



**THE BEHAVIOUR OF LDPE-MODIFIED
ASPHALT MIXTURE IN PAVEMENT
APPLICATION**

by

Tri Sudibyo

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ABSTRACT

Studies to improve bitumen performance are never-ending processes to answer the demands for better asphalt road performance. Rutting and fatigue cracking are the two most common asphalt pavement distresses that need continuous improvements. Rutting or permanent deformation on the pavement surface commonly happens due to heavy loading, high pavement temperature, slow-moving traffic or a combination of these factors. In comparison, fatigue cracking results from repeated traffic loads, even though minimal stress loads, in the years of the pavement service life. Therefore, better pavement resistance to rutting and fatigue will result in desirable, maintained long years of high-performance road services.

Modifying bitumen with specific methods using some additive material is widely recognised to achieve better bitumen performance. Low-density polyethylene (LDPE) is a popularly studied material to improve rutting resistance and modify bitumen fatigue resistance. The higher softening point, the lower penetration number, and the higher rutting resistance are the typical results of the LDPE-modified bitumen.

LDPEs are widely used packaging materials in plastic industries that available as purely made (virgin) or recycled from previous products. Many studies have incorporated processed and recycled LDPE as the bitumen modifier, resulting in better-performed bitumen and asphalt mixtures. Some other studies used virgin LDPE, which also improved bitumen performances. However, there is no direct comparison between recycled and virgin LDPE in modifying bitumen performance. This study tends to fill this gap and observe the difference between recycled and pure LDPE in affecting bitumen performance by using sets of standardized tests on bitumen and asphalt mixture to optimize the potential use of these materials.

This study started with the thermal characteristics tests using Dynamic Scanning Calorimeter (DSC) and chemical functional group through Fourier Transform Infrared Spectroscopy (FTIR) to identify the differences between the virgin and the recycled LDPE as the bitumen modifier. Then, 2%, 4%, 6%, 8% and 10% of the bitumen weight of virgin low-density polyethylene (LDPE) and recycled low-density polyethylene (rLDPE) modification were used to modify bitumen by using a high shear mixer at designed

temperature. At this stage, eleven bitumen were produced, consisted of ten modified bitumen and one unmodified bitumen as the control.

The Brookfield viscosity test measured the modified bitumen viscosity that represents the workability. The workability has become the primary consideration parameter for further analysis. Using DSR (dynamic shear rheometer) instrument, the amplitude and frequency sweep tests were carried out, and the bitumen resistance to permanent deformation was also studied using Multiple Stress Creep Recovery (MSCR) tests. The bitumen susceptibility to fatigue was also studied using the Linear Amplitude Sweep (LAS) test and the Double-Edged Notched Tension (DENT) test on the Ductilometer. FTIR observed the modification effect on the chemical functional group and the ageing process. The microscopy works studied the LDPE polymer dispersion in the bitumen.

The further stages were the asphalt mixture performance tests from the modified bitumen regarding resistance to permanent deformation and fatigue resistance. This stage tested the best-performed modified bitumen from the previous tests, with five asphalt mixture types from two virgin LDPE, two recycled LDPE, and one unmodified bitumen. Using the Nottingham Asphalt Tester (NAT), the Indirect Tensile Stiffness Modulus (ITSM) tested the non-destructive stiffness modulus, followed by the resistant to permanent deformation characteristic test on the Repeated Load Axial Test (RLAT) and the fatigue test on the Indirect Tensile Fatigue Test (ITFT).

This study resulted in the rheological property improvements of virgin and recycled LDPE-modified bitumen. Each LDPE type produces a different level of improvements at the same %w of bitumen. Similar trend of results also exhibited in the asphalt mixture performances. The modified asphalt mixtures have higher stiffness modulus, better-rutting resistance performance, and a longer cycle at the same stress level in the fatigue test compared to unmodified mixtures. Further tests are suggested to understand the physical properties of the recycled and virgin LDPE and their effects on the bitumen modification. This study also suggested using other material sources of the LDPE modifiers.

Keywords: LDPE modified bitumen, asphalt, rutting, fatigue

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Declaration

The research described in this thesis was conducted at the Nottingham Transportation Engineering Centre, the University of Nottingham between October 2019 and July 2023. I declare that the work is my own and has not been submitted for a degree at another university.

Tri Sudibyo

The University of Nottingham

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LIST OF ABBREVIATIONS

AASHTO	: American Association of State Highway and Transportation Officials
AC	: Asphalt concrete mixture design
ATR	: Attenuated Total Reflectance
CI	: Carbonyl index
COV	: Coefficient of Variation
CTOD	: Critical Top Opening Displacement
DENT	: Double-Edged Notched Tension
DMA	: Dynamic Mechanical Analysis
DSC	: Dynamic Scanning Calorimeter
DSR	: Dynamic Shear Rheometer
FTIR	: Fourier Transform Infrared Spectroscopy
HMA	: Hot Mix Asphalt
ITFT	: Indirect Tensile Fatigue Test
ITSM	: Indirect Tensile Stiffness Modulus (ITSM)
ITS	: Indirect Tensile Strength
Jnr	: Non-recoverable creep compliance
LAS	: Linear Amplitude Sweep
LDPE	: Low-density polyethylene
rLDPE	: Recycled low-density polyethylene
LLDPE	: Linear low-density polyethylene
MDPE	: Medium-density polyethylene
HDPE	: High-density polyethylene
LVDT	: Linear Variable Differential Transducer
MSCR	: Multiple Stress Creep Recovery
NAT	: Nottingham Asphalt Tester
PAV	: Pressure Ageing Vessel laboratory ageing procedure
PET	: Polyethylene terephthalate
PP	: Polypropylene
PVC	: Polyvinyl chloride
R ²	: Coefficient of Determination
RBT	: Rolling bottle test
RLAT	: Repeated Load Axial Test
RTFO	: Rolling Thin Film Oven laboratory ageing procedure
SI	: Sulfoxide index
TTSP	: Time-temperature superposition principle
VECD	: Viscoelastic continuum damage
T _c	: Crystallisation temperature
T _g	: Glass transition temperature
T _m	: Melting point
τ	: Maximum shear stress (N/mm ²)
T	: Torque (Nm)
r	: Radius of the parallel disks (mm)
γ	: Maximum shear strain
θ	: Deflection angle (radians)
h	: Gap between parallel plates (mm)

G^*	: Complex modulus
γt	: Dynamic oscillating shear strain
γ_0	: Peak shear strain
ω	: Angular frequency (rad/sec) = $2\pi f$, with f = frequency (Hz)
t	: Time (seconds)
σt	: Dynamic oscillating shear stress, Pa
σ_0	: Peak shear stress, Pa
δ	: Phase angle, degree
fr	: Reduced frequency, Hz
f	: Frequency, Hz
$a(T)$	: Shift factor in TTSP
W_T, W_E, W_P	: Total work, essential work & plastic work of fracture (J)
w_t	: Specific total work of fracture (J/m ²)
w_e	: Specific essential work of fracture (J/m ²)
w_p	: Specific plastic work of fracture (J/m ²)
%R	: MSCRT percentage of recovery
R0	: Unmodified bitumen
VL1, VL2, VL3, VL4, VL5	: 2%, 4%, 6%, 8% and 10% of virgin LDPE modified bitumen
RL1, RL2, RL3, RL4, RL5	: 2%, 4%, 6%, 8% and 10% of recycled LDPE modified bitumen

CHAPTER I: INTRODUCTION

1.1. Background

Rutting or permanent deformation along the road's wheel path is common distress in asphalt pavement. Another major deterioration is fatigue cracking caused by repeated traffic loading during the pavement service years. Many studies have been conducted to improve bitumen resistance to these deteriorations, and polymer-modified bitumen is one of the most popular methods to answer this need. The studies have used various polymers in the bitumen modification, including styrene-butadiene-styrene (SBS), styrene-butadiene-rubber (SBR), ethylene vinyl acetate (EVA), polyethylene, and others. These polymers produce better rutting and thermal cracking resistance and decrease fatigue damage, stripping and temperature susceptibility (Yildirim 2007).

Polymers are macromolecules formed through the chemical bonding of repeating smaller units of molecules known as monomers (Gad 2014; Kulkarni and Shaw 2016). This ingredient is very versatile, easily processed into complex shapes and widely used in many applications and products (Gad 2014; HILL 2005; Kulkarni and Shaw 2016). Plastic or thermoplastic is an example of synthetic polymer with a reversible ability from solid at one temperature to soften state at higher temperatures. Polyethylene, polystyrene, polyvinyl chloride, polypropylene, and polyurethane are examples of thermoplastic materials (Gad 2014). LDPE, or low-density polyethylene, is one example of plastic produced by a free radical polymerization method of ethylene monomer at 80–300°C under the pressure of 150–350 MPa (Pham 2021). This freshly made LDPE is considered pure or virgin LDPE plastic. Meanwhile, recycled LDPE (or other plastics in general) comes from melting and reforming steps of LDPE product wastes that had faced ageing or contamination in their previous use (Lin et al. 2022).

In modified bitumen and asphalt studies, there are various types of plastic used, with the majority types the high-density-polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), polyethylene terephthalate (PET or PTP), and polyvinyl chloride (PVC). Variations of studies have been conducted, including the mixing procedures (dry or wet), the plastic modifier form, additional materials, and another detail in the blending process.

Many researchers have conducted bitumen and asphalt studies incorporating plastic polymer, including the use of HDPE (Costa et al. 2019; Dalhat and Al-Abdul Wahhab 2017a; Khan et al. 2016; Movilla-Quesada et al. 2019a); LDPE (Almeida et al. 2020a; Dalhat and Al-Abdul Wahhab 2017a; Haider et al. 2020; Hu et al. 2018a; Khan et al. 2016; Lastra-González et al. 2016a, 2017; Padhan and Sreeram 2018; Wang et al. 2018a); Polypropylene (Dalhat and Al-Abdul Wahhab 2017a; Lastra-González et al. 2016a, 2017); PTP or PET (El-Naga and Ragab 2019a; Leng, Sreeram, et al. 2018a; Leng, Padhan, and Sreeram 2018; Movilla-Quesada et al. 2019a); PVC (Movilla-Quesada et al. 2019a; Ziari et al. 2019), pelleted mixed sources of recycled plastic waste (White and Reid 2018a, 2019a); and various recycled plastic waste of PET, LDPE, HDPE, PVC, PP and PS by Zakaria (2019). However, not all of these studies explicitly stated the source or origin of the plastic material, whether virgin (freshly made) or recycled plastic.

Compared to virgin plastic, recycled plastic has noticeable environmental benefits. According to the (Association of Plastic Recyclers 2018), per 1 kg of substituting virgin pellets to recycled polyethylene terephthalate (PET), polypropylene (PP), high-density polyethylene (HDPE) resins can reduce total global warming potential by 1.87 kg, 1.33 kg, and 1.31 kg CO₂, respectively. These recycled products also consume less energy for transportation or operation processes than virgin plastic (Benavides et al. 2018; The Association of Plastic Recyclers (APR) and Franklin Associates 2020).

Recycled plastics, however, have a drawback in the lack of quality compared to virgin material. For example, Eriksen et al. (2019) stated that over 58% of recycled plastic does not meet current market quality requirements. This condition is often caused by contamination, material ageing, and melting and reforming steps in the recycling process that limit its quality to replace virgin plastics (Ragaert, Delva, and Van Geem 2017). In addition, plastic recycling has main economic challenges of high collection costs, low capacity and efficiency of sorting operations, and limited volume of cheap, high-quality recyclable materials (Hennlock et al. 2015; Milios et al. 2018).

Each plastic polymer has a characteristic melting point that affects the bitumen blending, with some types having relatively higher melting points that require higher energy, such as polypropylene (160°C), polyethylene terephthalate (260°C), or polyvinyl chloride (290°C). Among the plastic polymer, polyethylene family: HDPE, which has a melting point of 130°C and LDPE, with a 110°C melting point, are commonly studied. Using these plastic

materials as bitumen modifier have a higher success potential as bitumen generally have suitable viscosity for modification at 150°C; thus, both LDPE and HDPE will be 'ready' to be incorporated in the bitumen blends, and many studies have concluded the benefits in their use as the bitumen modifier (Al-Hadidy and Yi-qiu 2009; García-Morales et al. 2006a; Hu et al. 2018b; Padhan and Sreeram 2018; Vargas et al. 2013a; Wang et al. 2018b). Although low-density polyethylene (LDPE), or polyethylene in general, is believed to improve the bitumen and mixture's rutting resistance and other properties, there is no clear understanding of the differences between virgin LDPE and recycled LDPE in the application.

The use of virgin and recycled LDPE has its advantages and disadvantages in terms of economical, environmental, and especially in its physical properties. Being freshly made, the virgin LDPE can be expected to have consistent and controlled physical properties. For bitumen modification, this can result in homogenous and more promising modified bitumen properties. On the other hand, the often lacking quality of recycled LDPE for industry (Eriksen et al. 2019; Ragaert et al. 2017) can potentially lead to unpredictable or poor results for bitumen modification compared to virgin LDPE.

However, there is no scientific proof that one material is superior to the other, and there is no direct comparison between the use of virgin to recycled LDPE in bitumen modification under the same modification procedure. The scattered studies of virgin or recycled LDPE-modified bitumen are difficult to compare because of different preparation, mixing temperatures, speed, duration or other detailed methods. This study tends to fill this gap by understanding the differences between virgin and recycled LDPE in affecting bitumen performance, emphasising rutting and fatigue performance.

1.2. Research gap in LDPE-modified bitumen/mixture

As a widely used bitumen modifier, polyethylene is well known to improve bitumen rheological performance (Al-Hadidy and Yi-qiu 2009; García-Morales et al. 2006a; Hu et al. 2018b; Padhan and Sreeram 2018; Vargas et al. 2013a; Wang et al. 2018b). Among the various polyethylene in bitumen and asphalt studies, based on Cole-cole diagram analysis, low-density polyethylene (LDPE) has the best compatibility with asphalt compared to LLDPE (linear low-density polyethylene), MDPE (medium-density polyethylene) or HDPE (high-density polyethylene) (Liang et al. 2021). In addition, LDPE has the lowest melting

point of all polyethylene, indicating the readiest to blend with bitumen in the modification process.

However, as there are two main groups of LDPE: the purely made virgin LDPE and the recycled LDPE from various products, no study directly compares them in affecting the modified bitumen performance. There are also needed more comprehensive understanding of how the LDPE-modified bitumen behaves on ageing, how the LDPE polymer disperses in the blend, how the bonding strength between bitumen and aggregates, and how these factors affect the mixture performance in rutting and fatigue resistance. This study tends to fill these gaps and further understand the LDPE-modified bitumen for better field applications regarding rutting and fatigue performance.

1.2.1. Overall behaviour and performance of plastic-modified bitumen

Various forms of LDPE and other plastics were used in bitumen and asphalt mixture studies. The mainly used in the bitumen modification were the small ground shape, powdered shape, and pelleted recycled plastic. The ground shape, the powdered shape or other physically prepared shapes are primarily used in studies incorporating waste plastic directly from urban dumping sites or recycling plants. The pelleted shapes were used where the plastic was provided by recycling companies. The tiny flakes or scrap form of plastic modifier were used by Almeida et al. (2020), Haider et al. (2020), El-Naga and Ragab (2019), Movilla-Quesada et al. (2019), Padhan et al. (2018), Hu et al. (2018), Lastra-González et al. (2017), Khan et al. (2016). The smaller or powdered form of the plastics was used by Ziari et al. (2019), Costa et al. (2019), Dalhat and Al-Abdul Wahhab, 2017), (Lastra-González et al. 2016b). There were also pelleted forms of recycled plastic modifiers (White and Reid 2018a, 2019a). A further review of these studies has been undertaken in the literature review chapter.

The mixing process of the bitumen, plastic modifier and aggregates is also one of the critical elements in plastic-modified bitumen and asphalt studies. The dry process is carried out by mixing the plastic directly with the heated aggregates, while the wet mixing process is carried out by mixing the plastic modifier with the bitumen. Some of the dry processes of modified asphalt studies were conducted by Almeida et al. (2020), Haider et al. (2020), El-Naga and Ragab (2019), White, Reid (2019a); White, Reid (2018a), Movilla-Quesada et al. (2019), Lastra-González et al. (2016b); Lastra-González et al. (2017). While

some of the wet process studies were done by Haider et al. (2020), Ziari et al. (2019), Padhan, Sreeram (2018), Leng, Padhan, et al. (2018), Leng, Sreeram, et al. (2018a), Hu et al. (2018), Dalhat, Al-Abdul Wahhab (2017a); Dalhat, Al-Abdul Wahhab (2016), Khan et al. (2016). The dry process is considered easier for application since there is no need for a particular mixing plant (Movilla-Quesada et al., 2019), while the wet process offers more significant improvement in modified bitumen properties (Haider et al. 2020). The wet method resulted in less coating loss, better tensile strength, and lower rut depth than the dry method. The literature review chapter critically reviews the wet and dry process.

