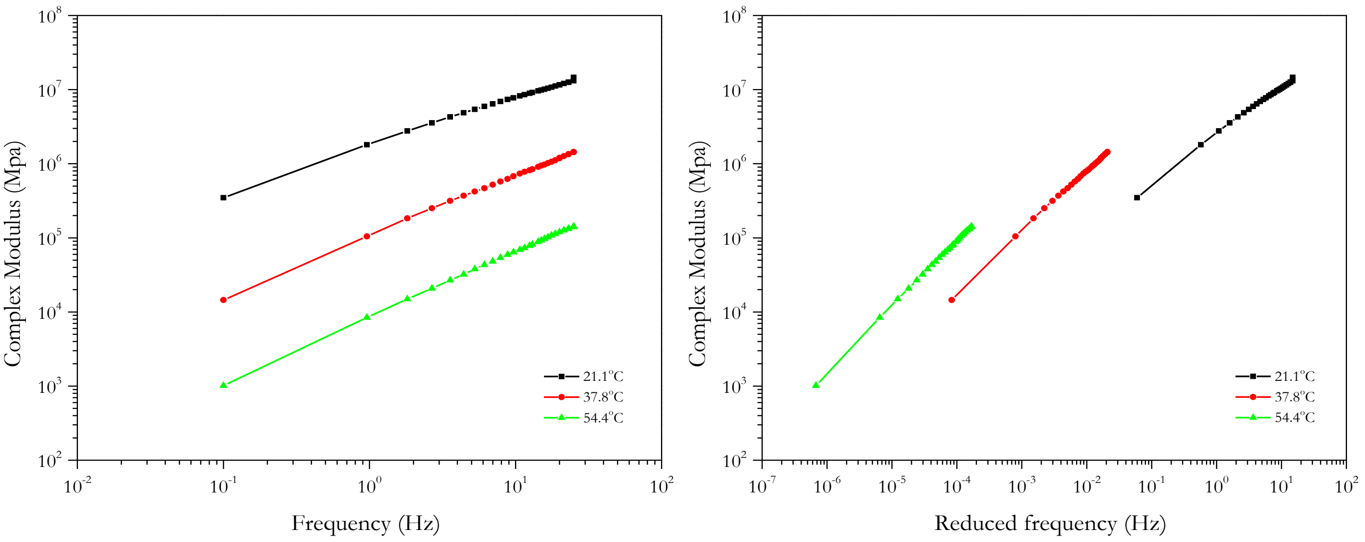
All the frequency sweep testing was done at strains using the prior minimum limiting strain (i.e. 1%) from AST to ensure LVE behavior during the dynamic testing.

The results of FST are presented with shear modulus (G*) master curves developed using the procedure outlined in sections IV of 3.3.3.3 in order to capture the effect of loading rate (frequency) and Temperature simultaneously. The shift factors calculated with a reference temperature of 20^{o}C using equation 3.6 are tabulated in the table below.

Table 4-5: Shift factors with T_{ref} = 20^{o}C

$\mathbf{a_{21.1}}$	$\mathbf{a_{37.8}}$	$\mathbf{a_{54.4}}$
0.5964	0.0008	6.7471E-06

Here is an example from the original unaged binder, to show master curve development procedure. After isothermal plots were developed using frequency and complex shear modulus at constant temperature for the three temperatures (see Figure 4.12 (a)), they were shifted using the shift factors in the table above to result a graph of G* and reduced frequency from equation 3.7 (see Figure 4.12 (b)).



(a) (b)

Figure 4.12. Isothermal plots of base bitumen (a) G* Vs frequency (b) G* Vs reduced frequency

The graph in Figure 4.12 (b) was then fitted to the sigmoid function optimizing the parameters (δ, α, β & γ) in Equation 3.8 using Excel-Solver to obtain a master curve as shown in Figure 4.13.

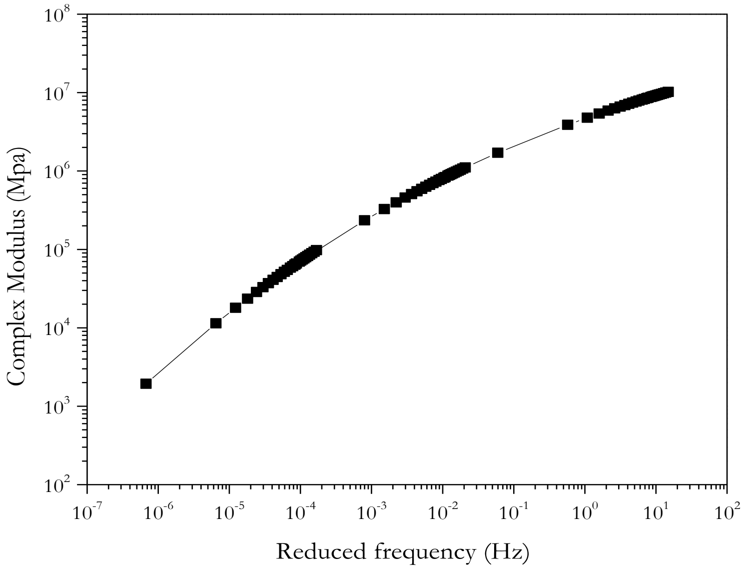


Figure 4.13. Master curve for unaged (base) bitumen (B)

Similar process was followed to obtain master curves for all 17 mastic samples using the shift factors in Table 4-5 and sigmoid parameters obtained from Excel solver for each type by minimizing the sum of squared errors (SSE) between log of predicted G* and experimental G*. The sigmoid parameters for each sample are given in with SSE for easy reference.

Table 4-6: Constants for sigmoid fitting function of B, AB and aged mastics

Sample	$\boldsymbol{\delta}$	$\boldsymbol{\alpha}$	$\boldsymbol{\beta}$	$\boldsymbol{\gamma}$	SSE
B	-30.7035	39.1705	-0.1868	-3.0339	2.0711
AB	-55.9290	64.8856	-0.1593	-3.2885	1.6429
AB+100L	-41.5456	51.3875	-0.1470	-3.0228	1.0796
AB+100O	-37.6983	46.4109	-0.2057	-3.4611	1.2649
AB+100P	-39.0871	47.8396	-0.2008	-3.4950	1.4341
AB+100RB	-45.3751	55.9160	-0.1264	-2.8651	1.9092
AB+100A	-45.1218	54.1021	-0.1681	-3.3725	1.6767
AB+75L25O	-53.1250	62.2685	-0.1666	-3.4362	2.5366
AB+75L25P	-26.6533	35.6530	-0.1920	-2.9813	1.3814
AB+75L25RB	-40.1690	50.0586	-0.1477	-2.9196	1.3148
AB+75L25A	-46.2939	55.0114	-0.1968	-3.5486	1.6994
AB+50L50O	-24.7446	34.8090	-0.1277	-2.4288	2.8653
AB+50L50P	-41.9149	51.5232	-0.1400	-3.0878	1.5487
AB+50L50RB	-51.0530	60.5070	-0.1558	-3.3415	1.9405
AB+50L50A	-35.1462	46.2455	-0.1201	-2.4740	1.5471
AB+25L75O	-42.8807	52.1188	-0.1702	-3.2531	0.9719
AB+25L75P	-22.5364	33.4754	-0.1076	-2.1047	1.8861
AB+25L75RB	-49.7273	58.7955	-0.1710	-3.4683	1.5770
AB+25L75A	-23.8696	32.0835	-0.2482	-3.3520	1.5641

