IKENNA DESMOND UWANUAKWA INVESTIGATION ON THE PERFORMANCE OF POLYMER MODIFIED ASPHALT BINDER NEU 2021

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A THESIS SUBMITTED TO THE INSTITUTE OF GRADUATE STUDIES OF NEAR EAST UNIVERSITY

By
IKENNA DESMOND UWANUAKWA

In Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in Civil and Environmental Engineering

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ABSTRACT

The modification of asphalt binder with polymer increases the performance of the asphalt binder and also increases the chemical complexity of the binder. Researchers have identified the polymer content and density besides other factors as the key influencing parameters on the behaviour of the polymer-modified asphalt binder (PMB). However, polymers such as styrene-butadiene-styrene (SBS) of a constant density are commercially available with different molecular weight. The effect of the molecular weight of the asphalt binder has not been fully investigated. In this study, the influence of SBS polymer molecular weight was investigated using three different SBS polymers of varying molecular weight and a constant density. The molecular weight and morphological characterisation of the SBS polymer were determined using the gel permeation chromatography (GPC) and Field Emission Scanning Electron Microscopes (FE-SEM). The softening point test, viscosity test, storage stability test at 163℃ and 180 ℃, and the mechanical dynamic test using the dynamic shear rheometer were performed on an unaged, rolling thin film oven (RTFO) and pressure aged vessel (PAV) samples. The softening point at 3% SBS content was found to be 4, 6.25 and 7℃ for binder modified with low, medium and high molecular weight SBS respectively. However, at higher SBS content, the softening were dependent on the SBS structure. The storage stability of the SBS modified binder decreased with an increase in the SBS molecular weight and reached up to 60℃ with a high molecular SBS binder at 7% polymer content. The change in the G*/Sinδ parameter was found to be dependent on the ratio of polystyrene to polybutadiene content of the SBS at 3% and 5% polymer content and the polymer molecular weight at 7% polymer content. The non-recoverable creep compliance (Jnr) parameter shows that a 5% SBS polymer content, modified binder with low, medium and high molecular weight SBS respectively recorded 71%, 90% and 92% reduction from the control binder Jnr parameter value at 1.0kPa stress level and 84%, 88% and 90% at 3.2kPa stress level. The machine learning model predicted the G*/sinδ and G*.sinδ parameters with 97% and 76% performance accuracy.

***Keywords*:** Molecular weight; polymer modified binder; SBS; rutting; fatigue

ÖZET

Asfalt bağlayıcının polimer ile değiştirilmesi, asfalt bağlayıcının performansını arttırır ve ayrıca bağlayıcının kimyasal karmaşıklığını arttırır. Araştırmacılar, polimer modifiye asfalt bağlayıcının (PMB) davranışı üzerinde anahtar etkileyen parametreler olarak diğer faktörlerin yanı sıra polimer içeriğini ve yoğunluğunu tanımlamıştır. Bununla birlikte, sabit yoğunluklu stiren-bünadien-stiren (SBS) gibi polimerler ticari olarak farklı moleküler ağırlıkla mevcuttur. Asfalt bağlayıcının moleküler ağırlığının etkisi tam olarak araştırılmamıştır. Bu çalışmada, değişen moleküler ağırlığa ve sabit yoğunluğa sahip üç farklı SBS polimer kullanılarak SBS polimer moleküler ağırlığının etkisi araştırılmıştır. SBS polimerinin moleküler ağırlığı ve morfolojik karakterizasyonu jel geçirgenlik kromatografisi (GPC) ve Alan Emisyon Tarama Elektron Mikroskopları (FE-SEM) kullanılarak belirlendi. Yumuşatma noktası testi, viskozite testi, 163°C ve 180 °C'de depolama stabilitesi testi ve dinamik kesme reometresi kullanılarak mekanik dinamik test, dayanıksız, yuvarlanan ince film fırını (RTFO) ve basınç yaşlı kap (PAV) numuneleri üzerinde gerçekleştirildi. %3 SBS içeriğinde yumuşama noktası, düşük, orta ve yüksek moleküler ağırlıklı SBS ile modifiye edilmiş bağlayıcı için sırasıyla 4, 6.25 ve 7°C olarak bulunmuştur. Bununla birlikte, daha yüksek SBS içeriğinde, yumuşama SBS yapısına bağlıydı. SBS modifiye bağlayıcının depolama stabilitesi, SBS moleküler ağırlığındaki artışla azaldı ve %7 polimer içeriğinde yüksek moleküler SBS bağlayıcı ile 60°C'ye kadar ulaştı. G*/Sinδ parametresinde yapılan değişikliğin polistirenin SBS'nin polibütadien içeriğine oranına %3 ve %5 polimer içeriğine ve polimer moleküler ağırlığının %7 polimer içeriğine bağlı olduğu bulunmuştur. Kurtarılamayan sürünme uyumluluğu (Jnr) parametresi, düşük, orta ve yüksek moleküler ağırlıklı SBS'li modifiye bağlayıcı olan %5'lik bir SBS polimer içeriğinin, kontrol bağlayıcısı Jnr parametre değerinden sırasıyla %71, %90 ve %92 azalma kaydettiğini ve 3,2kPa stres seviyesinde %84, %88 ve %90 oranında azaldığını göstermektedir. Makine öğrenimi modeli G*/sinδ ve G*.sinδ parametrelerini %97 ve %76 performans doğruluğu ile tahmin etti.

Anahtar kelimeler :Moleküler ağırlık; polimer modifiye bağlayıcı; SBS; izi; yorgunluk

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ANN	Artificial Neural Networks
APP	Atactic Polypropylene
ARP	Asphalt Rich Phase
ASTM	American Society For Testing And Materials
DSR	Dynamic Shear Rheometer
EBA	Ethylene Butyl Acrylate
EDX	Energy Dispersive X-Ray Analysis
EMA	Ethylene Methyl Acrylate
EPDM	Ethylene-propylene-diene terpolymer
EVA	Ethylene-Vinyl Acetate
FE-SEM	Field Emission Scanning Electron Microscopes
GPC	Permeation Chromatography
GPR	Gaussian Process Regression
MEPDG	Mechanistic-Empirical Pavement Design Guide
MSCR	Multiple Stress Creep And Recovery
NCHRP	National Cooperative Highway Research
PAV	Pressure Ageing Vessel
PVC	Polyvinyl Chloride
PE	Polyethylene
PMB	Polymer Modified Binder
PP	Polypropylene
PRP	Polymer-Rich Phase
PS	Polystyrene
RNN	Recurrent Neural Networks
RTFOT	Rolling thin film oven Test
SANS	Small-Angle Neuron Scattering
SAXS	Small-Angle X-Ray Scattering
SBR	Styrene-Butadiene-Rubber

SBS	Styrene- Butadiene-Styrene
SEBS	Styrene-Ethylene-Butadiene-Styrene
SIS	Styrene-Isoprene-Styrene
SVM	Support Vector Machine

CHAPTER 1

INTRODUCTION

1.1 Introduction

Asphalt, a by-product of the fractional distillation of crude oil used in the manufacturing of asphalt concrete for flexible pavement surfacing, and is a Newtonian fluid at high temperatures. Newtonian fluid here refers to compounds at a liquid state whose viscosity is independent of shear rate. Unmodified asphalt (neat asphalt) has been reported to exhibit Newtonian properties. Its viscosity is affected by temperature and independent of the applied shear stress (Lesueur, 2009). However, the use of neat asphalt in the construction of flexible pavement has been found to be susceptible to temperature change. At high temperatures, the viscosity of asphalt binder decreases resulting in permanent deformation under repeated loading. At low temperature, the binder becomes stiff and brittle, a problem associated with low temperature cracking in the flexible pavement (Polacco et al., 2015).

Modification of asphalt binder has improved its resistance to temperature change. Among such modification is the inclusion of polymer materials in the binder. The resulting polymer modified binder (PMB) has been reported to have different viscosity properties with respect to the base binder. While base binder is a Newtonian fluid at high temperatures, PMB is said to exhibit non-Newtonian characteristics at a corresponding temperature of the base asphalt. In Non-Newtonian behaviour, the viscosity is affected by shear rate. While existing standards for the selection of asphaltic concrete materials is based on properties of neat asphalt, the incorporation of PMB using these specifications result in high mixing and compaction temperatures. Asphalt mix design incorporates equiviscous temperature for estimation of mixing and compaction temperature. For example, Superpave (superior performing asphalt pavements) specified temperature corresponding to the viscosity at 0.17±0.02 and 0.28±0.03 Pa s for mixing and compaction respectively (Yildirim, 2007; Yildirim et al., 2006).

Since PMB is affected by shear rate, it is important to find a variable that correlates with the change observed in the modified asphalt binder.

Over the years researchers have identified polymer structure and density, polarity and solubility as factors affecting the rheology, compatibility and properties of polymer modified asphalt binder (Zhu et al., 2014). For example, high density (relative to asphalt) modifiers such as crumb rubber settle out at hot storage and increase the stiffness of the binder. On the other hand low-density, modifiers such as styrene-butadiene-styrene (SBS) tend to float about the neat asphalt, indicating that the degree of phase separation in proportion to the change in the polymer density (Liang et al., 2019; Z. Ren et al., 2020). However, a polymer of the same density and type are manufactured with a different molecular weight that controls the unique rheological characteristics of the polymer. Porter & Johnson, (1960) reported that the viscosity of the polymer increases with the molecular weight, which implies that the molecular of the materials increases its stiffness. In asphalt, studies have shown that oxidation of asphalt increases the molecular weight of the asphalt and precipitates asphaltene (Collins & Bouldin, 1992).

Since the molecular weight affects the viscosity and mechanical behaviour of asphalt and polymer, in a blended mix (polymer and asphalt), the inherent properties of individual materials would induce a significant effect on the blend. Therefore, in one part, this study seeks to investigate the effect of SBS polymer molecular weight on thermo-rheological properties of polymer modified asphalt binder and the economic benefits of modifying asphalt with polymer higher molecular weight.

In the other part, laboratory evaluation of asphalt binder and concrete properties are expensive despite the fact that asphalt is major road construction materials and road networks is an essential part of a nation's economy. The understanding of the behaviour of asphalt binder has not been fully explored and the modification of asphalt with a secondary material (e.g. polymer) increases the complexity of the material behaviour. The consideration of a less expensive approach to the determination of flexible pavement properties, Bari et al., (2006) proposed a regression model for the estimation of dynamic modulus (E*) for asphalt mix under level 2 mechanistic-empirical pavement design guide (MEPDG) structure. The proposed design is useful for estimating permanent deformation in asphalt pavement without laboratory evaluation. However, at Level 1 and volumetric design stage, experimental evaluation is required to select an appropriate binder to resist permanent deformation and fatigue cracking. Therefore, without a complementary model at the binder selection stage,

to select the binder using the rutting and fatigue parameters, the Witczak model becomes expensive to apply. Hence, this study seeks the explore the potentials of using the existing artificial intelligent tool in predicting the rutting and fatigue parameter of asphalt binder.

1.2 Problem Statement and Research Justification

The modification of asphalt binder with polymer leads to improved binder resistance to temperature change and SBS is widely used in the modification of asphalt as a result, there is an increase in the stiffness, reduction in temperature sensitivity and improvement in the elastic response of the blended binder (Zhu et al., 2014). However, several drawbacks such as thermal instability and phase separation have been attributed to SBS polymer-modified asphalt binder.

Thermal instability and phase separation of PMB is one of the major factors for consideration in the selection of a modifier especially for binder consider for long haulage or longer storage. Thermal instability between asphalt and the modifiers is accessed by storing PMB at elevated temperatures. This method delineates the thermodynamic stability of the modified binder mix. The difference in the softening point between the asphalt rich phase (ARP) and the polymer-rich phase (PRP) measures the degree of settling out that has occurred.

This drawback is consistent within the literature. For example, Ren et al., (2020) recorded 41.3℃ in the softening point difference at 6% stored at 163°C for 48h. Sun & Lu, (2003), stored 2 base asphalts modified with 4% branch SBS at the same condition and recorded 32.5 and 35℃ as the softening point difference between the ARP and PRP for the produced PMBs. Lu & Isacsson, (1997) and Lu et al., (2002) stored 19 samples produced from modification of 5 neat asphalt with 2 SBS polymer (linear and branch structure) at 180℃ for 72h. The SBS were incorporated at 3, 6, and 9% by the weight of the neat asphalt. The maximum softening point difference within the linear SBS PMB was 5℃ and increased to 37.5℃ and 50℃ for 6 and 9% linear SBS content respectively, while 6% branch SBS content reached 63.5℃. Data from Saad & Ahmed (2019) showed that at 5% SBS content the softening point difference was 10℃. The disparities could be attributed to the density, structure, and molecular weight of the polymer.

The influence of density and structure of polymer on the behaviour of PMB has been studied. However, the extent to which the polymer molecular weight influences the behaviour of asphalt binder is still unknown. These unknowns have further increased the complexity of PMB and make the selection of appropriate and economical modifier difficult.

Besides the selection of asphalt binder based on thermal stability, a binder is also selected based on its mechanical properties such as the rutting and fatigue parameters. The current method of evaluating the rutting and fatigue parameter involved laboratory experiments that are time-consuming. Bari et al., (2006) proposed a regression model for the estimation of dynamic modulus (E*) for asphalt mix under level 2 mechanistic-empirical pavement design guide (MEPDG) structure. The proposed design is useful for estimating permanent deformation in asphalt pavement without laboratory evaluation. However, the model is limited to asphalt concrete.

In this research, there is a need to quantify the effect of polymer molecular on the thermo-rheological behaviour of PMB. Such information in combination with existing knowledge would assist pavement designers in the selection of appropriate and economical modifiers for PMB. Also, there is a need for a predictive model for rutting and fatigue parameters for asphalt binder that will eliminate the laboratory produces in measuring these parameters.

1.3 Problem Question

The research questions arising from the introduction of the research statement of this research to be investigated;

1. What are the effects of polymer molecular weight on the thermo-rheological behaviour of polymer-modified asphalt binder?

2. Are dynamic test parameters sufficient for modelling rutting and fatigue parameters?

- And if so, what processes or methods can be applied to estimate the reliability of AI models for rutting and fatigue parameters?

1.4 Research Aim and Objectives

The research aims and objectives are fashioned to address the aforementioned research questions and contribute to the existing knowledge gap on the extent of polymer molecular weight effect on the behaviour of asphalt binder, and the possibility of modelling asphalt binder rutting and fatigue parameters. Therefore, the aim of this research is to provide detailed information through experimental evaluation on the effects of polymer molecular weight on the modified asphalt binder behaviour, and model rutting and fatigue parameters in a binder using the experimental data.

The research objectives are;

1. Select 3 different polymers with the same density but varying molecular weight for modification of asphalt binder at 3, 5 and 7 %. wt. polymer content.
2. To experimental investigated the influence of polymer molecular weight on the storage stability, softening point properties and thermo-rheological behaviour of modified asphalt binder.
3. To analyse the influence of polymer molecular weight on the ageing behaviour, rutting and fatigue properties of the modified asphalt binder.
4. To develop an artificial intelligence model using an existing artificial intelligent tool for rutting and fatigue parameters in the asphalt binder.
5. To evaluate the reliability of the developed artificial intelligent model in estimating the binder parameters.

1.5 Research Scope

This research is limited to;

1. Experimental evaluation of physical and rheological properties using the dynamic shear rheometer, viscometer, and softening point (ring and ball) equipment.
2. Binder short- and long-term ageing conditioning.
3. Binder storage stability at 163 and 180℃ for 48 and 72 hours.
4. Analysis of the experimental results and cost-benefit analysis for using PMB with varying molecular weight.

5. Artificial intelligence model for predicting rutting and fatigue parameters.

1.6 Research Methodology

This research involves a combination of experimental research (analytical) which ask the question “WHY” and “HOW” a system is affected, or influenced, by a particular variable, and predictive research that undertakes the process of extrapolating future results based on current information.

Therefore, a systematic approach was adopted to ensure a proper investigation, analysis and presentation of the findings to satisfy the justification of undertaking the research. The summary of the research program is presented in Figure 1.1.

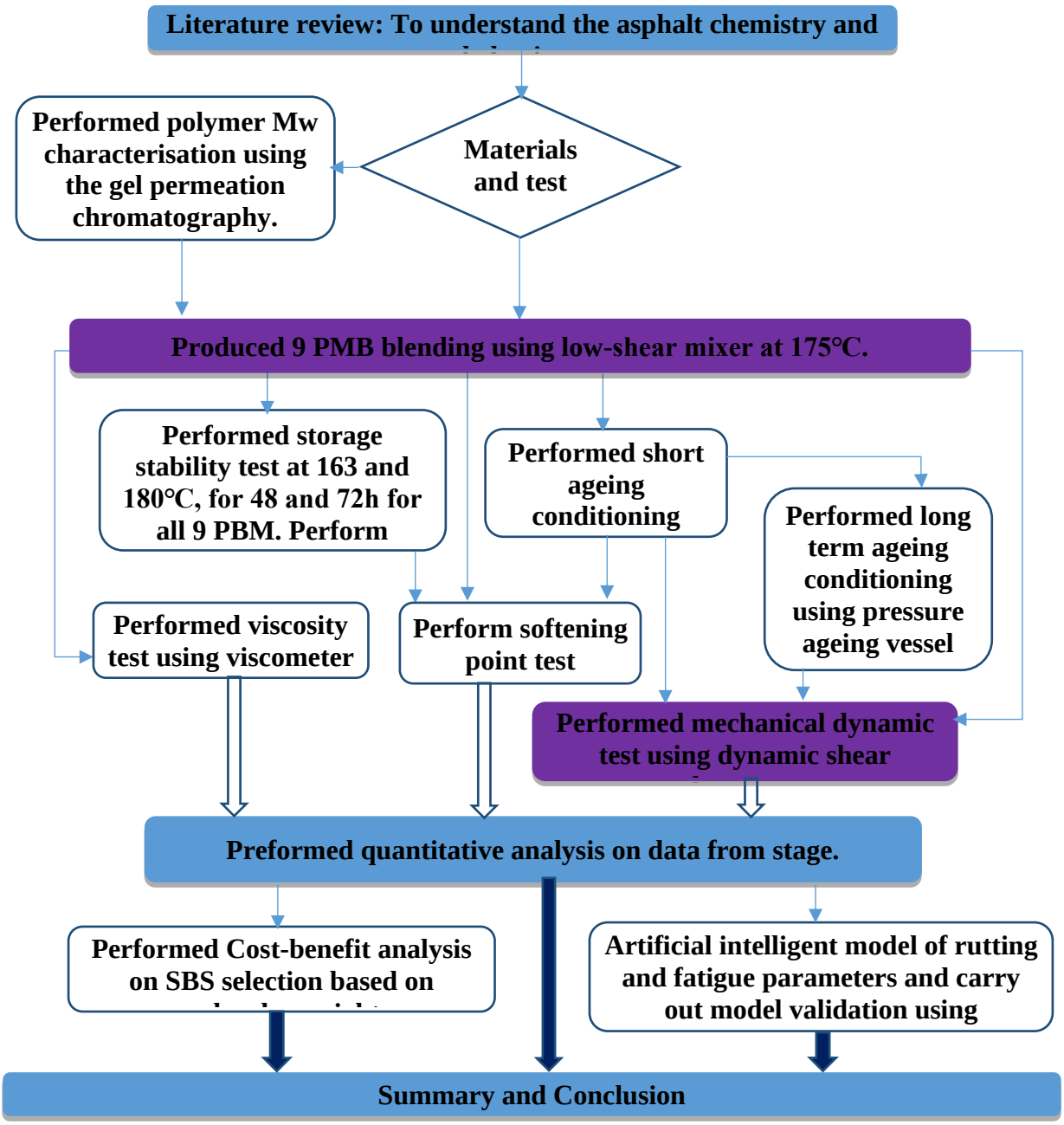


Figure 1.1: Research Program

1.7 Research Novelty Achievement

The contributions of this research are;

1. A detailed assessment of the influence of SBS polymer molecular weight on thermo-rheological behaviour of asphalt binder.

2. Cost-benefit analysis on the selection of SBS asphalt binder based on molecular weight.
3. Artificial intelligent model for predicting rutting and fatigue parameters using unaged binder data.

1.8 Thesis Structure

Chapter Two presents the existing findings and background information of the research.

In Chapter Three, the materials, methods, and standards are outlined and referenced accordingly. Also, the material characterisations were presented, which includes the polymer molecular and morphology characterisation, softening point and viscosity of the asphalt and PMB.

The results and discussions are presented in Chapter Four which includes; Thermo-rheology and dynamic behaviour analysis; cost-benefit analysis of using high molecular SBS for binder modification and the proposed machine learning models for the prediction of rutting and fatigue parameters of the binders.

Finally, the research conclusion was summarised in Chapter Five and recommendations were also proposed.

CHAPTER 2

ASPHALT AND POLYMER MODIFIED ASPHALT

2.1 Introduction

The use of the word asphalt should not confuse the reader that it implies a different material from that of bitumen. However, this study preferred asphalt since it is the commonly used term to express the residual product of petroleum crude oil. Similarly, where the word "oil" is used alone, the referred material will be defined otherwise it means petroleum crude oil and crude oil of fossil deposit used for manufacturing of petroleum products. This chapter presents literature background of asphalt chemistry and the composition and modification of asphalt.

2.2 Asphalt as a Construction Material

Asphalt is a naturally occurring compound and can also be manufactured artificially. The word "asphalt" in some literatures are interchanged with bitumen. With respect to material science, both defined the same material which is a by-product of fractional distillation of petroleum crude oil. Asphalt is a complex mixture of organic compounds found in nature or a residual product of the petroleum crude refinery process. It differs from the coal-tar or coal pitch in physical properties and behaviour.

Asphalt found in nature such as those of "lake asphalt" discovered in 1595 by Sir Walter Raleigh in Trinidad. The "Trinidad lake asphalt" contains 54 % wt. of binder, 36 % wt. of mineral matters and 10 % wt. of organic matters. Other natural asphalt includes Gilsonite with a large deposit in the state of Utah, USA; Buton natural rock asphalt found in South Sulawesi province of Indonesia; Rock asphalt used since the seventeenth century with large deposit across the globe (Hunter, 2015). Besides the naturally occurred asphalt, asphalts are extracted from residual petroleum crude oil through air blowing or by a solvent method. This asphalt according to the SHRP report (Robertson, 1991), "petroleum asphalt" is a high boiling vacuum distillation residuum that contains thousands of different molecular species.

Today, the use of asphalt stretched across several industries of which road construction is believed to consume about 85% of the world annual 87 million tonnes (Asphalt Institute. & European Bitumen Association., 2015). Other uses of asphalt (refined petroleum residua) include agriculture, buildings and industrial paving, hydraulics and erosion control, insulation and sealant industries, railways (ballast treatment) and recreation (lawn paving) (James G. Speight, 2016).

2.3 Asphalt Chemistry

The full characterization of asphalt chemistry is still ongoing. There are two principal schools of thought dominating the debate on the structure of asphalt; the colloids school of thought believed that asphalt has a colloid nature whereas this view is opposed by another group of researchers with the view that it is a homogenous fluid with no colloidal properties.

The properties and composition of a given asphalt are controlled by the petroleum crude source and method of manufacturing. Asphalt is a residual product of crude oil extracted as "long residue" from the distillation process of petroleum crude. An additional process is required for extraction of feedstock, used for asphalt from long residue in a vacuum distillation column at a reduced pressure to avoid thermal decomposition of the residue. The residue is further distilled between 10 -100 mmHg and 350 and 450 ^{o}C leaving a high viscous "short residue" (Hunter, 2015)

Depending on the properties of the short residue, a further pre-process of air blowing in the asphalt is carried out to convert the Low molecular weight (MW) maltenes into high MW asphaltenes which result in the reduction of the penetration value, and improve temperature susceptibility (Hunter, 2015).

The chemistry of asphalt cement is still under debate with several unknowns. One would have "believed that today's sophisticated analytical tools, computer-controlled instruments that work with milligrams of asphalt, should make the connection between asphalt composition and performance properties. Yet the complex chemical mix of even a single asphalt may never be adequately described"(Goodrich, Goodrich, & Kari, 1986). Boussingault in 1836 was the first to attempt the separation of native asphalt deposited in Bechelbroon, France into two separate units; petrolene and asphaltene at 230℃. The results

gave 85 and 15wt % of petrolene (distillable fraction) and asphaltene (solid fraction) (Boussingault, 1836, 1837; Lesueur, 2009).

Lesueur (2009), pointed out other works of (Richardson, 1913) that also identified asphaltene as the residue (insoluble) part of asphalt (bitumen) in a naphtha from paraffin petroleum of 62 or 88 Baume and the solute of matlenes. Furthermore, the petrolene is the distillable component of asphalt and maltenes is the asphalt fraction soluble in n-heptane. Further complexity of maltenes and asphalt structure are discussed in (Lesueur, 2009).

In the reviewed work by Polacco et al. (2015), the research classified asphalt into low-MW oil between 240 – 800 Da and high MW oil of 800 – 24000Da containing a high concentration of polycyclic and polyaromatics structures.