These studies concluded the mechanical properties improvement of the bitumen and the asphalt mixture. By incorporating different methods, plastic forms, aggregate gradation, and other variables, each study yielded specific bitumen or asphalt mixture properties but concluded the general agreement of higher bitumen stiffness and better rutting resistance. Regarding fatigue resistance, some studies stated an increase, while others stated no increase or lower fatigue resistance in the presence of LDPE or plastic modifiers. Among these studies, some have clearly stated the use of virgin or recycled plastic, while many did not clearly state which plastic was used. Therefore, it is difficult to directly compare which plastic type from these studies is better in improving rutting and fatigue performance.

1.2.2. Ageing effect of LDPE-modified bitumen

Bitumen ageing is an inevitable natural process that changes the properties and mechanical behaviour over a long period of the bitumen service life. As an important factor that affects the asphalt mixture performance, many studies in bitumen ageing are continuously conducted. Fourier-transform infrared spectroscopy (FTIR) is a widely used procedure to understand the ageing of bitumen. This procedure observes a molecular characteristic of material based on absorption or emission of the infrared spectrum. With the FTIR, the molecular structure changes of the bitumen related to the ageing degree in terms of aliphaticity, oxygenation rate and aromaticity can be quantitatively observed (Branthaver et al 1994, Huet, 1989, Lamontagne et al. 2001; Van den bergh 2011b). Studies of ageing and other purposes of bitumen by using FTIR have been conducted in various bitumen.

By using FTIR observation, (Nivitha, Prasad, and Krishnan 2016) stated that by conducting a laboratory ageing procedure, the evolving bitumen microstructure during the ageing can be recorded, and it could be entirely different for different modified binders. In the case of polyethylene under FTIR observation, instead of chemical differences, there were physical changes to the modified bitumen when waste polyethylene and carbon fibres (Zhang et al. 2016) and waste polyethylene (Fang et al. 2015) were used. Fang et al. (2015) also stated that, except for the ageing indications, there were similar chemical variations on base, modified, and RTFO-ed bitumen at different preparation temperatures. Among these studies, the ageing process of the bitumen is commonly associated with the carbonyl and sulfoxide functional group increase due to the oxidation effect (Hou et al. 2018).

LDPE-modified bitumen reportedly has a better rheological performance compared to base bitumen. While FTIR can be utilized to understand various aspects of the chemical functional group that represents the bitumen property, it will be interesting to understand the changes made by the LDPE-modified bitumen in the early age of the modification and after some ageing conditions. It is also interesting to observe the differences between the unmodified, virgin LDPE-modified and recycled LDPE-modified bitumen, as no studies directly compare them.

1.2.3. Dispersion of LDPE in modified bitumen

LDPE's ability to disperse in the bitumen phase is important in bitumen modification. In the case of low-density polyethylene, the good dispersion of the LDPE in the bitumen results in a homogenous modified blend (Liang et al. 2021; Polacco et al. 2005a). In this case, the material is compatible with bitumen and affects the modified bitumen performance (Liang et al. 2021). Although, (Polacco et al. 2005a) found that the less compatible polyethylene with rough dispersion tends to have better modification than the homogeneously dispersed polyethylene blend. The dispersion of modifiers in the bitumen is greatly related to how the two materials' particles or molecules interact and diffuse each other (Basfar and Idriss Ali 2006; Upadhyay et al. 2008).

Studies have stated that virgin or freshly made LDPE has different diffusion characteristics against other substances compared to the used-LDPE. By comparing virgin pellets to polypropylene pellets collected from the sea surface, (Mato et al. 2001) found different

behaviour in contamination distribution in the pellets' bodies. He proposed the polymer weathering may increase the effective diffusivity compared to virgin pellets. From a bitumen modification point of view, this could lead to potential benefits in using recycled plastics because the aged or reused plastic can be expected to have a better bitumen-polymer diffusion, leading to better modification results.

Another polyethene plastic study stated the weathered material's increase in crystallinity (Satoto et al., 1997; Guadagno et al., 2001) and density (Gulmine et al., 2003). Increasing these two properties means the weathered polyethylene can have a more compact structure and potentially better physical properties. Although, this might lead to a more difficult diffusion and interaction of bitumen into the polymer. This result was stated by D'Aniello et al. (2000), where a slower diffusion has been shown in the case of polypropylene. This condition is believed to be due to increased crystallinity. The slower diffusion rate due to a higher polymer crystallinity is generally expected (Young 1995). Similar results have also been presented in the comparative study of the sorptive behaviour of weathered pellets compared to virgin polyethylene (Karapanagioti and Klontza 2008).

These mixed study results raise questions about the potential difference between virgin and recycled LDPE dispersion in the modified bitumen. Also, how will these affect the modified bitumen and the properties of the corresponding asphalt mixtures.

1.2.4. The bond strength mechanism behind asphalt properties improvements or deteriorations

The failures of asphalt pavement can mainly be investigated through the adhesive properties of bitumen and aggregates. The aggregate and bitumen adhesion can be explained using mechanical, chemical, boundary layers theory, electrostatic and thermodynamic theories (Santhirasegaram and Weragoda 2018).

The adhesive work of bitumen and aggregates is a crucial parameter contributing to the overall asphalt mixture performance. A straightforward test to measure the bitumen – aggregate affinity can be used to determine the parameter. Haider et al. (2020) studied the LDPE and HDPE modified mixture and qualitatively tested the affinity of bitumen – aggregates using the boiling water test, rolling bottle test and water immersion test. They found that the aggregate's polarity, hydrophobicity, and acidity strongly influence the

bonding performance. They also stated that the wet mixing method was better with the lower aggregate coating loss, while the rutting and marshall stability was increased. Leng, Sreeram, et al. (2018a) used the hot water immersion test to observe the affinity between polyethylene terephthalate-based modified bitumen and aggregate. The study resulted in a lower coating loss of the plastic-based additives compared to unmodified virgin or RAP bitumen. Some other studies that used polyethylene terephthalate-based anti-stripping additives (Gürü et al. 2014; Padhan et al. 2013) also stated the increase in adhesion of bitumen and aggregates.

These results stated that polyethene plastic had increased the bonding strength or adhesion between the bitumen and aggregates compared to unmodified bitumen. These studies also stated that the bitumen and aggregates adhesion properties significantly influence the asphalt mixture performance. However, none of these studies has directly compared virgin to recycled plastic in the adhesion properties. Thus, no literature can clearly state which plastic type is better in improving adhesion of modified bitumen with aggregates that affect the asphalt mixture performance.

This study tends to fill these gaps by studying and comparing the adhesion of virgin and recycled LDPE-modified bitumen with the aggregates, which is vital in determining asphalt mixture performance.

1.2.5. The mixture performance

Studies have been conducted on plastic-based modification of bitumen or asphalt mixture. These studies were conducted on bitumen only (wet method), asphalt mixture (dry method), or both bitumen and asphalt mixture comparison in the wet or dry method. In some studies that used bitumen followed by mixture, a consistent result is commonly found between the bitumen and the mixture performance (Haider et al. 2020).

Increasing rutting resistance of asphalt mixture in the use of plastic-modified bitumen or asphalt has been reported by many. For studies on both dry and wet methods, a better rutting resistance has been reported by Haider et al. (2020) on HDPE and LDPE; Ziari et al. (2019) on PVC. The dry method rutting resistance improvement has been reported by: Almeida et al. (2020) on waste LDPE plastic; Movilla-Quesada et al. (2019) on mixed plastic scrap; El-Naga and Ragab (2019) on waste polyethylene terephthalate plastic; White, Reid (2018a) on pelleted recycled plastic.

Some studies have reported mixed results in fatigue resistance of plastic-modified asphalt mixture. Almeida et al. (2020a) stated the lower fatigue resistance of the modified mixture. Lastra-González et al. (2016a) stated no performance differences between the plastic-modified and unmodified mixtures. Meanwhile, many have stated the increasing fatigue resistance of the modified asphalt mixture (El-Naga and Ragab 2019c; Leng, Sreeram, et al. 2018a; Leng, Padhan, et al. 2018; White and Reid 2018b, 2019b).

These results promise the rutting resistance and potential fatigue resistance improvements of the asphalt mixture by using plastic modifiers either by wet or dry method. However, there are disagreements or inconsistencies between these studies about the mixture's fatigue performance. In addition, no study directly compares these performance parameters between virgin and recycled plastic, especially LDPE. Therefore, as the most compatible polyethylene for bitumen modification (Liang et al. 2021), this study will specifically use LDPE plastics as the modifier in the wet mixing method.

1.3. Research Aims and Objectives

1.3.1. Aims

To understand and differentiate the behaviour of virgin LDPE and recycled LDPE-modified bitumen and asphalt mixture to fatigue and rutting damage, this study will analyse the mechanical behaviour of bitumen and asphalt mixture experimentally at a centimetre scale based on a wide range of standardized laboratory tests that simulate rutting and fatigue damage.

1.3.2. Objectives

- 1) To investigate the best practice in LDPE-based bitumen modification by using high shear mixer
- 2) To investigate and differentiate the rutting and fatigue behaviour of virgin and recycled LDPE-modified bitumen and asphalt mixture
- 3) To investigate the factors that drive the rutting and fatigue behaviour of the modified bitumen and asphalt mixture through polymer-bitumen dispersion, ageing of the modified bitumen, and bitumen-aggregate adhesion
- 4) Differentiate the virgin and recycled LDPE properties that cause the different performance of the modified bitumen and asphalt mixture

1.4. Research Methodology

This research is a laboratory-based experiment that manufactures, tests and analyses the bitumen and asphalt performance on laboratory-scale specimens. Before producing or testing any material in the laboratory, comprehensive literature reviews and studies were conducted. Previous studies on plastic (in general) and polyethylene in bitumen modification were studied and elaborated. Earlier studies about the methodology used in polyethylene-based bitumen modification are summarized to conclude the most reliable method to adopt in this research. Further literature about bitumen rheological tests and results were studied to complete the relevant experiments plan to reach the aim of this study. Following the literature reviews and studies, the experiment and analysis steps can be listed as follows:

- 1) A high-shear mixing method will be conducted in the bitumen modification process with a detailed modification procedure based on previous studies and literature to produce LDPE-modified bitumen.
- 2) Tests to understand the bitumen properties will be conducted in standard penetration, softening point, viscosity, and Dynamic Shear Rheometer (DSR) works on bitumen sweep tests, rutting and fatigue resistance tests based on BSEN. The tests will also be conducted on laboratory-aged bitumen.
- 3) Provide a performance classification of the tested bitumen based on its workability and rheological properties to be carried on to asphalt mixture manufacture and tests.
- 4) To understand the ageing and chemical behaviour of the LDPE-modified bitumen, the bitumen's infrared spectrum band analysis will be conducted based on Fourier-transform Infrared Spectroscopy (FTIR).
- 5) The microscopy analysis of the LDPE-modified bitumen will be conducted to explain the physical and rheological property changes.
- 6) To understand the affinity between LDPE-modified bitumen and aggregates which influence the fatigue and rutting properties, the asphalt components' affinity or bonding strength analysis will be conducted based on the rolling bottle method.
- 7) Produce asphalt mixture specimens from the selected bitumen in the previous test phase by gyratory compaction based on BS EN.

- 8) Nottingham Asphalt Tester (NU14) will be used to understand the rutting and fatigue resistance of the asphalt mixtures.
- 9) Elaborate on the results of the bitumen properties and asphalt mixture performance using virgin and recycled LDPE in rutting and fatigue performances.

These laboratory experiments and analysis steps can be grouped into two main phases as follows:

1.4.1. Test Phase I: Bitumen modification and tests

In this phase, the neat bitumen and the modifier (virgin and recycled LDPE) were prepared for bitumen modification with the high-shear mixing method. This phase conducted standard bitumen tests of needle penetration number and the bitumen softening point at the early stage. The further tests were the bitumen viscosity, the Dynamic Shear Rheometer (DSR) works for various rheological properties, the ageing procedure of the bitumen, the observation of chemical functional group using FTIR, the microscopic photo and analysis of the bitumen, and finally, the Ductilometer tests. The obtained results were carried on to Phase II: the asphalt mixture tests.

1.4.2. Test Phase II: Asphalt mixture tests

The test phase II carried on the asphalt mixtures obtained from the selected bitumen from phase I. This phase conducted the asphalt mixing work, followed by the gyratory compaction to prepare the asphalt mixture specimens. The asphalt mixture tests were conducted regarding rutting and fatigue resistance. Further analysis of the findings in the two phases of the experiment was carried out to conclude the aim of this study. Details of the phases are exhibited in **CHAPTER III**.

1.5. Thesis Outline

Chapter I	:	This chapter explains the background of the research, current studies and research gap in similar topics, and the aim and objectives of this study. In addition, this chapter also describes the general research methodology and thesis outline.
Introduction		

Chapter II Literature Review	: This chapter summarizes the previously conducted studies from similar topics, literature related to bitumen and its rheological properties, previously conducted methodologies in bitumen modifications, literature about LDPE properties, and theories and methods related to observation for bitumen chemical functional group, ageing, and mixtures rutting and fatigue performance.
Chapter III Experimental Programme	: This chapter explains the experimental laboratory program to be conducted in the research. This chapter includes the tests on the materials in the bitumen modification, the phases (stages) in the experiments and tests, and the methods or standard codes used.
Chapter IV Modifier Characteristic and Bitumen Blending Results	: This chapter explains the modifier (LDPEs) characteristic in thermal changes (DSC) and FTIR. This chapter also presents the LDPE-bitumen blending (modification) process, the modification results, and the standard bitumen tests results.
Chapter V LDPE modified Bitumen Performance	: This chapter discusses the results of bitumen sweep tests, rutting resistance (MSCR), fatigue resistance (LAS), and fatigue fracture (DENT) characteristics, the polymer dispersion and polymer network, and FTIR test result on unaged, short-term aged (RTFOT), and long-term aged (PAV).
Chapter VI LDPE modified Asphalt Mixture Performance	: This chapter explains procedures and findings related to the LDPE-modified bitumen mixtures and compaction with aggregates. This chapter also discusses the result of ITST, ITFT and RLAT tests on asphalt mixtures.

Chapter VII	:	This chapter briefly discusses and concludes the
Conclusion		findings of this study and the potential further
		research to conduct.
References	:	List of references in the Thesis.

CHAPTER II: LITERATURE REVIEW

2.1. Introduction

This literature review elaborates on the recent research on a similar topic and the approaches and methodology to achieve the aim of this study. This chapter starts with brief descriptions of the constituent materials, the general agreements about the plastic-modified bitumen, and the successfully proven method used in the modification process. Then, this chapter provides the theories and approaches to understanding bitumen and asphalt mixture rutting and fatigue performances. These include the bitumen rheology, microstructures, the affinity of bitumen and aggregates, and the asphalt mixtures' permanent deformation and fatigue failure. The evaluation of bitumen performance in rutting resistance is explained through the bitumen's ability to recover in multiple stress creep and recovery tests and from the complex modulus master curves from the dynamic mechanical analysis. The fatigue resistance is approached by the Linear Amplitude Sweep test and by the essential work of fracture (EWF) theory from the Double-Edge Notched Tension test results. This chapter also describes the thermal changes characteristics and the chemical functional groups to characterise the LDPE modifiers and understand bitumen ageing. Furthermore, the approaches to observe asphalt mixture rutting and fatigue performance are explained.

2.2. Constituent Materials

This study incorporates two primary materials: bitumen and low-density polyethylene (LDPE) as the modifier. Furthermore, two types of LDPE are used in this study: freshly made (virgin) LDPE and recycled LDPE. The following sub-chapters elaborate on these two materials' general properties and characteristics.