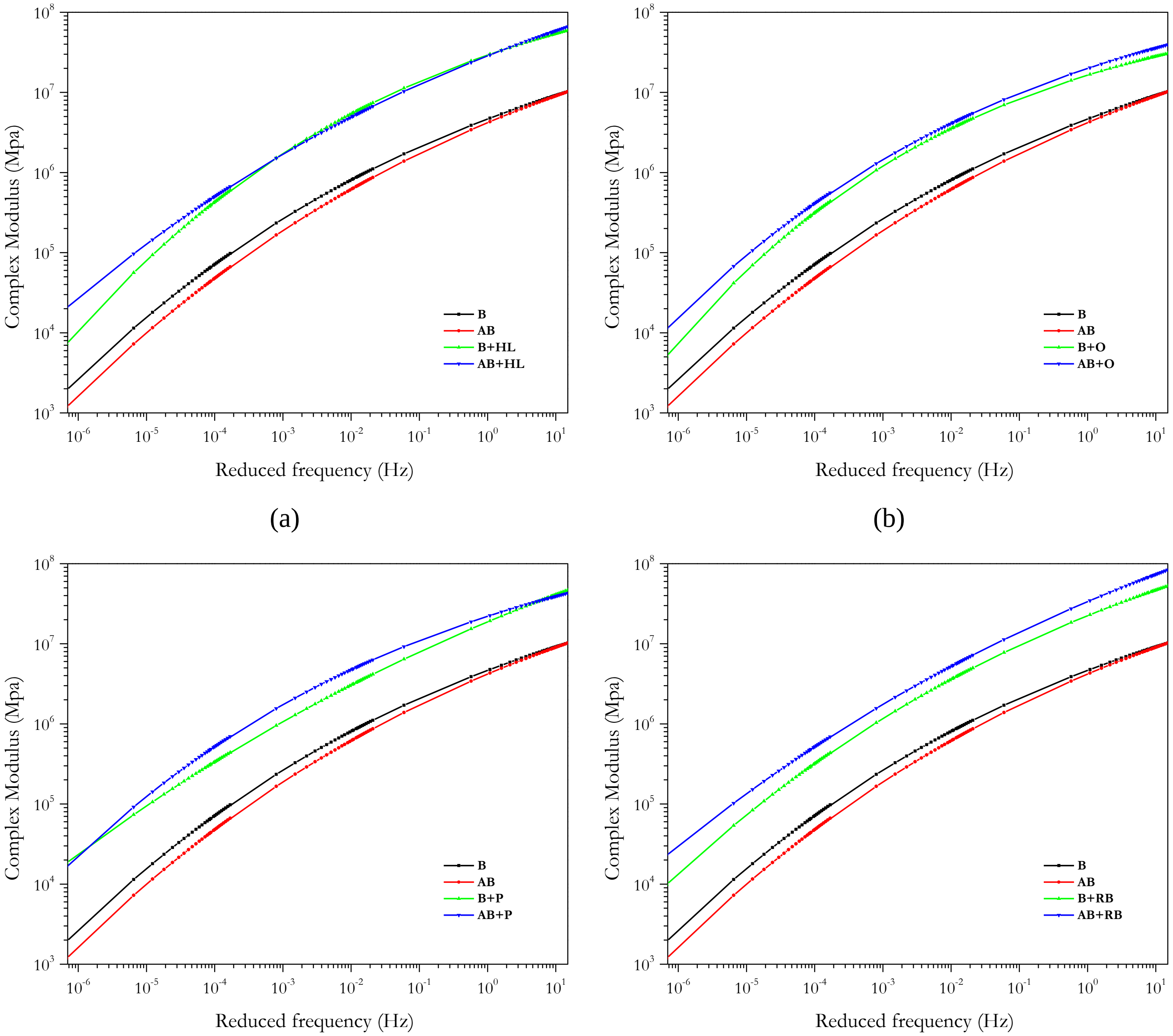
The analysis of master curves here is divided into three parts. The first of these parts is to investigate the effect of each filler on ageing properties of bitumen-filler matrix. Master curves of mastics constituting each filler are presented in Figure 4.14 for this purpose along with the master curves of neat bitumen before and after ageing.

It can be observed from the figures that shear stiffness generally decreases with increase in temperature and decrease in frequency almost in a similar manner. That is, all fillers led to increase in stiffness in both high temperature/low frequency and low temperature/high frequency regions since the master-curves corresponding to the mastics offset towards higher values of the G* compared to the neat bitumen curves. In addition, almost all of them have the tendency to increase the stiffness of their corresponding aged mastics relative to the unaged ones. The improvement in shear modulus (especially at higher temperatures and slow-moving vehicles) is apparently a positive indication on reduction of susceptibility to rutting though it is not enough since the distress is a condition requiring a long-term process.

Among the fillers, it was the red brick filler (RB) that caused largest increase in the stiffness of aged mastics in both high temperature/low frequency and low temperature/high frequency regions. The limestone filler (L) being the second largest contributor to this effect; however, has more pronounced effect in low temperature/high frequency region of the master curves. Which means that they would affect the mastic properties more when there is low temperature or during application with higher loading rates. As for the other fillers, wood ash filler relatively did not do much to aged mastic stiffness in most of the master curve regions. The other two fillers (i.e. OPC and PPC) gave almost similar results even though it was OPC which has made the least decrease in high temperature/low frequency regions.