Table 2.1: Analysis of asphalt compounds (Mortazavi & Moulthrop, 1993).

Origin		**AAA-1 Canada**	**AAB-1 USA**	**AAC-1 Canada**	**AAD-1 USA**	**AAF-1 USA**	**AAG-1 USA**	**AAK-1 Venezuela**	**AAM-1 USA**
C	wt.%	83.9	82.3	86.5	81.6	84.5	85.6	83.7	86.8
H	wt.%	10.0	10.6	11.3	10.8	10.4	10.5	10.2	11.2
H + C	wt.%	93.9	92.9	97.8	92.4	94.9	96.1	93.9	98.0
H/C	Molar	1.43	1.55	1.57	1.59	1.48	1.47	1.46	1.55
O	wt.%	0.6	0.8	0.9	0.9	1.1	1.1	0.8	0.5
N	wt.%	0.5	0.5	0.7	0.8	0.6	1.1	0.7	0.6
S	wt.%	5.5	4.7	1.9	6.9	3.4	1.3	6.4	1.2
V	ppm	174	220	146	310	87	37	1480	58
Ni	ppm	86	56	63	145	35	95	142	36
Mn	g/mol	790	840	870	700	840	710	860	130

In addition to MW, asphalt compounds can be classified with respect to their polarity.

From Table 2.1, typical asphalt molecules contain about 90% hydrocarbon and 9% heteroatoms; nitrogen, sulphur oxygen vanadium and metals. The presence of these heteroatoms influences the polarity of asphalt molecules. According to Robertson (1991), products formed after oxidation of asphalt due to the ageing or blowing process contributes to the polarity of the asphalt molecules.

With respect to the polarity of an asphalt, Table 2.1 illustrates the percentage by weight of heteroatom required to induce polarity in asphalt. According to Lesueur (2009) review of related literature, sulphur in asphalt is in the form of sulphides, thiols and sulfoxides. Oxygen is in presented as; keteones, phenols and carboxylic acids. Nitrogen as; pryrolic and pyridinic structures whereas metals are present as metalloporphyrins. However, the functional group of the polar atoms do not exceed 0.1 mol/l for straight-run asphalt which increases with the increase in ageing of the asphalt. The density of asphalt at room temperature is estimated between 1.01 – 1.04 g/cm^3 and glass transition about -20℃ which could vary within a wider range from + 5℃ to – 40℃ depending on the source of the petroleum crude oil (Lesueur, 2009).

Over the years, chemists have developed a major way to characterise asphalt composition with the SARA (saturate, aromatics, resins and asphaltenes) method. SARA can further be categorised into maltenes and asphaltenes. Maltenes is composed of saturates, aromatics and resins that are soluble in n-heptane leaving asphaltenes as insoluble.

2.3.1 Saturates

For asphalt binders, saturates are colourless or lightly coloured liquid at room temperature, which accounts for 5 -20 wt.% of the asphalt, with a very low glass transition of about – 70℃. Saturates could be said to have traces of heteroatoms, or do not have heteroatoms at all which gives it a nonpolar behaviour (Corbett, 1969; Hunter, 2015; Lesueur, 2009; Polacco et al., 2015). They consist of straight and branched-chain aliphatic hydrocarbons as well as cycloaliphatic compounds, with a molecular weight between 470 – 880 g/mol and with H/C ratio of approximately 2 (Hunter, 2015; Lesueur, 2009)

Table 2.2: Analysis of chemical SARA fractions (Branthaver et al., 1993; Corbett, 1969; Ecker, 2001; Koots & Speight, 1975; Lesueur, 2009; Michon et al., 1997; J. G. Speight, 2004)

	H/C	**C**	**H**	**O**	**N**	**S**	**M_n**	**Solvent in ASTM D4124**
	–	**%**	**%**	**%**	**%**	**%**	**g/mol**	
Bitumen	1.5	80–88	8–12	0–2	0–2	0–9	600–1500	–
Saturates	1.9	78–84	12–14	< 0.1	< 0.1	< 0.1	470–880	n-heptane
Aromatics	1.5	80–86	9–13	0.2	0.4	0–4	570–980	toluene and toluene/methanol 50/50
Resins	1.4	67–88	9–12	0.3–2	0.2–1	0.4–5	780–1400	trichloroethylene

	H/C	C	H	O	N	S	M_n	Solvent in ASTM D4124
	–	%	%	%	%	%	g/mol	
Asphaltenes	1.1	78–88	7–9	0.3–5	0.6–4	0.3–11	800–3500	n-heptane insoluble

2.3.2 Aromatics

In asphalt compounds they constituent 40 – 60wt% of the total asphalt with the lowest molecular weight of nephthene aromatics fraction, and usually a dark-brown in colour (Hunter, 2015). At room temperature, they are viscous than saturates and with a glass transition of – 20℃. The molecular weight ranges from 570 -980g/mol (Table 2.2). Aromatics contain nonpolar carbon chains which are slightly aliphatic with condensed aromatics rings (Hunter, 2015; Lesueur, 2009). Also, in asphalt, aromatics provides dispersion for the peptised asphaltenes (Hunter, 2015).

2.3.3 Resins

They are dark-brown polar aromatics with a small quantity of heteroatoms (Hunter, 2015). It consists of 30 – 45wt.% of the total asphalt, and is also a dispersing or stabilizing agent for asphaltenes in asphalt (Hunter, 2015; Lesueur, 2009). The proportion of resins to asphaltenes in asphalt controls the amount of the "solution" or "gelatinous" behaviour of the asphalt which in asphalt chemistry is referred to as "gel" or "sol" (Hunter, 2015). The H/C ratio is between 1.38 to 1.69 and it forms a black solid at room temperature with a molecular weight of 780 – 1400 g/mol (Lesueur, 2009). Polacco et al. (2015), suggested that due to the presence of fused aromatic structures within the resins molecules, which is also found in asphaltenes the boundary between resins and asphaltenes is not clearly defined.

2.3.4 Asphaltenes

Asphaltene is of great interest to pavement binder chemists and is the most studied SARA fraction. Their presence in asphalt significantly affects the rheological behaviour of reference asphalt; an increase in asphaltenes content increases the hardness, viscosity and softening point, whereas the penetration is decreasing (Hunter, 2015). Asphaltenes among the SARA fractions has the highest molecular weight between 800 – 3500 g/mol (Lesueur, 2009). Langevin & Argillier (2016), defined asphaltenes as the "oil fraction precipitated by addition of paraffin solvents, usually pentane or heptane". It is believed to consist of 5 –

25wt.% of the total pavement asphalt binder and also with the lowest H/C ratio between 0.98 to 1.56 (Hunter, 2015; Polacco et al., 2015). The molecular constituents of asphaltenes are polar groups complex metal and polycyclic aromatics groups with an average of about 7 rings attached to linear or branched hydrocarbons chains (Langevin & Argillier, 2016). The polarity of asphaltenes is controlled by the presents of about 5 – 8 wt.% of sulphur in the rings in thiophenic groups; 1.5wt.% of the nitrogen in the rings of pyrrolic and pryridinic groups and about 1 wt.% of oxygen in form of carboxylic groups and phenols; and traces of transition metals (Ni, Va, Fe,..) from small ppm up to a tenth of wt.% in form of metallo-porphyrins (Langevin & Argillier, 2016; Lesueur, 2009). At room temperature, asphaltenes form a black powder responsible for the colouration of base asphalt and do not exhibit glass transition (Lesueur, 2009).

2.4 Asphalt as a Colloid

The nature of asphalt as reviewed by Polacco et al., (2015), are in two schools of thought; the colloids and disperse polar fluid. The latter is less favoured, hence in this study, asphalt will be reviewed as colloids.

"Colloid is a homogeneous system consisting of nanoscale (1–100nm) or mesoscale (from 100nm to hundreds of microns) molecules or particles dispersed through a medium (or second phase)"(Yang & Yang, 2015). From the above definition, a colloidal system consists of two phases; the disperse and continuous phase. Dispersion is defined as a "two-phase solid system, the particles of which are colloidal, distributed in a continuous". Note that dispersion differs from suspension which is "a heterogeneous two-phase system, of buoyant particulate solid, not colloidal, distributed in a continuous liquid".

The formation of micelles of Nano-sized colloids of asphaltenes has been confirmed with small-angle X-ray scattering (SAXS) and small-angle neuron scattering (SANS). They have been identified in organic solvents, crude oi and in asphalt (Lesueur, 2009). The asphaltene nano-aggregate are said to be formed as a result of interaction between the p-electron of the rings and flocculate into a larger aggregate as the concentration increases. The asphaltene with higher polarity is located at the centre whereas the less polar asphaltene surrounds at the boundary (Langevin & Argillier, 2016).

The aggregation results in the formation of micelles which are found in the disperse phase in maltenes. Lesueur (2009) review suggests that at the glass transition state of asphalt, asphaltene remains a disperse solid. This hypothesis was based on the temperature behaviour of different fractions of asphalt at glass transition state; asphalt and its aromatics have close glass transition temperature.

Another contrasting theory to that of the colloidal model is the dispersed polar fluid model which "proposed that polar molecular fractions are uniformly dispersed within the asphalt"(Little et al., 2018), which will not be covered in this dissertation. For a detailed description of the colloidal theory and others see Lesueur (2009).

2.5 Asphalt Modification

The need to enhance the performance of neat asphalt has driven the concept of modifying asphalt with chemical and nonchemical modifiers. At severe weather conditions of exposure, neat asphalt fails to meet design performance requirements as well as account for increasing axle load and traffic intensity. The increase in traffic load and associated issues have resulted in the reduction of in-service life quality of the flexible pavement structure. This usually increases the need for frequent road maintenance and re-paving(Polacco et al., 2015).

The modification of asphalt with modifiers are carried out to improve the mechanical and thermo-rheological properties of binders used in the production of asphalt concrete. In the literature, chemical modifiers have proved to improve the elastic recovery properties, higher resistance to low-temperature cracking and permanent deformation at elevated temperatures. Besides these improvements, some asphalt modifiers have drawbacks such as thermal storage instability, phase separation and increase binder cost (Kraus, 1982; Porto et al., 2019a; Zhu et al., 2014).

Since the first quarter of the twentieth century when the asphalt was modified with natural rubber, other modifiers have been applied to improve the performance of asphalt binder. Synthetic modifiers application did not start until after the end of the second world war with several breakthroughs in polymer science (Read & Whiteoak, 1995; Zhu et al., 2014). Literature shows that elastomers account for 75% of melt modification, 25% by plastomers and 10% by waste rubber crumbs and the remaining percentage are other mechanical

materials (G. D. Airey, 2004). Table 2.3 shows the list of materials that have been used or researched for modification of asphalt binder.

Table 2.3: List of asphalt modifiers

Modifier Parent Group	Modifier	Reference
Thermoplastic elastomers	Styrene-butadiene-styrene (SBS)	(Adedeji et al., 1996; G. D. Airey, 2004; Al-Hadidy & Yi-qiu, 2011; Al-Rabiah et al., 2016; Xiaohu Lu & Isacsson, 1997; Tian et al., 2020; W. Zhang et al., 2019)
	Styrene-butadiene-rubber (SBR)	(Abedini et al., 2016; AH Albayati, 2011; CT Shih, 1996; Gogoi et al., 2016; Khadivar & Kavussi, 2013; Z. Ren et al., 2020; Salehfard et al., 2017; Teltayev et al., 2019; Velayudhan & Yameni, 2012)
	Styrene-isoprene-styrene (SIS)	(H. H. Kim et al., 2019; Mazumder et al., 2020; F. Zhang et al., 2018)
	Styrene-ethylene-butadiene-styrene (SEBS)	(Isacsson & Lu, 1999; Xiaohu Lu & Isacsson, 2000; Rahi et al., 2015; Wei et al., 1996)
	Ethylene-propylene-diene terpolymer (EPDM)	(Ghoreishi et al., 2020; Khalaf et al., 2018; Kumar et al., 2020)
	Isobutene-isoprene copolymer	(Elbashbishy et al., 2015; Read & Whiteoak, 1995)
	Natural rubber	(Al-Mansob et al., 2014; Al-Sabaeei et al., 2019; Atul Narayan et al., 2017; Azahar et al., 2016; Rahi et al., 2015;

		S. Ren et al., 2019; Sani et al., 2019; Wen et al., 2017)
	Crumb tyre rubber	(B. Huang et al., 2002; S.-C. Huang & Pauli, 2008; H. H. Kim et al., 2017a, 2017b; H. H. Kim & Lee, 2015, 2016; Hyunhwan Kim et al., 2014; S.-J. Lee et al., 2008; Palit et al., 2004; Shen & Amirkhanian, 2005; Xiang et al., 2009)
	Polybutadiene	(Read & Whiteoak, 1995)
	Polyisoprene	
Thermoplastic polymers	Ethylene-vinyl acetate (EVA)	(Domingos & Faxina, 2014; Isacsson & Lu, 1999)
	Ethylene methyl acrylate (EMA)	(Aguirre et al., 2016; Y. Chen et al., 2015)
	Ethylene butyl acrylate (EBA)	(Isacsson & Lu, 1999; Zhu et al., 2014)
	Atactic polypropylene (APP)	(Belak & Stout, 1964; Nekhoroshev et al., 2001, 2017)
	Polyethylene (PE)	(Brasileiro et al., 2019; García-Travé et al., 2016)
	Polypropylene (PP)	(Brasileiro et al., 2019; Giavarini et al., 1996; Yeh et al., 2005)
	Polyvinyl chloride (PCV)	(Brasileiro et al., 2019)
	Polystyrene (PS)	

Thermosetting polymers	Epoxy, Polyurethane, Acrylic, Phenolic resin	(Apostolidis, Liu, Erkens, et al., 2020; Apostolidis, Liu, Marocho, et al., 2020; P. Cong et al., 2011, 2019; Y. Liu et al., 2017; Peiliang et al., 2010)
	resin	(L. Cong et al., 2019; M. Sun et al., 2018; R. Yu et al., 2018; Z. Zhang et al., 2020)

Besides the materials itemised in Table 2.3, other modifiers include, organo-metallic compounds, Sulphur, lignin, Cellulose, alumino-magnesium silicate, glass fibre, asbestos, polyester, amides, phenols, gilsonite, hydrated lime, lime, fly ash, silica fume, carbon black, rock asphalt and Trinidad Lake asphalt.

2.6 Polymer Modification of Asphalt Binder

Polymer materials which could be natural or synthetic materials refer to identical or similar units (mer or monomer) joined together. In nature, the polymer includes cellulose, silk, bitumen, shellar or rubber. However, most of the available polymer materials are synthesised polymers often known as plastics.

The application of synthetic polymer dates backs to 1820 when Thomas Hancock found the process to make natural rubber fluid at high shear forces, a state necessary for blending with other materials to occur, followed by vulcanisation process natural rubber in 1939 by Charles Goodyear (Young & Lovell, 2011). By the mid-20th century, different polymer materials were discovered and developed, also scientist has begun to gain useful insight into the behaviour of polymer and the method of synthesizing it.

In general, a polymer is defined as “a substance composed of molecules which have long sequence of one or more species of atoms or groups of atom linked to each other by primary, usually covalent bonds” (Young & Lovell, 2011)

Two distinct ways of classifying polymers are based on their thermal response; thermoplastic and thermosetting. However, this method of classification further has three classes such as thermoplastic, elastomers and thermosetting. This section and subsequent section would only attempt the properties of the polymer used in binder modification. For an in-depth review on polymer refer to Young and Lovell (2011) and Fried, (2014). A broader form of classification was given by Pyshyev et al., (2016) that grouped polymer compounds used in modifying asphalt into four groups; elastomers, thermoplastic elastomers, thermosetting plastics and thermoplastics. Table 2.3 provides a list of polymers that have been applied in asphalt modification. Among these polymers, SBS polymer has attracted the highest research and it is the focus of this study.

2.6.1 Review of SBS modified asphalt binder

Modification of asphalt binder with SBS polymer has been researched extensively. But there remain several unexplained phenomenons that require further studies. One of the earliest research on asphalt modification with SBS polymer was done by Piazza et al., (1980) according to Google Scholar search results. The search investigated the mechanical and viscoelastic behaviour of SBS polymer-modified asphalt binder using penetration grade test, softening point test, Fraas breaking point test and Tensil test that focused on yield stress and elongation at the breakpoint. It concluded that the addition of SBS polymer minimised softening at low temperatures and reduced brittleness. This behaviour is dependent on asphalt quality (especially aromatic content) and mixing procedures. To provide a concise review of SBS polymer-modified asphalt binder, this section will be subdivided into rutting, fatigue cracking, storage stability and moisture damage behaviour of SBS polymer-modified asphalt binder.

a. *Rutting resistance characterisation of SBS polymer-modified asphalt binder*. Rut formation which is a durability problem of asphalt pavement at a higher temperature above 30 ℃ is a serious problem. Asphalt binder is a thermoplastic viscoelastic material that forms part of the load-bearing components of asphalt pavement concrete. However, at high temperatures, asphalt pavement is subjected to varying forms of deformation such as rutting, which occurs as a result of accumulated strain in the asphalt binder. According to Fatin & Mahmoud (2004), rutting in asphalt pavement is defined as the continuous accumulation of

longitudinal depression along the wheel path under repeated loading. Rutting occurs as a compressive pavement deformation of the underlying pavement subgrade or as plastic deformation of the asphalt layer near the surface. The plastic deformation of the pavement surface is dependent on time, temperature and stress level. In relation to this, asphalt binder within the asphalt pavement concrete dominates the viscoelastic response of the permanent deformation that takes place in the mixture (Anderson, Christensen, Bahia, Dongre, Sharma, Antle, et al., 1994).

In 1987, the "Strategic Highway Research Program" (SHRP) was initiated to provide performance criteria for quality pavement design, the programme came up with "Superior Performance Asphalt Pavement (Superpave®)" specification which has received wider acceptance (Anderson, Christensen, Bahia, Dongre, Sharma, Antle, et al., 1994; McGennis et al. 1994). The Superpave ® performance criteria specified the use of |G*|/Sinδ parameter at 10 rad/s for the selection of paving binder resistance to rutting. However, the use of |G*|/Sinδ parameter according to Bahia et al., (2001), is not sufficient to evaluate rutting in asphalt pavement since the parameter have a lower correlation ($R2 = 0.2377$) with the mixture accumulated strain. The multiple stress creep and recovery (MSCR) was developed as an alternative to |G*|/Sinδ parameter. The test also eliminates the need to perform an elastic recovery test on the binder. The multiple stress creep and recovery uses the non-recoverable creep compliance (Jnr) parameter is the evaluation of the susceptibility of asphalt binder to rutting.

Valkering et al.,(1990) evaluated rutting susceptivity of SBS polymer-modified asphalt binder using a modified static creep test by introducing a dynamic loading and laboratory test track on the mixture. The results showed improved mechanical stability and reduced temperature susceptibility. The increased elastic recovery and improved temperature susceptibility are attributed to the formation of polymeric networks in asphalt polymer blends (M. G. Bouldin et al., 1991). At the sample polymer content, SBS block copolymer was found to have developed polymeric networks as compared to SBR (latex) and have improved resistance to permanent deformation and reduced creep compliance due to the developed networks (M. G. Bouldin et al., 1991; Tarefder & Yousefi, 2016). Asphalt polymer networks are dependent on the critical polymer content whereas, for a polymer melt

solution, its molecular weight is a significant factor that controls the critical concentration (M. Bouldin et al., 1988; M. G. Bouldin et al., 1991). On the other hand, the double bond of the butadiene part of SBS gives SBS polymer modified binder the desirable properties when the PMB is subjected to thermal degradation at higher temperatures (Johansson & Linde, 1991). Furthermore, the polymeric network also enhances the elastic recovery in an asphalt/polymer binder in addition to improved thermal degradation resistance. According to Yildirim (2007), the elasticity of asphalt is a measure of recovery from original properties after the application and release of stress. This characteristic is a significant factor that is considered in sections where permanent deformation in asphalt pavement is envisaged.

Researches in the past and recent time have supported Bouldin et al., (1991) theory that SBS block copolymer formation of a polymeric network could enhance its elasticity properties and resistance to permanent deformation. Anjan et al., (2011) compared the mechanical behaviour of asphalt binder modified with SBS and crumb rubber on asphalt mixture using the dynamic modulus (NCHRP-9-19) test, dynamic creep test, static creep test and wheel tracker tests. The elastic recovery test conducted at 15℃ unaged binder shows 77% and 68% recovery for SBS and crumb rubber modified binder respectively. The PMBs after rolling thin film oven test (RTFOT) ageing conditioning, the percentage of recovery decreased by 22% and 29% for SBS and crumb rubber modified binder respectively. In general, the modification with SBS was found to have a significant reduction on the temperature susceptibility up to 10%, whereas the crumb rubber modified asphalt was a 9.8% improvement from the unmodified binder. At 60℃, the dissipated energy for SBS PMB was also lower than the crumb rubber and unmodified binder. Although in (Anjan kumar & Veeraragavan, 2011) the loading frequency and temperature were identified as a significant factor influencing the SBS modified asphalt binder resistance to permanent deformation, other research researchers have reported base binder has a more significant influence on the permanent deformation-resistant of SBS PMBs (J.-S. Chen et al., 2002; Wong et al., 2004).

b. *Fatigue cracking resistance characterisation of SBS polymer-modified asphalt binder:* Fatigue cracking develops in asphalt pavement due to the build-up of damage under repeated traffic loading (Safaei & Castorena, 2017). The initiated micro fatigue crack progresses as the material is subjected to repeated stresses and strain leading to rupture of the material

(Bessa, 2017). According to the Federal Highway Administration (2016) report, factors that influence the initiation and progress of fatigue cracking in asphalt pavement are; poor base and subgrade design, aggregate and binder properties, frequency and intensity of load and strain tolerance of the pavement under in-service ageing effect.

In asphalt mixture, fatigue cracking resistance is a measure of fracture life (Nf) or service life (Ns).In the laboratory different test methods have been used to estimate fatigue cracking in asphalt mixture they include; 4-point bending beam fatigue, AMPT push/pull fatigue, indirect tensile strength (IDT), disk-shaped compact tension [DC(t)], Texas overlay, dissipated creep strain energy and Semi-Circular Bending (SCB). In the Superpave design, National Cooperative Highway Research Program (NCHRP) developed the dynamic modulus (|E*|), flow number, and flow time to measure the permanent deformation and cracking in the mixture. On the other hand, the program also developed the |G*|.Sinδ parameter at 10 rad/s for the selection of binder resistance to fatigue cracking in asphalt pavement at intermediate temperatures (Federal Highway Administration, 2016). The |G*|.Sinδ parameter is an important parameter highlighted in the structure of the Superpave mix design system for all levels in the binder selection criteria at the volumetric design (Cominsky, 1994).

The modification of asphalt with polymer has resulted in an increased fatigue resistance on asphalt and the improvement dependent on asphalt content and aggregate properties. The finer asphalt mix is also reported to have a more prolonged improvement in fatigue life (Bessa, 2017). Fakhri et al., (2013), modified a 60/80 pen grade asphalt with 5% SBS polymer and investigated the effect of loading frequency for the assessment of fatigue life in asphalt mix using a four-point bending beam test. It was discovered that the addition of SBS polymer increased the fatigue life of the asphalt mix three times more than the control asphalt mix. The study further suggests for modified asphalt the use of 65% for the criterion of a decrease in stiffness instead of the conventional 50% and to consider the effect of temperature on the fatigue behaviour of PMB mixes. Khattak & Baladi, (1998), reported that the fatigue life of PMB mixes increased significantly at 20℃. On the other hand, in a stone matrix asphalt composite mix such as the inclusion of coconut and cellulose fibre, Awanti

(2013) reported that SBS modified composite mix fatigue life was 36% higher than neat asphalt composite mix. The fibres were introduced to prevent the drain down of asphalt.

In binder selection, the Superpave |G*|.Sinδ parameter measure at 10 rad/s for PAV conditioned binder is conventionally used. The limit value is 5000 kPa and studies have shown that SBS modified asphalt binder have higher |G*|.Sinδ values, in such cases neat asphalt binder is preferred (Gordon D. Airey, 2004; Xiaoming Liu et al., 2018; Mazumder et al., 2016).

c. Storage stability characterisation of SBS polymer-modified asphalt binder: Storage stability of PMB is one the major factors for consideration in the selection of modifiers especially for binder considered for long haulage or longer storage. Storage instability or rather incompatibility between asphalt and the modifiers is accessed by storing PMB at elevated temperatures. This method delineates the thermodynamic stability of the modified binder mix. The difference in the softening point between the asphalt rich phase (ARP) and the polymer-rich phase (PRP) measures the degree of settling out that has occurred. Polymers of different structures and behaviour have been used to modify asphalt. They include thermoplastics, thermoplastic elastomers, natural and synthetic rubber and thermosets. Among these polymers, thermoplastic elastomers have been widely researched with SBS reported having high storage instability at high temperatures (Xiaohu Lu et al., 2002; D. Sun et al., 2006; Zhu et al., 2014, 2018)

According to (Xiaohu Lu et al., 2002; Zhu et al., 2018), the base binder influences the compatibility of the asphalt-SBS polymer blend. They concluded that an increase in the asphaltene content with increased SBS content is proportional to phase separation whereas the blend with higher aromatic shows an increase in the phase separation with respect to softening point test. Lesueur (2009), also reported that the high average molecular weight of asphaltene in the SARA (saturate, aromatics, resin and asphaltene) composition of asphalt affects its viscosity and stiffness.