2.2.1. Bitumen

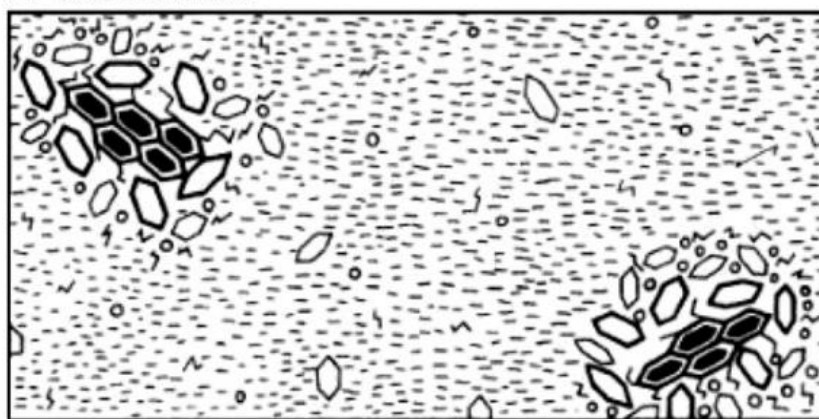
Bitumen is a well-known, reliable, and widely used material in road pavement construction. It is a viscous liquid at a high temperature and a solid glassy material at a low temperature. Bitumen is obtained mainly from a petroleum refinery, with some sources also from natural deposits such as asphalt lakes or mining stones, for example, The Pitch Lake in Trinidad and Tobago and Buton Island in Indonesia. The main components of bitumen are hydrocarbon with various other compositions depending on

the origin. Bitumen consists of 82-88% of Carbon, 8-11% of Hydrogen, 0-6% of Sulphur, 0-1.5% of Oxygen and 0-1% of Nitrogen (Rahman 2004). The general chemical components of bitumen are groups of molecules based on size and polarity known as SARA (Saturates, Aromatics, Resins and Asphaltenes), with resins, aromatics and saturates also known as one group of 'maltenes'. The composition of maltenes and asphaltenes is the key to determining the bitumen types: SOL or GEL. Asphaltenes are the dispersed components in the maltenes that represents the bitumen type. GEL is the bitumen type that has relatively lower resins and aromatics. The asphaltenes form a large-scale network as they are not fully dispersed in the bitumen, forming a GEL (gelatinous) bitumen type. The SOL (solution) type is the one that has sufficient maltenes that disperse the asphaltenes to develop the whole oily bitumen (Hunter, Self, and Read 2015). Figure 2.1 shows the schematic representation of SOL type and GEL type bitumen. The characteristic of each bitumen component is described as follows (Read and Whiteoak 2003):

- **Saturates.** Saturates are white non-polar viscous oil that gives the fluid characteristic to the bitumen. Bitumen mass usually constitutes 5% to 20% of saturates with a molecular weight range of 300 g/mol to 1500 g/mol. With its fluid characteristic, saturates generally give the bitumen the ability to reform broken bonds.
- **Aromatics.** This component has black or brown characteristics and has 300 to 20000 g/mol molecular weight. Aromatics have both polar and non-polar oily fluid. The polar aromatics are generally darker and more viscous, while the non-polar aromatics are less viscous and have yellow to orange in colour. Aromatics are a solvent for asphaltenes and resins, and with 40-65% of bitumen weight, they are the significant proportion in the bitumen. Aromatics are also considered a bitumen plasticiser and help protect the oils from oxidation during the bitumen ageing process.
- **Resins.** Resins are black or brown solid or semi-solid components with very polar characteristics and high molecular weight of 500 – 50000 g/mol. Its high polarity makes resins very adhesive and acts as co-solvent agents or peptisers for the asphaltenes. The resins' adhesive attribute serves as a stabiliser that holds the components in the bitumen. The proportion of resins and asphaltenes determines the type of bitumen as SOL or GEL bitumen type. In bitumen oxidation, the volatilization and oxidation of resins harden the bitumen due to the conversion of resins into more polar molecules.

- Asphaltenes. Asphaltenes are black or brown with the highest molecular weight of all components, from 1000 to 100000 g/mol. They tend to form an aggregation of 20000 to 1000000 g/mol micelles, with 5% to 25% of all bitumen mass. Asphaltenes give the bitumen stiffness and acidity behaviour. Higher asphaltenes produce a harder bitumen with lower penetration, higher softening point, and higher viscosity. The gel structure of the asphaltenes micelles tends to break down on heating and reform on cooling. Therefore, the performance of asphaltenes changes with temperature.

A Sol bitumen



B Gel bitumen

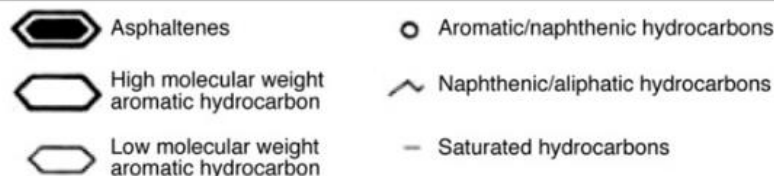
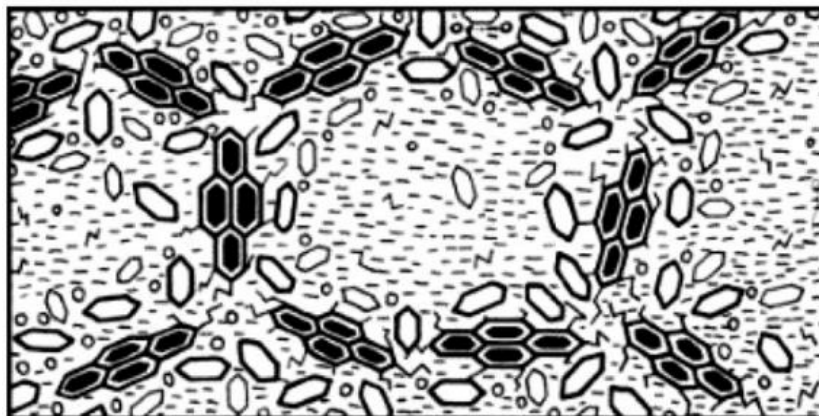


Figure 2. 1: Schematic representation of SOL type and GEL type bitumen (Read and Whiteoak 2003)

The rheology of the bitumen can change in the changes of the asphaltenes and maltenes proportion. The general characteristic changes of bitumen in the changes of its components can be described as follows (Read and Whiteoak 2003):

- 1) The bitumen shear susceptibility reduces with the increase of aromatic and the constant ratio of saturates and resins
- 2) Harder bitumen, higher softening point and viscosity, lower pen number and lower shear susceptibility can be produced by increasing the resins
- 3) Softer bitumen can be made by increasing saturates and keeping the resins and aromatics ratio

2.2.2. Low-Density Polyethylene

‘Plastics’ are materials that are widely used in worldwide industries. There are various commonly used plastics, such as Polyethylene, Polystyrene, Polypropylene, Polyethylene terephthalate (PET) and others. On the world scale, polyethylene has the highest share of total production. Low-density or Linear-low density polyethylene (LDPE/LLDPE) is one of the polyethylene that also has the highest use proportion in the EU compared to other plastic types (EC DG ENV 2011). In the UK, the increasing use of plastic is followed by a higher capacity of its recycling fourfold since early 2000 to 2021. However, the UK is still reliant on exports for recycling at 47% (WRAP 2023). This illustrates the challenges in plastic recycling or reuse. Figure 2.2 shows the world thermoplastic production and the type in the EU, and its recycling rate in the UK.

Polyethylene is made from ethylene polymerization. Ethylene is the term for hydrocarbon substance of C_2H_4 or double bond of two methylene $CH_2 = CH_2$. The chain structure of the ethylene, $-CH_2 = CH_2-$, and the manufacturing technologies determine the polyethylene type. High-density polyethylene (HDPE) is the one that has few branches of chain structures, has a more compact structure, higher density and can reach a high amount of crystalline, thus having a higher melting point. High crystallinity means a high degree of ordered polymer chain alignment. On the other hand, LDPE has a higher number of chain structure branches, thus producing a material that hardly forms into a crystalline fraction and has a lower melting point than HDPE (Agboola et al. 2017; Nagy and Belina 2018).

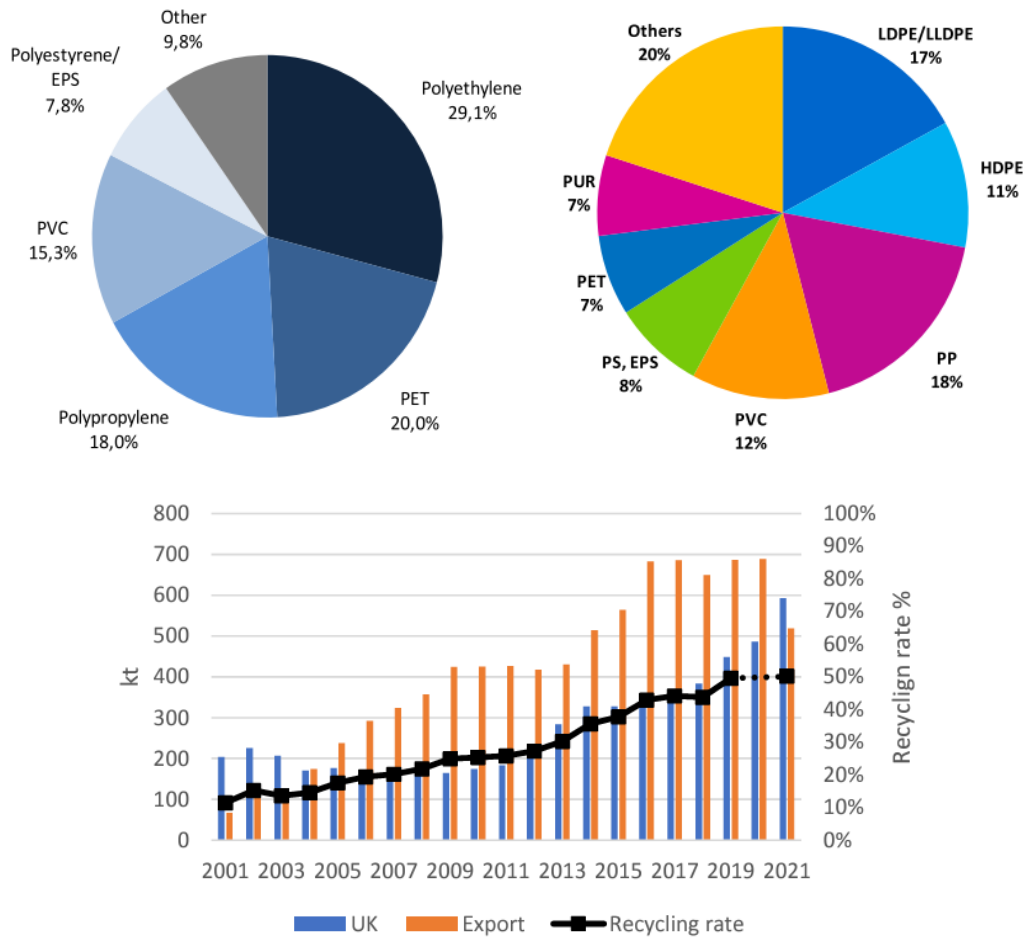


Figure 2. 2: World thermoplastic capacity, plastic demand in the EU (EC DG ENV 2011) and the UK plastic recycling rate (WRAP 2023)

Figure 2.3 depicts the illustration of polyethylene chain structures with different degrees of branching. The linear non-branching is the model of high-density polyethylene while the low density showed long, unordered branches of the ethylene, $-CH_2 = CH_2 -$, surrounding the main polyethylene structure. Some other classifications mentioned medium-density polyethylene (MDPE) and Linear-low polyethylene (LLDPE) that generally have properties between the LDPE and HDPE with their structural illustration are presented in Figure 2.4.

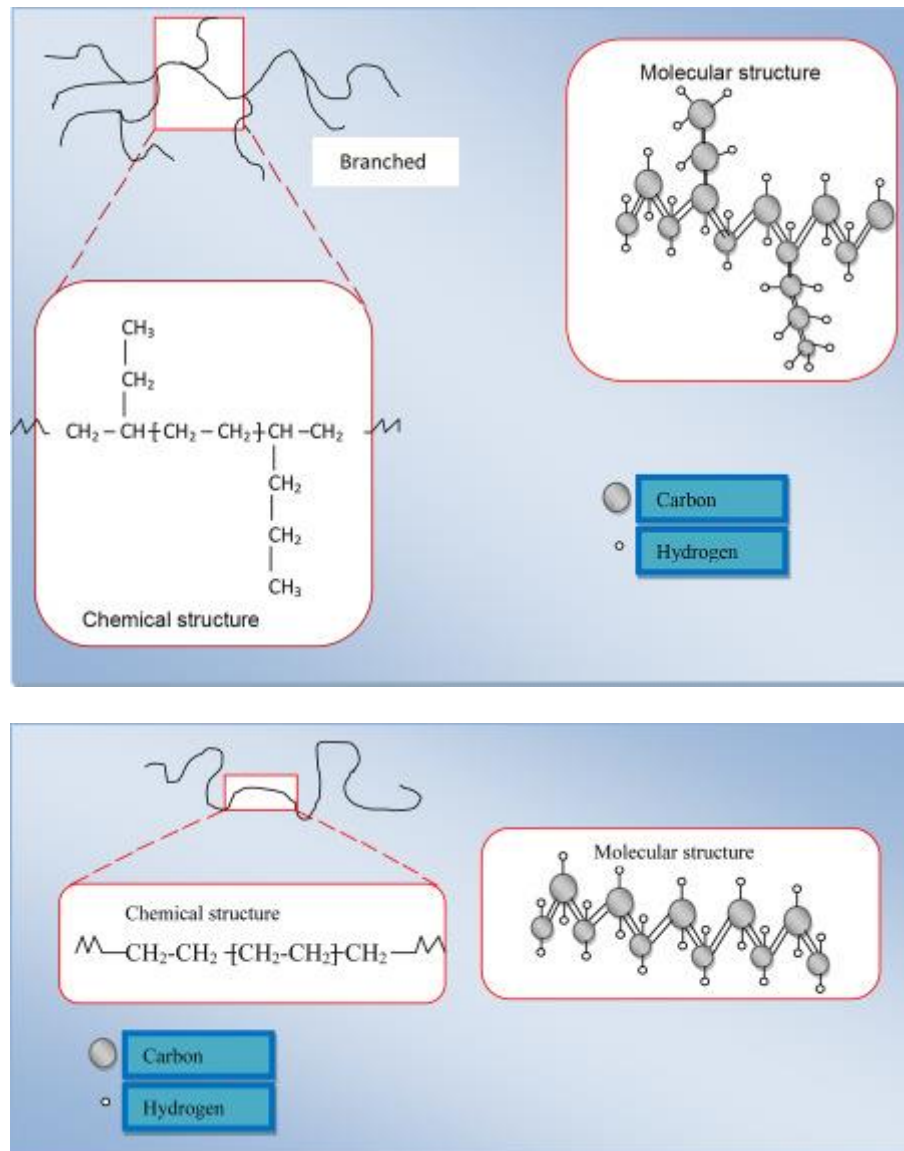


Figure 2. 3: A linear form of polyethylene with branches (Low-density polyethylene) and without branches (high-density polyethylene) (Agboola et al. 2017)

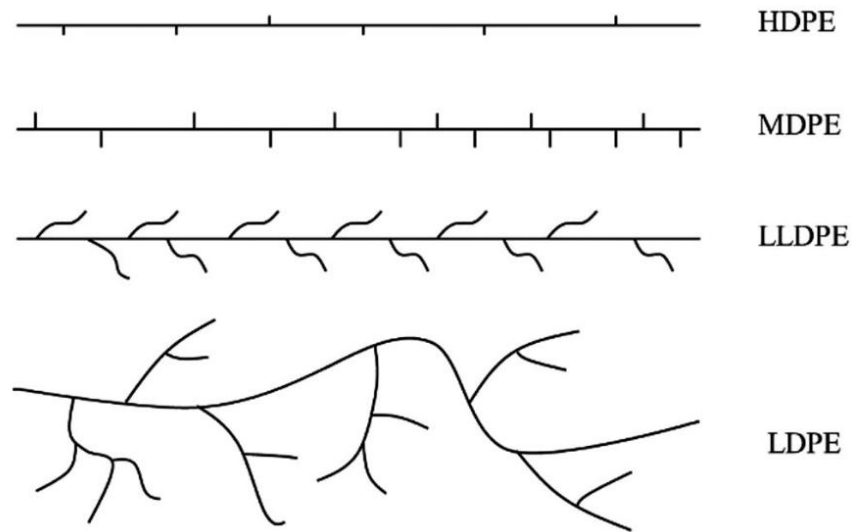


Figure 2. 4: Schematic illustration of various PE molecule structures (Liang et al. 2021)

LDPE is efficiently manufactured at low cost and widely produced mainly as a packaging material such as groceries bags and plastic wraps because it has semi-rigid properties, are water and weather-proof, tough, and has good chemical resistance. LDPE has a melting point of $\pm 110^{\circ}\text{C}$ and can continuously withstand a high temperature of $80\text{--}95^{\circ}\text{C}$.

2.3. Plastic modified bitumen

Due to the increasing demand for better quality and durability for higher traffic volume and heavier loads, bitumen and road pavement technology has continuously grown. Polymer-modified bitumen is one of the most popular modifications, and its demand has increased tremendously (D'Angelo 2009). It has been widely recognised that adding polymers into bitumen can overcome its deficiencies by improving viscoelastic behaviour while maintaining its performance. In addition, polymers can increase the resistance to permanent deformation, fatigue cracking, and various important properties (Behl, Sharma, and Kumar 2014; Kalantar, Karim, and Mahrez 2012a).