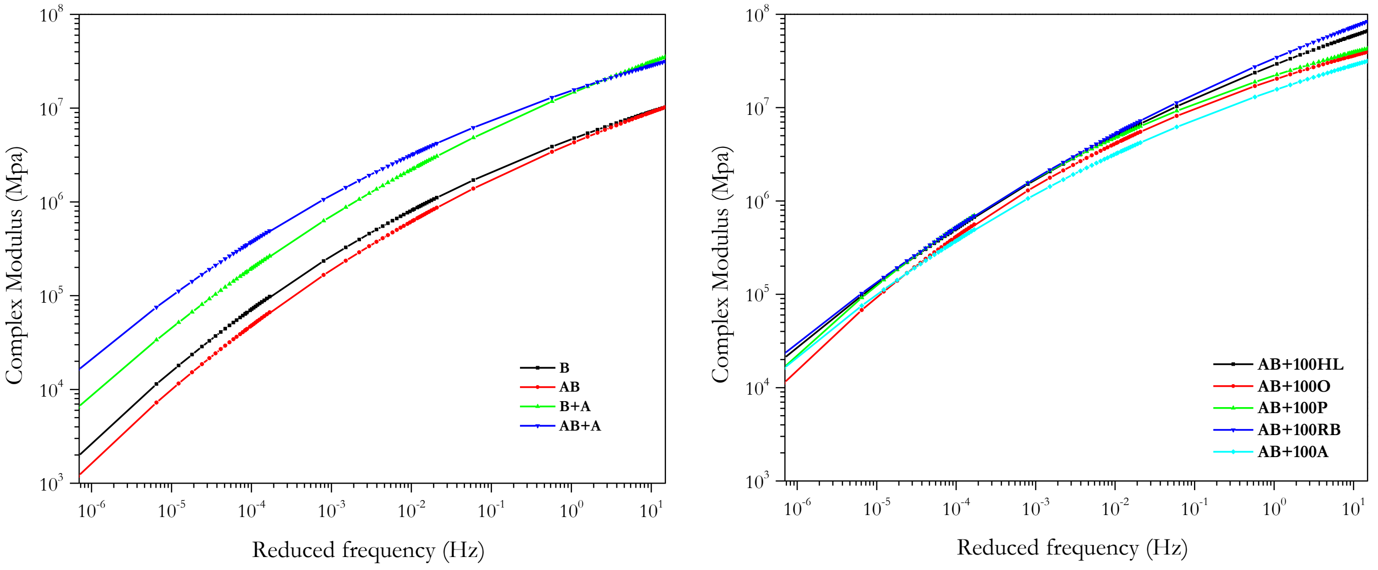
The rheological results can be related with the chemical, microscopic morphology and other physical properties of the fillers. It was previously stated that mastics prepared with the fillers L, A, OPC and PPC all had higher or almost higher peaks in the carbonyl region than the aged bitumen and it is an indication of the catalysis of bitumen oxidation in these mastics. These in combination with the rheological evaluation of the ageing level of these materials verify the existence of an anti-ageing mechanism that is related to the interactions between the filler particles and the bitumen. This mechanism refers to the adsorption of polar bitumen components apparently the ones formed upon oxidation, by the filler particles [120]. As a result, the viscosity-build-up promoters are removed from the bitumen matrix, thus leading to apparent less aged mastics than the bitumen. More specifically, fillers L, A, OPC and PPC catalyzed the oxidation of bitumen, leading to higher concentration of carbonyls in their aged mastics compared to the aged bitumen. Thus, the lower ability of wood ash fillers in stiffening and having a larger ability to catalysis of oxidation may be its inability to adsorb and hold the polar functional groups from bitumen (e.g. carbonyls) on their particles' surface due to their lower SSA. Similarly, the large stiffening effect of RB-fillers may be the result of their inability to catalyze the formation of oxidation compounds and their larger SSA.

The difference in the stiffening effect of different fillers can be also related to their critical concentration for it is the ones that have higher critical concentration which had higher ability to stiffen the mastics.


Complex Modulus (Mpa)
Reduced frequency (Hz)
10^3
10^4
10^5
10^6
10^7
10^8
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
B
AB
B+HL
AB+HL
B+O
AB+O
B+P
AB+P
B+RB
AB+RB

(a) (b)

(c) (d)



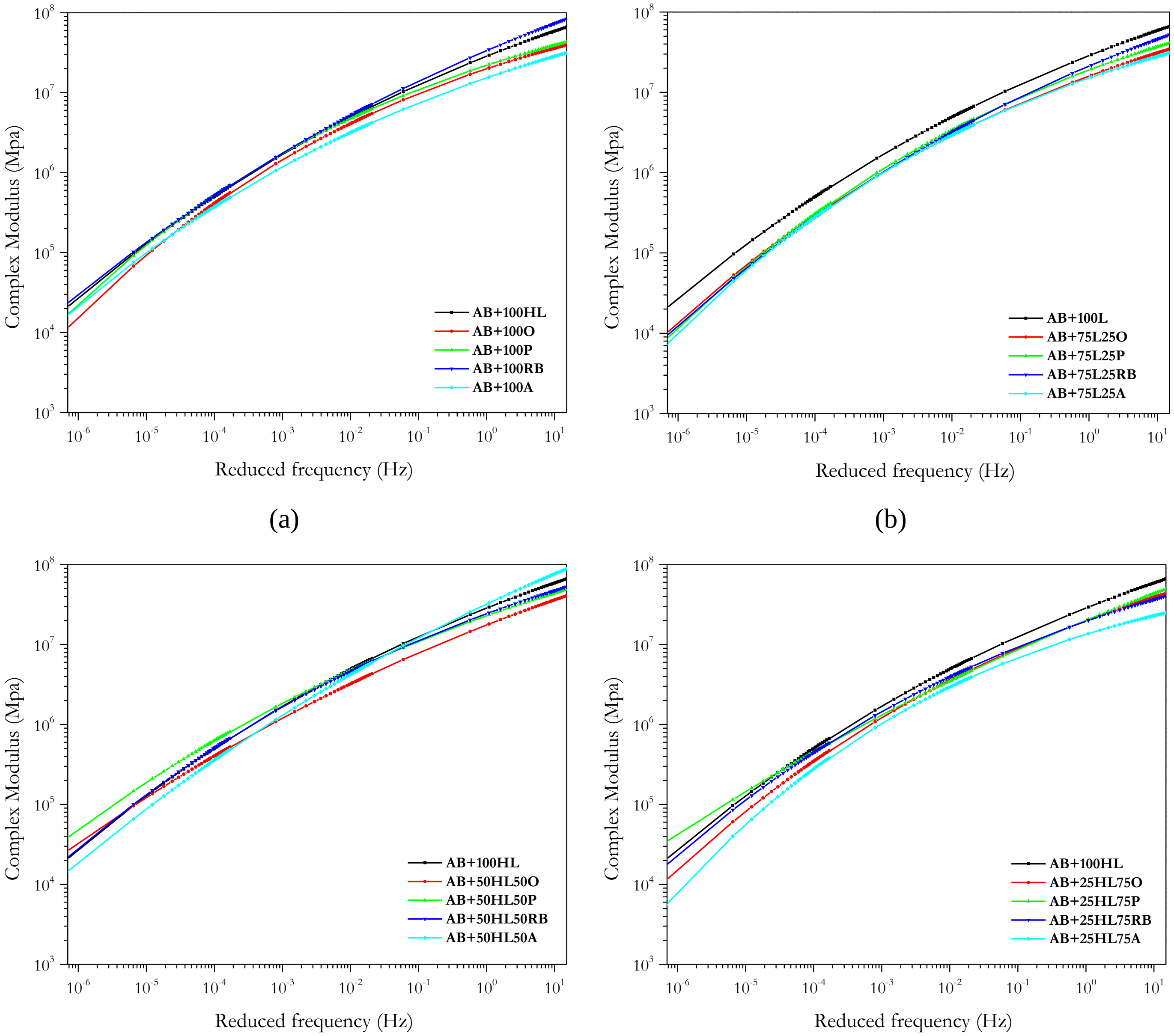
(e) (f)

Figure 4.14. Master curves for filler type effects (a) L (b) OPC (c) PPC (d) RB (e) A (f) comparison

The second group of master curves are presented in Figure 4.15 to analyze the effect of mineral filler proportion in view of percentages of replacing the limestone filler (L). The effect of completely replacing L has been discussed above. From the figures, it can be understood generally that replacing L in any proportion reduces the effect L had increasing the stiffness of aged mastic.

The effect of replacing 25% of L is shown in Figure 4.15 (b) and it can be concluded that replacing 25% of L by other fillers decreased the effect that L had in increasing the stiffness of aged mastic more than replacing 50% or 75% of it. Besides, it can be seen that this effect is more noticeable in high temperature/low frequency region. Conforming to the effect of individual fillers discussed before, it is RB filler replacement which resulted an effect nearer to the effect of L filler. Furthermore, the difference in the effect of each individual filler at this percentage of replacement is more evident in low temperature/high frequency (loading rate).