2.7 Thermorheological and Ageing Evaluation of Asphalt Cement Binder

The thermorheological behaviour of asphalt cement (neat and modified asphalt binder) measures the deformation and flow over a given temperature. The thermorheological test

methods include the viscosity, softening point, penetration, ductility, recovery and other mechanical dynamic tests. The mechanical dynamic test can be carried using the dynamic shear rheometer (DSR) and bending beam rheometer (BBR). The DSR measures the mechanical dynamic response at intermediate and high temperatures, while the BBR measurement considers the response at low temperatures.

The background literature in this section will be limited to viscosity, DSR, ageing and storage stability tests carried out in this research.

a. *The dynamic shear measurement*: The dynamic shear measurement of asphalt cement was developed to measure the linear viscoelastic moduli of the binder at different applied stress or strain, test temperatures and the test loading frequencies under sinusoidal loading behaviour. The measurement is limited within the linear region. Although asphalt cement exhibits non-linear behaviour and complex flow, the quantification is beyond the scope of this research.

The modelling of asphalt cement with the linear viscoelastic region has been found to be sufficient for engineering design purposes (Lesueur, 2009). As a viscoelastic material, asphalt cement has both inherent viscous and elastic properties. For example, under creep loading conditions, the material is expected to deform immediately on the application of load, such behaviour correlates with its elastic properties. The deformation is also expected to progress into time-dependent deformation that has both complete viscous elements and delayed elastic components. Only the delayed elastic part is recovered (slowly) at a decreasing rate upon removal of applied load (Anderson, et al., 1994).

In the measurement of the viscoelastic response of asphalt cement using the DSR device, a parallel or cone plate may be used in the measurement. The parallel plate is commonly used with a diameter ranging from 8mm to 25mm. The 8mm plate is suitable at intermediate temperature (4 to 40°C) and at high test temperatures (46 to 82°C), the 25mm plate is preferred. According to Anderson et al., (1994), the thickness of the sample depends on the modulus of the binder. The schematics of the DSR device is presented in Figure 2.1.

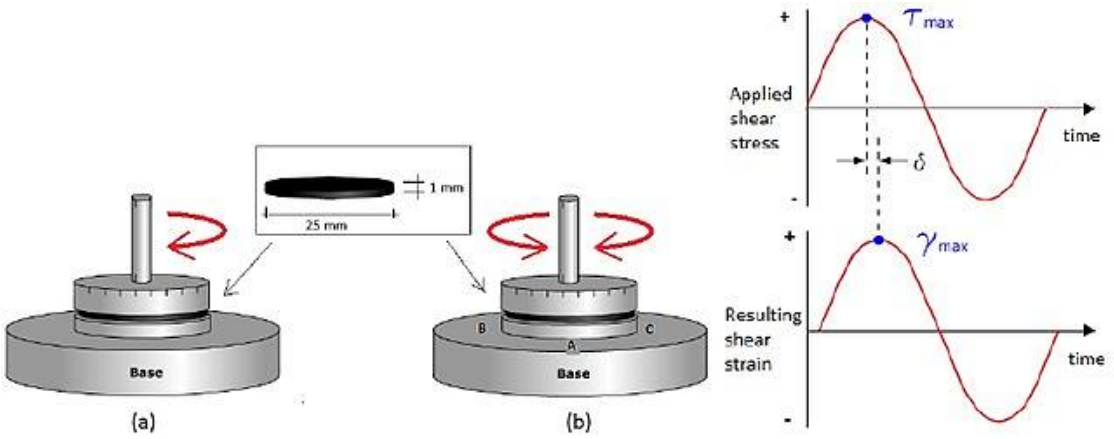


Figure 2.1: Schematics of the dynamic shear rheometer (a) viscosimeter (b) oscillation (Yener & Hınıslıoğlu, 2014)

From the graph in Figure 2.1, the complex shear modulus and the phase angle (δ) can be estimated;

$$G* = \frac{(\tau_{max} - \tau_{min})}{(\gamma_{max} - \gamma_{min})} \qquad 2.1$$

Where τ is the shear stress (Pa) and γ shear strain (%).

The complex shear modulus specify the binder resistance to deformation with respect to stiffness, while the phase angle measures the lag in the stress response in contrast to applied strain. In other words, it delineates the elastic and viscous properties of a material. The value of the phase angle at a given loading condition expressly assist in characterising a viscoelastic material; where 0° and 90° indicates purely elastic and viscous material.

b. *Binder viscosity evaluation*. The viscosity of a fluid measures its resistance to flow. In asphalt cement and modified asphalt cement, the viscosity is an important parameter in the determination of the asphalt mixture (binder and aggregate) mixing and compaction temperature required to achieve maximum density within a given compaction effort. Unaged asphalt cement can be characterised using capillary viscometry since its behaviour at elevated temperature is within the Newtonian region (independent of shear rate).

c. *Storage stability elavaution*. Asphalt modification with different materials usually has compatibility problems when stored at elevated temperatures. The modification of

asphalt is carried out after preheating asphalt (usually above 165°C) and the modifier is dispersed within the asphalt matrix using a high or low shear mixer. The resultant modified asphalt binder is stored (short-term) or transported directly to a job site for pavement construction and asphalt concrete mixture manufacturing.

Neat asphalt has a complex chemical composition, and its modification with polymer has been reported to have improved resistance to pavement distresses. The modification of asphalt increases its chemical complexity leading to incompatibility with modifiers (G. Airey, 1997; Ma et al., 2017; Mohd Hasan et al., 2019; Porto et al., 2019a; Sani et al., 2019; Topal et al., 2017). Asphalt and its modifier may have different properties such as density. This disparity in material properties often results in thermal instability and immiscibility between the two materials. The increase of the storage temperature weakens van der Waals forces that held the micelles of the modified binder components together (Z. Ren et al., 2020). The reviewed previous state of art studies on asphalt and modified asphalt suggest that the source of the neat asphalt affects the compatibility and mechanical properties of the polymer-modified binder (PMB) (Lesueur, 2009; Polacco et al., 2015). However, it has been reported in the literature that the principal factor affecting the compatibility of PBM has not been found (Zhu et al., 2018).

The compatibility between the asphalt and modifiers is significant in the management of pavement construction, especially during the hot storage at the temperature range of 130° - 168°C. Storage stability of PMB is one of the major factors for consideration in the selection of a modifier especially for binders consider for long haulage or longer storage duration to avoid segregation (Francken, 2004; Refined Bitumen Association, 2012). The term compatibility describes the “level of interaction” between biphasic asphalt/polymer mixture in which the “polymer-rich-phase (PRP) formed by maltenes-swollen-polymer is dispersed in an asphaltene-rich-phase (ARP)”(Liang et al., 2015). In the literature, (Polacco et al., 2015)storage stability is defined as the macroscopic compatibility of the biphasic asphalt/polymer mixture, evaluated from the phase separation of the PRP and ARP stored under quiescence, which does not include other charges such as ageing.

The hot storage instability or rather incompatibility between asphalt and its modifiers is accessed by storing PMB at elevated temperatures. This process delineates the

thermodynamic stability of the modified binder composite. The difference in the softening point between the asphalt rich phase (ARP) and the polymer-rich phase (PRP) after phase separation, indicates the degree of settling out that has occurred as detailed in ASTM D7173 (ASTM D7173, 2011).

Researchers have sort ways to characterise the hot storage instability and the two commonly used methods are; ASTM D7173 and EN13399. In the ASTM D7173, the modified asphalt cement is stored in an aluminium tube, approximately 25mm in diameter and between 125mm to 140mm long. The sample is stored vertically at 165±5°C for a period of 48±1h. at the end of the hot storage period, the sample is transferred to a freezer at -10±10°C and the vertical position is maintained up to 4h and divided into 3 equal portions. Further analysis is carried out on the top and bottom portions of the sample to characterise the stability of the sample. A stable sample is expected to have a softening point difference of 2°C between the top and bottom sections and a similar methodology is outlined in EN 13399 with slight modification in the storage container, duration of 72h and 180°C storage temperatures. In EN13399, the softening point difference for a stable sample must be below 5°C.

According to Airey (2003), the phase separation found in SBS modified asphalt binder is attributed to the insufficient quantity of light asphalt components required to completely peptize the asphaltene and modifier micelles and can be improved with an increased aromatic content of the asphalt or by the addition of aromatic oil to the blend (Kraus, 1982; Zhu et al., 2014).

On the other hand, the phase separation can be improved by adding a crosslinking agent to the blend. Ren et al., (2020), added nano-montmorillonite to crumb rubber, SBS and SBR modified asphalt binder and achieved 98%, 50% and 31% improvement respectively on the storage stability. Chen & Huang (2007), significantly reduced phase separation in SBS modified asphalt binder from 60℃ to less than 5℃ of bi-phase softening point difference through vulcanization of the blend using 5% (by .wt of SBS) sulfur.

d. *Binder ageing conditioning evaluation.* Ageing in asphalt is a complex process. It is an irreversible change in the chemical components of the asphalt cement in form of oxidation, polymerisation or evaporation of lighter components of the asphalt cement. In

general, asphalt cement ageing results in the hardening of the material (Lesueur, 2009). Ageing of asphalt cement starts from the manufacturing process, through mixing and in-service life period. However, only the mixing and the service-life ageing process are evaluated in the laboratory.

At the manufacturing of the asphalt concrete, usually at temperatures above 160℃, rapid chemical ageing occur in the asphalt cement resulting in a change in the rheological behaviour. In the laboratory, the asphalt cement ageing that occurs during the mixing stage, usually known as short-term ageing is simulated using the ASTM D2872 or the BS EN 12607 - rolling thin film oven test (RTFOT). The experiment is conducted at 163℃ for 85 mins. The resultant samples have reported having increased viscosity, hardening, increase in the molecular weight and yielding up to 4 wt.% asphaltenes (G. Airey, 1997; Lesueur, 2009; López-Montero et al., 2018).

The in-service simulation is typically known as long-term ageing and the laboratory simulation is expected to mimic ageing conditions up to 8yrs of in-service conditions. The pressure ageing vessel (PAV) is used in accordance with ASMT D6521 or BS EN14769 to condition the asphalt cement in the laboratory. The resultant materials have increased complex modulus indicating loss of light components and hardening of the asphalt cement (Lesueur, 2009; Xiao et al., 2020; Yildirim, 2007).

2.8 Machine Learning Modelling Application in Asphalt binder Parameters

Machine learning within the last few years has made its presence felt in various sectors; on the internet (Cui et al., 2018), communication systems (Björnson & Giselsson, 2020; Qin et al., 2019), vision and voice recognition(Guo et al., 2016; Li & Zhao, 2019; Pingel & Ha, 2017; Voulodimos et al., 2018), smart device and instrumentations(Cao et al., 2018), as well as other varying engineering applications (Pinar Akpinar & Khashman, 2017; Khashman & Akpinar, 2017). Its deployment has witnessed unprecedented results and a revolution in the artificial intelligence field. Computational methods available in the machine learning field include artificial neural networks (ANN), support vector machine (SVM), Gaussian process regression (GPR), recurrent neural networks (RNN) and others.

The ANN is a nonlinear statistical model data modelling using the abstraction of the biological neural networks. Although ANN performance in literature has been reported to have good predictive results, it is often criticised to have high computational cost (iteration tuning) and often trapped at a local minimum. Further, data overfitting is also another disadvantages critics of ANN cite; the inability of the model to correctly map new inputs to corresponding target values (Berka et al., 2009; Xi-zhao et al., 2013). To overcome these problems, a non-parametric approach such as the Gaussian process minimises the data overfitting by defining a distribution function and setting an initial distribution to unlimited possibilities over the function directly (Asante-Okyere et al., 2018). Comparative studies of GPR and other machine learning tools such as ANN and SVM shows that the algorithm is an efficient machine learning tool with higher accuracy on the generalisation data set (Asante-Okyere et al., 2018; Aye & Heyns, 2017; Caywood et al., 2017; Chaurasia et al., 2019; Richardson et al., 2017; Wang et al., 2006; H. Yu et al., 2016).

In the asphalt technology field, machine learning models have been widely reported to have higher predictive accuracy over regression models (C. L. Chen & Tai, 2010; El-Badawy et al., 2018; Ghasemi et al., 2019; J. Liu et al., 2018; Souza, 2018). The traditional artificial neural networks, support vector machine and decision tree algorithm have been applied in different study areas, with higher predictive accuracy over regression models.

In the review of existing literature for the application of machine learning modelling in asphalt binder and HMA concrete, Ghasemi et al., (2019) predicted hot mixed asphalt (HMA) concrete dynamic modulus using the ANN and multivariable regression models. The study's selected input variables were drawn from features of volumetric and particles size gradation of 9 mixes to extract 243 data points. Further, the principal component analysis was used for orthogonal transformation and resulting principal components were used to calibrate the ANN and multivariable regression models. The results of the fitted test data show that the ANN model satisfactorily estimated the dynamic modulus (E*) of the HMA. Daneshvar and Behnood, (2020) on the other hand, compared the performance random forest algorithm with the Witczak model in the prediction of E* of HMA. Using the statistical parameters (R2 and average errors), the study concluded that the developed model improved the E* as compared to the Witczak models. El-Badawy et al., (2018) compared the

traditional ANN and three existing regression models (Witczak NCHRP 1-37A, Witczak NCHRP 1-40D and Hirsch) in the prediction of E* in HMA concrete using 25 mixes each, from the Kingdom of Saudi Arabia and Idaho State. A total of 3,720 cases were extracted from the 50 mixes to build the research database. Three ANN models were evaluated using input variables from the three-existing regression of models. The research concluded that Witczak models are more effective in the prediction of E* when compared with the Hirsch model. Further, the input parameters in Witczak NCHRP 1-37A were reported to show a more dynamic effect on the sensitivity scale when compared with Witczak NCHRP 1-40D model inputs variables that were dominated by binder properties. The three evaluated ANN models proved to have improved E* value when compared with the corresponding regression models. Similar research to El-Badawy et al., (2018) was conducted by Liu et al., (2018) with the incorporation of recycled asphalt shingles and comparison of ANN model and modified Witczak E* model developed by Yu, (2012). The developed ANN model also showed improved E* values when compared with Yu, (2012) RSA model. Further, few studies (Alas and Albrka Ali, 2019; Yan and You, 2014; Kok et al., 2010) on machine learning prediction of complex modulus and phase angle did not account for ageing conditioning in asphalt binder. This limited their findings in the prediction of rutting and fatigue parameters in the asphalt binder.

CHAPTER 3

RESEARCH METHODOLOGY AND MATERIALS CHARACTERISATION

3.1 Introduction

This chapter outline the research methodology employed in this research in achieving the research objectives and the materials characterisation. The research is analytically based research that involves experimental, predictive and simulation approaches. The experimental approach involves thermo-rheological behaviour evaluation of SBS modified asphalt binder. Three different SBS with constant density and different molecular weight was used at different polymer content. On the other hand, in predictive methodology, the performance of four different machine learning algorithms was assessed in the modelling of rutting and fatigue parameters using un-aged and short-term aged data extracted in the experimental research. Finally, the simulation of the developed model with independent data was performed to access the reliability and the application of the developed model.

3.2 Materials

Materials used in this study are 60/70 pen grade neat asphalt, Kraton ® D1152 ESM, Kraton ® D1101 ASM and Kraton ® D1184ASM.

The neat asphalt was obtained locally from the Penang region of Malaysia. The asphalt grade is also been utilized in local construction works. The SBS polymer was supplied by Kraton Polymers Nederland BV in the form of porous pellets. The Kraton D1152 ESM and D1101 ASM are linear polymers, while Kraton D1184ASM is a branched polymer. The physical properties of the neat asphalt and the SBS polymers are presented in Table 3.1.

There are two sets of materials used in this research; asphalt and polymer. The asphalt material used was locally supplied 60/70 Pen grade asphalt used in pavement construction works in the Penang region of Malaysia. The asphalt material has been used in several publications (Mohd Hasan et al., 2019; Poovaneshvaran, Mohd Hasan, & Putra Jaya, 2020; Poovaneshvaran, Mohd Hasan, Sani, et al., 2020; Sani et al., 2019).

Polymer used were supplied by Kraton ® polymer in form of pellets. Three styrene-butadiene-styrene (SBS) polymer was selected, having two linear and one branched structure. The linear structured polymer is Kraton ® D1152 ESM and Kraton ® D1101 ASM, while the branched structured polymer is Kraton ® D1184ASM. The polymers were either dusted with talcum or silica.

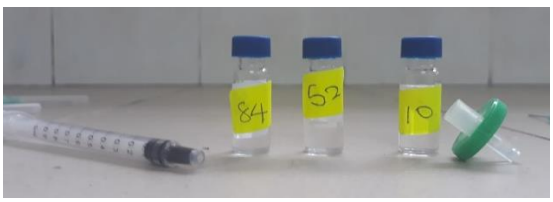
Table 3.1: Physical characteristics of the study polymers

Parameters	D1152 ESM	D1101 ASM	D1184 ASM
Solution Viscosity @25 (ºC) (Pa.s)	1.0	1.24	4.2
Structure	Linear	Linear	Branch
Styrene-butadiene ratio	29.5/70.5	31/69	30/70
Melt flow rate 200 ºC /5000g (g/10min)	7.2	-	-
Particle size < 200µm % wt.	4.8	10	7

3.3 Gel permeation chromatography (GPC)

The characterisation of the polymer molecular weight can be done using osmometry techniques(membrane and vapour pressure osmometry), light scattering technique, gel permeation chromatography (GPC), viscometry and proton NMR spectroscopy. Among these techniques, the GPC is widely used and have been applied a number of research works (Neira-Velázquez, Rodríguez-Hernández, Hernández-Hernández, & Ruiz-Martínez, 2013), and was used in this research to evaluate the molecular weight of the SBS polymers.

The samples were prepared by dissolving 0.1 % wt. of tetrahydrofuran (THF) solution in 1.5 µm vial and filtered through 0.2µm filter to remove undissolved polymer (Ding, Deng, Cao, Yu, & Tang, 2019). The characterisation was carried out with Agilent 1260 Infinity Quaternary LC gel permeation chromatography.



(a)

(b)

Figure 3.1: GPC experimental setup: (a) 1.5 μm vial with filter and (b) Agilent 1260 Infinity Quaternary LC equipment

3.4 Field Emission Scanning Electron Microscopes (FE-SEM)

The field emission scanning electron microscopes (FE-SEM) is a microscopic analytical tool fit for investigating structural features of smaller than 1 nm on the material surface. The FE-SEM operates with the aid of electrons with a negative charge in place of light as seen in an optical microscope. The technic was used to provide the surface morphology of the polymer materials. In order to access the morphology of the polymers with FE-SEM, the polymers were first transformed to conduct electricity. This is done by coating the materials with a thin-film layer of gold. The coating was carried using the device in Figure 3.2 b. The FE-SEM picture is as shown in Figure 3.2a.

(a) (b)

Figure 3.2: (a) FE-SEM setup; (b) gold coating device.

3.5 Research Mix Design And Procedure

In Figure 3.3, the schematics of the study mix design is outlined. The production of PMB in this study was carried out using a low shear mixer. The control binder mentioned in section 3.2 is referred to as “BB” within this research. The control binder was modified with 0%, 3%, 5 % and 7 % of the SBS polymer added by weight of the asphalt. The mixing processes were divided into three stages; preheating of the mixing containers, premixing of the asphalt without SBS polymer and mixing after the addition of polymer.

Stage 1: Two ovens were used in this stage. Oven-1 was preheated to 180℃ temperature for 2 hours while oven-2 was preheated to 165℃ for 2 hours and the low shear mixer preheated for 1hr at 180℃ temperature. The mixing container was placed in oven-1 for an hour while the control binder was placed in oven-2 for 1 hour. The required quantity of the control binder for batch mixing was measured into the mixing container and transferred to the mixer.

Stage 2: Mixer temperature was reduced to 175℃, and the asphalt was stirred for 20 mins at 2000rmp.

Stage 3: The required SBS polymer percentage for modification was added gradually and the binder was stirred for another 60mins. At the end of the mixing process, the produced binder was stored in an airtight container and labelled accordingly.

Table 3.2: PMB sample details and code identification

Binder Category	Mix code	Polymer type	Polymer % in the mix
Control binder	BB	-	-
Modified binder	PMB-I-3	D1152 ESM	3
	PMB-I-5	D1152 ESM	5
	PMB-I-7	D1152 ESM	7
	PMB-II-3	D1101 ASM	3
	PMB-II-5	D1101 ASM	5
	PMB-II-7	D1101 ASM	7
	PMB-III-3	D1184 ASM	3
	PMB-III-5	D1184 ASM	5
	PMB-III-7	D1184 ASM	7

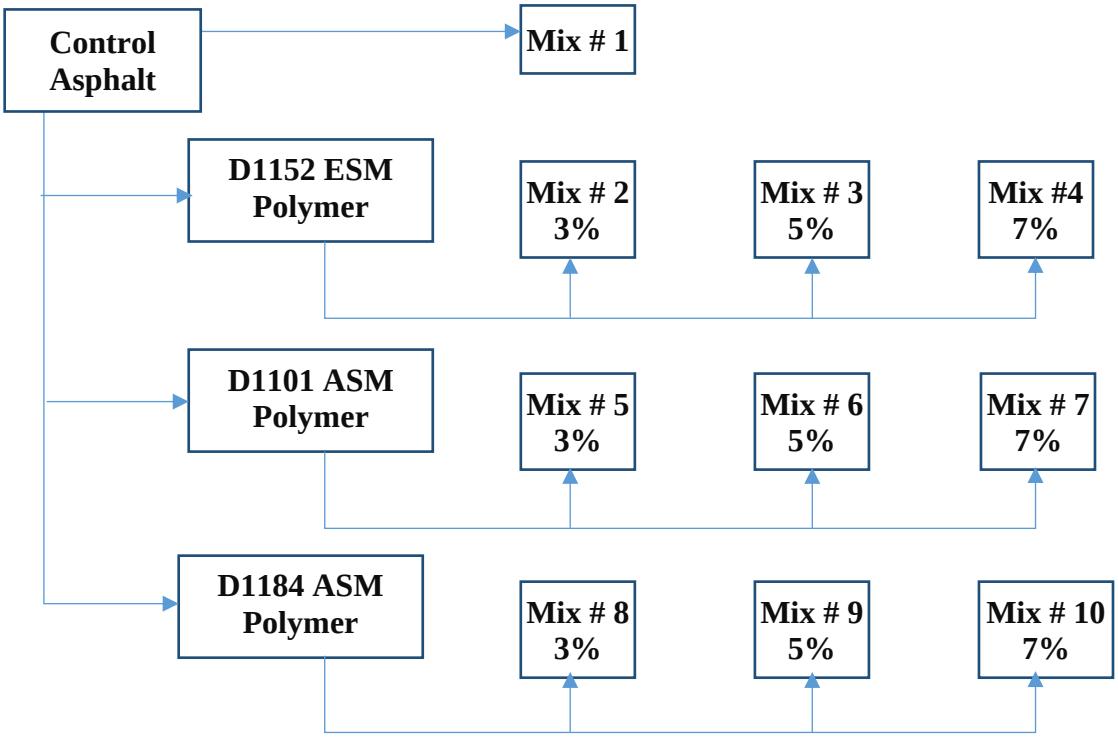


Figure 3.3: Research mix design

(a) (b)

Figure 3.4: (a) Oven (b) the low-shear mixer.

3.6 Asphalt Binder Softening Point Test

The asphalt binder softening test was conducted in accordance with the ASTM D36-2000 standard specifications. The apparatus used in the test include; the rings, pouring plate, balls. ball-centring guides, glass beaker, ring holder assembly, thermometer and hotplate. The reagents used were distilled water and glycerine.

a. Sample preparation: A sample of the asphalt binder is placed in a small container and transferred to a preheated oven (110 C) and allowed to melt and gain sufficient fluidity to pour. The sample is stirred carefully and poured into the rings. The samples in the rings were allowed to cool gradually to room temperature. A hot straight edge is used to level the sample poured in the rings. All samples achieved sufficient fluidity within 60 mins.

b. *Equipment setup*: The test equipment is set up as shown in Fig 3.3 with rings containing the samples placed in the ring holder. The ball centring guides are placed over the rings. The balls were carefully placed, with the centring guide holding the balls in position. The setup apparatus is placed in the glass beaker. The liquid bath is poured into the beaker to submerge the ring and the ball completely. The thermometer is placed in the beaker to measure the temperature. The starting temperature of the distilled water and glycerine bath samples was 5 ±1°C and 30 ±1°C respectively. Before the heating processes, the starting temperature was kept constant for 30 min to achieve temperature equilibrium in both the samples and apparatus.