Polymers that are mainly studied as bitumen modifiers are styrene butadiene styrene (SBS), styrene-butadiene rubber (SBR), ethylene vinyl acetate (EVA), polyethylene, which improves the rutting, thermal cracking, fatigue damage and stripping resistance (Yildirim 2007). Plastic materials such as HDPE, LDPE, PP, PET or PTP and PVC as a form of polymer have also been studied as bitumen modifiers with various positive results (Almeida et al. 2020a; Costa et al. 2019; Dalhat and Al-Abdul Wahhab 2017a; El-Naga and Ragab 2019a;

Haider et al. 2020; Hu et al. 2018a; Khan et al. 2016; Lastra-González et al. 2016a, 2017; Leng, Sreeram, et al. 2018a; Leng, Padhan, et al. 2018; Movilla-Quesada et al. 2019a; Padhan and Sreeram 2018; Wang et al. 2018a; White and Reid 2018a, 2019a; Ziari et al. 2019). According to Liang et al. (2021), low-density polyethylene (LDPE) has the best compatibility with bitumen compared to other PE families such as LLDPE (linear low-density polyethylene), MDPE (medium-density polyethylene) or HDPE (high-density polyethylene). The least compact main structure chain that provides the lowest rigidity and hardness is believed to cause LDPE to become more compatible than other polyethylene plastic (Liang et al. 2021). LDPE also has the lowest melting point of all plastic, indicating the highest potential blending with bitumen in the shear mixing temperature.

2.3.1. Preparation and modification procedures of plastic-modified bitumen

Plastic modification in the pavement can be done in the wet and dry mixing method. Studies on both methods have shown that the wet method is commonly better than the dry method (Haider et al. 2020). However, the dry method offers an easier procedure (Movilla-Quesada et al. 2019b), and both procedures result in improvements in the final product than the unmodified bitumen or asphalt mixture (Haider et al. 2020). Therefore, both methods have their advantages and disadvantages.

2.3.1.1. Dry method

The dry process is conducted with the plastic polymer directly added to the group of heated aggregates before being mixed with bitumen. This method is considered simpler than the wet method and can commonly be carried out in most asphalt plants. The dry method commonly uses higher plastic content (can be >15% by bitumen weight) than the wet method, and the aggregate coating by the plastic is the critical element of the modification process. The plastic coating enhances the bitumen binding, resulting in a better asphalt mixture performance (Zakaria 2019).

The flexible film of any plastic can be used in this method (Zakaria 2019). However, Movilla-Quesada et al. (2019) stated that plastic waste must be scrapped and smaller than 2 mm to perform the best result in the dry mixing process. Also, this plastic sizing procedure is needed to prevent the possibility of incompatibilities between polymer and bitumen (Lastra-González et al. 2016a; Movilla-Quesada et al. 2019a).

Using LDPE waste plastic, Almeida et al. (2020b) conducted dry method mixing, resulting in a higher indirect tensile strength on dry (normal) and wet-conditioned asphalt mixture specimen. The author also stated the higher result in stiffness modulus and rutting resistance. However, the modification had a drawback in lower workability or difficulties in the preparation. In addition, the modification also reduced the fatigue cracking performance compared to unmodified mixtures.

Movilla-Quesada et al. (2019) reported that the plastic scrap-modified mixtures have a higher stiffness, perform better in the Marshall stability test, and have a higher permanent deformation resistance. Similar results have also been reported by El-Naga and Ragab (2019), where polyethylene terephthalate waste increased the bitumen stiffness, enhanced asphalt mixture performance in rutting resistance, and potentially reduced the asphalt layer thickness requirements for the same service life compared to the unmodified mixture. Another recycled plastic waste-modified mixture study also stated the increase in the asphalt mixture's stiffness, moisture damage resistance, and rutting resistance (White and Reid 2018a). Also, the modified mixtures can potentially reduce the construction cost.

There are agreements in these study results that plastic modification generally increases the asphalt mixture stiffness, increases the rutting resistance, and potentially improves the fatigue resistance. These characteristics suit medium and higher climatic temperature zones but are potentially more prone to cracking damage in cold or lower temperature areas (Movilla-Quesada et al. 2019a). The use of plastic modifier in dry method generally uses small cut or pelleted material. Table 2.1 summarises the modifier shape, modification rate and property changes of the modified asphalt mixtures.

Table 2. 1: Dry method modification and the general results

No	Modifier shape/size	% Modification	Property changes
1	±2 mm cut plastic flakes/scrap	10% & 20% of bitumen weight (Movilla-Quesada et al., 2019) 1% of aggregate volume (Lastra-González et al., 2016a)	Generally similar property changes are obtained by all modifier shape/size: higher stiffness, higher rutting resistance, slightly lower workability. Some

		2, 4, 6, 8% of bitumen weight (Almeida et al. 2020b)	stated slightly lower fatigue resistance.
		2, 4, 6, 8, 10 & 12% of bitumen weight (El-Naga and Ragab, 2019)	
2	Pelleted plastic (recycled)	6% bitumen weight (White and Reid 2018a)	

2.3.1.2. Wet method

The wet mixing method is another term for bitumen modification before the modified product is applied to the asphalt mixture. This procedure requires specific material treatment and mixing, such as high-temperature and high-speed shear mixing, to obtain stable mixtures (Al-Adham and Al-Abdul Wahhab 2018). In this method, the plastic must be sufficiently compatible with the bitumen to successfully produce modified bitumen and avoid phase separation after the modification/blending process has finished (Zakaria 2019).

Table 2. 2: The melting point of plastic materials (Dalhat and Al-Abdul Wahhab 2017b)

Plastic type	Melting point (°C)	Blending temp. (°C)
LDPE	110	160
HDPE	132	180
PP	162	190
PET	250	-
PVC	298	-
PS	>300	-

HDPE, LDPE, PET, PVC, PP, and PS are common types of plastic material in which the LDPE, HDPE, and PP are the only suitable plastic material in the wet mixing of bitumen modification due to the melting point of 110°C, 132°C and 160°C respectively Dalhat, Al-Abdul Wahhab (2017a). Table 2.2 shows the melting point of each type of plastic and the possible blending temperature in the wet mix process.

According to Dalhat, Al-Abdul Wahhab (2017a), in the wet process, bitumen modification of plastic is carried out by preparing the tiny powder-like ground shape for easier blending. Figure 2.5 shows the ground shape of LDPE, HDPE, and PP. At 5000 rpm shearing speed, the optimal blending procedure for PP, HDPE, and LDPE are at 190°C, 180°C, and 160°C, respectively, with 50, 60 and 30 minutes long Dalhat, Al-Abdul Wahhab (2017a).

Figure 2.6 (a) shows how LDPE, HDPE, and PP modifiers affect the bitumen viscosity in the variable of blending time. In the case of LDPE, the stable viscosity is reached after approximately 30 minutes of shear mixing. A further additional time of shearing does not significantly affect the viscosity. Therefore, the LDPE modifier has a relatively shorter high-shear mixing time to obtain constant viscosity than HDPE and PP, which require a longer blending time of approximately 60 minutes.

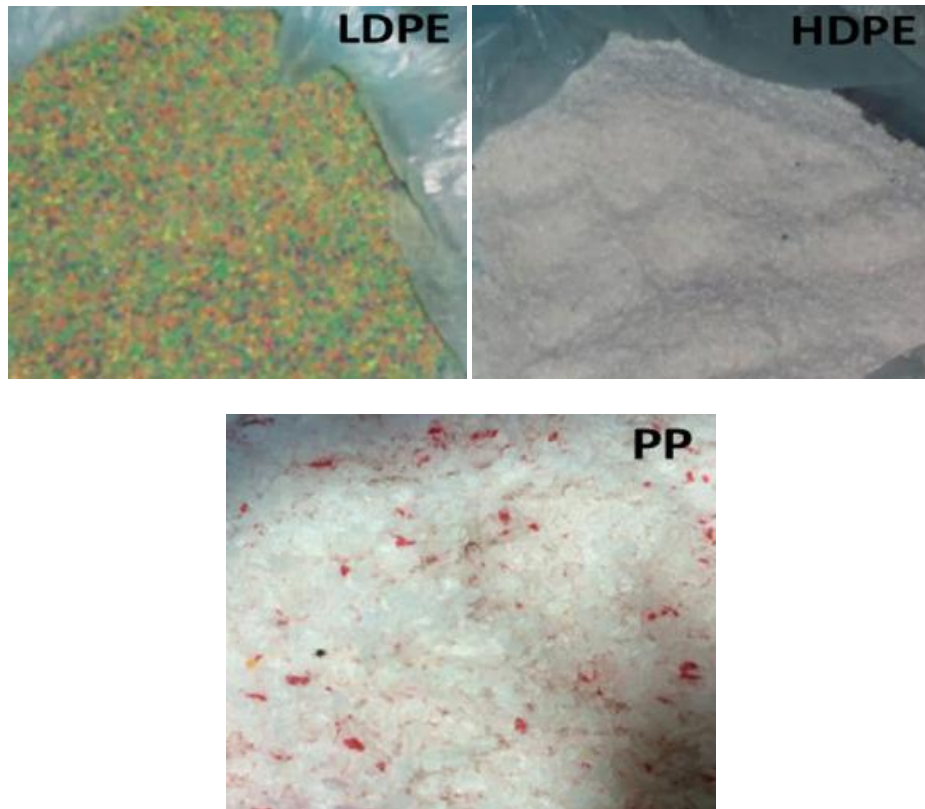


Figure 2. 5: Ground LDPE, HDPE and PP (Dalhat and Al-Abdul Wahhab 2017b)

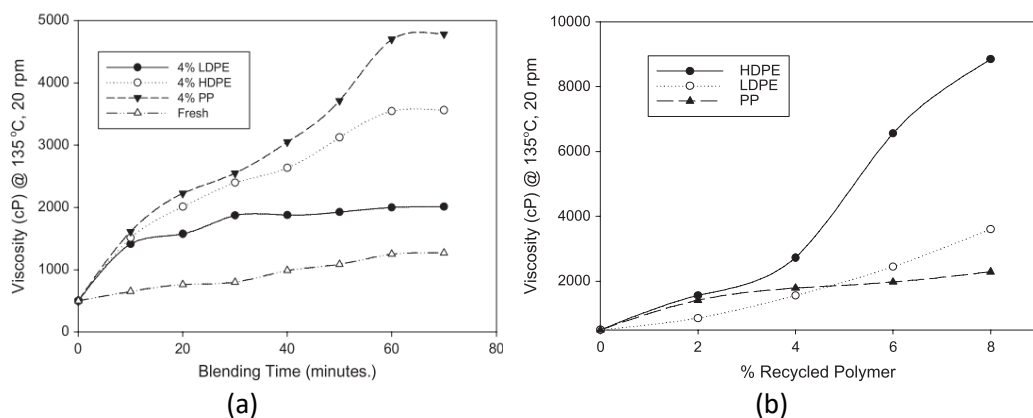


Figure 2. 6: The mixing and %weight effect to plastic modified bitumen viscosity (Dalhat and Al-Abdul Wahhab 2017b)

Figure 2.6 (b) shows how the HDPE modifier significantly raised the bitumen viscosity when more than 4% of bitumen weight was implemented. In contrast, the LDPE modifier is relatively slighter in increasing the modified bitumen viscosity at 4, 6 or 8% of LDPE modifier content.

2.3.2. General improvements in plastic-modified bitumen and asphalt mixture

Rutting or permanent deformation along the wheel path is one of the most common distresses in asphalt pavement due to heavy loading, high pavement temperature and slow-moving traffic. Another major asphalt pavement deterioration is fatigue cracking caused by repeated traffic loading in the years of the pavement service life. Studies in plastic-modified bitumen/asphalt have been conducted to understand how the modification affects the asphalt mixture rutting and fatigue performance.

2.3.2.1. Rutting resistance

Asphalt studies with various types of plastic modifiers and mixing procedures frequently stated the improvement of the rutting resistance. Almeida et al. (2020) conducted tests of a modified asphalt mixture using LDPE waste in plastic flakes form with an ageing procedure. Compared to the unmodified mixture, the unaged or aged plastic-modified mixture presents a higher rutting resistance under the wheel tracking test than the reference mixture.

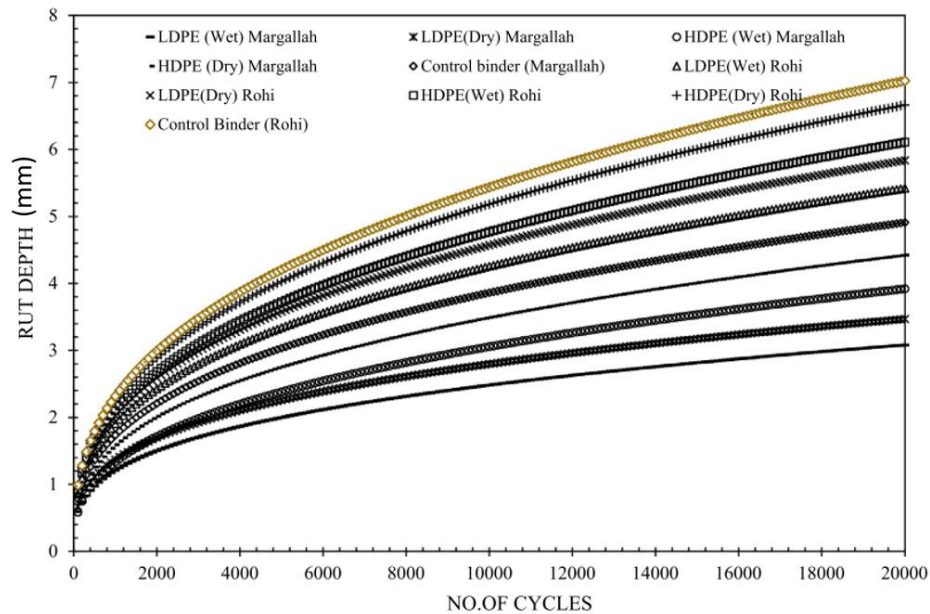


Figure 2. 7: Rutting resistance results from neat and plastic-modified asphalt (Haider et al. 2020)

A similar result was obtained by Haider et al. (2020), who conducted the HDPE and LDPE-modified bitumen and asphalt by using dry and wet mixing methods. Both modifiers produced higher rutting resistance in both mixing methods, with the wet mixing found to be better than the dry mixing. Figure 2.7 shows the rutting resistance improvement of all plastic-modified asphalt compared to unmodified asphalt.

Another study by Movilla-Quesada et al. (2019) used waste plastic scrap of PET, HDPE, and PVC as the modifier to the asphalt mixture in the dry mixing method and partially replacing the bitumen resulted in the similar result of improvement in rutting resistance as shown in Figure 2.8. Plastic modifiers (PF1, PF2, PG1, PG2) decreased the rut depth of more than half of the reference mixture (REF, REF1) under the wheel tracking test.