Replacing 50% of L filler in the mastics has made justice to the effect each filler had replacing L in low temperature/high loading rate and high temperature/low loading rate regions. This is because of the fact that relative the other replacement cases, the fillers had different effect in the regions and the band of master curves is almost uniform in the two regions. This means that, a 50% replacement of L filler by some other filler will would have a reduced effect than L filler in increasing stiffness of aged mastic while having a higher effect on the other region. Among the fillers 50% replacement by PPC increased the stiffness of mastic in this category better than any other filler (even L-filler itself) during high temperature or low loading rate while A-filler was the least performer in this aspect and region. In the low temperature/high frequency case it was A-filler which performed well while OPC's performance was the least. A-fillers performance is not outlier here.



(a) (b)

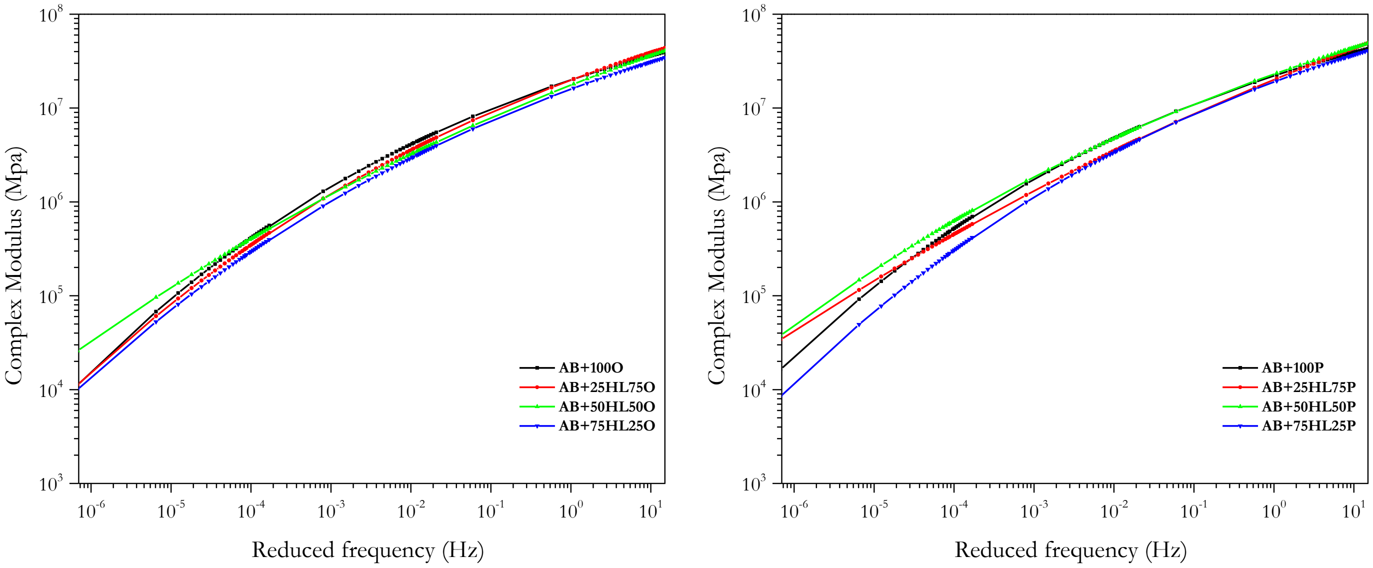
(c) (d)

Figure 4.15. Master curves for filler proportion effects (a) Mastics without L replacement (b) Mastics with 25% of L replaced (c) Mastics with 50% of L replaced (d) Mastics with 75% of L replaced

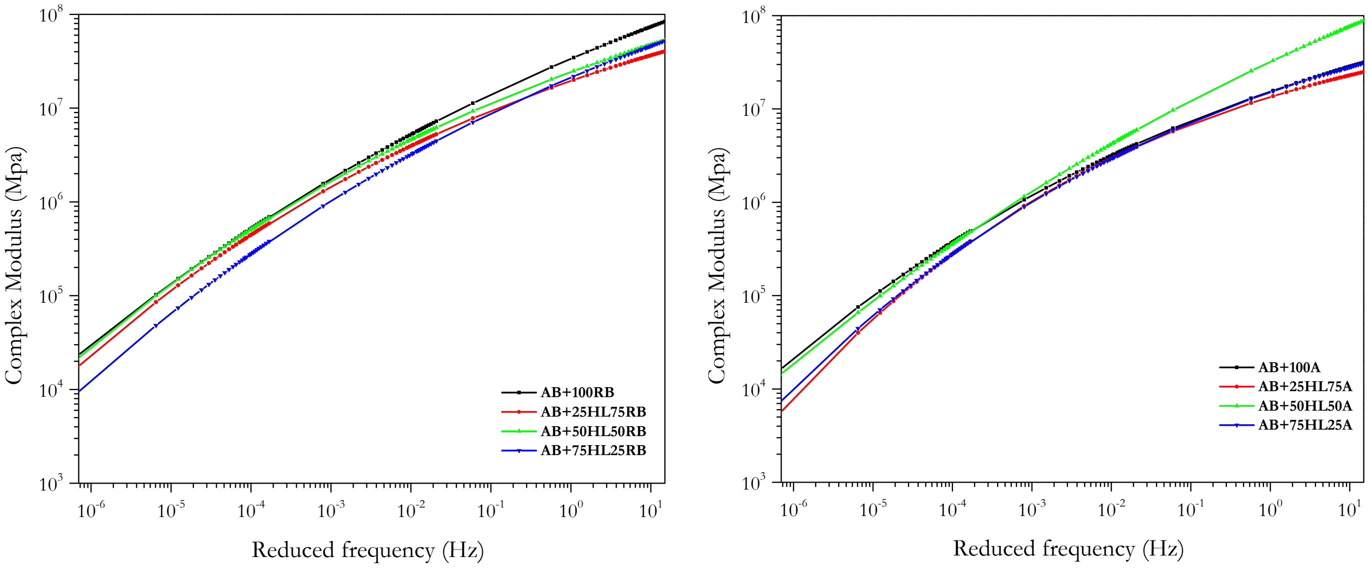
Regarding the replacement of 75% of L-filler, the difference in the effect of the fillers in increasing mastic stiffness is large in both extreme regions while lower in middle temperature-frequency cases. The effect of other fillers in increasing stiffness is less than L-filler with lower temperature/high frequency while it is again A-filler which is the worst performer among the fillers in both low temperature/high loading rate and high temperature/low loading rate conditions.

The third category of master curves is provided to show the effect of proportioning with respect to each filler type. It can be said that replacing 50% of L-filler on average results a better increase in complex shear modulus (shear stiffness) while a 25% replacement gives the least increase in stiffness of the aged mastic.

Among the filler types, replacing OPC in different proportions does not result much difference in the G* master curves. The largest un-uniformity is observed in A-filler master curves. RB-filler master curves have similar trend with the master curves of OPC but the band is a bit wider in RB-filler. The PPC filler results a greater difference in master curves in high temperature/low frequency region while the difference is very minimal on the other end.