(a) (b)

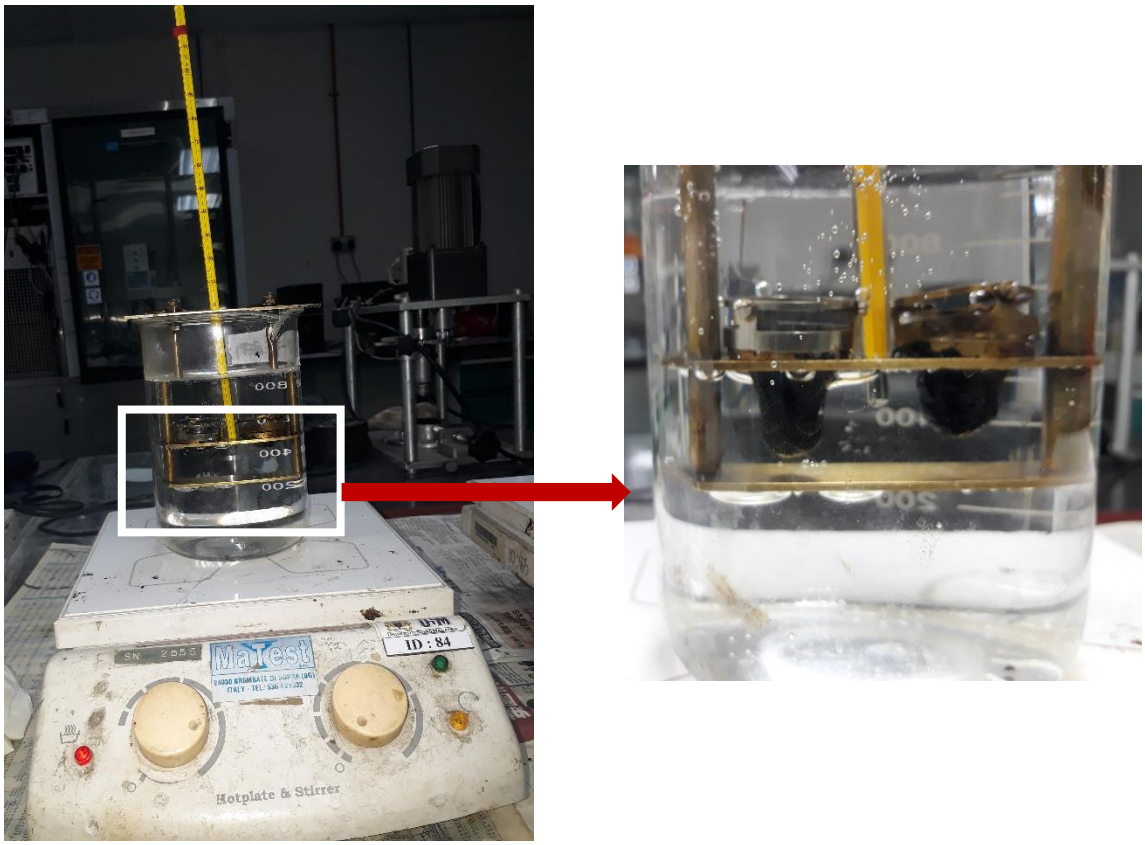


Figure 3.5: (a) Softening point test setup (b) softening point measurement

b. *Sample heating*: After the temperature equilibrium, the beaker containing a sample with two rings is gradually heated from under at a constant temperature rise. The temperature increase was kept at 5 ±1°C/min.

b. *Softening point calculation*: The temperature at which a ball touches the base of the ring holder is the softening point. The mean temperature of the two rings is calculated as the softening point of a sample. Where the softening point temperature difference exceeds 1°C between the two rings, the test is repeated.

3.7 Asphalt Binder Viscosity Test

The asphalt binder viscosity test was conducted in accordance with the ASTM D36-2000.

Figure 3.6: Asphalt binder viscosity test setup

3.8 Hot Storage Stability Test Method

The hot storage stability of the PMB samples was evaluated using the aluminium foil of 36mm in diameter and 150 mm in height. The preparation of the samples for the hot storage stability for the polymer-modified binder was in accordance with BS EN 13399(Bitumen and Bituminous Binders. Determination of Storage Stability of Modified Bitumen, 2010). The aluminium tube was filled between 100 to 120 mm height and allowed to cool to room temperature and stored vertically for 2 and 3 days at 163℃ and 180℃. The hot stored samples were removed from the oven and cooled to room temperature, thereafter stored for 4hrs at – 5℃. After the removal of the aluminium foil, the samples were divided into three equal portions as shown in Figure 4.1 and the softening point (Figure 4.2) test was performed on the top and bottom parts in accordance to ASTM D36 (ASTM, 2011).

Figure 3.7: Storage stability experiment setup

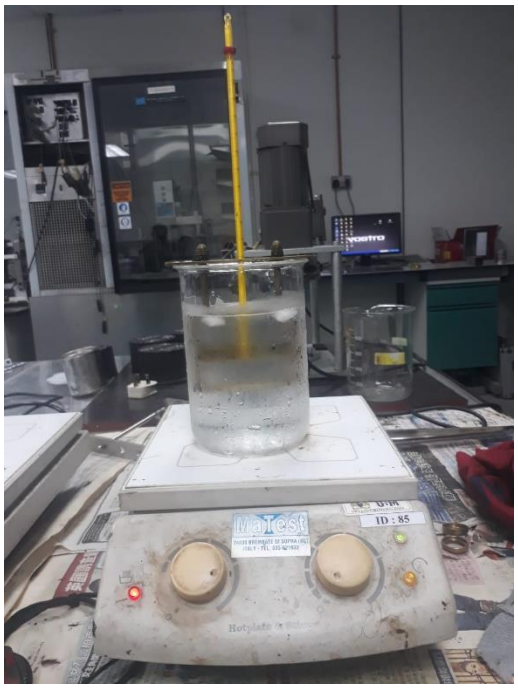


Figure 3.8: Softening point test experimental setup

3.9 Asphalt Binder ageing Conditioning

Ageing in asphalt is the rheological properties change that results due to variation in the chemical composition during production and service life of the material (Sirin et al., 2018). In asphalt mixture, two types of ageing occur; short-term ageing and long-term ageing. The short-term ageing occurs at high-mixing temperatures and fasts during the production of

asphalt concrete. On the other hand, the ageing process that occurs during the service life of the asphalt pavement is called long-term ageing. It occurs relatively at a lower temperature than the short-term ageing and over an extended period of time.

In this research, the rolling thin film oven test (RTFOT) and pressure ageing vessel (PAV) test were used to stimulate short and long term ageing respectively, in the laboratory.

The RTOFT was conducted in accordance with ASTM D2872 specification standard. The PAV test was conducted in accordance with ASTM D2872 specification standard.

(a)

(b)

(c)

Figure 3.9: (a) PAV device setup, (b) asphalt sample, (c) sample rack holder.

3.10 Mechanical Dynamic Test

The mechanical dynamic test performed in this research are oscillation, and creep and recovery test. In the oscillation test method, the complex dynamic modulus and the phase

angle were measured for the assessment of rutting and fatigue parameters in the control and modified binders. The creep and recovery test was used to assess the multiple creep recovery of the asphalt binder.

3.11 Summary of Experimental Methodology

The research summary of the research experimental evaluation procedures are presented in Figure 3.10.

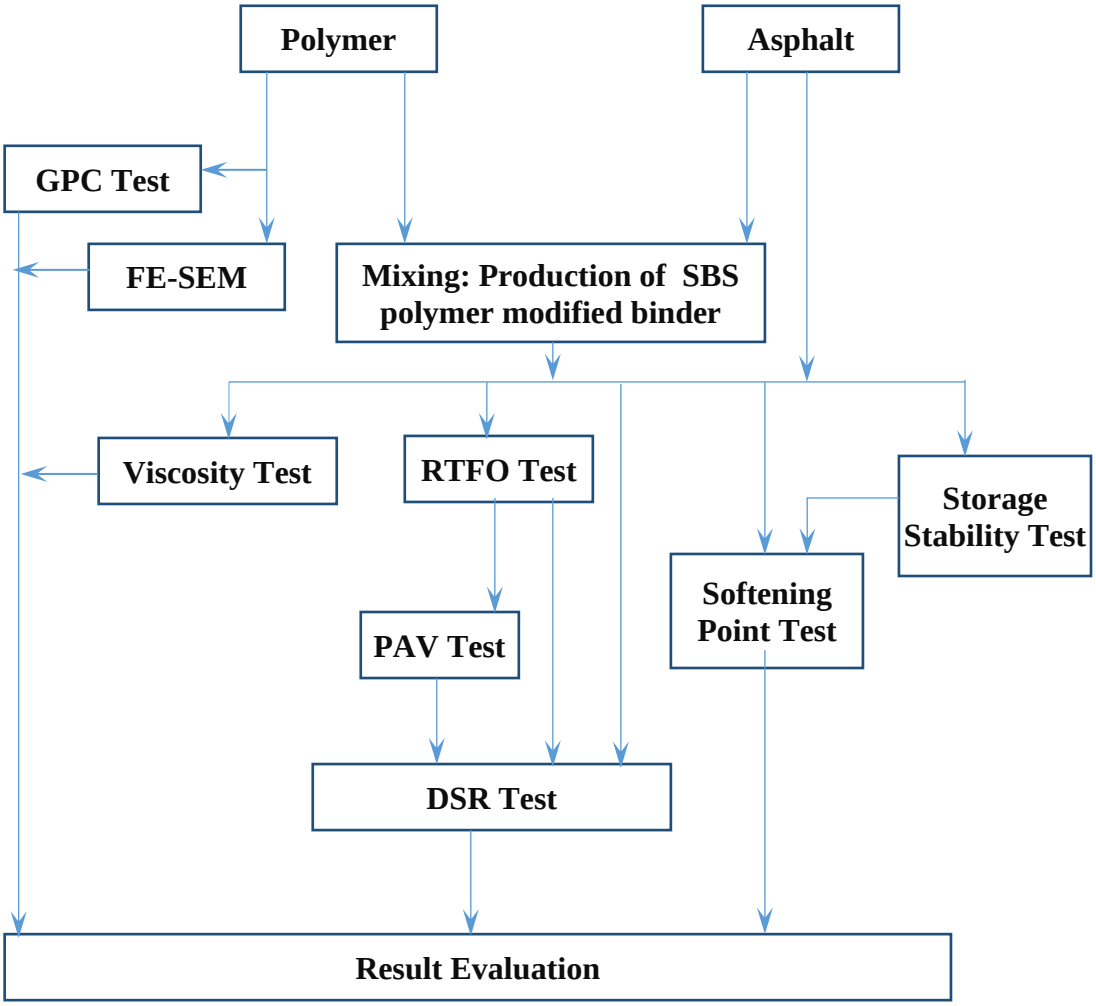


Figure 3.10: Experimental research schematics

3.12 Data Preparation and Model Architecture

The results of the material characterisation and mechanical dynamic test were used to build the database for the machine learning modelling. The input variables consist of 16 variables;

softening point (°C), viscosity (Pa.s) at 135°C, DSR test frequency (rad), temperature (°C), phase angle (°) and complex shear modulus (kPa) at test temperatures between 46–76°C at 6 °C increments. The databases consist of 1980 and 1668 data points for the modelling rutting and fatigue parameters respectively. The database was divided into training and simulation sets. The training set was further divided into training-testing-validation subsets. The output for the first case study (1) was the Superpave® rutting parameter (G*/sinδ), and for the second (2) and third (3) case studies were the Superpave® fatigue parameter (G*.sinδ). The descriptive statistic of the data used is presented in Table 3.3. After data collection, the binary normalisation was applied to both the input and output variables independently. While the normalisation is important to reduce early saturation during training, it can also reduce the importance of certain variables with smaller numeric values. In order to avoid scaling down of any variables, the normalisation was applied within the variables (P. Akpinar & Uwanuakwa, 2020; Pinar Akpinar & Uwanuakwa, 2016).

3.13 Machine Learning Research Model

Three models consisting of the Gaussian process regression (GPR), artificial neural networks (ANN) and recurrent neural networks (RNN) using the MATLAB software for all the algorithms.

The research model architecture is presented in Figure 3. 11. In the model development, the model was trained with the research data, while 3% and 6% latex modified asphalt binder mixes dataset from Sani et al., (2019) were used to simulate the developed model. The idea is to assess the performance of the model with an independent test replica dataset that was not used to calibrate the model. The independent dataset provides a measure of the accuracy of a trained model.

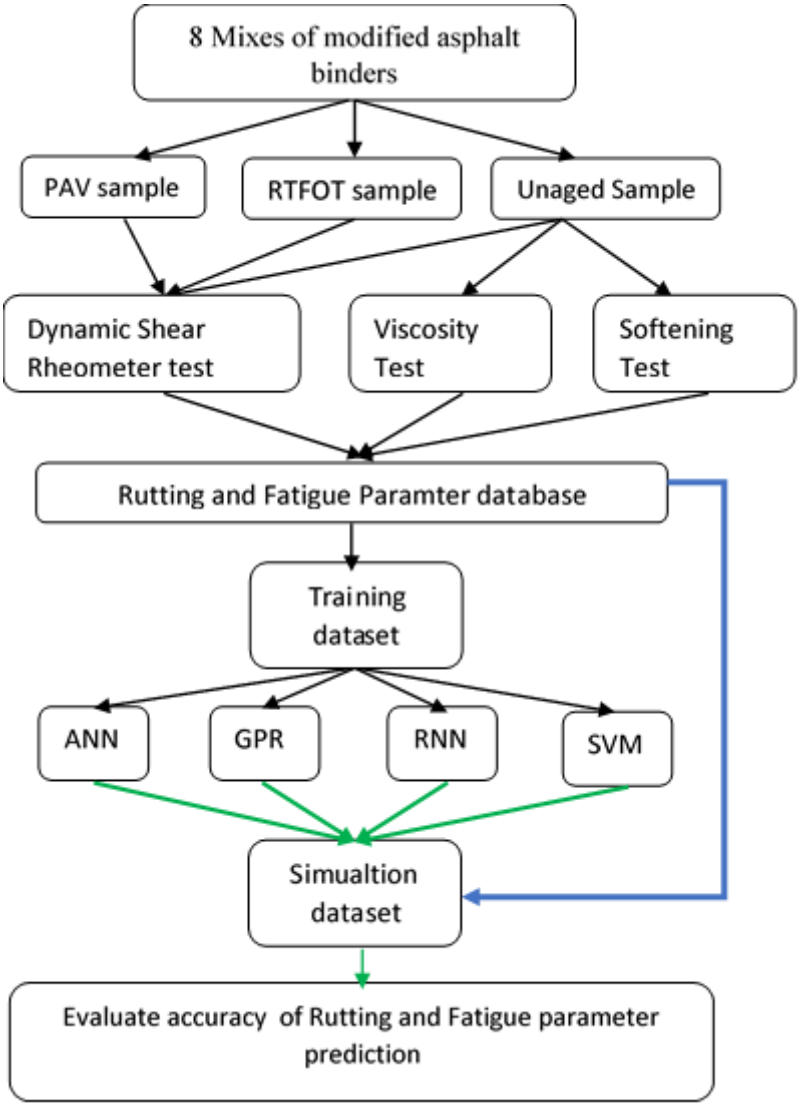


Figure 3.11: Model Architecture.

The developed model performance was measured using a cost function that penalises or reward the network. The network mean-square-error (MSE) was the cost function used in this research. Further, the ANN and RNN samples were divided into mini-batches in a ratio of 60:20:20 and 70:15:15 training:testing: validation sets respectively. Five-fold cross-validation was applied to the GPR models and trained using the regression learner App in the MATLAB software. The network parameters were obtained and updated through trial and error. A total of 12 hidden neurons were found to be sufficient for ANN and RNN models. The GPR kernel function was set to square exponential. The computations were carried out on Intel Corei3, 2.10 GHz CPU on Windows 10 with 12 GB RAM.

Table 3.3: Statistical description of the measured 18 input variables and the outputs.

	Modelling of Rutting with Unaged Binder Inputs				Modelling of Fatigue with Unaged Binder Inputs				Modelling of Fatigue with RTFOT Binder Inputs			
Variables	**Min**	**Max**	**Mean**	**Std. Deviation**	**Min**	**Max**	**Mean**	**Std. Deviation**	**Min**	**Max**	**Mean**	**Std. Deviation**
Frequency (rad)	0.63	62.80	15.06	18.44	0.63	62.80	15.06	18.44	0.63	62.80	15.06	18.44
Softening point (°C)	50.00	70.25	57.63	6.82	50.00	70.00	57.63	6.82	54.00	79.00	62.17	8.16
Viscosity (Pas)	1131.50	3204.30	1926.99	689.74	1132.00	3204.00	1926.99	689.78	1131.50	3204.30	1926.99	689.78
G* @ T46 °C (kPa)	5070.00	294,000.00	78,123.08	72,387.62	5070.00	294,000.00	78,123.08	72,391.49	12,000.00	637,000.00	145,668.60	135,273.40
G* @ T52 °C (kPa)	1990.00	149,000.00	38,442.69	36,095.25	1990.00	149,000.00	38,442.69	36,097.18	4500.00	290,000.00	70,249.23	64,701.79
G* @ T58 °C (kPa)	775.00	79,700.00	18,902.45	18,644.12	775.00	79,700.00	18,902.45	18,645.12	1620.00	152,000.00	32,862.05	31,843.26
G* @ T64 °C (kPa)	333.00	48,400.00	10,366.33	10,690.06	333.00	48,400.00	10,366.33	10,690.63	690.00	75,600.00	18,163.12	17,692.36
G* @ T70 °C (kPa)	153.00	28,300.00	5606.22	5897.43	153.00	28,300.00	5606.22	5897.74	312.00	47,800.00	9935.94	9943.40
G* @ T76 °C (kPa)	78.50	16,500.00	3351.97	3465.50	79.00	16,500.00	3351.97	3465.69	156.00	27,000.00	6029.82	5871.54
δ @ T46 °C (°)	40.10	88.90	63.10	9.07	40.00	89.00	63.10	9.07	37.20	88.40	58.48	8.38
δ @ T52 °C (°)	48.50	85.30	66.63	8.12	49.00	85.00	66.63	8.13	39.00	77.40	62.14	7.82
δ @ T58 °C (°)	51.40	88.20	69.54	8.54	51.00	88.00	69.54	8.54	49.00	81.90	65.52	7.18
δ @ T64 °C (°)	48.00	89.80	71.68	9.55	48.00	90.00	71.68	9.55	48.60	85.60	68.41	8.52
δ @ T70 °C (°)	28.40	89.60	72.02	12.74	28.00	90.00	72.02	12.74	22.80	89.60	69.34	11.85
δ @ T76 °C (°)	22.80	89.90	72.15	14.77	23.00	90.00	72.15	14.77	14.30	89.90	69.17	15.95
Temperature °C	46.00	76.10	61.00	10.25	16.00	31.00	23.20	5.57	16.00	31.20	23.20	5.56
Output (kPa)	0.16	796.56	55.34	95.48	30,328.00	1,555,500.00	361,493.90	277,693.70	30,327.70	1,555,500.00	361,493.90	277,693.70

3.14 Model Evaluation Criteria

In machine learning modelling, different evaluation criteria are used to quantify the performance of the model. According to Wu and Chau (2013), evaluation of model performances should include absolute and relative error measurements of the model (Wu & Chau, 2013). In this study, two traditional statistical tools were used: the coefficient of determination (R^2); the root mean squared error (*RMSE*) and the mean absolute error (*MAE*).

$$R^2 = \frac{SSR}{SST} \tag{3.1}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(Y_{Predi} - Y_{Obi})^2}{n}} \tag{3.2}$$

$$MAE = \frac{1}{n}\sum_{i=1}^{N}|Y_{Obi} - Y_{Predi}| \tag{3.3}$$

where *n* is the number of observed values, $Y_{Pred1.}\ Y_{Pred2.}\ \ldots\ldots Y_{PredN}$ are predicted values; $Y_{Ob1.}\ Y_{Ob2.}\ \ldots\ldots Y_{ObN}$ are the observed values; SSR is the sum of squared regression derived by $\sum(Y_{Predi} - \bar{Y})^2$; SST is the total variation contained in the dataset derived by $\sum(Y_{Obi} - \bar{Y})^2$ and $\bar{Y}$ is the mean of Y value

3.15 Material Characterisation

3.15.1 Polymer physical and morphological characterisation

The physical and chemical characterisation was carried using a Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (FESEM-EDX). scanning electron microscopy uses a high-resolution image method to map out the topographic and morphological structures of a sample material, which include the surface area feature, shape and particle size at the nanoscale. However, the incorporation of the energy dispersive x-ray spectroscopy EDX, enhances the ability of the FESEM-EDX to characterise the chemical composition of the sample material is expressed in weight percentage or by the atomic percentage (Restivo et al., 2014).

Figure 3.12 and 3.13, shows that the morphological characterisation Kraton ® D1101 ASM has a larger particle size as compared to the particles sizes of Kraton ® D1152 ESM and Kraton ® D1184ASM. The influence of their particles sizes is not considered in this research, since the materials evaluation studies were conducted on samples at melt state. However, it is important to show their various shapes and topographical features which is similar to among the polymers and relevant for the purpose of comparison.

A similar trend was observed in the features for of the polymers at 100µm FE-SEM magnification.