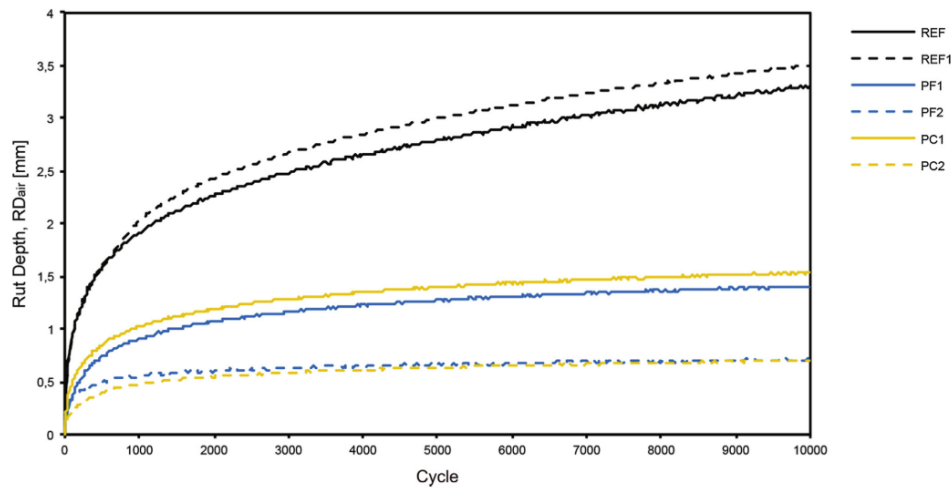


Figure 2. 8: Rut depth comparison of neat and plastic-modified asphalt mixture (Movilla-Quesada et al. 2019a)

Dalhat and Al-Abdul Wahhab (2017) utilized PP, HDPE, and LDPE recycled plastic waste in bitumen modification under the wet mixing procedure. The study resulted in a similar conclusion of rutting resistance improvement compared to the neat asphalt mixture. Other conducted asphalt studies of different plastic modifiers resulted in a similar trend of rutting resistance improvement. El-Naga and Ragab (2019) utilized PTP (polyethylene terephthalate) by dry mixing in the asphalt modification. The PTP modification produced a lower rut depth compared to the neat asphalt mixture. Costa et al. (2019) utilized ethylene vinyl acetate (EVA), high-density polyethylene (HDPE) and styrene butadiene styrene (SBS). All modifiers produced better rutting resistance, with the HDPE being the highest compared to the other mixtures. Utilized PVC and EAF (electric arc furnace) dust as the bitumen modifier, Ziari et al. (2019) stated the improvement in the rutting resistance of the bitumen and the mixture. Hu et al. (2018) used polyethylene waste packing tape material as a 60/70 penetration bitumen modifier using 2%, 4%, 6% and 8% by neat bitumen weight, producing higher rutting resistance compared to the unmodified mixture. Wang et al. (2018) implemented polyethylene and anti-rutting agents (ARA) as a modifier to the bitumen and produced a higher rutting factor. White, Reid (2018) used AC20 base course and SMA10 surface course asphalt mixture, replacing 6% of bitumen weight with the plastic waste product of MR6, MR8 and MR10. All mixtures were reducing the rut depth. Leng, Sreeram, et al. (2018b) produced waste polyethylene terephthalate additives derived through an aminolysis process and applied the material into crumb

rubber-modified asphalt. The modification increased the mixture rutting resistance. Khan et al. (2016) utilized LDPE, HDPE, and crumb rubber to modify neat bitumen. Under the DSR test (without asphalt mixture), the modified bitumen improved the rutting resistance. Lastra-González et al. (2016b) utilized polyethylene (PE), polypropylene (PP), polystyrene (PS), and waste rubber tyres in dry mixing asphalt modification. All modifications resulted in lower rutting deterioration.

2.3.2.2. Fatigue resistance

Similar to rutting resistance, the fatigue resistance tests of various plastic modifications were popularly conducted. For example, Almeida et al. (2020) stated that the modified asphalt mixture has slightly lower fatigue resistance than the unmodified reference mixture. Figure 2.9 shows the 4PB test of asphalt fatigue, which results in lower ε_6 (the estimation of strain at 10^6 cycles) for unaged plastic modified but higher in aged plastic modified.

Costa et al. (2019) and Wang et al. (2018a) stated a similar result of potential lower fatigue resistance, especially at a lower temperature. The different results were stated by Lastra-González et al. (2016a). Incorporating the polymeric wastes did not modify the fatigue resistance; the modified mixture had the same performance as the reference mixture. Figure 2.10 shows the relatively same result of strain under 4PB tests and statistically has no significant differences.

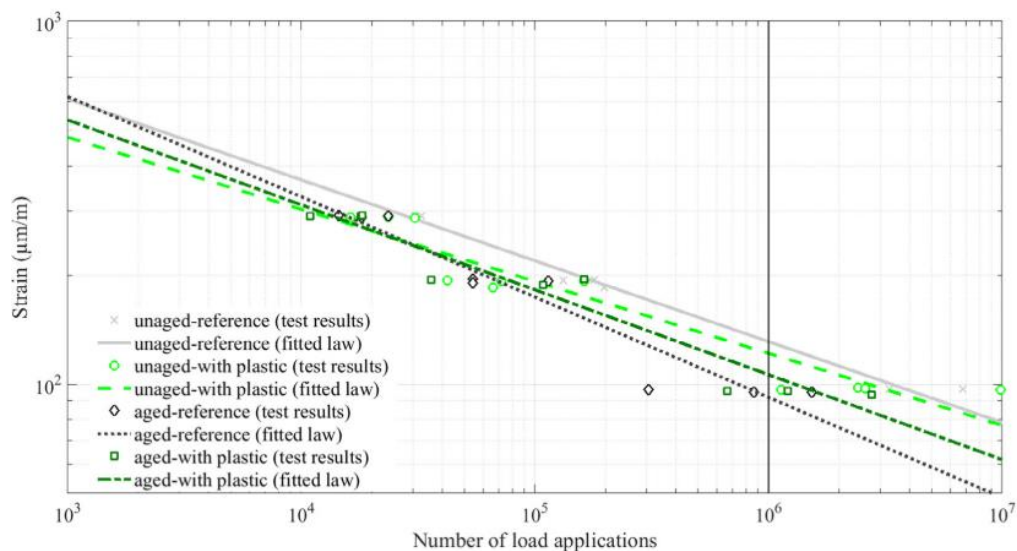


Figure 2. 9: The fatigue test result of neat and LDPE-modified asphalt (Almeida et al. 2020b)

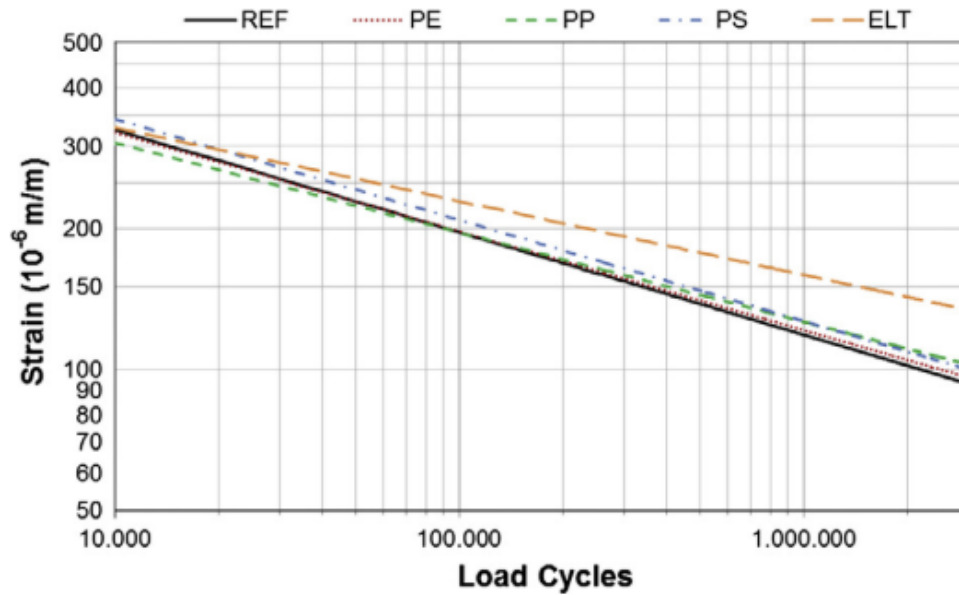


Figure 2. 10: Fatigue lines from 4PB test (Lastra-González et al. 2016c)

Unlike the previously mentioned results, El-Naga and Ragab (2019) stated the improvement of the cracking resistance of PTP-modified asphalt. White, Reid (2018a, 2019a) stated the improvement in fatigue resistance based on cracking resistance from the force ductility investigation and fracture toughness test. Leng, Padhan, et al. (2018) and Leng, Sreeram, et al. (2018a) stated the fatigue resistance improvement when utilizing PET-based additives and crumb rubber-modified asphalt. Hu et al. (2018a) stated the fatigue resistance improvement at the low strain level on polyethylene-modified bitumen. Ziari et al. (2019) stated the fatigue-resistant improvement of PVC and EAF dust-modified bitumen based on the LAS test.

Dalhat and Al-Abdul Wahhab (2017) stated the fatigue cracking improvement of LDPE, HDPE and PP-modified bitumen compared to a neat mixture. Khan et al. (2016) also stated the improvement of fatigue resistance in LDPE, HDPE and crumb rubber-modified bitumen compared to neat bitumen.

A brief compilation of plastic-modified bitumen and asphalt mixtures in terms of the most common parameters is presented in the following Table 2.3.

Table 2. 3: Plastic modifier effect to bitumen and asphalt mixture

Plastic modifier	R&B, penetration number, or other parameters	Rutting resistance	Fatigue resistance	References
HDPE	Increasing softening point and decreasing penetration number mentioned by (Costa et al. 2019) Better adhesion between the aggregate and bitumen (Awwad and Shbeeb 2007)	Higher rutting resistance mentioned by all	(Costa et al. 2019) stated potential lower fatigue resistance on low temperature. (Awwad and Shbeeb 2007), (Dalhat and Al-Abdul Wahhab 2017a) and (Khan et al. 2016) stated higher fatigue resistance. The fatigue resistance concluded better in a high-temperature environment.	(Movilla-Quesada et al. 2019a) (Costa et al. 2019) (Dalhat and Al-Abdul Wahhab 2017a) (Khan et al. 2016) (Awwad and Shbeeb 2007) (Kalantar, Karim, and Mahrez 2012b)
LDPE	Increasing softening point and decreasing pen number mentioned by (Dalhat and Al-Abdul Wahhab 2017a; Haider et al. 2020) Better adhesion between the aggregate and the bitumen (Awwad and Shbeeb 2007)	Higher rutting resistance mentioned by all	(Almeida et al. 2020a) stated slightly lower especially on a lower temperature. (Awwad and Shbeeb 2007), (Dalhat and Al-Abdul Wahhab 2017a) and (Khan et al. 2016) stated higher fatigue resistance.	(Almeida et al. 2020a) (Haider et al. 2020) (Dalhat and Al-Abdul Wahhab 2017a) (Khan et al. 2016) (Awwad and Shbeeb 2007) (Kalantar et al. 2012b)
PE	Increasing softening point and decreasing pen number mentioned by (Hu et al. 2018a; Padhan	Higher rutting resistance mentioned by (Hu et al. 2018a; Lastra-González et al. 2016a;	(Hu et al. 2018a) stated increasing the fatigue resistance. (Wang et al. 2018a) conclude the decrease of	(Padhan and Sreeram 2018) (Wang et al. 2018a) (Hu et al. 2018a) (Lastra-González et al. 2016a)

Plastic modifier	R&B, penetration number, or other parameters	Rutting resistance	Fatigue resistance	References
	and Sreeram 2018; Wang et al. 2018a) More resistance to UV aging and rutting (Mohammadiro udbari et al. 2016) Aging resistance (Becker, Mendez, and Rodriguez 2001)	Wang et al. 2018a) (Fang et al. 2012; Fuentes-Audén et al. 2008; González et al. 2002; Mohammadiro udbari et al. 2016)	fatigue resistance in low temperature.	(Fuentes-Audén et al. 2008; González et al. 2002) (Kalantar et al. 2012b) (Becker et al. 2001)
PP	Increasing softening point and decreasing pen number mentioned by (Dalhat and Al-Abdul Wahhab, 2017)	Higher rutting resistance mentioned by (Dalhat and Al-Abdul Wahhab, 2017)	No clear/significant result to conclude.	(Lastra-González et al. 2017) (Dalhat and Al-Abdul Wahhab 2017a) (Lastra-González et al. 2016a)
PTP or PET	Increasing softening point and decreasing pen number mentioned by (El-Naga and Ragab 2019a; Leng, Sreeram, et al. 2018a; Leng, Padhan, et al. 2018)	Higher rutting resistance mentioned by all	All increasing fatigue resistance except (Movilla-Quesada et al., 2019) not conducting the test.	(El-Naga and Ragab 2019a) (Movilla-Quesada et al. 2019a) (Leng, Padhan, et al. 2018) (Leng, Sreeram, et al. 2018a)
PVC	Increasing softening point and decreasing pen number mentioned by (Ziari et al. 2019)	Higher rutting resistance mentioned by all	(Ziari et al. 2019) stated the increase of fatigue resistance. (Movilla-Quesada et al., 2019) not	(Ziari et al. 2019) (Movilla-Quesada et al. 2019a)

Plastic modifier	R&B, penetration number, or other parameters	Rutting resistance	Fatigue resistance	References
			conducting the test.	
Pelleted recycled plastic	Increasing softening point and decreasing pen number mentioned by (White and Reid 2019a)	Higher rutting resistance mentioned by all	Fatigue resistance increased mentioned by all	(White and Reid 2019a) (White and Reid 2018a)

2.3.3. Significant properties of different variables in plastic-modified bitumen

Studies have been conducted with different variables including plastic type, plastic content or mixing methods. Zakaria (2019) has conducted recycled waste plastic (RWP) modified bitumen of LDPE, HDP and PP at different content with low shear mixing rates. The study concluded that all RWP-modified bitumen properties show a similar trend. Based on standard bitumen tests, the RWP properties were more greatly affected by the RWP content than the RWP types. However, on specified tests on rutting and fatigue performance, each RWP performed different results.

2.3.3.1. Plastic type

Different plastic types have been widely studied in modifying bitumen and asphalt mixture. Plastic-modified bitumen and asphalt mixture generally provide a higher stiffness and rutting resistance than unmodified bitumen. In terms of fatigue property, on the other hand, the modification presented different results between studies, especially at a low testing temperature. At low temperatures, the plastic-modified bitumen is generally stiffer and thus more prone to crack.

HDPE modification studies resulted in increasing softening point (Costa et al. 2019), better rutting resistance (Awwad and Shbeeb 2007; Costa et al. 2019; Dalhat and Al-Abdul Wahhab 2017a; Kalantar et al. 2012b; Khan et al. 2016; Movilla-Quesada et al. 2019a), better fatigue resistance (Awwad and Shbeeb 2007; Dalhat and Al-Abdul Wahhab 2017a;

Khan et al. 2016), lower fatigue resistance (Costa et al. 2019), better adhesion between aggregate and bitumen (Awwad and Shbeeb 2007).

Similar to HDPE, LDPE modification studies resulted in an increase in softening point and a decrease in pen number (Dalhat and Al-Abdul Wahhab 2017a; Haider et al. 2020), better rutting resistance (Almeida et al. 2020a; Awwad and Shbeeb 2007; Dalhat and Al-Abdul Wahhab 2017a; Haider et al. 2020; Kalantar et al. 2012b; Khan et al. 2016), better fatigue resistance (Awwad and Shbeeb 2007), (Dalhat and Al-Abdul Wahhab 2017a) (Khan et al. 2016), lower fatigue resistance, better bitumen and aggregate adhesion (Awwad and Shbeeb 2007).

Polyethylene modified studies also resulted in the similar outcome of increasing softening point and decreasing penetration number (Hu et al. 2018a; Padhan and Sreeram 2018; Wang et al. 2018a), increasing rutting resistance (Fang et al. 2012; Fuentes-Audén et al. 2008; González et al. 2002; Hu et al. 2018a; Lastra-González et al. 2016a; Mohammadiroudbari et al. 2016; Wang et al. 2018a), increasing fatigue resistance (Hu et al. 2018a), and decreasing fatigue resistance at low temperature (Wang et al. 2018a).

Studies on other plastic, such as polyethylene terephthalate (PET), polypropylene (PP), and polyvinyl chloride (PVC), also concluded similar results. PET-modified bitumen has higher rutting resistance (El-Naga and Ragab 2019a; Leng, Sreeram, et al. 2018a; Leng, Padhan, et al. 2018; Movilla-Quesada et al. 2019a) and higher fatigue resistance (El-Naga and Ragab 2019a; Leng, Sreeram, et al. 2018a; Leng, Padhan, et al. 2018). Studies also stated higher rutting resistance on PP and PVC (Dalhat and Al-Abdul Wahhab 2017a; Movilla-Quesada et al. 2019a; Ziari et al. 2019) and higher fatigue resistance on PVC (Ziari et al. 2019).

These results illustrated that, regardless of type, plastic modified bitumen resulted in typical improvement in stiffness (pen number), softening point, and rutting resistance. Lower fatigue resistance generally occurs at a lower temperature. This result is similar to (Zakaria 2019), which used various types of recycled waste plastic, resulting in relatively the same trend of improvements. (Becker et al. 2001) presented several polymer modifiers' advantages, disadvantages, and applications, as shown in Table 2.4. This table only shows the plastic polymer part of the whole presented polymers.