(a) (b)



(c)

(d)

Figure 4.16. Master curves for filler type and proportion effects (a) L (b) OPC (c) PPC (d) RB (e) A

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In conclusion, five fillers (limestone filler, OPC, PPC, red brick filler and wood ash) were selected and made to form a mastic with a 60/70 penetration grade bitumen. Physical, microscopic and chemical tests were conducted in order to characterize the bitumen and fillers before mastic formation. The fillers were used individually and as a replacement for limestone filler (control) different (25%, 50% and 75%) proportions. Moreover, master curves were constructed from rheological tests of mastics and neat binders to compare the effect of filler type and proportion at different temperature and loading rate (frequency) ranges. Consequently, the following conclusions are made after a thorough analysis of the master curves:

1. The unconventional fillers, red brick powder (RB) and wood ash (A), have shown different characteristics. RB was found to have a very good mitigating effect towards short-term ageing of the mastics while the wood ash has given the worst performance relative to the control limestone filler. The relatively good mitigating effects of RB are attributed to its ability to retard catalysis of oxidation products such as compounds containing carbonyl functionalities and its rough textured angular particles which would provide larger specific surface area to adsorb (remove) polar bitumen molecules which are intern would have promoted in building-up viscosity. The wood ash has the tendency to catalyze the formation of oxidation products beside its inability to adsorb polar bitumen molecules due to its low specific surface area from the relatively large flaky particles it was made of. This made it to perform relatively lower than the other fillers even when used with the limestone filler as a replacement.
2. The Portland cements most of the time had a medium performance between RB and wood ash. The had the tendency of catalyzing oxidation which balanced by their capacity to adsorb polar molecules. As a result, it would be fair to replace some limestone at any proportion possible with these cements considering their abundance in the construction industry.

3. The difference in the stiffening effect of different fillers can be also related to their critical concentration for it is the ones that have higher critical concentration which had better ability to stiffen the mastics. However, more fillers and Cc/Cv ratios need to be considered before a major conclusion.
4. Proportioning in replacing mineral filler should be performed with great care get an optimum result from the replacements. This is from the fact that, replacing 50% of L-filler on average resulted a better increase in complex shear modulus (shear stiffness) and a uniform band of master curves while the other proportions resulted different effects on different regions of the master curves.

5.2. Recommendations for Further Research

Though this research, with the materials and pavement conditions considered, can be a significant contribution by itself to the literature on the area, additional fields need to be explored in order to complement it. Consequently, practical recommendations encompassing all possible materials, conditions and performance mechanisms can be suggested. Based on the work provided in this research the following can be recommended for future work:

1. Although short term ageing could provide an insight into the effect of mineral fillers on asphalt ageing, the conditioning by definition covers a short state in a life time of pavement mixtures. As a result, studies considering long term ageing need to be considered to give definitive recommendation on the effect of mineral fillers.
2. This research was conducted on bitumen-fillers mastics with the anticipation that mastic rheology would give better prediction of asphalt mixture rheology than pure bitumen. The ease to conduct experiments was also a major a factor. However, the research could give a better approximation to the actual pavement conditions if asphalt mixtures were used. A relation between ageing of bitumen, mastic and mixture could be generated to conform the consideration in this thesis. Besides, the effect of different mix design methods on ageing can be simultaneously studied with the effect of fillers. Thus, research considering neat bitumen, bitumen mastic and bituminous mixtures is recommended.
3. Studies to compare the effect of volume proportioning using “critical concentration” with traditional weight proportioning on ageing of mastics could provide on appropriate proportioning methods. Hence, it is recommended that conducting such researches even

before any of the previously mentioned recommendations would save resources and give a push on the notion of research for practice.

4. Finally, since comprehensive mathematical and numerical models encompassing different range of fillers and ageing conditions could help to ease the selection fillers for required function modelling studies considering chemical. microstructural and rheological properties of bituminous mixture and its constituent materials is needed.

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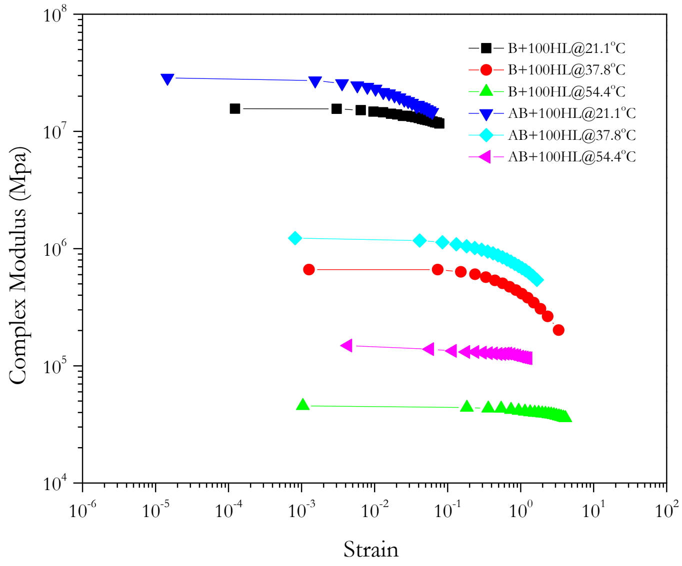
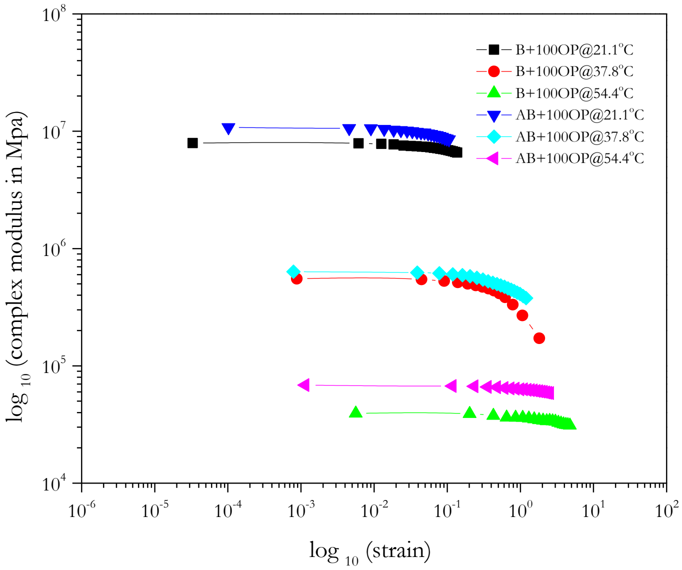
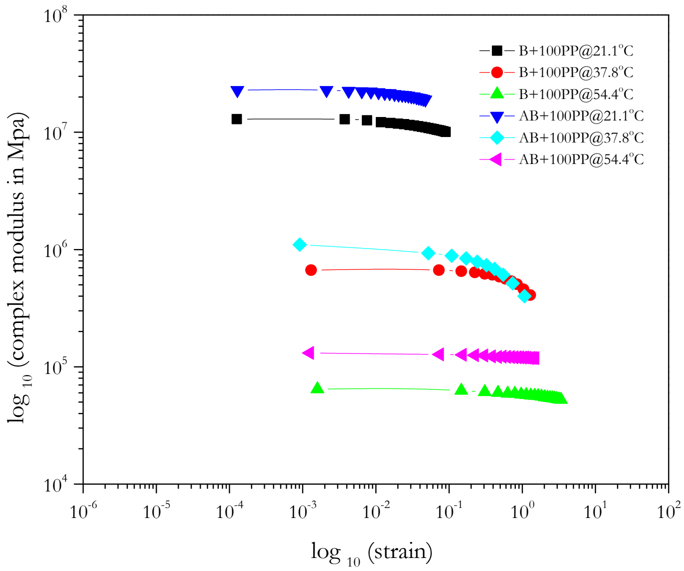
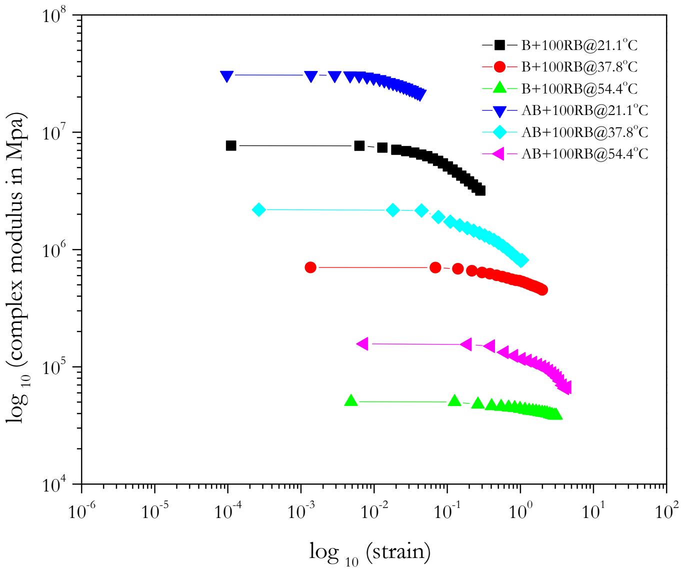
APPENDIX