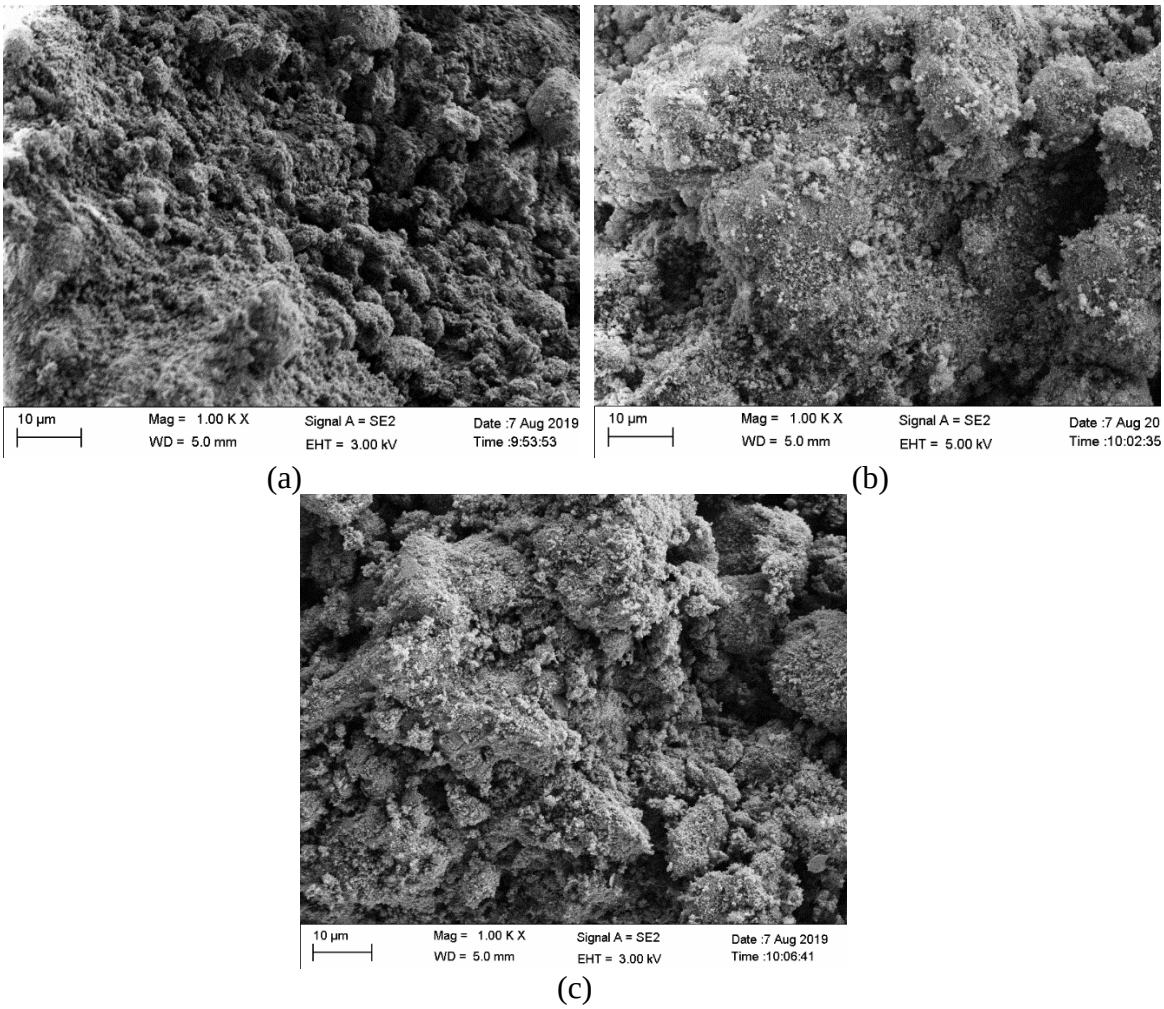


Figure 3.12: FE-SEM morphological characterisation of the polymers at 10µm for (a) D1152 ESM (b) D1101 ASM and (c) D1184ASM

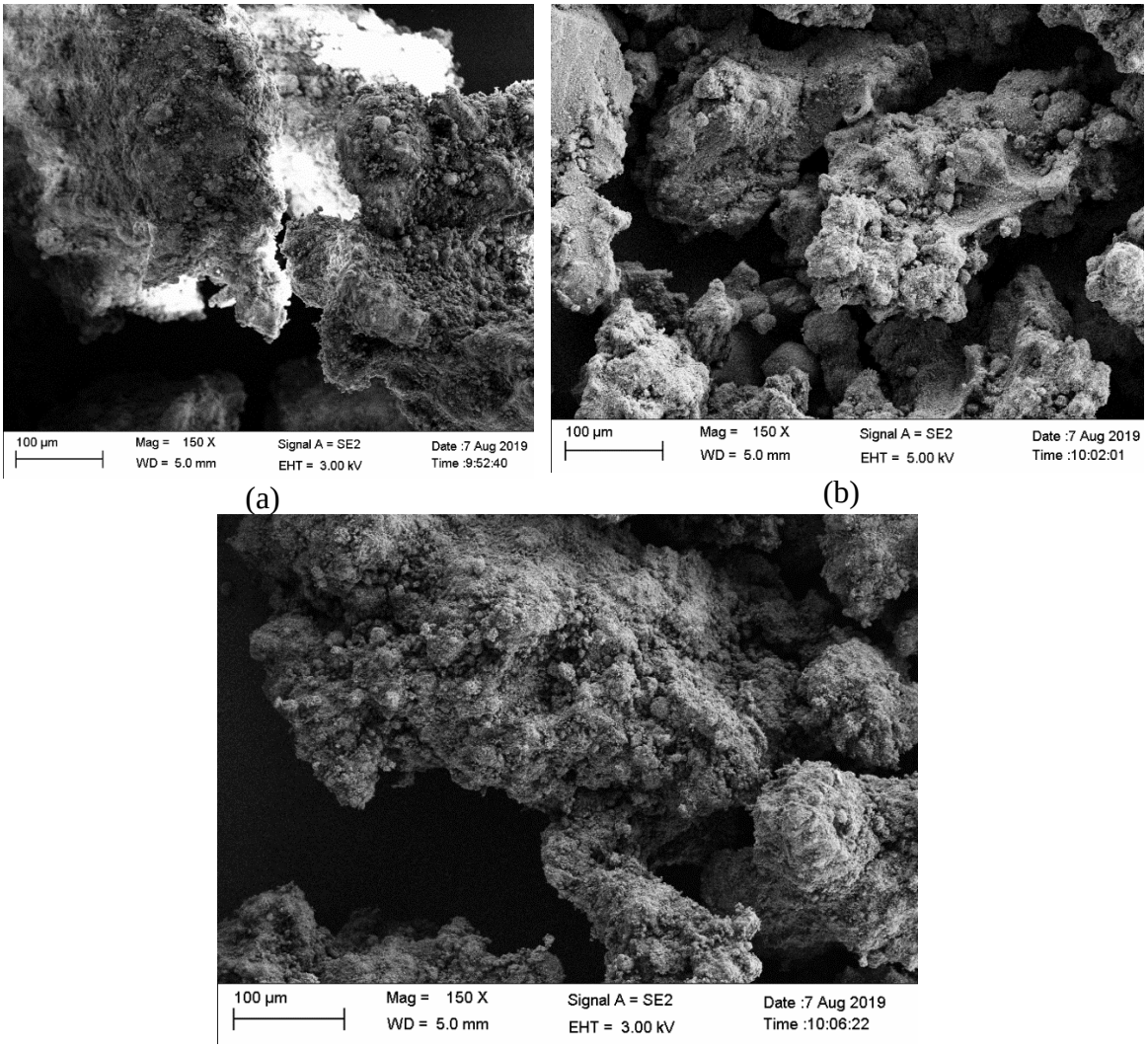
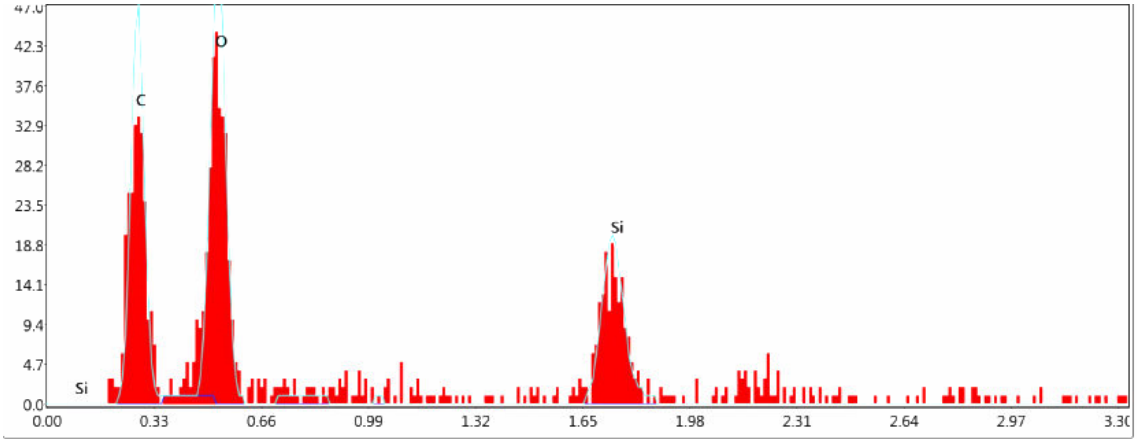
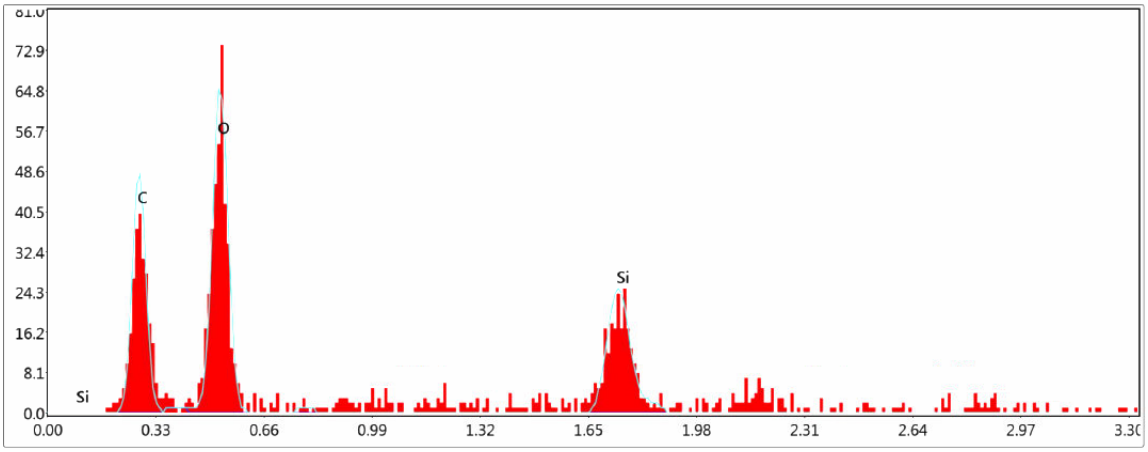


Figure 3.13: FE-SEM morphological characterisation of the polymers at 100µm for (a) D1152 ESM (b) D1101 ASM and (c) D1184ASM

The energy-dispersive x-ray spectroscopy EDX analysis are presented in Figure 3.14. The results show that Kraton D1184ASM with silicon, oxygen and carbon contents of 48.12 %, 37.17% and 16.70 % respectively, have the highest molecular weight of 505 kDa. Although the results of the EDX cannot be used to estimate the molecular weight, however, it provided insight into the elemental composition of the samples.



(a)



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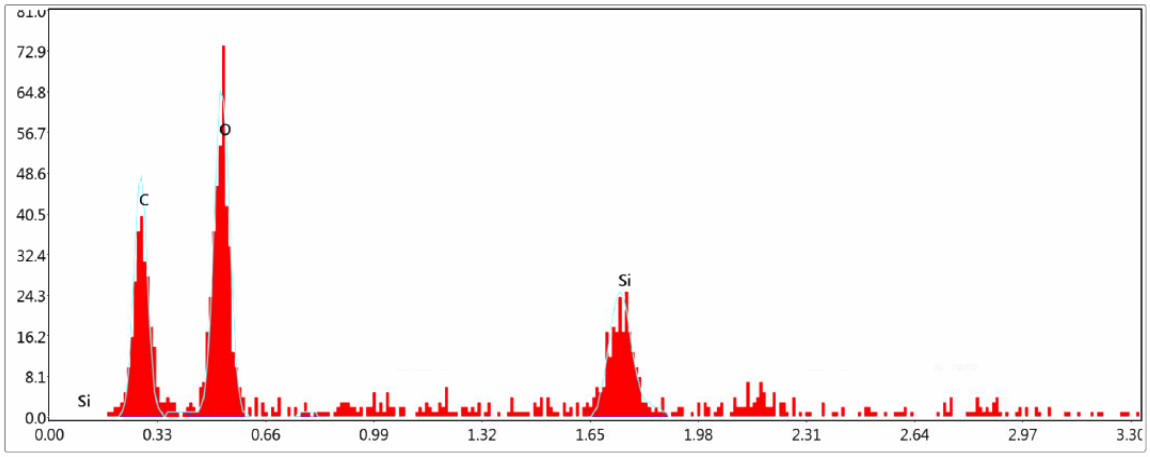


(c)

Figure 3.14: EDX element analysis of the polymer samples

3.15.2 Polymer molecular weight characterisation

The Agilent 1260 Infinity Quaternary LC equipment software calculates the values of the molecular weight, the results are presented in Table 3.4.

Table 3.4: Properties of the SBS polymers

Parameters	D1152 ESM	D1101 ASM	D1184 ASM
Solution Viscosity @25 (ºC) (Pa.s)	1.0	1.24	4.2
Structure	Linear	Linear	Branch
Styrene-butadiene ratio	29.5/70.5	31/69	30/70
Melt flow rate 200 ºC /5000g (g/10min)	7.2	-	-
Particle size < 200µm % wt.	4.8	10	7
Molecular weight, Mn (g/mol)	1.5822E5	3.5680E5	5.0557E5
Molecular weight, Mw (g/mol)	1.5827E5	3.5760E5	5.0692E5
Molecular weight, Mz (g/mol)	1.5833E5	3.5840E5	5.0829E5
Polydispersity Index	1.00	1.00	1.00

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Empirical Binder Characterization

The empirical binder characterisation is presented in this section. Only the softening point and the viscosity of the binder are considered. The result results are presented in Table 4.1 and analysed below.

Softening point test: The softening point test evaluates the tendency of the material to flow at elevated temperatures usually encountered in service of the asphalt pavement. The details of the test are outlined in ASTM D36.

Dynamic Viscosity Test: The dynamic viscosity test measures the apparent viscosity of asphalts required for mixing, compaction and handling of the asphalt. The test was performed at 135 C, 155 C and 175˚C test temperature. The detailed procedure for the test experiment is contained in ASTM D 4402.

Table 4.1: Results of empirical binder characterization

Samples	Softening point Test ASTM D36 ˚C	Dynamic Viscosity Test ASTM D4402 Pa.s			
		Shear rates^{-1}	135℃	155℃	175℃
		3.81	0.488	0.200	0.113
BB	46	6.76	0.456	0.206	0.094
		16.91	0.443	0.198	0.095
PMB-I-3	50	6.76	1.132	0.450	0.206
		3.81	1.713	0.700	0.338
PMB-I-5	53.5	6.76	1.650	0.656	0.300
		16.91	1.587	0.630	0.303
PMB-I-7	61	6.76	2.357	0.950	0.456
PMB-II-3	52.25	6.76	1.188	0.506	0.250

		3.81	1.853	0.800	0.413
PMB-II-5	59	6.76	1.800	0.787	0.400
		16.91	1.738	0.735	0.358
PMB-II-7	70.25	6.76	3.204	1.337	0.644
PMB-III-3	53	6.76	1.269	0.450	0.213
		3.81	2.642	0.613	0.275
PMB-III-5	55	6.76	2.100	0.740	0.288
		16.91	1.940	0.710	0.335
PMB-III-7	72	6.76	3.922	1.356	0.475

4.1.1 Control and PMB binder softening point analysis

The results in Figure 4.1 presents the softening point for unaged and RTFOT conditioned samples. The results show that the increase in the molecular weight concentration for a given polymer content increases the softening point of the binder. For example, at 3% polymer content, there was a 4, 6.25 and 7℃ increase in the softening point from the control binder for PMB-I, PMB-II and PMB-III respectively. Similarly, at 5% and 7% polymer content, within the samples (PMB-I and PMB-II) modified with linear SBS polymer, a similar trend was observed. Further, PMB-II-5 modified with linear SBS polymer increased by 13℃ from the control binder, while PMB-III-5 modified with branch polymer increased by 9℃. The results suggest that the structure of the polymer could have a potential influence on the binder.

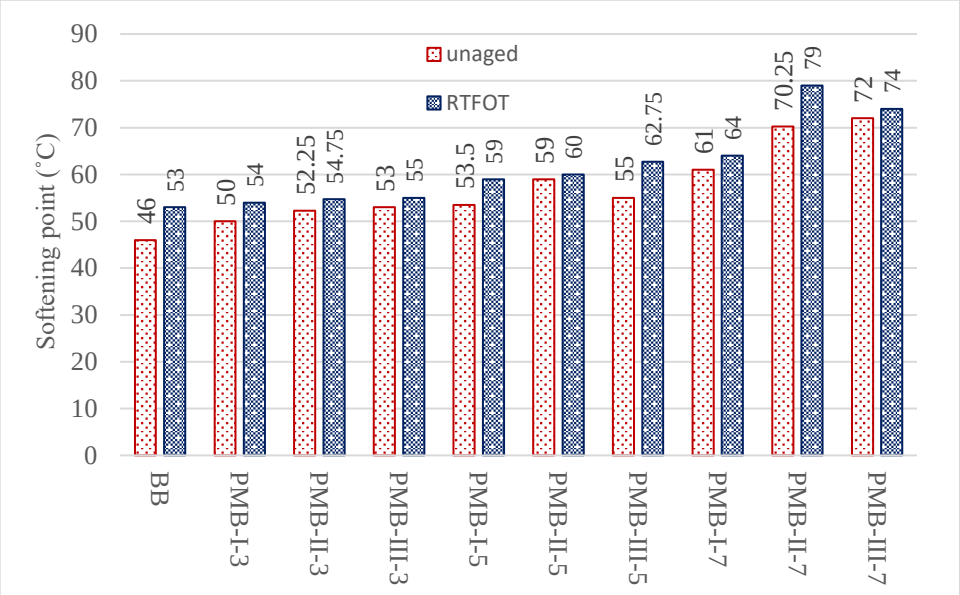


Figure 4.1: Softening point results of unaged and RTFOT samples

Further, for the samples modified with linear SBS polymer, it was observed that the increasing molecular concentration of the samples increased the softening point of the binder for RTFOT conditioned samples. Figure 4.1, also suggest that the structure of the polymer could influence the softening point of the polymer-modified binder.

4.1.2 Control and PMB binder viscosity test analysis

The first aspect of the mechanical dynamic analysis studied the influence of the molecular weight on the viscosity of the modified binder. The quiviscous temperature for asphalt concrete construction was developed by the Asphalt Institute in 1962 which recommended the mixing and compaction temperatures for a binder with the viscosity of 0.17 ± 0.02 and 0.28 ± 0.03 Pa s respectively. These values are applied to both the Marshall mix and SuperPave mix designs (Yildirim et al., 2006). However, the SuperPave manual noted that this viscosity value range is not valid for use for modified binder mixing and compaction temperatures. The manual recommended the manufacturers specifications for modified binders (Yildirim et al., 2006).

The effect of the molecular weight on the binder viscosity was investigated at135ºC temperature using a Brookfield viscometer between 3.38 to 16.91 1/s shear rate on 5% polymer content.

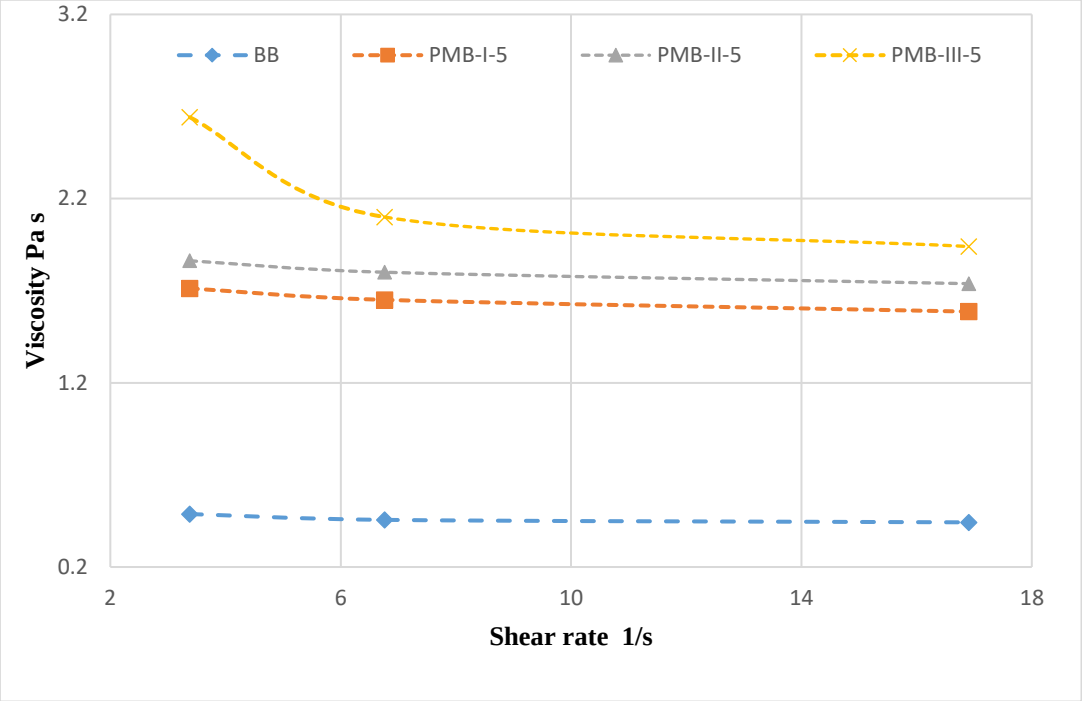


Figure 4.2: Variation of viscosity with shear rate at 135 ºCfor neat asphalt and 5 % content of modified binder.

The results in Figure 4.2, shows the variation of viscosity with the shear rate at a different at 5% SBS content with different molecular weight. For the case of the control binder, the increase in shear rate does not affect the viscosity of the neat asphalt. However, at a lower concentration, for PMB-I-5 and PMB-II-5, there was a slight deviation in the values of the viscosity from the Newtonian region towards the non-Newtonian region which is governed by the shear rate. The increase in the molecular weight of the SBS polymer for PMB-III at 5% content, showed a clearer transition from the non-Newtonian to Newtonian region. Also, the Newtonian plateau zone decreases faster with the increase in the molecular weight of the modified binder.

The modification of the neat asphalt altered the molecular structure of the asphalt from Newtonian to a non-Newtonian fluid. The behaviour of non-Newtonian fluid is a complex one, the stress tensor, as well as its derivatives, is a function of the velocity gradient (Binesh et al., 2015). Furthermore, it was observed that the dependence of the viscosity of the PMB on the molecular weight decreases as the shear rate increases.

The viscosity dependence of the SBS modified binder on the shear rate could be attributed to the crosslink networks between asphalt and polymer formed through polymer entanglement(Usmani, 1997), unlike neat asphalt which has a weak bond between the asphalt molecules(Jones & Kennedy, 1991). The networks tend to deform by shear yielding resulting in to decrease in viscosity as can be observed in Figure 4.2.

4.2 Storage Stability Characterization SBS Modified Asphalt Binder

A hot storage test conducted in this research was used to determine the degree of phase separation between the asphalt and polymer-rich phases. The test was conducted at temperatures 163°C and 180°C for 2 and 3days. The results were evaluated based on the softening point difference between ARP which settled out from the PRP. In Figure 4.3(a), the results of the samples stored at 163°C for 2 and 3days show that phase separation did not occur with the sample designated as low Mw at 3% content (PMB-I-3), the softening points of the ARP and PRP were found to be consistent indicating good hot storage stability. With the increase in the Mw of the SBS (PMB-II and PMB-III), it was observed that the 3% addition resulted in phase separation. For a storage duration of 2 days (48hr), the softening point difference between the ARP and PRP for PMB-II and PMB-III at 3% content of the polymer was 19°C and 45°C respectively. However, PMB-III did not show an appreciable increase at the 3% content when the storage duration was increased to 3days (72hr), unlike PMB-II which has a 14% increase from 48hr to 72hr.

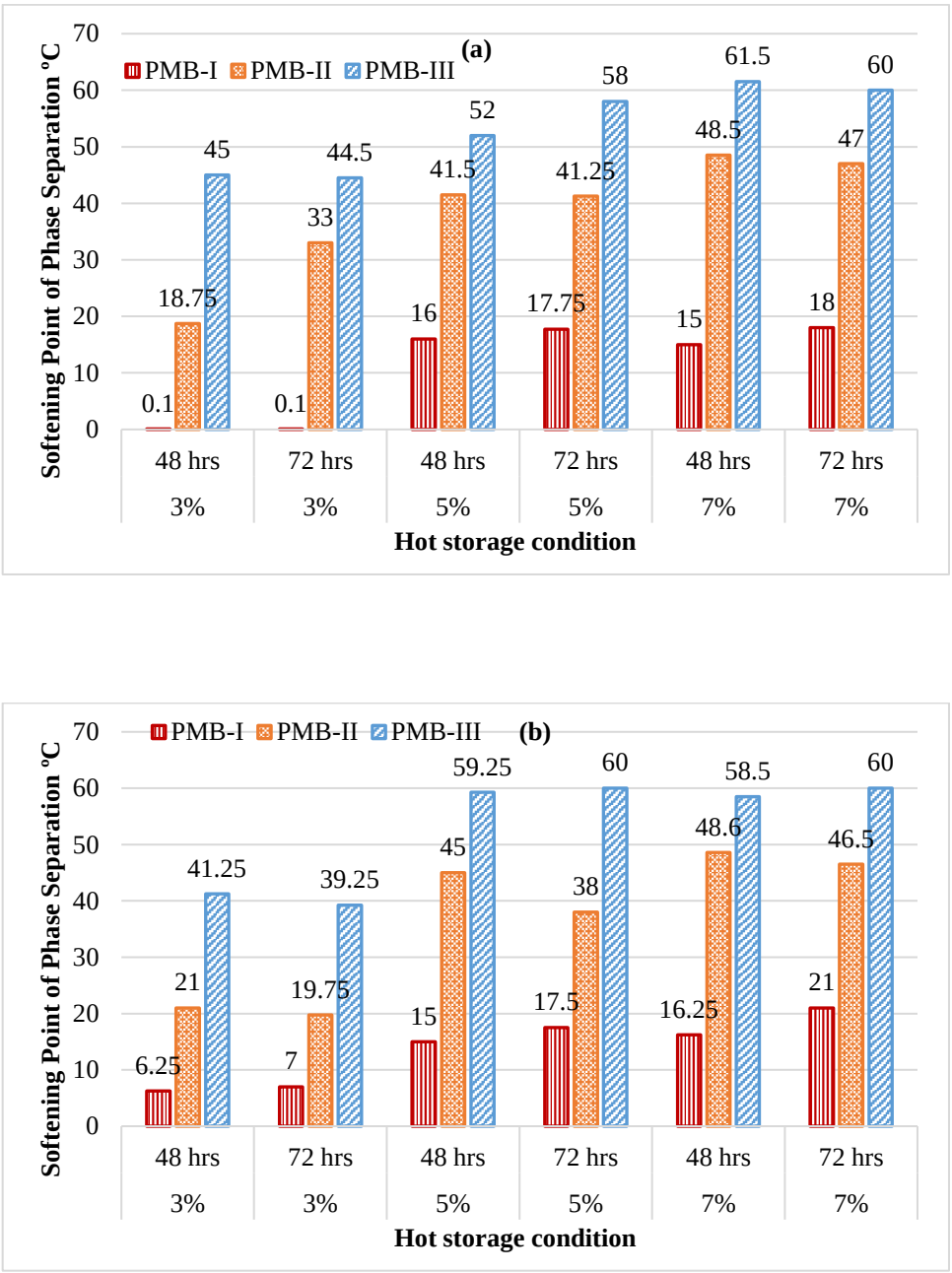


Figure 4.3: The softening point difference between ARP and PRP for (a) 163ºC and (b) 180ºC

The increase in the storage temperature from 163ºC to 180ºC resulted in phase separation at 3% concentration for PMB-I. However, for PMB-II and PMB-III, the degree of phase separation obtained at the temperature of 163ºC also changed when the storage temperature was increased to 180ºC. The result further indicated that at higher polymer content and molecular weight, the increase in temperature did not have a significant effect. For example,

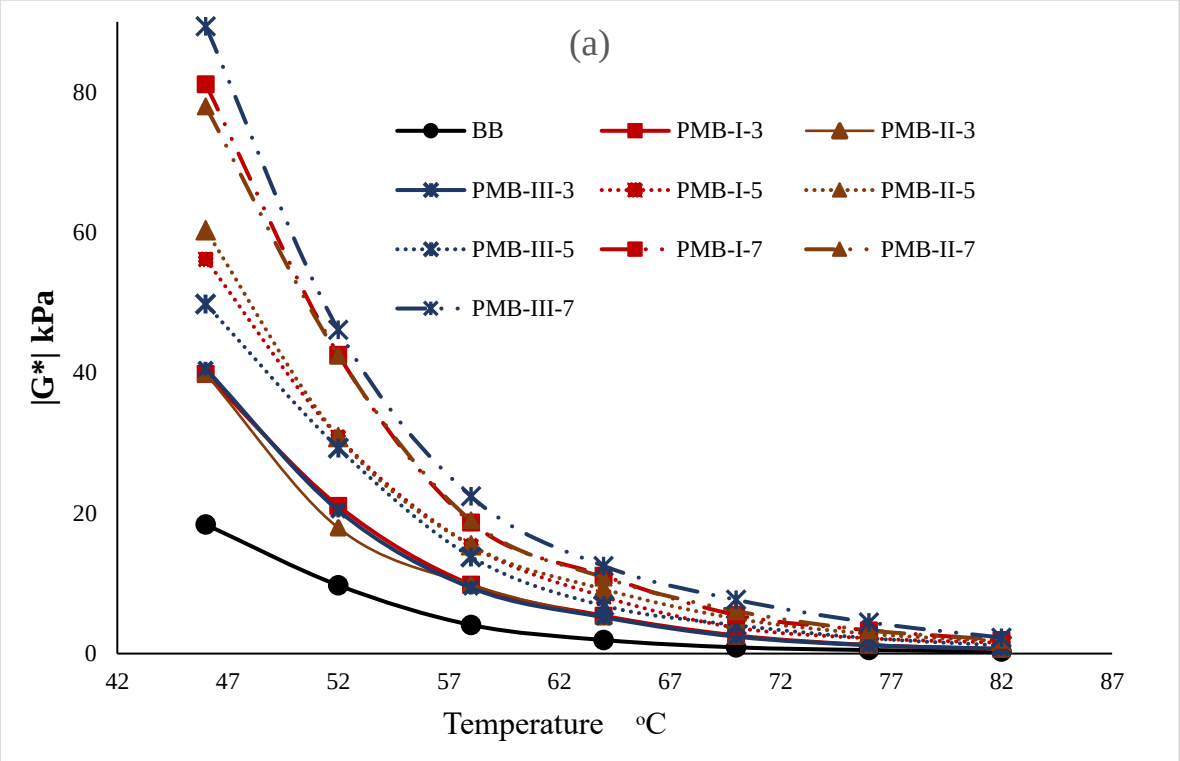
phase separation that occurred in PMB-III at 3% content for 163℃ and 180℃ was 45℃ and 41.25℃ respectively after 48h storage period, and 44.5℃ and 39.25℃ respectively after 72h hot storage time. The same trend was observed with PMB-III 3% content.