Table 2. 4: Advantages, disadvantages, and uses of several plastic polymers in bitumen modification

Polymer	Advantages	Disadvantages	Uses
Polyethylene (PE)	- High temperature resistance - Aging resistance - High modulus - Low cost	- Hard to disperse in the bitumen - Instability problems - High polymer contents are required to achieve better properties - No elastic recovery	- Industrial uses - Few road applications
Polypropylene (PP)	- No important viscosity increase even though at high amounts of polymer - ease of handling and layout - High R&B Low penetration - Widens the plasticity range and improves the binder's load resistance	- Separation problems - No improvement in elasticity or mechanical properties - Low thermal fatigue cracking resistance	- Atactic PP is used for roofing - Isotactic PP is not commercially applied
Ethylene-vinyl-acetate (EVA) Ethylene-methacrylate (EMA)	- Outstanding compatibility in some cases - Minimal viscosity changes compared to competitive products	- No improvement in elastic recovery	- Paving and roofing

Polymer	Advantages	Disadvantages	Uses
	- Thermally stable at normal mixing and handling temperatures - Low cost compared to block copolymers - Increased tack		
PVC	- Lower cracking	- Acts mostly as filler	- Not commercially applied.
Mixed systems (most used systems include SBS in their Formulation. Systems with PE have also been used)	- Improvements that may not be possible with a single modifier	- Compatibility and instability problems	- Paving

2.3.3.2. Plastic content

Studies on plastic-modified bitumen or asphalt mixture used various plastic content from 2% to 20% or more by bitumen weight, depending on the modification method (dry or wet) and plastic types. González et al. (2002) used 5% bitumen weight of HDPE and LDPE plastic, resulting in a higher elastic modulus of modified bitumen. A wider range of modifier content was done by Fuentes-Audén et al. (2008), which used recycled polyethylene blending with 2, 5, 15, 25, and 50% weight of 150/200 pen bitumen. The study resulted in enhanced permanent deformation or rutting and increased thermal and fatigue cracking for 5-15% modification. Another study by Khan et al. (2016) used 2, 4, 8 and 10% by bitumen weight of LDPE and HDPE, resulting in an optimum modified bitumen with 10% of LDPE and 4% of HDPE for rutting resistance behaviour. A higher than 4% of HDPE resulted in a lower rutting resistance. Compared to the LDPE, the higher density of ethylene (i.e. HDPE) has better modified the bitumen at low %content while reducing the rutting behaviour at higher %content in the bitumen. Similarly, Dalhat, Al-Abdul Wahhab (2017a) studied bitumen modification at 2, 4, 6, and 8% of bitumen weight using HDPE, LDPE and PP. The study showed relatively little property improvement using 2% content, while the 8% modification resulted in high-viscosity bitumen. Another study by Costa et

al. (2019) used 5% bitumen weight of HDPE plastic, EVA and SBS in the wet method. The study resulted in better rutting resistance of HDPE-modified bitumen compared to unmodified bitumen. While the studies above used virgin bitumen, Leng, Sreeram, et al. (2018b) used 2% PET to modify virgin and RAP-modified bitumen, resulting in a reduced strip, better rutting and fatigue characteristics. The PET also potentially rejuvenated the bitumen.

In the dry mixing method, Awwad, Shbeeb (2007) used 6, 8, 10, 12, 14, 16, and 18% of bitumen weight of LDPE and HDPE. The author stated that the optimum dry method is at 12% plastic modifier of bitumen weight. Instead of using bitumen weight to determine the modifier content, Lastra-González et al. (2016a) replaced 1% of aggregate volume with the plastic waste of PE, PP and PS by dry mix method. PP and PE resulted in similar with 60% higher stiffness and 60% more resistance to plastic deformation than the reference mixtures, with no changes in fatigue performance. A relatively higher plastic content was done by Movilla-Quesada et al. (2019a) using 10% and 20% of waste plastic scrap in dry mixing, resulting in better rutting resistance on higher plastic content. Another study by Almeida et al. (2020a) used 2, 4, 6 and 8% plastic waste by weight of bitumen in the dry mixing method, resulting in better rutting resistance AC mixtures compared to unmodified mixtures.

There were also studies in both dry and wet mixing methods. White, Reid (2019a) and White, Reid (2018a) used the wet and dry method in two separate studies to modify bitumen using recycled waste plastic at 6% of bitumen replacement (dry) and 4%, 6% and 8% of bitumen weight (wet). Both methods improved the fracture and deformation resistance of the modified asphalt mixtures. Meanwhile, El-Naga, Ragab (2019a) used PTP at 2, 4, 6, 8, 10 and 12% of bitumen weight in wet mixing and 10, 11, 12, 13, and 14% in the dry mixing process. The PTP-modified mixtures exhibited higher Marshall stiffness modulus, rutting resistance, and indirect tensile strength. Similarly, Haider et al. (2020) used LDPE and HDPE at 3, 6, 9 and 12% of bitumen weight in dry and wet mixing methods. The study concluded that the wet method performs better than the dry method in the percentage of coating loss, Marshall stability and rutting resistance.

It can be stated from these studies that for various type of plastics, the wet mixing method commonly use modifiers at a range of 2% to 10% of bitumen weight. 2% of plastic contents generally produce low modification effects (Dalhat and Al-Abdul Wahhab 2017a), while

the higher content (4-8%) produces higher rutting resistance property of the modified bitumen, regardless of the plastic type. The workability issue of the modified bitumen starts emerging at around 8 to 10% modification. A higher plastic content than 10% commonly results in a highly viscous bitumen and is considered impractical for mixtures application.

In contrast to the wet method, the dry method can use a plastic modifier higher than 12% of bitumen weight. Some studies used up to 18% (Awwad and Shbeeb 2007) or 20% (Movilla-Quesada et al. 2019a), which improved asphalt mixtures rutting resistance. Finally, these studies concluded that the plastic content of 0 to 10% of bitumen weight is the most suitable range for wet mixing due to viscosity and workability reasons, while >10% is applicable in dry mixing to satisfy the aggregate coating by the plastic modifiers.

2.3.3.3. Mixing method

The wet or dry mixing method in the plastic-modified bitumen or asphalt mixture determines the suitable plastic types, plastic content, and the final modified products. González et al. (2002) successfully modified bitumen using HDPE and LDPE plastic with 1200 rpm blending at 180°C for 6 hours. Using the same polyethylene-family plastic and 150/200 pen bitumen, Fuentes-Audén et al. (2008) blended the material at 180°C in a standard bitumen mixer for <25% of bitumen weight and 'highly viscous substances' mixer for 50%, resulting in a better rutting resistance modified bitumen. A study on similar plastic of LDPE and HDPE by Khan et al. (2016) was conducted using a laboratory mixer at 165°C for two hours. The LDPE and HDPE were ground into powder form of 0.15-0.75mm before the modification. Similarly, Dalhat, Al-Abdul Wahhab (2017a) studied bitumen modification using HDPE, LDPE, and PP. The study suggested 60 minutes of mixing at 180°C for HDPE, 50 minutes at 190°C for PP, and 30 minutes at 160°C for LDPE to successfully modify the bitumen into a homogenous blend and enhanced properties. Meanwhile, Costa et al. (2019) modified the bitumen with HDPE plastic, EVA and SBS using a low-shear mixer of 600 rpm for one hour at 180°C. This method results in satisfying polymer dispersion in the bitumen. A different method has been done by Leng, Sreeram, et al. (2018b) in modifying virgin and RAP-modified bitumen by a high shear mixer at around 150°C for 2 h at a mixing rate of 4000 r/min. A short laboratory wet mixing was conducted by White, Reid (2019a) and White, Reid (2018a), where the pelleted-plastic mixing with 170°C bitumen was only 30 seconds.

In the dry mixing method, Awwad, Shbeeb (2007) added the polyethylene of LDPE and HDPE into 180-190°C heated coarse aggregate. The heated plastic melted and coated the aggregates into polyethylene-textured surfaces. Then, the coated aggregates were used with the bitumen in asphalt mixture fabrications. A similar method was used by Lastra-González et al. (2016a) on PE, PP and PS; Haider et al. (2020) on LDPE and HDPE; Movilla-Quesada et al. (2019a) by mixing the plastic at 150°C for 1 minute; and White, Reid (2019a); White, Reid (2018a) on pelleted waste plastics. These studies concluded improvements in the modified asphalt mixtures compared to the unmodified in various parameters, including coating loss, Marshall stability and rutting resistance. In the use of PTP with a high melting point (300°C), El-Naga and Ragab (2019) heated the aggregates for 2 hours at 250°C before adding PTP to melt and coat the aggregates. Then, the bitumen was added at 140°C into the aggregates to produce the mixes.

These studies were conducted on wet and dry mixing methods. The dry mixing method generally emphasises the coating of the aggregates by the plastic modifier. This coating is achieved by heating the aggregate above the melting point of the plastic (generally 160-180°C), thus, the plastic will melt and coat the aggregates' surface when added. The higher melting point of the plastic, for example, polyethylene terephthalate ($\pm 250^\circ\text{C}$), requires the higher aggregates' pre-heating. The plastic-coated aggregates are expected to have better adhesion with the bitumen and enhance the asphalt mixture properties.

In the wet method, the plastic addition to the bitumen is generally conducted at low viscosity of the bitumen (0.17 – 0.28 Pa.s according to BS EN 12697-35) or around 160-190°C depending on the pen number. There are commonly two types of mixing, low-shear mixing and high-shear mixing. Even though there is no exact definition of the shear mixing speed, the 'low shear' term is commonly used for mixing speed at 250, 500, 800 or other 'hundreds' rpm, while high shear mixing uses 2500, 4000 or even 5000 rpm. The high-speed shear mixing is conducted relatively at a shorter duration (Dalhat and Al-Abdul Wahhab 2017a), for example, 30 minutes, 45 minutes, or 60 minutes. Meanwhile, the low shear speed mixing can use 2 hours or even 6 hours (González et al. 2002) to achieve the desired homogenous bitumen-plastic blends.

2.3.4. Comparison to other polymer modification

Bitumen modification with polymer generally incorporates two main polymer types: elastomer and plastomer. Examples of elastomers are styrene–butadiene–styrene (SBS), styrene–isoprene–styrene (SIS), and styrene–ethylene/butylene–styrene (SEBS). Meanwhile, the commonly used plastomers are polyethylene (PE), polypropylene (PP), ethylene–vinyl acetate (EVA), ethylene–butyl acrylate (EBA), atactic polypropylene (APP) and isotactic polypropylene (IPP) (Fawcett et al. 1999; Fawcett and McNally 2000; Polacco et al. 2005b, 2006a; Zhu, Birgisson, and Kringos 2014a).

Elastomer has the advantages of improving elastic response and increasing stiffness, rutting and fatigue resistance. However, elastomers are relatively high-cost, have storage instability problems, and are incompatible with some bitumen. Styrene–butadiene–styrene (SBS) is the most popular elastomer in bitumen modification. SBS has repeatedly been reported to have good dispersibility or solubility in bitumen and resulted in excellent SBS-modified bitumen properties. However, the SBS can also have compatibility problems when applied to bitumen with insufficient maltenes components. This is because the SBS elastomer competes with asphaltene in absorbing maltenes of bitumen, which can lead to phase separation (Airey 2003). In this case, the appropriate amount of aromatic oils can be added to improve the SBS and bitumen compatibility. Another problem of SBS-modified bitumen is its performance deterioration due to heat, oxidation and ultraviolet (UV) light (Li et al. 2010), commonly occurring in aged bitumen. The observed shift towards more soft and viscous aged SBS bitumen can be attributed to the SBS copolymer degradation (Airey 2003). Despite the disadvantages, SBS as a polymeric elastomer is popularly accepted as a bitumen modifier.

Another polymer group type is plastomer. Plastomer has the advantages of good high-temperature properties, relatively low cost, and high resistance to rutting. Although, it also has the disadvantages of poor storage stability and limited enhancement in low-temperature properties (Zhu, Birgisson, and Kringos 2014b). Polyethylene, including its family members: high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE), is one of the plastomer that is widely studied as a bitumen modifier. These materials enhance bitumen properties and have the benefits of being widely available at a relatively low cost. In addition, using a recycled product of

this material, i.e. recycled waste plastic, can also be considered a sustainable and environmentally friendly act. However, due to its non-polar nature, polyethylene has compatibility issues with bitumen, leading to immiscible behaviour, limited elasticity improvement and storage stability problems (Polacco et al. 2005a, 2006b).

2.3.5. Storage stability of plastic-modified bitumen

Due to compatibility and different density between bitumen and polymer modifiers, the phase separation between these two materials in the polymer-modified bitumen is one of the main drawbacks. In plastic-modified bitumen, due to plastic generally having a lower density (0.91-0.97 g/cm³) than pure bitumen (1.01-1.05 g/cm³), there is a phase separation between the materials when the modified bitumen is stored in high temperature with no stirring. The LDPE's non-polar nature also affected the material to be immiscible in the bitumen blends that drove the separation (Polacco et al. 2005a). The separation occurs with the particles of plastic polymers tend to coagulate and float on top of the hot bitumen, resulting in a different proportion of polymer blend between the upper and bottom part of the modified bitumen.

According to (Kalantar et al. 2012b), blends of bitumen and polymer may be incompatible, slightly compatible, or compatible with bitumen. Incompatible polymer results in a heterogeneous mixture where the particles are practically separated from the bitumen. In this blend, the modified bitumen does not have enough cohesion and ductility due to the polymer affecting the chemical equilibrium of the bitumen. Slightly compatible blends of bitumen and polymers are achieved under special mechanical, chemical and thermal processes. This type of compatibility usually requires a certain temperature, duration, and high shear mixing to produce the intended homogenous modified bitumen. In a fully compatible polymer, the homogenous and physically stable blends of bitumen and polymer are achieved by conventional mixing techniques. This type of blend is commonly undesirable as bitumen's physical properties may or may not be improved. In the case of purely compatible polymer and bitumen, the modified bitumen properties are almost the same as the initial bitumen (Brion Brule, Bernard., 1986) thus, partial miscibility or 'slightly compatible' of bitumen and polymer are preferred compared to total miscibility of these materials (Lesueur 2009).

Compatibility and phase separation are directly related; higher compatibility produces lower phase separation and vice versa. Therefore, polymer-modified bitumen is preferable to have good compatibility to avoid phase separation and to improve the physical properties. However, phase separation may still happen in polymer-modified bitumen, especially during storage at high temperatures without stirring.

Some studies tend to increase the storage stability of polyethylene-modified bitumen by adding some reactive copolymer such as glycidylmethacrylate (Polacco et al. 2005a) to increase reactivity with bitumen. However, there was no sufficient improvement in the stability or homogeneity of the PE-bitumen blends. Padhan, Sreeram (2018) used trans-polyoctenamer and sulphur to increase the reactivity of polyethylene and bitumen, which led to storage stability increments. However, adding the reactivator is only suitable for low polymer content (less than 2%). Improving the stability of polyethylene-modified bitumen is difficult due to the differences in the molecular weight and structure, density, and viscosity of the blends' constituents (Giavarini et al. 1996). Besides the materials' nature, the blending procedures are also essential to bitumen stability (Lu and Isacson 1997).

2.3.6. Polymer dispersion and bitumen structural changes

The dispersion of the polymer in the bitumen is related to the compatibility of both materials. Extensive swelling can occur at high bitumen and polymer compatibility, where the polymer-rich phase forms as the matrix and the asphaltene-rich fraction becomes the dispersed phase. This 'inversion of phase' phenomenon is well known to be highly desirable in the modified bitumen as it produces an enhanced polymer-modified bitumen. However, compatibility is also needed to be at some level where it does not make the polymer entirely dissolved in the bitumen, resulting in a non-improved modified bitumen (Giuliani et al. 2009).

One of the most common ways to understand the compatibility of a polymer with bitumen is by using fluorescence or optical microscopy observation. The microscopy visualisation results of the blend microstructure can be used to understand the different performed polymer-modified bitumen. Figure 2.11 presents 4% SBS-modified bitumen produced on compatible and incompatible bitumen. The compatible bitumen and polymer system resulted in a homogenous blend that can be observed in microscale

observation (a). The opposite is a heterogeneous blend (b) that shows a different phase of material in the blend, resulting in a different rheological property of the product compared to the homogenous one.