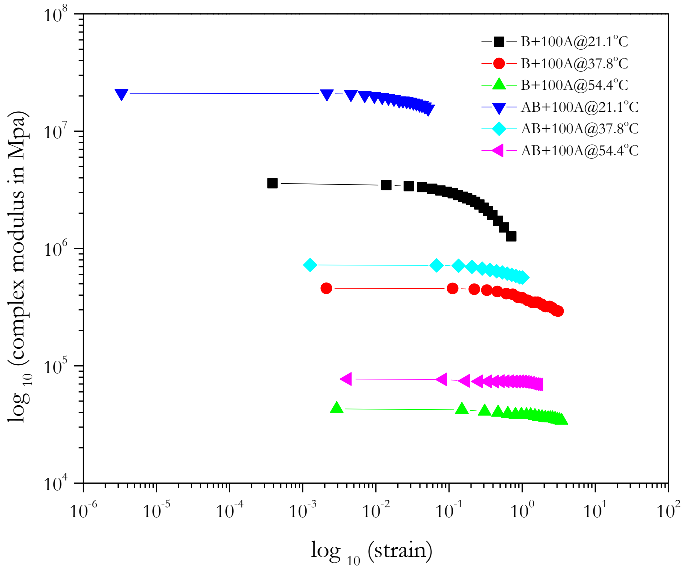
Amplitude sweep test results used for LVE range determination