Consequently, from the results of Figure 4.3 (a) and (b), the increase in the storage time from 2 to 3 days affects the asphalt/polymer biphasic stability for SBS PMB studied. Similar trends reported by (Hakseo Kim & Lee, 2013; Zani et al., 2017)are in agreement with the findings observed in Figure 4.3, in which the temperature and time affect the stability of hot storage.

The addition of SBS polymer with higher molecular weight into the asphalt at a temperature lower than the SBS disassociation temperature will form micelles dispersed within the ARP. This action increased the Mw of micelles (asphaltene and polymer micelles) within the matrix(Lesueur, 2009; Polacco et al., 2015). At higher storage temperature, un-peptised micelles of the polymer due to excessive molecular weight disassociate from the matrix leading to segregation between ARP and PRP. The disassociation is caused by weak London-van der Waals force at a high temperature which was formed through polymer entanglement which held the biphasic asphalt/polymer network(Usmani, 1997).

4.3 Characterization Unaged Asphalt Binder

The characterization of the unaged asphalt binder was carried out using the oscillatory results of the dynamic shear rheometer performed between 46 to 82°C temperatures at the frequency of 10 rads. The results are presented in Figure 4.4. The results show that the increase in the SBS content increased the stiffness of the binder as can be observed in the increasing complex shear modulus and the decreasing phase angle. Further analysis shows that PMB-III with the highest molecular weight has the highest stiffness.



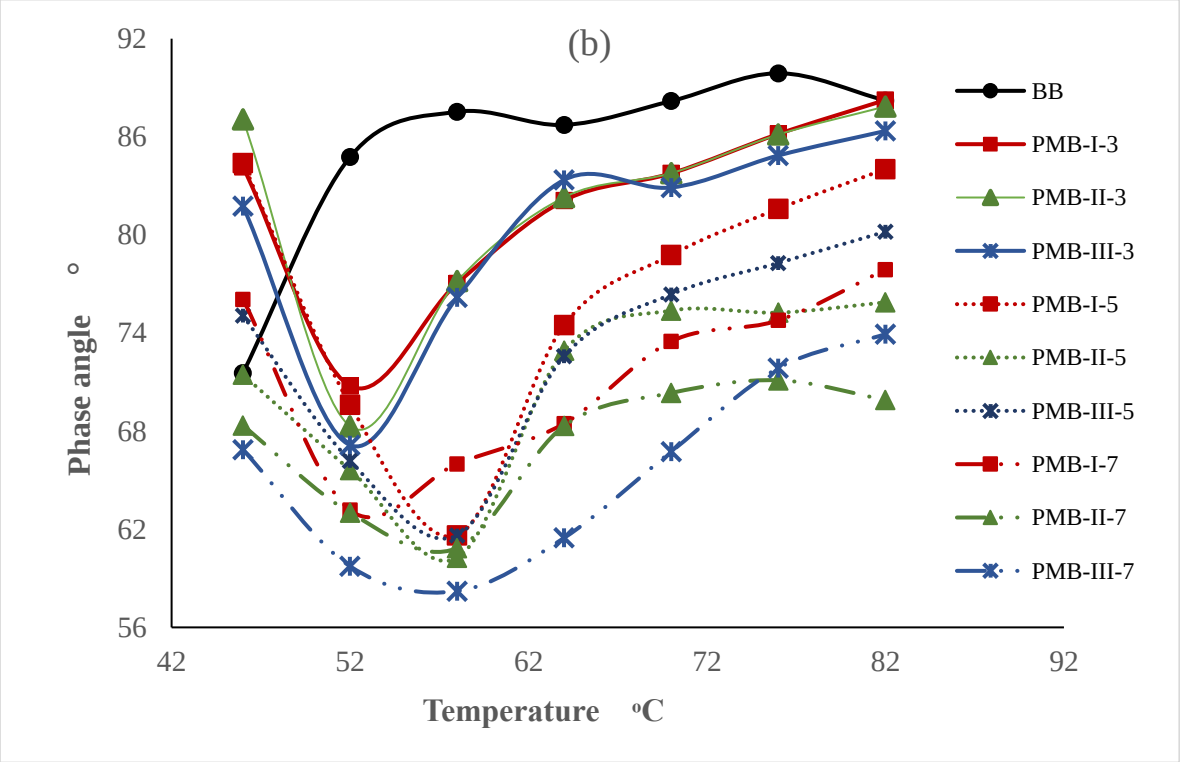


Figure 4.4: Unaged binder plot of (a) complex shear modulus (G*) and (b) phase angle against temperature.

4.4 Rutting Parameter Characterization of SBS Modified Asphalt Binder

The G*/Sinδ of an asphalt binder extracted from the DSR test is recognised by Superpave specification for the evaluation of the rutting performance of a binder. The specification requires a minimum value of 1.0 and 2.2 kPa for the original and RTFOT binder respectively at the reference pavement temperature (AASHTO M 320, 2010) to meet the rutting resistance performance of asphalt pavement. The results obtained for varying SBS polymer molecular weight are presented in Figure 4.5 for the RTFOT samples.

The results show that the increase of the testing temperature, led to a decrease in G*/Sinδ value, while the increase in the molecular weight of the polymer increased the G*/Sinδ. The control binder failed to meet the requirement at 70℃ temperature. The PMB-II and III met the requirement up to 76℃ temperature indicating a good resistance to rutting in the pavement.

The higher value of the G*/Sinδ parameter associated with PMB-III with a higher Mw indicates the dependency of binder stiffness on the Mw for a given PMB at constant density.

Further analysis shows that the glass transition temperature of the SBS monomers influences the rutting parameter. The PMB-II with 31% polystyrene content have higher rutting resistance, this could be attributed to the behaviour of the polystyrene monomer. It is important to note that SBS exhibit two glass temperatures; -100℃ and 70℃ for polybutadiene and polystyrene phase respectively, and expected to shift the glass transition temperature of asphalt (Nivitha & Murali Krishnan, 2016). This phenomenon was observed between 46℃ to 70℃ at 5% polymer content. PMB-II recorded the height G*/Sinδ value.

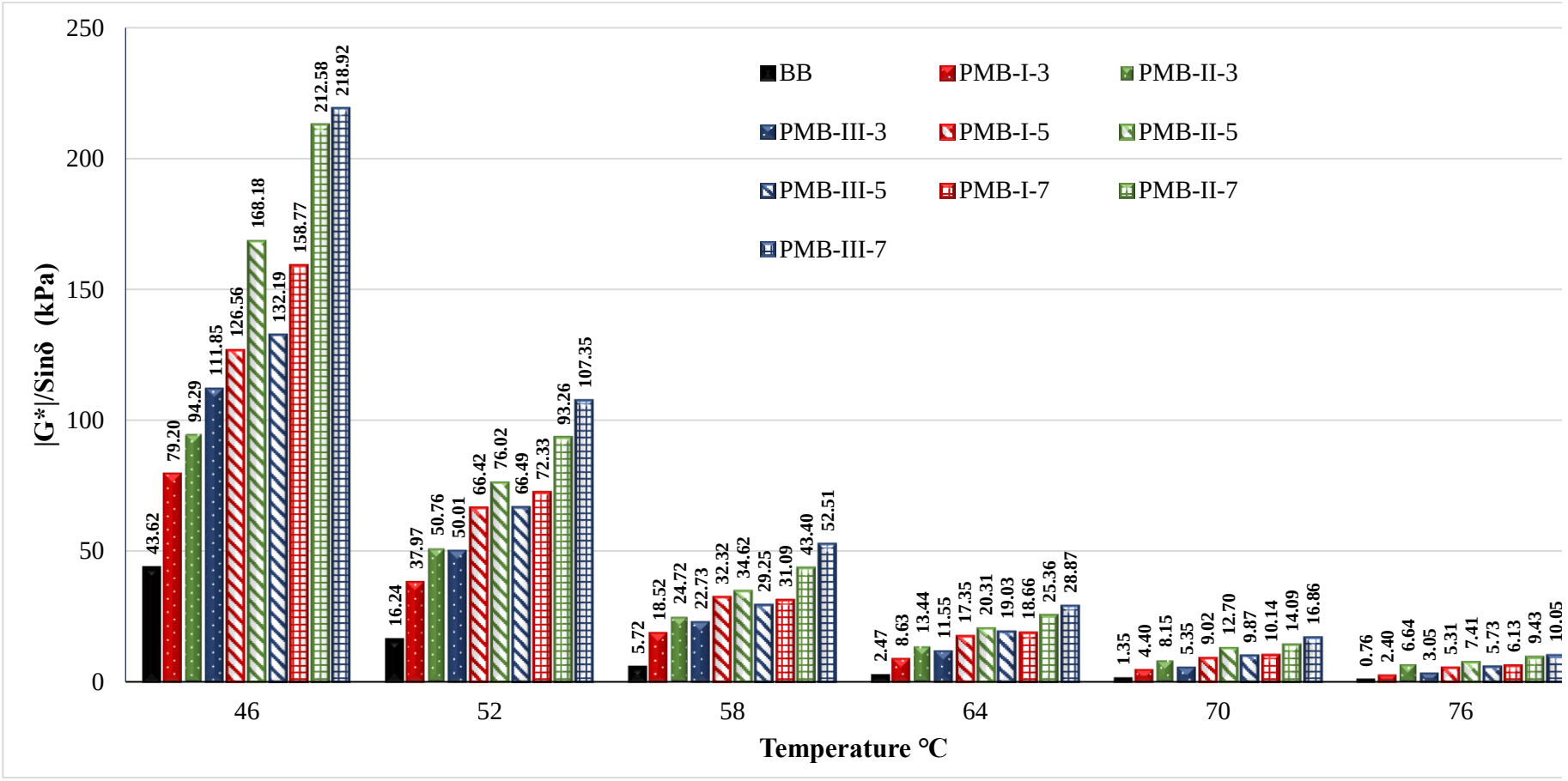


Figure 4.5: Variation G*/Sinδ with temperature for RTFOT samples.

4.5 Multiple Stress Creep Recovery Characterization Of SBS Modified Asphalt Binder

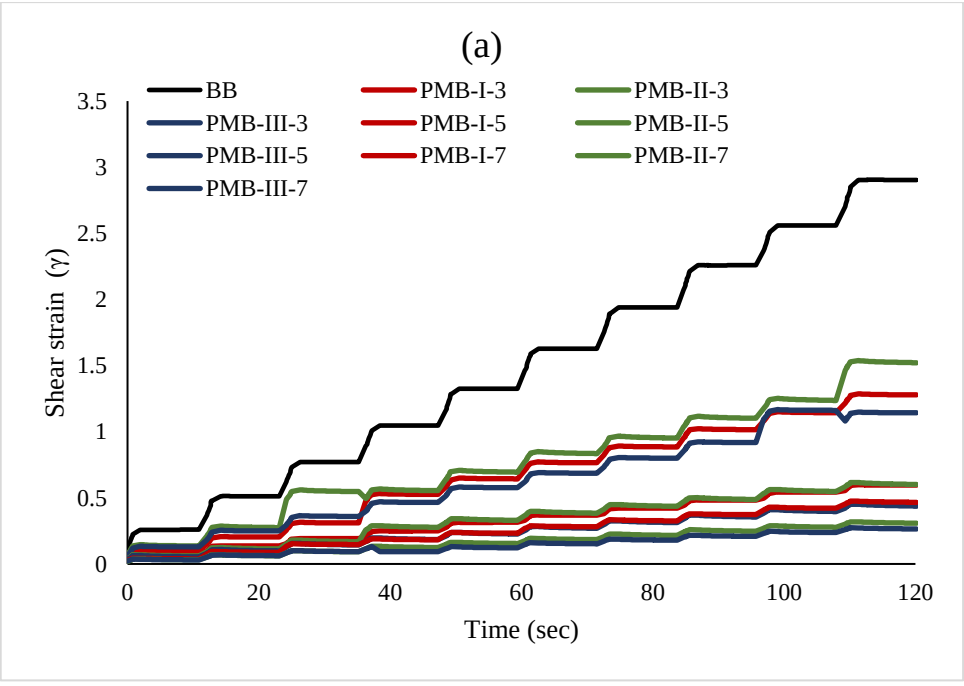
The Multiple Stress Creep Recovery Test is wildly used in the evaluation of the rutting performance of an asphalt binder (Ashish & Singh, 2018; García-Travé et al., 2016; Jafari et al., 2017; Shafabakhsh et al., 2015). Within this research, the commonly used standard stress level of 0.1 and 3.2 kPa were applied at 64 ℃ and corresponding induced strain were measured accordingly.

The importance of the MSCR test is to investigate the stress sensitivity of an asphalt binder for a given traffic load condition using the non-recoverable creep compliance (Jnr) parameter. The parameter (Jnr) can be calculated using equation (1) for both 0.1 and 3.2 kPa stress levels;

$$J_{nr}(kPa^{-1}) = \frac{1}{10}\left\{\sum_{i=1}^{10}\left(\frac{e_{10}}{\tau}\right)_i\right\} \qquad 4.1$$

where e10 = adjusted strain after recovery for each cycle and τ is the applied stress level.

A detailed approach for the estimation of the Jnr is given in (Soenen et al., 2013).



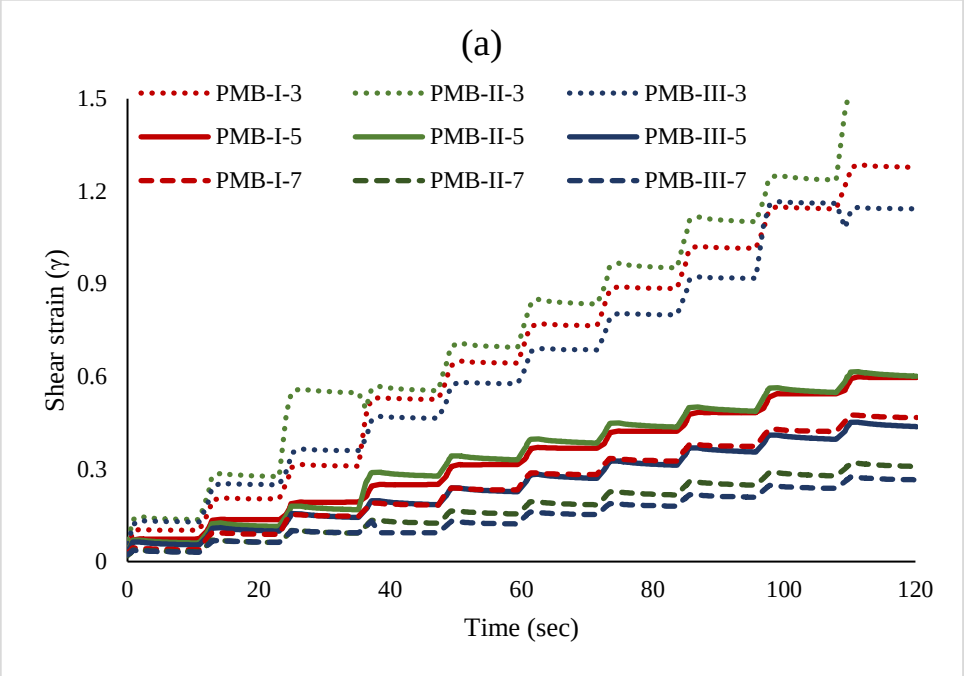


Figure 4.6: Variation of the strain response at 0.1 kPa stress levels

In Figures 4.6 and 4.7, the respective induced strained for the measured stress level of 0.1 and 3.2kPa are presented for RTFOT samples. The increase in the value of the measured strain infers the susceptive of an asphalt binder to rutting at a given pavement traffic loading condition. The results further show that the increase in the molecular weight of the SBS reduces the tendency of the modified binder susceptive to rutting.

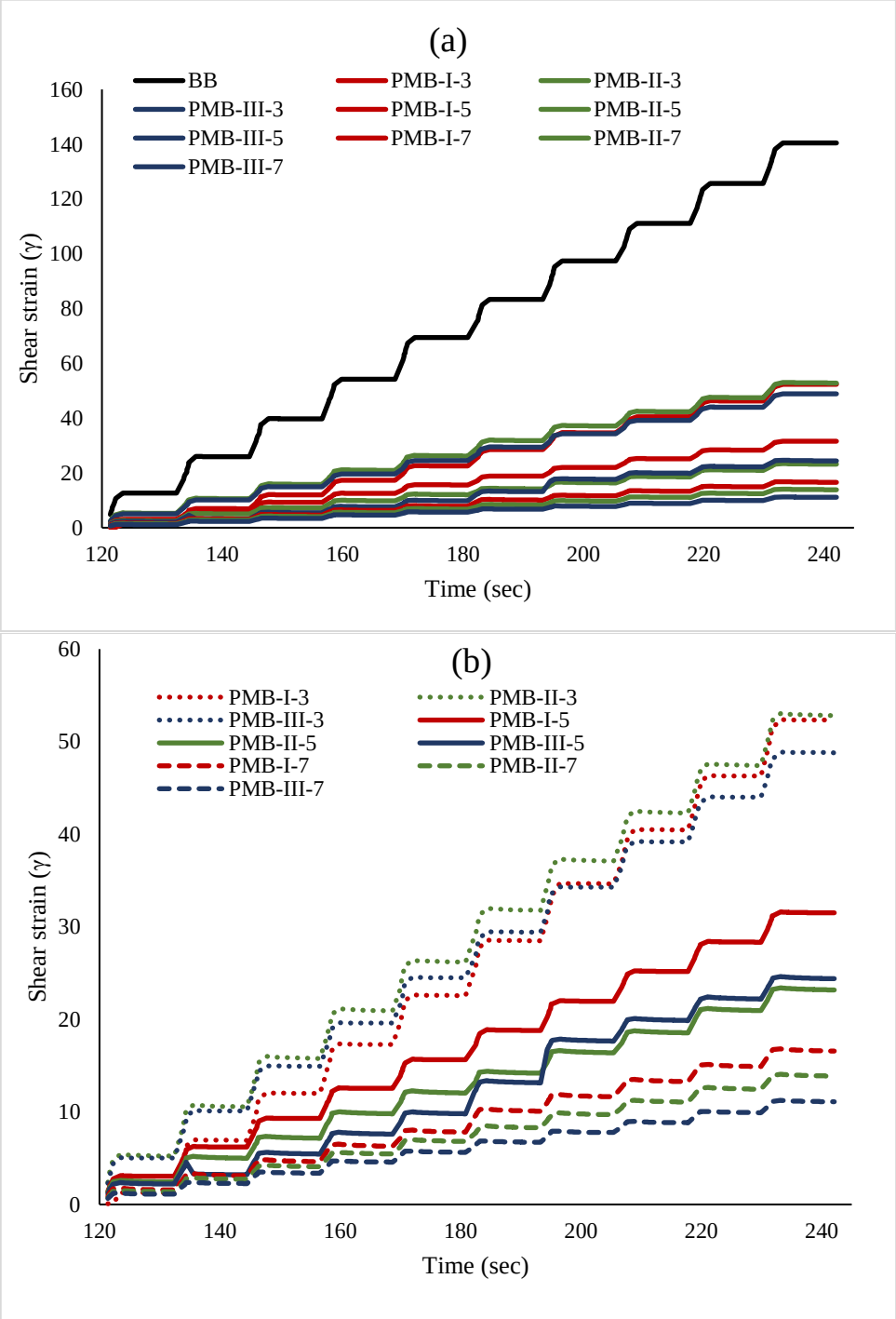


Figure 4.7: Variation of the strain response at 3.2 kPa stress levels

For the stress level of 0.1 kPa and at 5% SBS content, the induced strain at the end of the first cycle creep loading 0.02239, 0.0692, 0.0698, and 0.0632, for the control, PMB-I-5, PMB-II-5 and PMB-III-5respectively. This, in essence, shows a slight reduction in the strain value with the increase in the molecular concentration when evaluated within a given

polymer content. Subsequently, at the end of the unloading (recovery) for the first cycle of 0.1kPa stress level, the respectively recovered strain values for the control, PMB-I-5, PMB-II-5 and PMB-III-5 are -0.002, 0.00043, 0.00919 and 0.00943. Further, for the given SBS with constant density, the increase in molecular weight resulted in increased recovered strain. The same trend was observed for the 3.2kPa stress level.