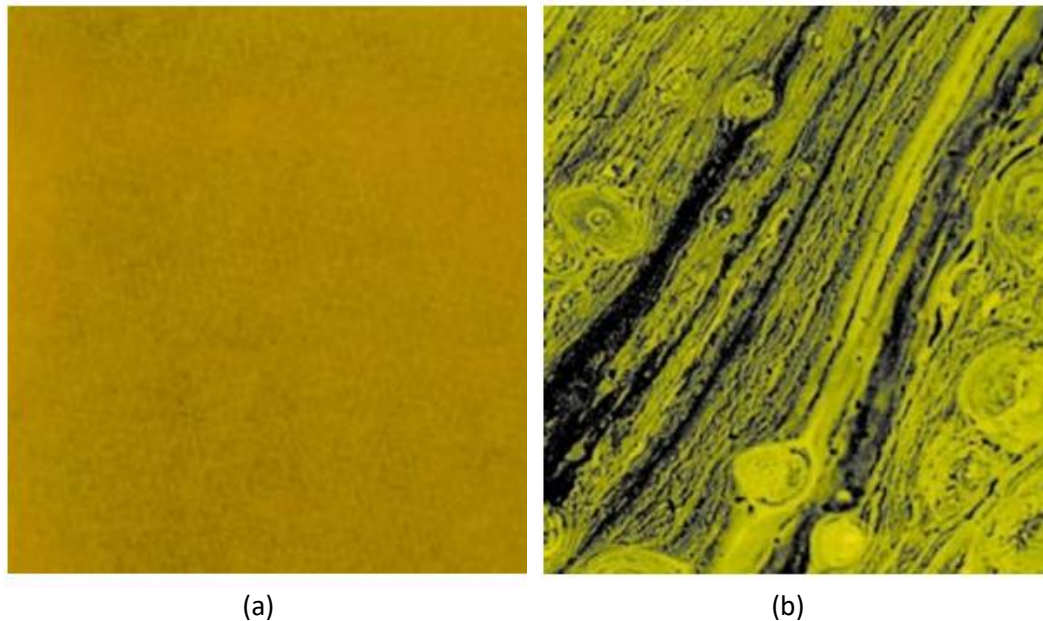


Figure 2. 11: 4% SBS on (a) compatible system and (b) incompatible system (Becker et al. 2001)

The immiscible condition can also happen in a visually homogenous blend, as stated by (Polacco et al. 2005a), as shown in Figure 2.12. The author used polyethylene-based polymer modifiers. The study noted that some modifiers resulted in a homogenous product, but the polymer particles were not blended with the bitumen. Figure 2.12 shows how the particles are separated from each other within the bitumen phase, producing a well-dispersed particle in the modified bitumen. Although the product (modified bitumen) is visually homogenous, the bitumen and the modifiers are separated, and this condition can only be seen under microscopy. In this case, the modified bitumen's performance is commonly changed insignificantly.

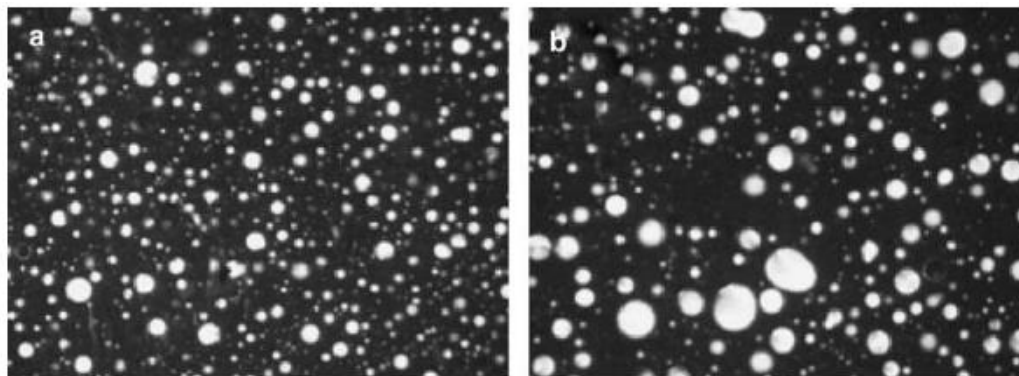


Figure 2. 12: (Polacco et al. 2005a) presented various polyethylene-modified bitumen dispersion under fluorescence microscopy

2.3.7. Differential Scanning Calorimeter

Differential scanning calorimeter is widely used in the materials' thermal analysis, a method to study the materials' behaviour as a function of temperature or time. This method measures the energy a material releases during cooling or absorbed during heating and is widely used in various materials and a broad range of temperatures. By using this method, the glass transition temperature (T_g), melting point (T_m), the heat of melting (H_f), crystallisation temperature (T_c), the heat of crystallisation (H_c), and heat absorbed or evolved during cure or decomposition reactions as typically shown in Figure 2.13 can be measured.

In the transition process, a melting solid material into a liquid state will absorb energy (endothermic). On the other hand, the material will transfer out excess energy (exothermic) in the crystallisation process. The DSC instrument measures the differences in absorption or extraction energy compared to the reference that defines the test material's thermal characteristics. In the process of material thermal state transition, the area under or upper the curves can be measured to determine the number of heat of crystallization, the melting, or the degradation process (Leyva-Porras et al. 2019).

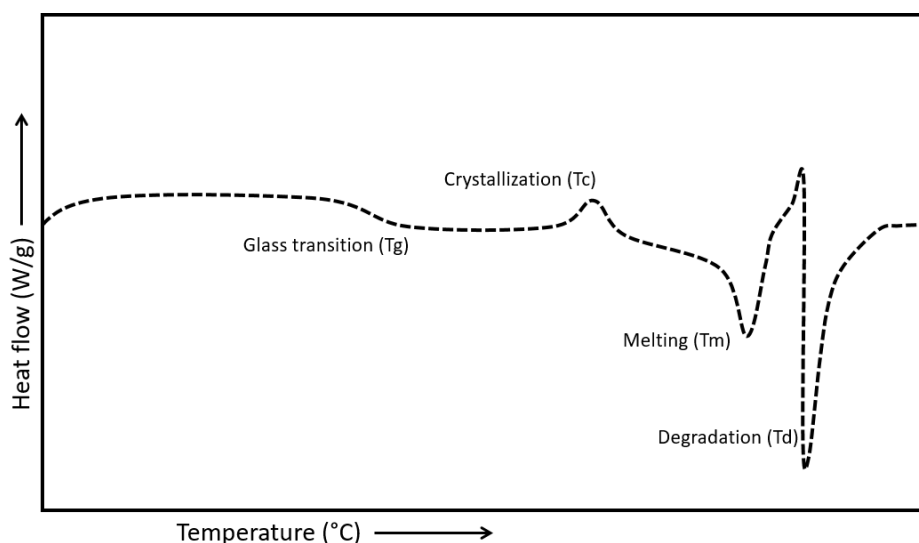


Figure 2. 13: Typical DSC graph of material transition

In the application of understanding the bitumen modifiers, this method can be used to measure the melting point of the materials that can be used to determine the blending temperature with the bitumen. Since every material or polymer has specific thermal transition characteristics, this method can also be used to differentiate the bitumen modifiers.

2.4. Plastic ageing, degradation and recycling

The term recycled polyethylene (or recycled plastic in general) refers to plastic made from previously used plastic products. This previously used product could be formed from virgin plastic or recycling of other previously used products. This means recycled plastics have faced various ageing or deterioration factors that might degrade their physical integrity (Ravve 2012).

2.4.1. Plastic ageing and degradation

The deterioration of plastic as a polymeric material depends not only on its previous functionality but also on the environment and natural conditions they interacted with, such as temperature, rain, atmospheric pollution, thermal cycling, solar radiation, the oxygen content of air, humidity, ionic radiation, hydrolysis and mechanical shear (Ravve 2012; Satoto et al. 1997). These conditions mainly occurred on plastic subjected to outdoor exposures. Among these external natural factors that degradate plastic polymer, solar radiation (ultraviolet light) is believed to be the leading cause (Farrukh S. Qureshi et

al. 1990; La Mantia 1996). However, even though solar radiation initiates the degradation, the temperature is a more critical factor in the further steps of the degradation process (Satoto et al. 1997).

Solar or UV radiation can break the plastic molecular bonding and induce photo oxidation that degrades the material (Satoto et al. 1997). The solar radiation initiates the degradation process, and the following auto-oxidation further deteriorates the plastic material. A higher temperature can accelerate this process and is strongly affected by the air's oxygen level. The degradation propagation can be distinguished by the formation of carbonyl structure (Guadagno et al. 2001; Satoto et al. 1997) as the result of the oxidation process. Without the presence of oxygen, plastic degradation is relatively minimal. For example, polyethylene is a stable material under UV exposure. This is because, after the chain scission by the UV, the chain branching, chain termination and ageing propagation are very slow without the oxidation process. It is also believed that the degradation mechanism is mostly occurred in the amorphous region without changing in the crystalline part of the plastic. This explains the phenomenon of crystallinity increase that believed as the result of chain rearrangement of the amorphous region of the plastic after the scission by photo degradation (Satoto et al. 1997).

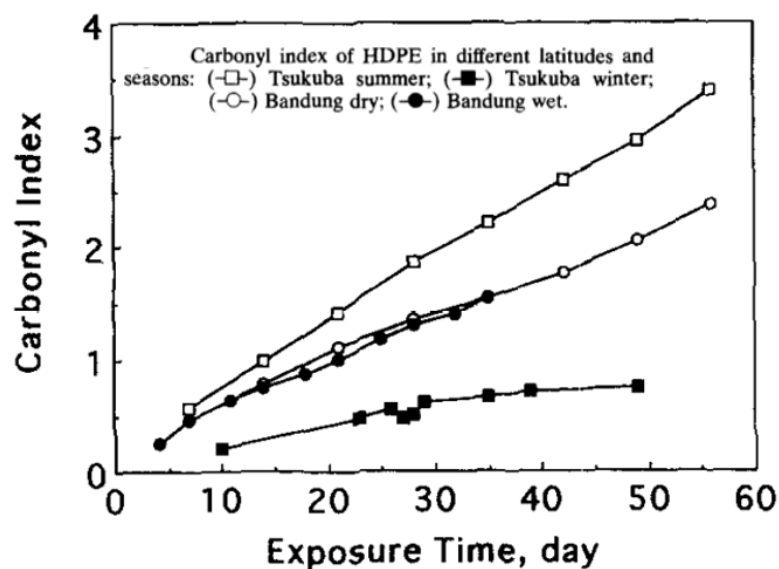


Figure 2. 14: Carbonyl index of HDPE aged in different seasons and latitudes (Satoto et al. 1997)

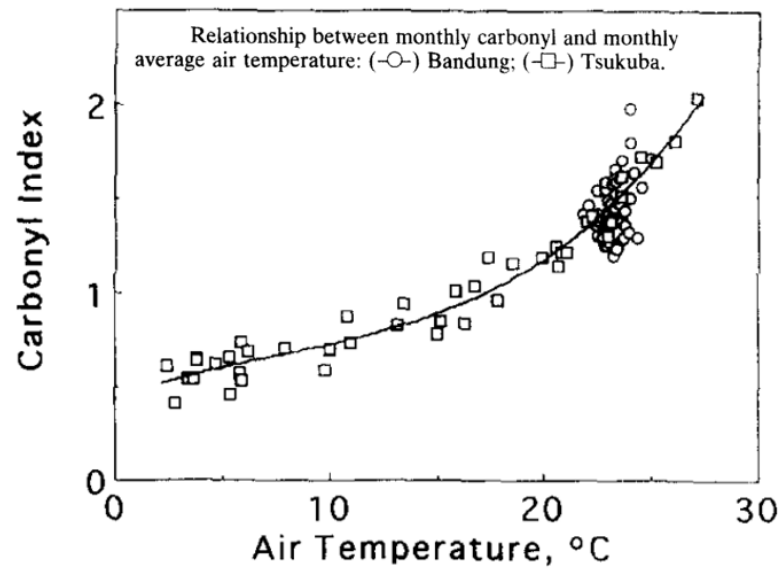


Figure 2. 15: The temperature effect on carbonyl index (Satoto et al. 1997)

Figure 2.14 shows that the HDPE plastic presented different carbonyl indexes when aged at different seasons and latitudes. The graph indicates that the ageing indicator is unaffected by the wet and dry seasons but significantly different in winter and summer. The carbonyl index shows dependencies on natural temperature during the summer and winter. The higher temperature results in higher oxidation and, thus, the carbonyl index. A more evident air temperature correlation to the carbonyl index as an indication of oxidation can be seen in Figure 2.15 where the average air temperature has significantly affected the carbonyl index.

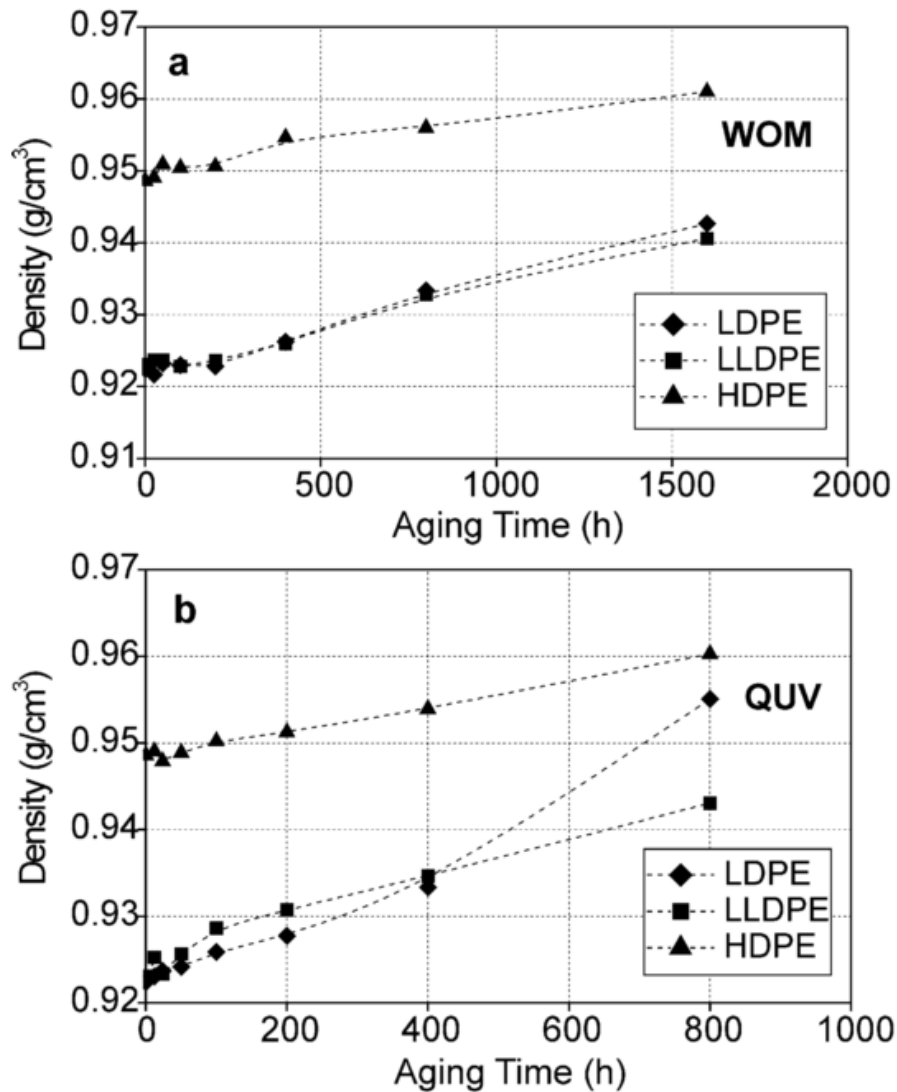


Figure 2. 16: Variation in density changes of different polyethylene versus artificial ageing time (Gulmine et al. 2003)

The various chemical reaction and processes in plastic ageing resulted in a higher molecular weight of the material (Gulmine et al. 2003). This is due to the incorporation and bonding of oxygen with high molecular weight into the polymer's chain structure during oxidation. This condition is identifiable from the increased formation of carbonyl structure (Guadagno et al. 2001). Another cause is the rearrangement of the truncated chain of the amorphous region into a more arranged crystalline structure. This branching rearrangement resulted in more dense particles with higher molecular weight (Satoto et al. 1997) (Gulmine et al. 2003).