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B+100A@54.4°C
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AB+100A@54.4°C
$\log_{10}$ (complex modulus in Mpa)
10^8
10^7
10^6
10^5
10^4
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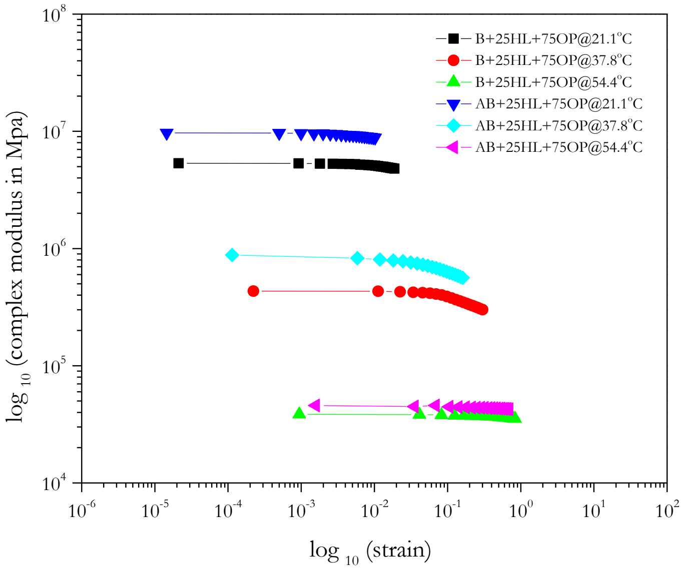
10^2
$\log_{10}$ (strain)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$\log_{10}$ (complex modulus in Mpa)
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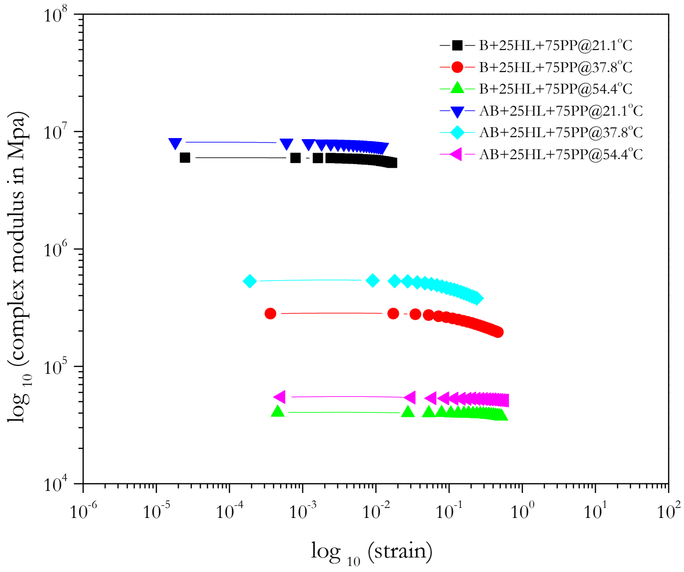
10^1
10^2
$\log_{10}$ (strain)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$\log_{10}$ (complex modulus in Mpa)
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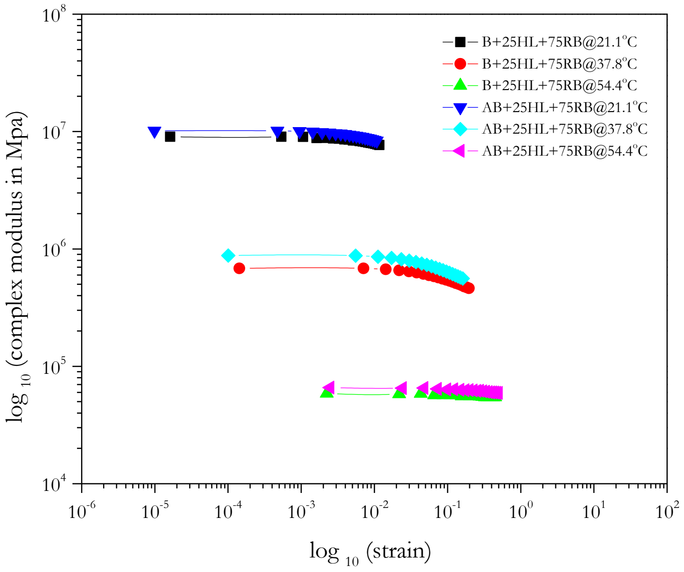
$\log_{10}$ (strain)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$\log_{10}$ (complex modulus in Mpa)
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10^4
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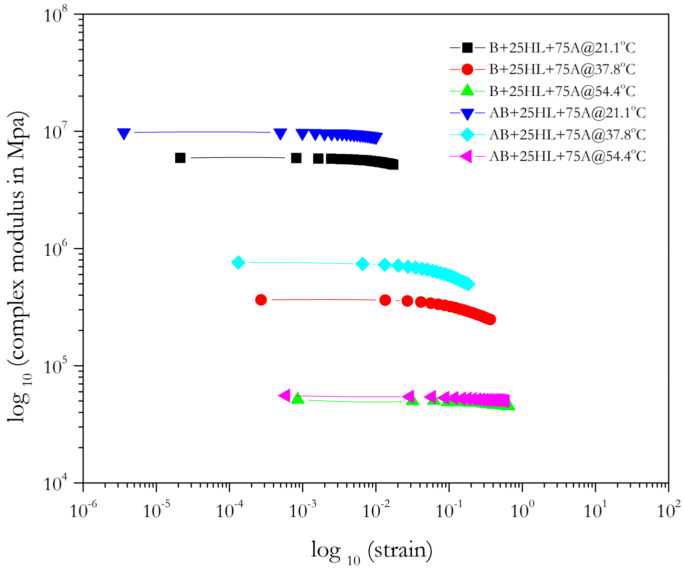
10^1
10^2
$\log_{10}$ (strain)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AB+25HL+75A@54.4°C
log 10 (complex modulus in Mpa)
log 10 (strain)
10^{8}
10^{7}
10^{6}
10^{5}
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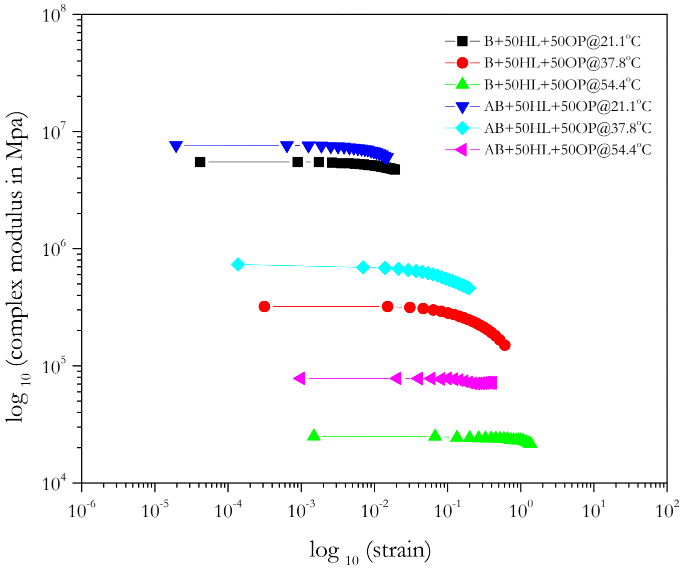
10^{2}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AB+50HL+50OP@54.4°C
log 10 (complex modulus in Mpa)
log 10 (strain)
10^{8}
10^{7}
10^{6}
10^{5}
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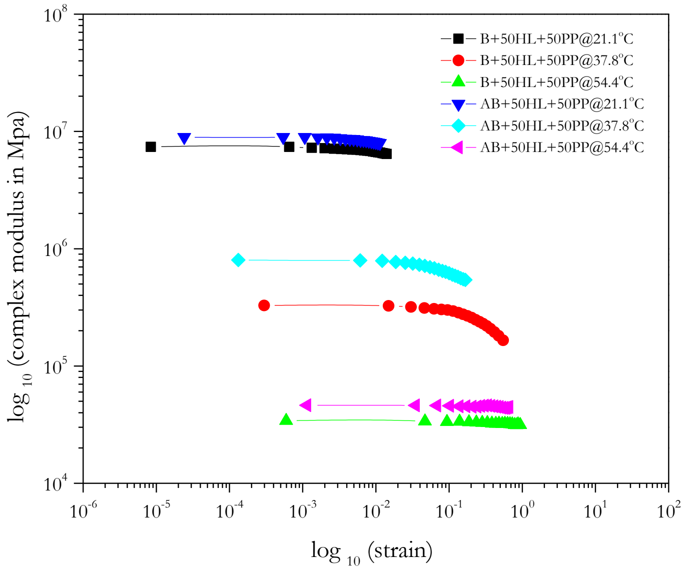
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log 10 (complex modulus in Mpa)
log 10 (strain)
10^{8}
10^{7}
10^{6}
10^{5}
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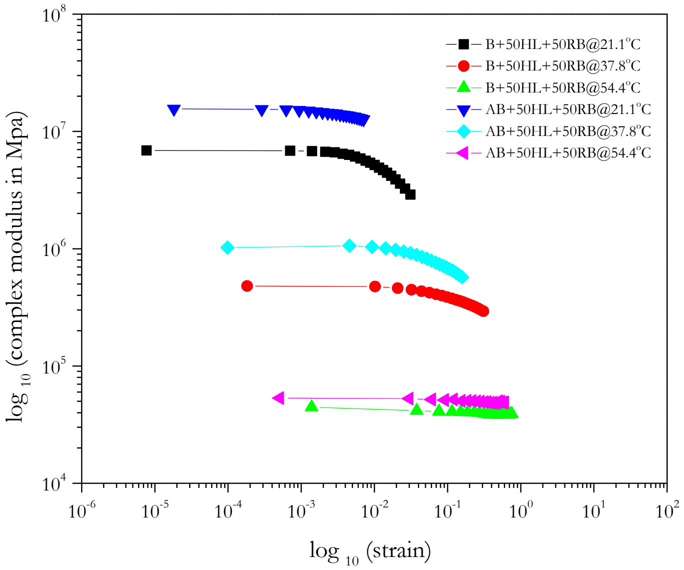
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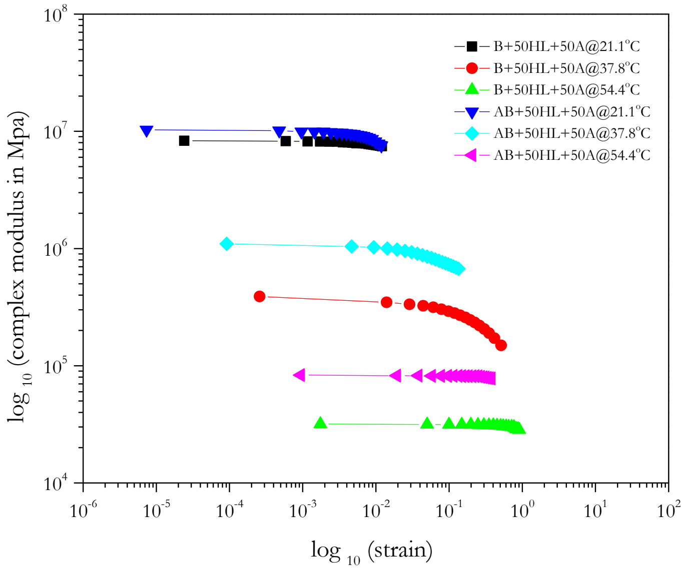
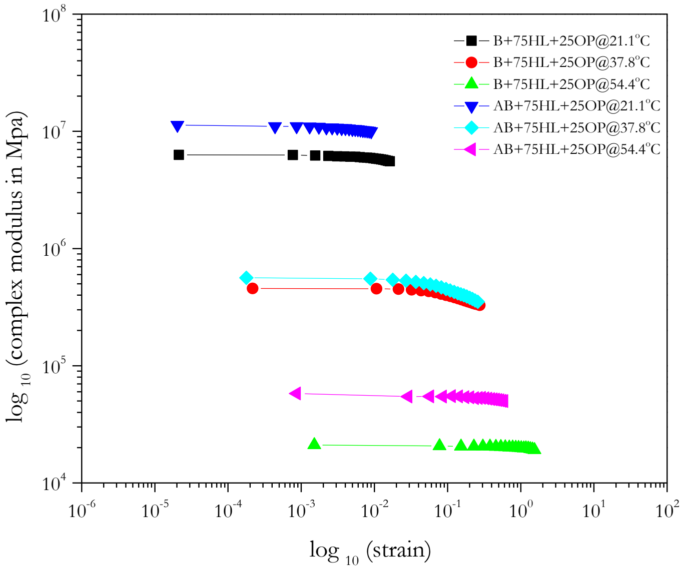
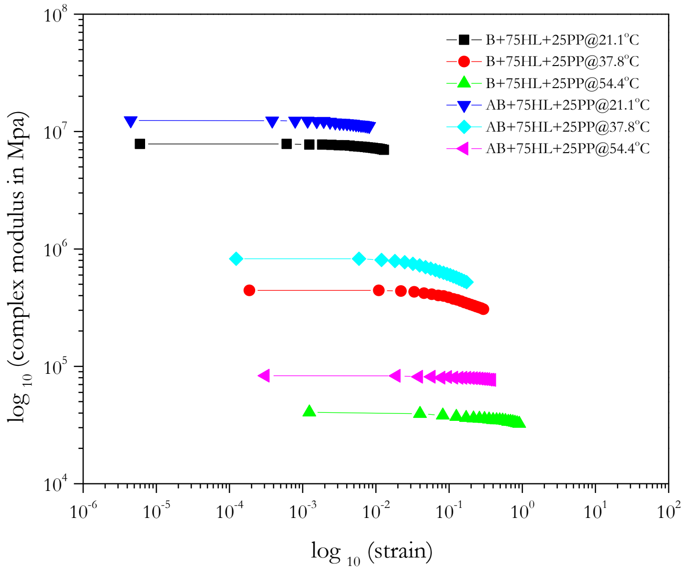
log 10 (complex modulus in Mpa)
log 10 (strain)
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}