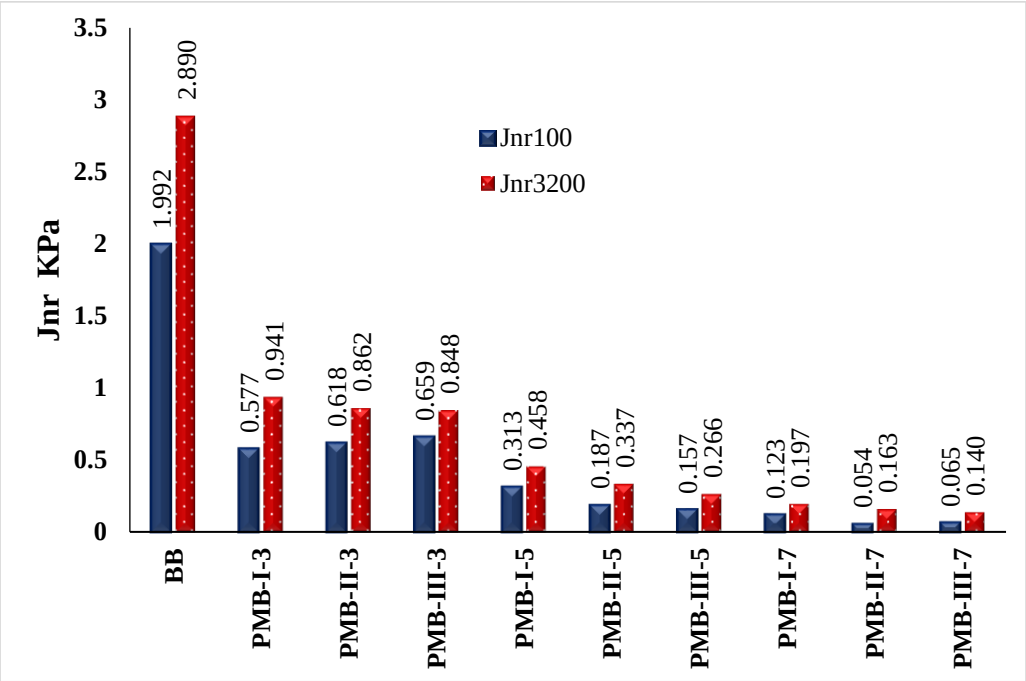


Figure 4.8: J_{nr} Value for studies samples

The non-recoverable creep compliance (Jnr) parameter measures the ratio of the strain that is not recovered at the end recovery section to the applied strain. The results of the Jnr at 1.0 and 3.2kPa stress levels recommended by AASHTO MP19 for evaluation of binder for different traffic conditions are presented in Figure 4.8. It can be seen that the increase in the molecular weight of the SBS content resulted in a decrease in Jnr values. There was a significant reduction in the value of the control Jnr and the modified binders.

At 5% SBS content of the study, Figure 4.8 further shows that there was a 71%, 90% and 92% reduction from the control binder Jnr at 1.0 kPa for PMB-I-5, PMB-II-5 and PMB-III -5 respectively. Further, at 3.2 kPa stress level, the Jnr reduction from the control binder for PMB-I-5, PMB-II-5 and PMB-III-5 were 84%, 88% and 90% respectively. This indicates

that the increase in the SBS molecular weight decreases the Jnr parameter of the binder and improves its susceptivity to permanent deformation.

The statistical analysis results of two-factor ANOVA on the variation test samples with Jnr100 and Jnr3200 are presented in Table 4.2. The higher variation between F-value and F-critical, and the reduced P-value lower than alpha value resulted in the rejection of the proposed null hypotheses that the mean of observation is the same, in favour of the alternative that there is a variation with the mean. This suggests that the increase in Mw has a significant effect on the variation of Jnr of the asphalt binder.

Table 4.2: Two-factor ANOVA on the samples Jnr100 and Jnr320

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	8.900934	9	0.988993	31.94582	8.97E-06	3.178893
Columns	0.277348	1	0.277348	8.958731	0.015124	5.117355
Error	0.278626	9	0.030958			
Total	9.456908	19				

4.6 Fatigue Parameter Characterization of SBS Modified Asphalt Binder

Figure 4.9 shows the variation of |G*|.sinδ parameter with the temperature for all studied samples, for the measured fatigue response of the binder. The |G*|.sinδ parameter of an asphalt binder is used in the evaluation of the fatigue property of the binder as detailed in the AASHTO M 320 specification. The standard specified a maximum |G*|.sinδ value of 5000 kPa for a given asphalt binder to meet the anti-fatigue performance criteria. It can be seen that the value of |G*|.sinδ of the control binder was lower than the SBS modified binder except for PMB-III at 3% polymer content. It is evident that all the modified samples are not suitable for resisting fatigue at a temperature below 22℃ except for PMB-III-3. From the 5000 kPa limiting line in Figure 4.7, and within each SBS content, PMB-III with a higher Mw was observed to have reduced |G*|.Sinδ parameter when compared with the corresponding PMB-I and PMB-II. This tends to indicate resistance to binder ageing.

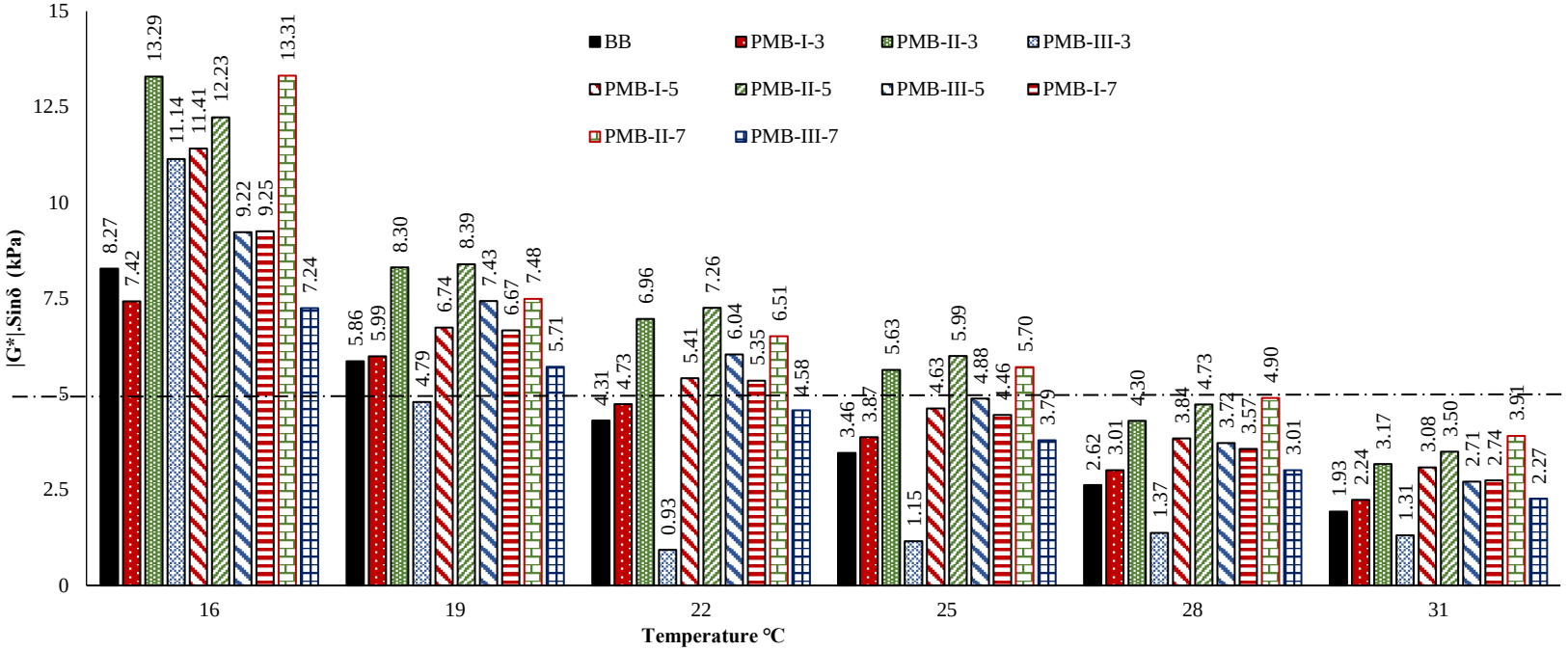


Figure 4.9: Variation |G*|.Sinδ with temperature

The fatigue failure temperature for PMB-I and PMB-III at 5% SBS polymer content was 25℃, both modifiers have a similar polystyrene-polybutadiene ratio of approximately 30/70. However, the PMB-III failure temperature at 7% polymer content was 22℃.

4.7 Cost-Benefit Analysis

In this chapter, the principles of cost-benefit analysis (CBA) are outlined. The cost-benefits of the modification of asphalt with polymers of varying molecular weight was analysed and the results were discussed with respect to rutting and fatigue properties of asphalt binder.

4.7.1 The Methodology of The Cost-Benefit Analysis

The philosophy of cost-benefit analysis is to provide an economic outlook on an alternative system based on the evaluation of cost, benefit and effectiveness of the system. The cost-benefit analysis in this research was estimated to ascertain the economic suitability of modifying 60/70 penetration grade asphalt with SBS polymer of different molecular weights. The analysis took into consideration the rutting and fatigue parameter and the ageing that occur during the mixing of asphalt concrete.

The polymer material cost was obtained from Kraton polymer and the asphalt cost was obtained from alibaba.com. the price of asphalt obtained from alibaba.com did vary with location and suppliers. Although there are limited 60/70 pen grade suppliers on alibab.com online market, however, the price range difference within each location is within 15 EUR/Mt. The average price obtained from suppliers from Turkey is 224.49 €//Mt.

Other costs that were associated with polymer modification include heating and mixing of the polymer and asphalt. The estimation was carried out based on technical data of IKA PMB Plant DR 2000/10 PB, electricity tariff and labour in Turkey. According to Enerjisa 2019 Annual Report, Turkey average electricity tariff was 0.063 €//kWh and the IKA PMB electricity input and production output is 25 kW and 2500 L/h.

Estimation cost of electricity per hour = 25 * 0.063 = 1.575 €/

Total output per hour = 2500L

The volumes were converted to mass by multiplying with the density. The density of the two mixture is estimated as follows;

$$\frac{1}{\rho} = \frac{mass\ fraction\ of\ polymer}{density\ of\ polymer} + \frac{mass\ fraction\ of\ asphalt}{density\ of\ asphalt} \qquad 4.2$$

Determination of mass fraction at varying polymer content;

$$= \%\ conc * 1000cm^3 * density \qquad 4.3$$

Assume 5 € for labour per hour to produce PMB. Therefore, the cost of producing PMB at different polymer content is 302 €/mt for PMB-I and PMB-II, and 312€/mt for PMB-III for all polymer content. The machine hourly rate was 5 € per hour.

4.7.2 Estimation of Cost-Effectiveness Analysis

The cost-effectiveness analysis was carried out by comparing the cost incurred to obtain the benefit and cost of the existing system. In this study, a simplified approach was adopted to calculate the cost-effectiveness;

$$cost - effectiveness = \frac{expected\ performance}{unit\ cost} \qquad 4.4$$

The cost-benefit was determined by taking the ratio of the cost-effectiveness of the base binder to that of the modified binder. The ratio was estimated between 46 ℃ and 64 ℃ for rutting resistance and Jnr parameter.

The results of the cost-effectiveness of modifying asphalt with SBS polymer with varying molecular weights with respect to rutting resistance are presented in Figure 4.10. From the Figure, it can be observed that at 46 ℃ pavement temperature, the benefits of modifying 60/70 pen grade asphalt with Kraton D1152 polymer at 3, 5 and 7 % polymer content were 1.53, 2.23 and 2.5 respectively. Further, for binder PMB incorporated with Kraton D1184, which have high molecular weight, the gained benefits at 46 ℃ were 2.12, 2.26 and 3.30 for 3, 5 and 7% polymer content respectively. This is an indication that increases polymer content has a significant increase in the economic benefit. Also, the increase in the molecular

weight of the polymer was observed to yield a significant benefit across the test temperatures.

At high temperature, the cost-benefit was observed to increase significantly with an increased molecular weight of the polymer. For example, the cost-effectiveness ratio of PMB-III-7 increases at an average of 1.46 from 46℃ to 64℃ temperatures. The PMB-II-7 and PMB-I-7 increased at an average of 1.24 and 0.89 respectively from 46℃ to 64℃ temperatures. Similarly, the trend was also observed with 3 and 5% polymer content. The results of the cost-effectiveness ratio is in agreement with data presented in M. I. Souliman et al., (2017) and Mena I. Souliman et al., (2016) which reported a 2.6 cost-effectiveness ratio for polymer modified asphalt concrete.

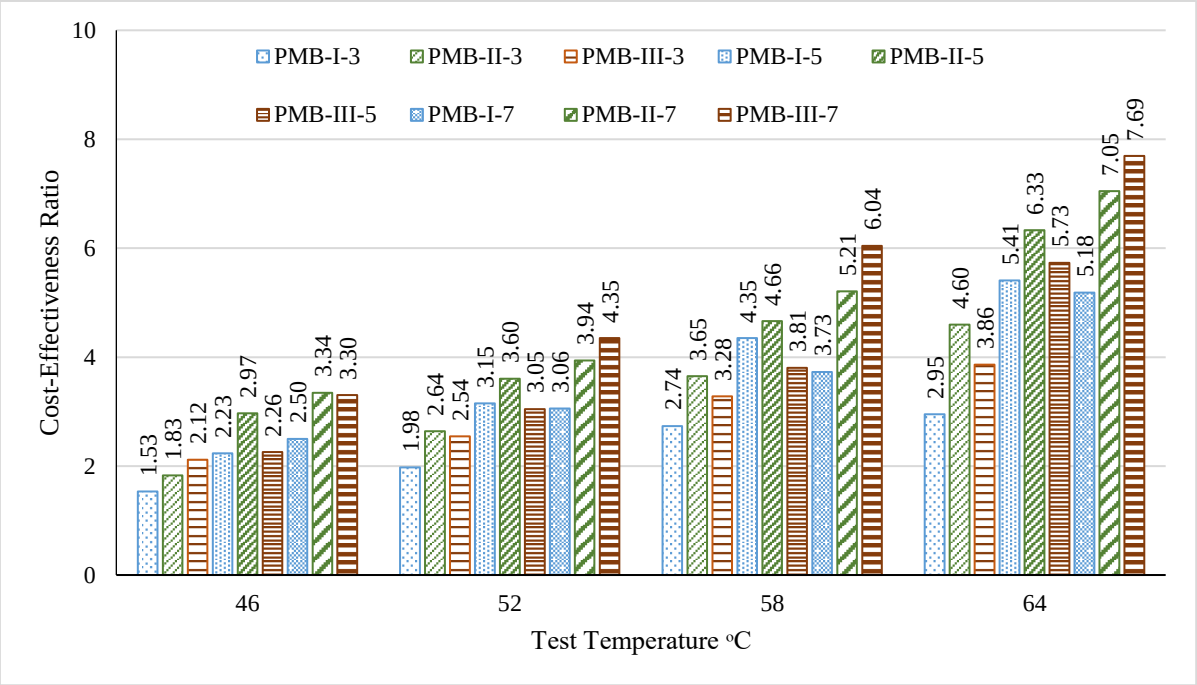


Figure 4.10: Cost-effectiveness ratio for rutting parameter

The gained benefits calculated using the Jnr parameter are presented in Figure 4.11. The Cost-effectiveness values obtained for 3 % polymer content shows 4.09, 3.82 and 3.66 gain for using PMB-I, PMB-II and PMB-III respectively. However, at 5% and 7% polymer content, PMB-III shows 17.05 and 63.20 respectively for 1.0kPa stress level, and at 3.2kPa, 14.60 and 31.37. The benefit decreased as the SBS molecular weight decreased. It is worth

note that using SBS with high molecular weight would increase the cost-benefit of the pavement surfacing.

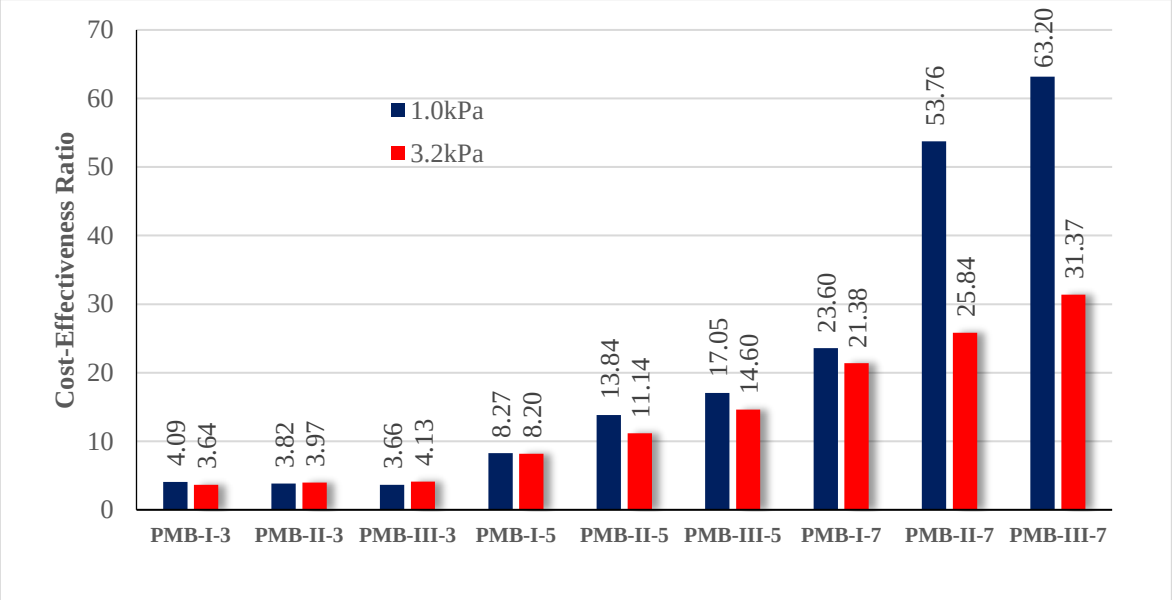


Figure 4.11: Cost-effectiveness ratio for Jnr parameter

4.8 Machine learning Modelling

In asphalt pavement construction, the selection of appropriate asphalt binder with the required properties to mitigate the challenges of pavement deterioration is critical in prolonging the service life of the asphalt pavement exposed to ageing conditions. Asphalt binder, within the asphalt, dominates the viscoelastic properties of the asphalt pavement subjected to various pavement distresses. Rutting and fatigue cracking are serious pavement distresses facing asphalt pavement that are exposed to intermediate and high temperatures prevailing in the tropical regions (Behiry, 2012; Khan et al., 2013; Y. R. Kim, 2008; Mirzababaei et al., 2017; Sani et al., 2019). Rutting in asphalt pavement occurs as a result of accumulated strain which induces a non-recoverable deformation along the wheel path of the pavement (Rahman & Gassman, 2019). The plastic deformation that is formed along the wheel path creates discomfort to the road user and reduces the service life of the pavement. On the other hand, fatigue cracking develops in asphalt pavement due to repeated loading on the asphalt pavement surface. Fatigue cracking is caused by weak, sub-grade, base and poor material design, and reduced strain tolerance of the asphalt mixture resulting from long-

term field ageing (Behiry, 2012; Brown et al., 2009). The selection of appropriate asphalt binder has been reported to enhance the resistance of hot mix asphalt (HMA) concrete when subjected to rutting and fatigue (Khan et al., 2013; Polacco et al., 2015; Porto et al., 2019a). Further, laboratory testing of rutting and fatigue in asphalt binder requires advanced testing equipment that is not readily available in the developing countries within the tropical regions. However, governments are saddled with the responsibility of providing quality pavement structures with the limited available budget. In such cases, the application of a predictive model would reduce project costs and deliver quality pavement structure.

The Witczak model can predict E* using parameters that can be extracted from a basic experiment and manufacturer's specifications. The model is cost-effective in a mechanistic-empirical pavement design guide (MEPDG) (Bari et al., 2006). However, predictive models for the design of mixture parameters cannot standalone without a complimentary binder model.

4.8.1 Prediction of Rutting Parameter Using Unaged Parameters

The results of the prediction of the Superpave® rutting parameter are presented in Table 4.3 and Figure 4.12. The main motivation of this section is to explore the possibilities of using an unaged input parameter to predict the Superpave® (G*/sinδ) rutting parameter. As stated in the previous section, the G*/sinδ parameter is valuable in estimating rutting susceptive in asphalt binder. However, experimental measurements to determine the values of G*/sinδ at different PG (performance grade) temperatures is expensive and involve advanced equipment.

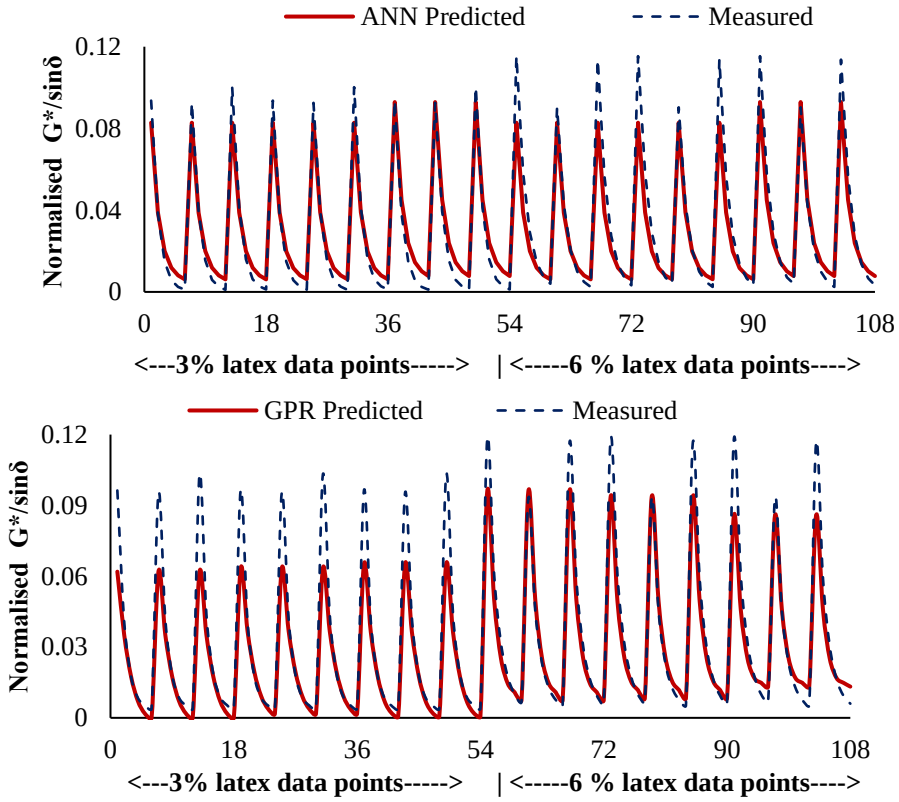
Four different approaches were used for modelling the G*/sinδ parameter at different PG temperatures. The proposed GPR algorithm, RNN, SVM and the ANN were the modelling tools used.

In the results, it is worth noting that the overall training performance of the four methods was satisfactory considering the normalized RMSE, MSE and MAE values and coefficient of determination (R^2) of the models. The statistical goodness of fit parameters is presented in Table 4.3. A comparison was made between the GPR and RNN predictive accuracy and traditional ANN and SVM models. Figure 4.12 shows the point by point comparison of the

simulation dataset results of the unaged dataset prediction of the rutting parameter. As seen from the graph for the simulation dataset, the ANN model was able to simulate the corresponding measured rutting parameters better than the GPR, RNN and SVM with respect to R^2 values of 0.99 and 0.96 for the 3% and 6 % latex modification respectively. The normalised RMSE and MAE were also found to be lower than the other models, The overall performance of all the models was substantially high.

Table 4.3: Performance results for the prediction of G*/sinδ parameters using unaged dataset.

Model	**Training Results**			**Simulation Results**					
				3% Latex Dataset			**6% Latex Dataset**		
	R^2	RMSE	MAE	R^2	RMSE	MAE	R^2	RMSE	MAE
ANN	0.96	0.024	0.013	0.99	0.007	0.006	0.96	0.012	0.008
GPR	0.95	0.026	0.012	0.97	0.015	0.008	0.97	0.010	0.007
RNN	0.97	0.019	0.010	0.96	0.016	0.008	0.96	0.008	0.005
SVM	0.95	0.028	0.013	0.95	0.016	0.012	0.95	0.011	0.008



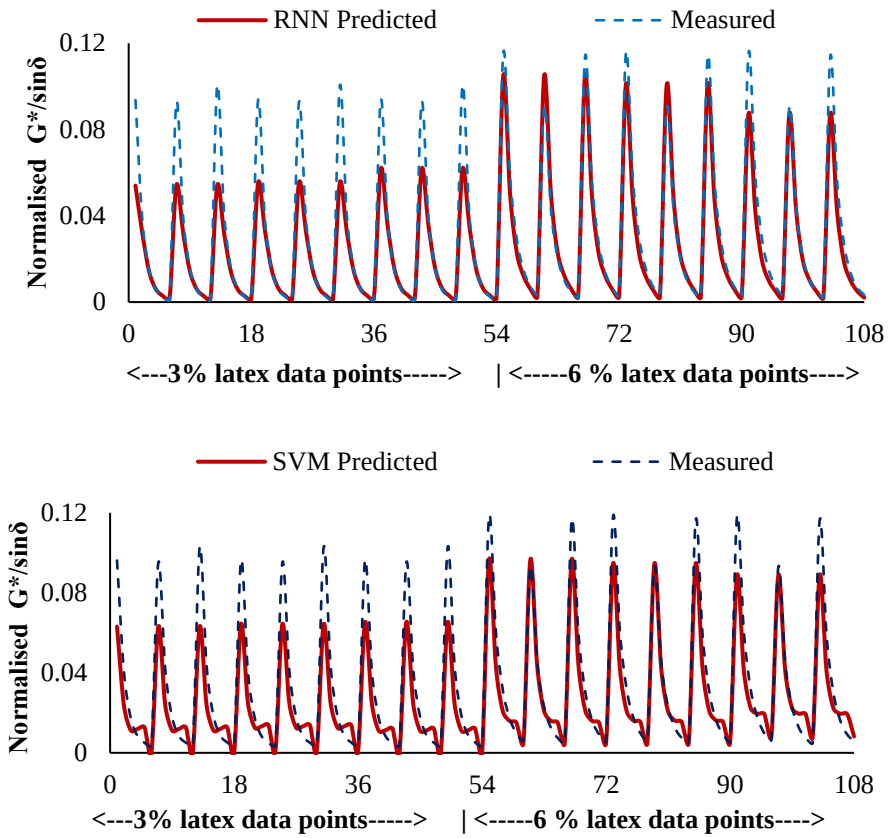


Figure 4.12: The comparison of predicted vs. measured G*/sinδ parameters using the unaged dataset.