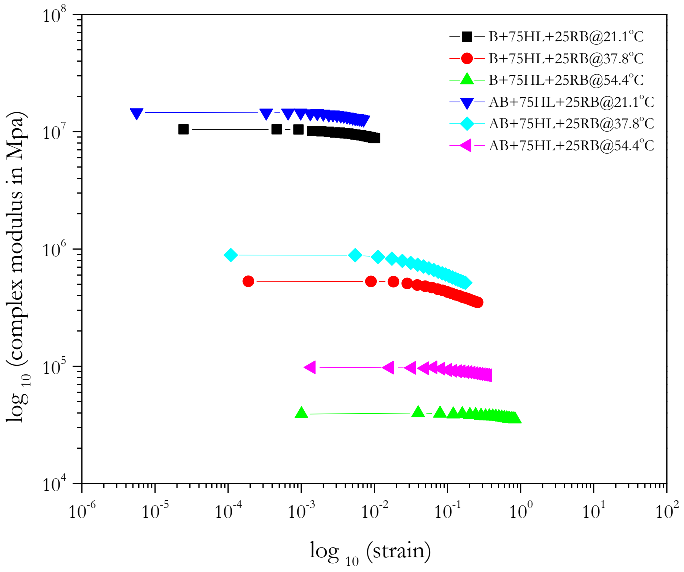
B+50HL+50A@21.1°C
B+50HL+50A@37.8°C
B+50HL+50A@54.4°C
AB+50HL+50A@21.1°C
AB+50HL+50A@37.8°C
AB+50HL+50A@54.4°C
10^4
10^5
10^6
10^7
10^8
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
log 10 (complex modulus in Mpa)
log 10 (strain)



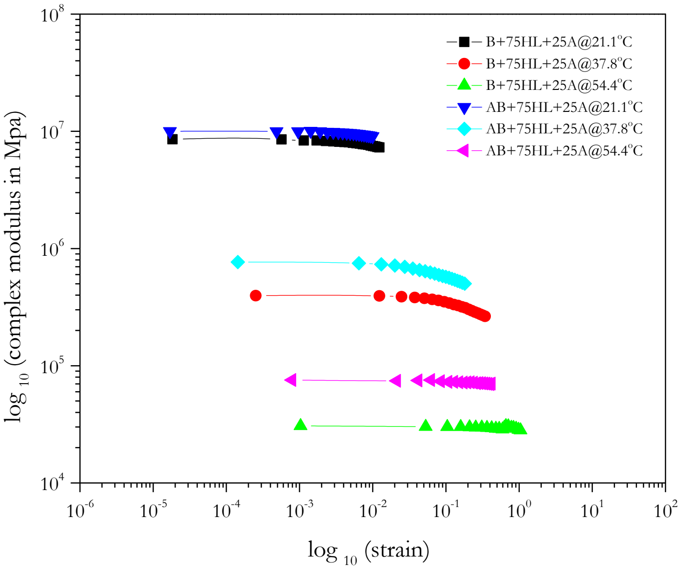
B+75HL+25OP@21.1°C
B+75HL+25OP@37.8°C
B+75HL+25OP@54.4°C
AB+75HL+25OP@21.1°C
AB+75HL+25OP@37.8°C
AB+75HL+25OP@54.4°C
10^4
10^5
10^6
10^7
10^8
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
log 10 (complex modulus in Mpa)
log 10 (strain)



B+75HL+25PP@21.1°C
B+75HL+25PP@37.8°C
B+75HL+25PP@54.4°C
AB+75HL+25PP@21.1°C
AB+75HL+25PP@37.8°C
AB+75HL+25PP@54.4°C
10^4
10^5
10^6
10^7
10^8
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
log 10 (complex modulus in Mpa)
log 10 (strain)



B+75HL+25RB@21.1°C
B+75HL+25RB@37.8°C
B+75HL+25RB@54.4°C
AB+75HL+25RB@21.1°C
AB+75HL+25RB@37.8°C
AB+75HL+25RB@54.4°C
10^4
10^5
10^6
10^7
10^8
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
log 10 (complex modulus in Mpa)
log 10 (strain)


■ B+75HL+25A@21.1°C
● B+75HL+25A@37.8°C
▲ B+75HL+25A@54.4°C
▼ AB+75HL+25A@21.1°C
◆ AB+75HL+25A@37.8°C
◀ AB+75HL+25A@54.4°C
log 10 (complex modulus in Mpa)
log 10 (strain)
10^4
10^5
10^6
10^7
10^8
10^-6
10^-5
10^-4
10^-3
10^-2
10^-1
10^0
10^1
10^2