4.8.2 Prediction of Fatigue Parameter Using Unaged Parameters

A major objective of evaluating the methods for predicting fatigue resistance in asphalt binders is to eliminate the laborious laboratory works involved in measuring fatigue performance in the binder. The modelling of fatigue resistance of the asphalt binder is critical in prolonging the service life of the pavement. The evaluation of binder fatigue resistance requires short and long term aged conditioning resulting in physical and chemical changes in the binder.

The performance of the models is presented in Table 4.4 and a graphical representation of the point by point comparison of the predicted and measured values for the simulation dataset is in Figure 4.13.

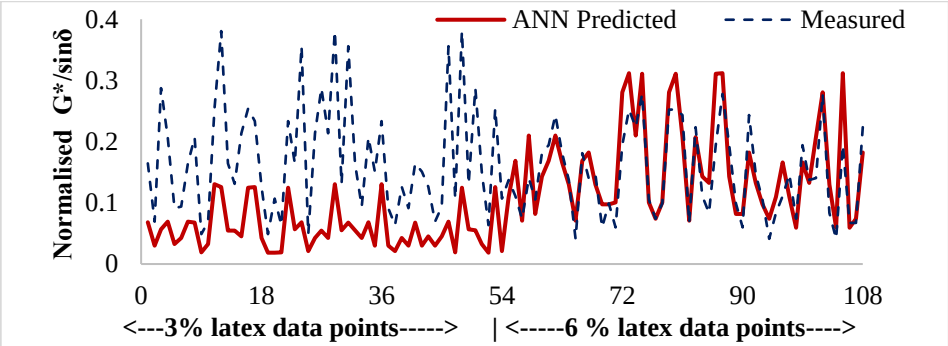
The results in Table 4.4 show that all model training performed substantially well. However, high model training accuracy does not translate to performance with a simulation of a new

dataset that was not previously used in the model calibration. All the models did not perform well with 3% latex simulation dataset extracted from (Sani et al., 2019). However, the proposed GPR within the dataset used for simulation performed better than ANN, RNN and SVM models. The poor performance of the models at 3% latex modification could be attributed to complex chemical and physical changes that take place during short and long term binder ageing conditioning.

With a 76% correlation between the predicted and the measured value of G*.sinδ parameter using the GPR model, it is possible to eliminate the ageing conditions (PAV and RTFOT) test required in the selection of a suitable binder that meets specified PG temperature criteria for medium and low-density traffic. This could be beneficial to the developing countries within the tropical region that need to use the manufacture specification data to design pavement structures.

Table 4.4: Performance results for the prediction of fatigue parameter (G*.sinδ) parameters using unaged dataset.

Model	Training Results			Simulation Results					
				3% Latex Dataset			6% Latex Dataset		
	R^2	RMSE	MAE	R^2	RMSE	MAE	R^2	RMSE	MAE
ANN	0.98	0.028	0.020	0.49	0.116	0.090	0.70	0.039	0.032
GPR	0.96	0.036	0.024	0.60	0.120	0.019	0.76	0.38	0.032
RNN	0.98	0.028	0.020	0.61	0.142	0.121	0.70	0.071	0.061
SVM	0.96	0.037	0.025	0.49	0.116	0.090	0.70	0.039	0.032



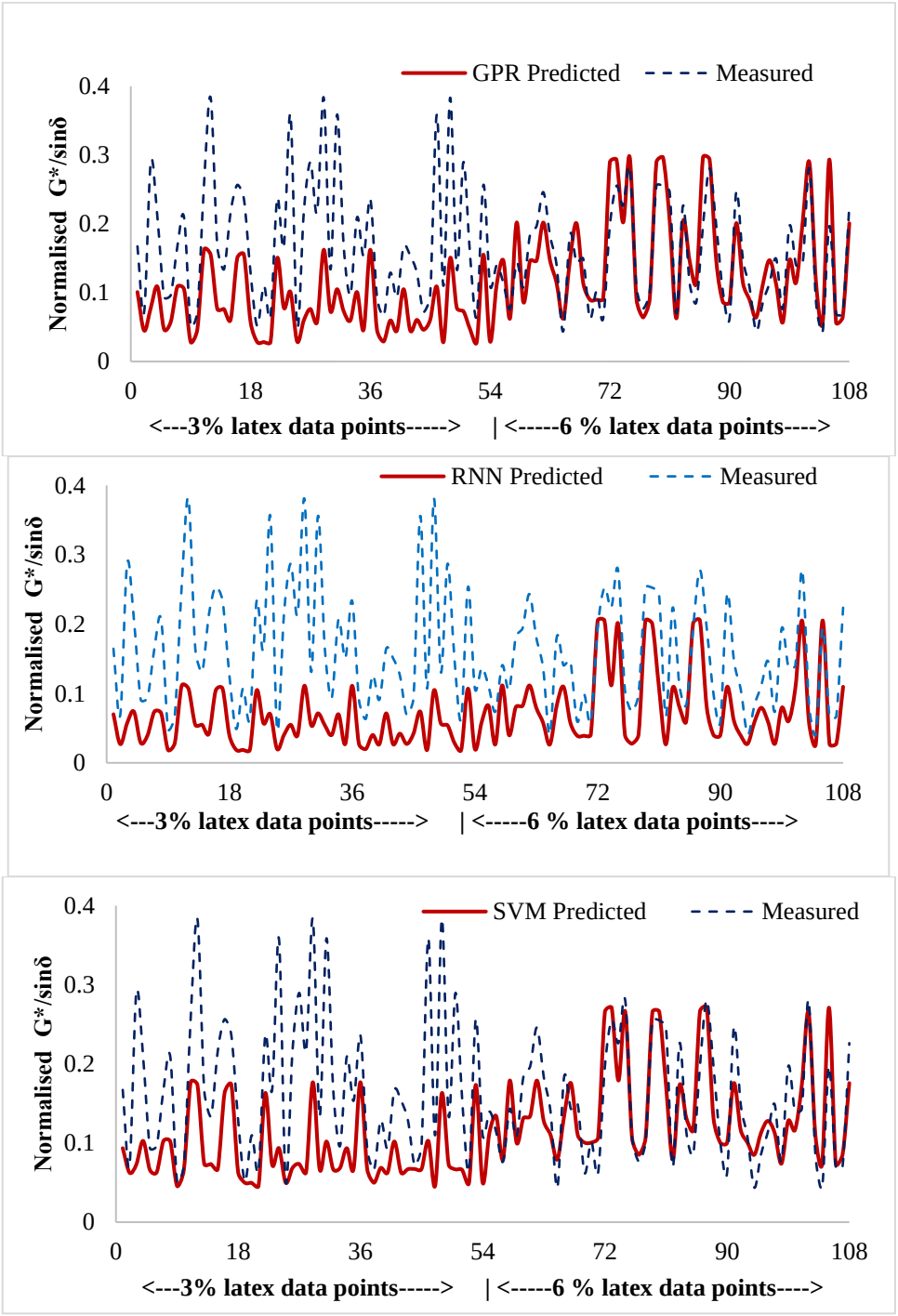


Figure 4.13: The comparison of predicted vs. measured G*.sinδ parameters using the unaged dataset.

4.8.3 Prediction of Fatigue Parameter Using Short-Term Aged Parameters

Further, in the previous section, the essence of using the unaged input variables is to reduce the prediction cost for the prediction of the fatigue parameter. However, in this case, study,

the RTFO conditioned dataset was used to evaluate the progress of the G*.sinδ parameter in the asphalt binder. Although the modelling cost is higher, this research aimed to investigate the reliability of modelling the G*.sinδ parameter using the GPR algorithm.

The results of the four algorithms show higher training accuracy for the modelling of the G*.sinδ parameter using the short-term aged input variables as shown in Table 4.5 and Figure 4.14. As observed in Section 4.8.1, the simulation performance was lower than the training performance. The poor performance of the models especially, with 3% latex modification implies that the training dataset is insufficient for extracting the complex chemical and physical changes features that take place during binder ageing. The complexity of binder ageing can be seen in the behaviours of the model with 3% latex modification.

Table 4.5: Performance results for the prediction of fatigue parameter (G*.sinδ) parameters using short-term aged dataset.

Model	**Training Results**			**Simulation Results**					
				3% Latex Dataset			**6% Latex Dataset**		
	R^2	RMSE	MAE	R^2	RMSE	MAE	R_2	RMSE	MAE
ANN	0.98	0.027	0.019	0.50	0.225	0.214	0.68	0.044	0.035
GPR	0.96	0.036	0.025	0.60	0.136	0.116	0.64	0.050	0.040
RNN	0.97	0.029	0.021	0.52	0.132	0.110	0.71	0.077	0.063
SVM	0.96	0.035	0.025	0.50	0.201	0.187	0.66	0.045	0.036

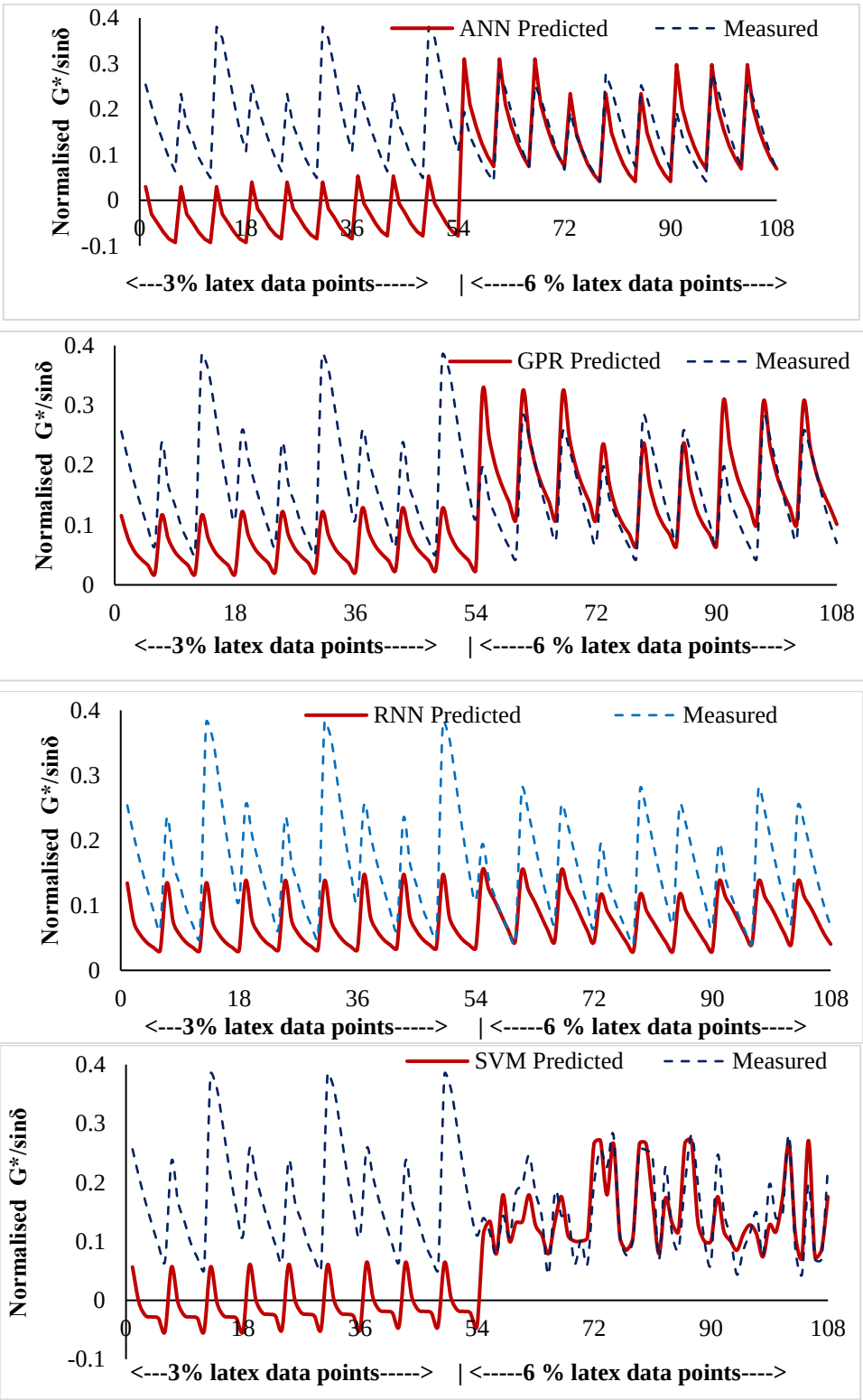


Figure 4.14: The comparison of predicted vs. measured G*.sinδ parameters using the short-term aged dataset.

4.8.4 Parameter Sensitivity Analysis

Computational models have, in recent times, paved the way for providing optimal solutions to a design problem. Its reliability is dependent on the features of the selected model parameters that add uncertainty to the model output. However, model parameter uncertainty on the output can be evaluated using a structural optimisation design method called sensitivity analysis (SA). Global sensitivity analysis (GSA) is a class of SA that provides valuable global insight on how the model output variance is dependent on the uncertainty of a particular model parameter by allowing more than one factor to vary at the same time (Al et al., 2019; Xinnan Liu et al., 2020).

In this study, the GSA was applied using the easy GSA MATLAB solution. The study by Al et al. (2019) contains a detailed development with research data for easy GSA. The Sobol first and total order indices were used to estimate model parameter sensitivity to output variance. The Sobol index is a sensitivity index that decomposes the output variance and estimates the importance of a single or specific set of variables in the uncertainty of the model output (X. Y. Zhang et al., 2015). The first order accounts for individual effects on the variance of the dependent variable. On the other hand, the total indices account for the overall dependent variable effect on the model output variance and also inter-variable interactions (Saltelli et al., 2008).

a. *Sensitivity analysis of rutting model parameters*

With respect to the unaged parameters on the G*/sinδ, which was the scope of Case Study-1, Figure 4.13 shows that the temperature, softening point and test frequency are the most influencing parameters. Further, the influence of phase angle showed a unique trend with the phase angle at T58 °C recording the highest STi value. The results are in agreement with the standard laboratory values; an increase in test temperature and frequency decrease the G*/sinδ values of asphalt binder. Further, the importance of viscous and elastic properties of asphalt binder influences the rutting behaviour observed in the phase angle and softening point values.

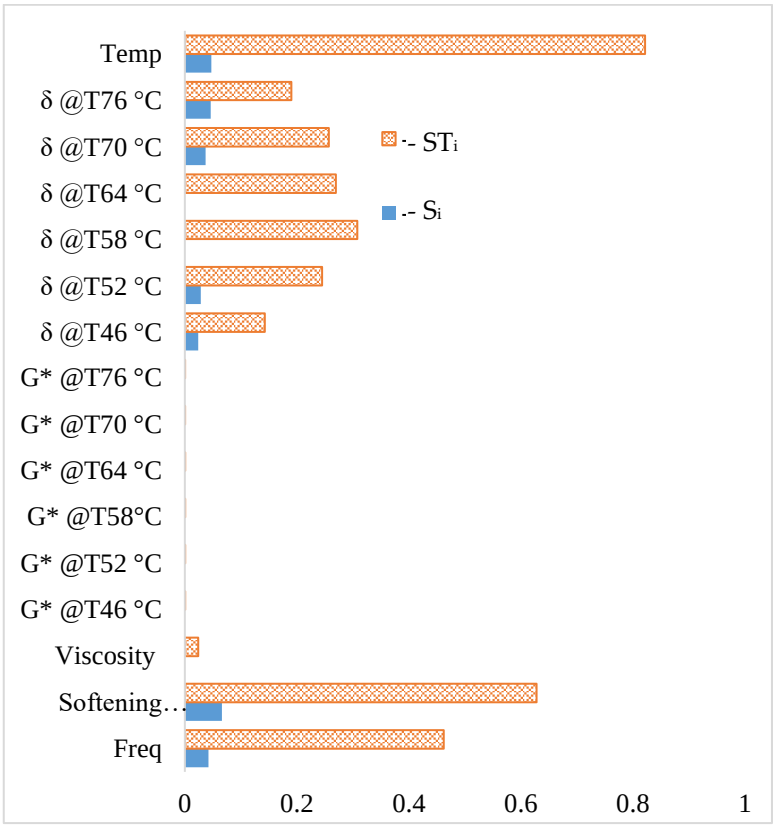


Figure 4.15: Sobol indices obtained for rutting model parameters.

b. Sensitivity analysis of fatigue model parameters

The objectives of Case Studies 2 and 3 were to predict the fatigue cracking using unaged and short-aged (RTFOT) parameters respectively. This study only focused on the prevailing temperature range affecting tropical regions. As obtained in Case Study 1, the phase angle, softening point and test temperature and frequency showed high sensitivity to the variation of G*.sinδ parameter. The Sobol indices showed low sensitivity of G* and viscosity of the binder to the variation of G*.sinδ parameter as shown in Figure 4.16.

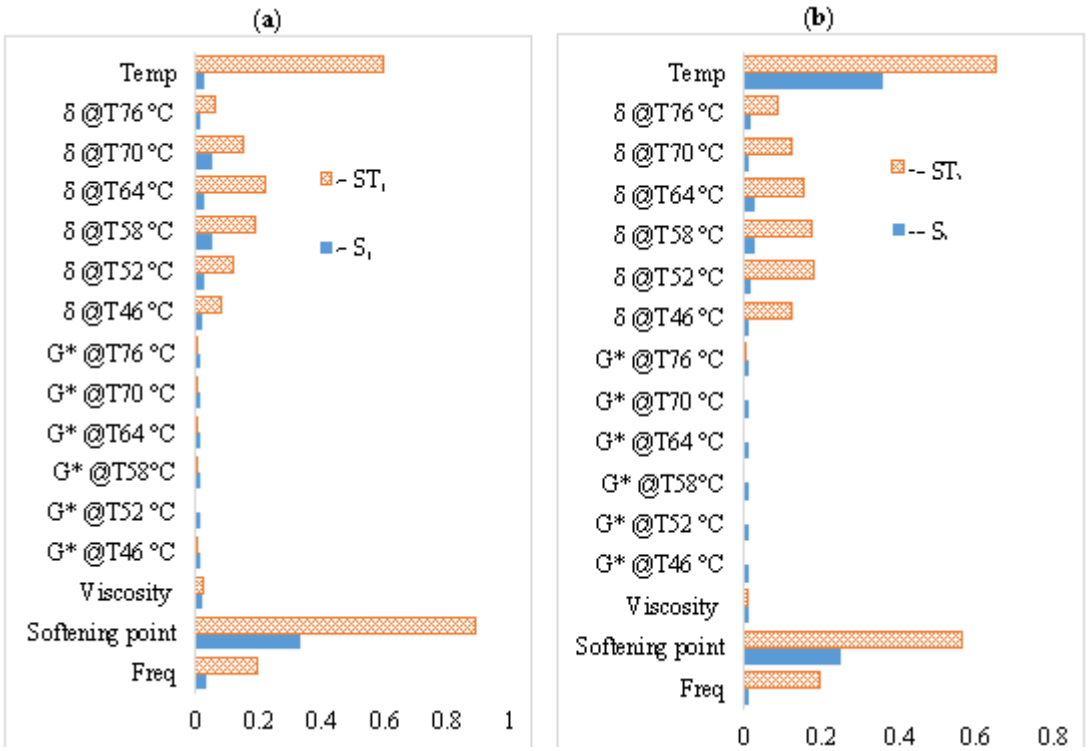


Figure 4.16: Sobol indices obtained for fatigue model using (**a**) unaged parameters and (**b**) RTFOT parameters.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The modification of asphalt with polymer results in a significant variation in the binder properties.SBS polymer among other materials is used for the modification of asphalt binder. Besides the polymer content, researchers have also identified that the density of the modifier is an influencing parameter controlling the behaviour of asphalt containing the different modifications. However, a given polymer such as SBS used in asphalt modification is produced with different molecular weight. The molecular weight of material that measures the mass per mole differs from the density that measures the mass per volume.

In this study, the influence of molecular weight on the behaviour of polymer-modified asphalt binder was investigated. Since the density is dependent on the molecular weight, to avoid the effect of density, three SBS polymer designated as PMB-I, PMB-II and PMB-III with constant density was used in the investigation.

The softening point test, viscosity test, mechanical dynamic and ageing test were performed on the control and modified asphalt binder at 3%, 5% and 7% SBS content. Based on the results of the investigation, the following conclusions were drawn;

- The softening point results analysis show that at low 3% SBS content, the increase in the modified binder softening point is dependent on the molecular weight of the SBS. The PMB-I, PMB-II and PMB-III were observed to have 4, 6.25 and 7℃ softening point temperature increases respectively from the control binder.
- However, at 5% and 7%, the softening point temperature was found to be dependent on the polymer structure.

- With respect to the viscosity, as reported in the literature, the control binder behaviour at the test temperature of 135 ℃ is within the Newtonian region and the

increase in the SBS led to the departure into the non-Newtonian region. This effect is higher at a lower shear rate.

- The SBS molecular weight has a strong influence on the storage stability behaviour of the modified binder. The results of the samples stored at 163℃ and 180℃ at 48h and 72h show that a modified binder with 3% SBS polymer content with an average molecular weight of 150kDa is a stable binder at 163℃ storage temperature.
- Binders with high SBS polymer content and average molecular weight are not suitable for long storage and high storage temperatures.
- The change in the G*/Sinδ parameter was found to be dependent on the ratio of polystyrene to polybutadiene content of the SBS at 3% and 5% polymer content and the polymer molecular weight at 7% polymer content.
- The non-recoverable creep compliance (Jnr) parameter which measures the ratio of the strain that is not recovered at the end of the recovery section after applied strain, shows that a 5% SBS polymer content, PMB-I, PMB-II and PMB-III respectively recorded 71%, 90% and 92% reduction from the control binder Jnr parameter value at 1.0kPa stress level.
- At the 3.2kPa stress level, and at the same 5% SBS polymer content, PMB-I, PMB-II and PMB-III respectively recorded 84%, 88% and 90% reduction from the control binder Jnr parameter value, indicating the influence of the SBS polymer molecular weight on the Jnr value of the binder.
- The cost-benefit of using SBS polymer with high molecular weight was evaluated. The results indicate that there is a significant benefit to using high molecular weight SBS polymer. For the G*/sinδ parameter, the cost-effectiveness ratio of PMB-III-7 increases at an average of 1.46 from 46℃ to 64℃ temperatures. The PMB-II-7 and PMB-I-7 increased at an average of 1.24 and 0.89 respectively from 46℃ to 64℃ temperatures. For the Jnr parameter, for PMB-II with an average molecular weight of 500kDa at 5% and 7% for 1.0kPa stress level was 17.05 and 63.20 respectively. At a higher stress level of 3.2kDa, the benefit decreased to 14.60 and 31.37 respectively. The PMB-II and PMB-I cost-effectiveness value was lower than that of PMB-III indicating an economic potential of using SBS with high molecular weight.

- The prediction of the G*/sinδ and G*.sinδ parameters were investigated using ANN, GPR, RNN and SVM. The validity of the proposed models was accessed using a simulation dataset after the calibration of the model. The performance accuracy of the models show that GPR model accuracy was 97%, and higher than the other model for prediction of G*/sinδ parameter using unaged input variables.
- The G*.sinδ parameter modelling also show a higher performance for the GPR model with an R^2 of 0.76 and a mean square error of 0.032. The performance of the G*.sinδ parameter modelling using the short-term aged input variables was low, RNN model recorded 71% prediction accuracy and 0.063 mean square error.
- The sensitivity analysis indicated phase the input variable significant controlled the output variance in this order; temperature, softening point, test frequency, phase angle and the complex shear modulus.
- The viability of the proposed machine learning models can be applied at the project preliminary stage and also at locations with limited resources. Pavement designers can rely on the model to select appropriate binders where applicable.

5.1 Recommendations

Due to limitations enumerated in Chapter one, other binder and characterisation tests could not be performed. Further research on asphalt binder and mixture is recommended in order to exhaust the effect of polymer molecular weight on the behaviour of asphalt binder and concrete.

In the literature (Choi et al., 1999; Jenkins et al., 2013; J. H. Lee et al., 2016) polymer adhesive energy increases with an increase in molecular weight. This could provide an insight into the key-dependent variables on the moisture susceptivity of the asphalt mixture.

Furthermore, the influence of Mw should be investigated on PMB modified with different polymer types (elastomer and plastomers)with constant density and varying Mw to ascertain the extent of the effect on asphalt behaviour.

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