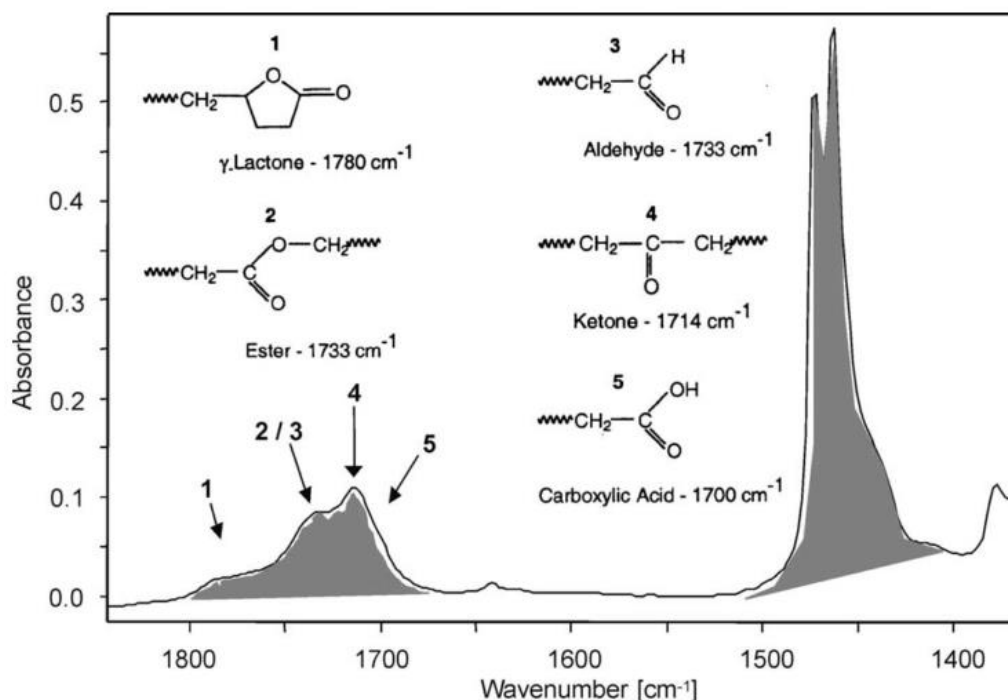


Figure 2. 17: The various carbonyl band from the ATR-FTIR spectrum of aged LDPE
(Gulmine et al. 2003)

The density increase of polyethylene plastic due to ageing has been reported by Gulmine et al. (2003). The study used two artificial natural ageing equipment, Weather-Ometer (WOM) and Weathering Tester (QUV), on HDPE, LLDPE and LDPE plastics. Figure 2.16 shows the density increase of LDPE, LLDPE and HDPE from WOM and QUV equipment. The plastic's density increase has been shown for all specimens and weathering equipment, which is believed to result from increased crystallinity, crosslinking reaction, and the incorporation of oxygen that produce a heavier polymer. As shown in Figure 2.17, the ATR-FTIR test from the study also presented the various carbonyl groups formed by the polymer oxidation process, which was also previously stated by Komitov et al. (1989). Furthermore, the study also stated that LDPE had shown greater instability against ageing, followed by LLDPE and HDPE.

2.4.2. Plastic recycling

Recycled plastic polymer generally suffers two types of degradation: during the lifetime and mechanical degradation during the recycling process (La Mantia 1996). Degradation during the lifetime (or ageing), as explained in the previous subchapter, is because of factors before the recycling process. Meanwhile, mechanical degradation is caused by a

combination of heat and mechanical shear in the recycling process (Beyler and Hirschler 2002).

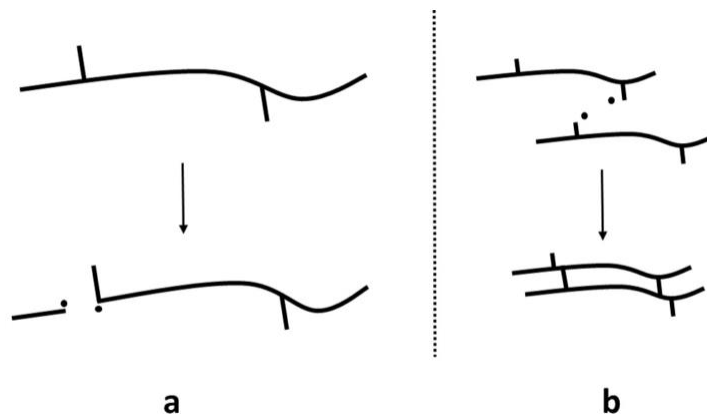


Figure 2. 18: (a) Chain scission and (b) crosslinking branching (Ragaert et al. 2017)

Similar to ageing due to environmental or natural conditions, the mechanical degradation of plastic includes the process of chain scission and chain branching (Ragaert et al. 2017). Chain scission mostly occurs in the polymer's main structural chain and reduces the polymer's molecular weight and properties. The scission produces truncated structures or free radicals that can undergo chemical reactions such as branching or crosslinking. Crosslinking is the bonding between the main truncated structural chain or free radicals that result in a denser structure, thus increasing the molecular weight. Figure 2.18 illustrates the process of chain scission and crosslinking of the polymer. According to Pinheiro et al. (2004), polyethylene is an example of a plastic polymer more prone to chain branching due to thermal-mechanical degradation. Another effect of thermal-mechanical degradation is the changes in mechanical, rheological, and thermal properties, such as melting temperature and crystallization, and appearances or physical properties, such as surface properties and colour (Ragaert et al. 2017).

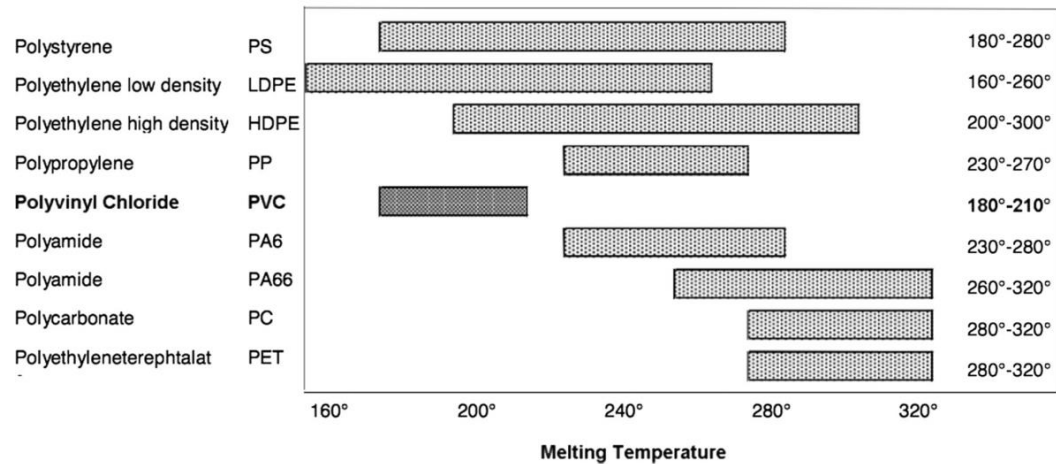


Figure 2. 19: Processing temperatures for common plastics (Moller and Jeske 1995)

Plastic recycling is also common to have a mixed type of plastic waste. Figure 2.19 shows various plastics' processing temperature range mainly related to their melting point. The differences between the melting point and processing temperatures in the mixed recycled plastic can affect the lower melting plastic components due to overheating. This condition can reduce the final properties of the recycled product (Ragaert et al. 2017).

Because waste or post-consumer plastics have experienced ageing and degradation, it is a common practice to add additives in the recycling process for various purposes. For example, heat stabiliser additives are generally added because most of them have been 'consumed' during the lifetime or the recycling process itself; thus, the plastic becomes more prone to heat degradation (Ulutan 2003). Other additives can also be added to facilitate recycling, including impact modifiers (restoring properties), reinforcements, pigments, and fillers. These additives can help to enhance the properties of plastic recovered from waste (Murphy 2001).

2.5. Bitumen performance characterisation

Durable and long-lasting satisfactory traffic services are always expected from road pavements. The performance of asphalt pavement is highly reflected from the selected aggregate properties and the chosen bitumen performance that bonds in the asphalt mixtures. Various bitumen modifications have been studied to improve its properties, thus producing a better asphalt pavement. Therefore, continuous development on the testing method of bitumen characterisation to reliably predict asphalt performance has also been demanded. These tests must be suitable for a neat and polymer-modified

bitumen by understanding its fundamental engineering properties (Airey and Brown 1998) (Airey 2002). For this purpose, the dynamic shear rheometer (DSR) is usually used to fundamentally understand bitumen's viscous and elastic properties at high and intermediate service temperatures. The DSR can assess the physical and rheological data required to characterise bitumen performance that cannot be achieved by using traditional empirical tests, such as Fraass breaking point for low temperature, capillary viscosity for intermediate temperature and softening point for high temperature. Also, the traditional empirical methods do not sufficiently provide enough information on bitumen's physical and rheological data, especially for polymer-modified bitumen, because of its more complex response (Subhy 2017).

2.5.1. Dynamic Shear Rheometer (DSR)

Dynamic Shear Rheometer (DSR) has been widely used in bitumen studies to understand the viscoelastic response (stiffness, viscosity, phase angle) at specified loading and temperature setting. Depending on the need, different loading states can be applied by using DSR, such as oscillatory (sinusoidal) or creep and relaxation mode. There are generally two testing modes in the DSR use: controlled stress and strain. In the controlled stress mode, a fixed torque load is applied to the bitumen, producing a magnitude of shear stress on top of the bitumen via the oscillating plate or spindle. In this mode, the magnitude of shear strain is measured. Creep tests are an example of stress-controlled mode applications. In strain-controlled mode, the applied load is a small magnitude of strain within a linear viscoelastic range, and the resulting stress is measured. The sinusoidal load tests are an example of a strain-controlled mode. Figure 2.20 shows the schematic illustration of the DSR specimen, base (bottom) plate, spindle (top) plate and the rotation/oscillation of the applied loads.

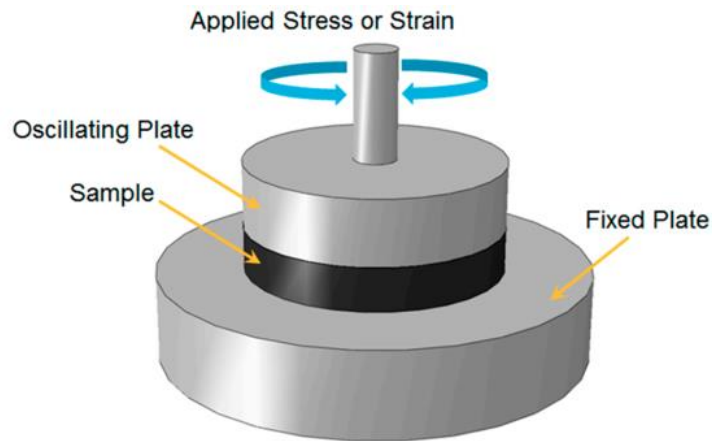


Figure 2. 20: The schematic illustration of DSR testing (Majidi et al. 2016)

The bitumen sample is sandwiched between the fixed bottom plate and the oscillating spindle/top plate. The data measurement of DSR is based on the torque and angular rotation of the spindle. The angular rotation from applied stress at creep load or the stress magnitude from applied strain at oscillation load is measured and computed to give bitumen rheological data.

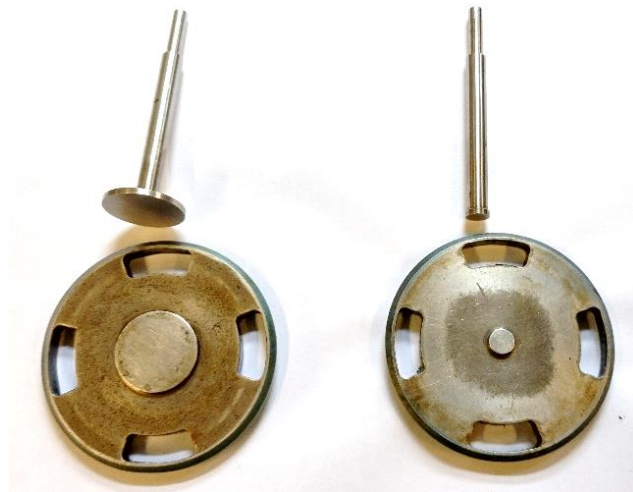


Figure 2. 21: The pair of 25mm and 8mm size spindle and base plate

The DSR data calculation depends on the spindle size (or sample diameter) and the gap between two parallel plates (or sample height). In the bitumen testing, there are two most common spindle sizes: 8 mm with a 2 mm testing gap and 25 mm with a 1 mm testing gap, depending on the testing temperature and the expected stiffness of the bitumen. Figure 2.21 shows the example of the spindle (top plate) and bottom plate (base plate)

with 25mm and 8mm in size. With this configuration of spindle and base sizes of the DSR, the stress, strain and complex modulus are calculated based on these measurements:

$$\tau = \frac{2T}{\pi r^3} \quad \text{Eq. 2. 1}$$

$$\gamma = \frac{\theta r}{h} \quad \text{Eq. 2. 2}$$

$$G^* = \frac{\sigma_{max}}{\gamma_{max}} \quad \text{Eq. 2. 3}$$

Where:

- τ = maximum shear stress (N/mm²)
- T = torque (Nm)
- r = radius of the parallel disks (mm)
- γ = maximum shear strain
- θ = deflection angle (radians)
- h = gap between parallel plates (mm)
- G^* = complex modulus

The above equations suggest that the shear stress τ and shear strain γ are dependent on the radius of the parallel plate r and the gap between the lower plate and the oscillating plates h . For this matter, different parallel plates (spindle size) are used in the bitumen DSR testing. On a stiffer bitumen or at a low temperature, a smaller spindle with a higher gap is generally preferable, while a softer bitumen or higher temperature is suitable for a bigger spindle with a smaller gap. Strategic Highway Research Program/SHRP-A-369 (Anderson et al. 1994) suggested the use of spindle size and the gap as follows:

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

It is possible to use the same testing geometry for various bitumen and a wide range of temperatures. However, the limitation of precision results should be noted due to potential compliance errors (Airey 2002). In addition, for some polymer-modified bitumen, such as rubberised bitumen, the potential presence of undissolved particles may result in an unreliable measurement when using a small (1 mm) gap (Subhy, Lo Presti, and Airey 2016). Therefore, a larger gap size minimum of three times higher than the

maximum dimension should be used as a rough practical rule for this bitumen (Presti 2011).

2.5.2. Dynamic Mechanical Analysis (DMA)

The term dynamic mechanical analysis refers to studying and understanding a material's rheological properties. In the bitumen study, this method widely uses a dynamic shear Rheometer (DSR) as the instrument. The use of dynamic mechanical analysis on the bitumen results in different rheological properties on different load rates and testing temperatures. At lower temperatures ($<60^{\circ}\text{C}$), bitumen rheology works as a function of temperature and loading rate, while at higher temperatures ($>60^{\circ}\text{C}$), its properties are more dependent on the temperature (Airey 1997), as illustrated in the Figure 2.22.

In the presence of polymer in the modified bitumen, this phenomenon becomes even more complicated where the temperature and loading rate affect the mechanical properties at a temperature below 60°C (Airey 1997) (Subhy 2017). In this case, a wider range of temperatures and loading times are needed to understand and predict the bitumen rheological performance (Subhy 2017).

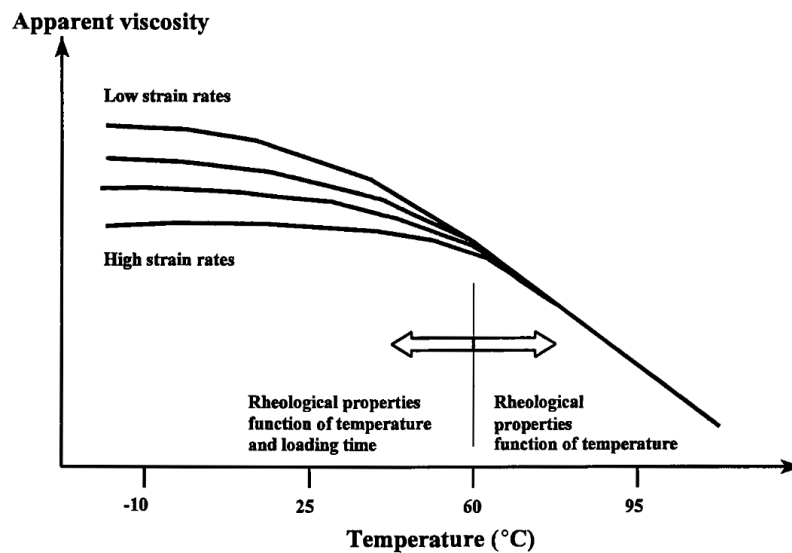


Figure 2. 22: Rheological behaviour of bitumen (Airey 1997)

The dynamic mechanical analysis utilises oscillatory stress or strain load of the DSR to the bitumen within the linear viscoelastic region. With the sandwiched bitumen specimen oscillate-loaded with a specified angular loading frequency ω , the strain can be presented as follows:

$$\gamma_t = \gamma_0 \sin \omega t \quad \text{Eq. 2. 4}$$

Where:

- γ_t = dynamic oscillating shear strain
- γ_0 = peak shear strain
- ω = angular frequency (rad/sec) = $2\pi f$, with f = frequency (Hz)
- t = time (seconds)

With the applied load, the bitumen responds with oscillatory stress with some delay

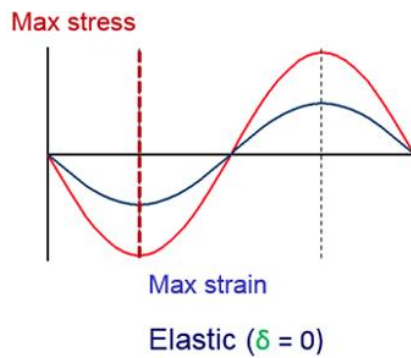
defined as phase angle δ , which is presented in the equation as follows:

$$\sigma_t = \sigma_0 \sin(\omega t - \delta) \quad \text{Eq. 2. 5}$$

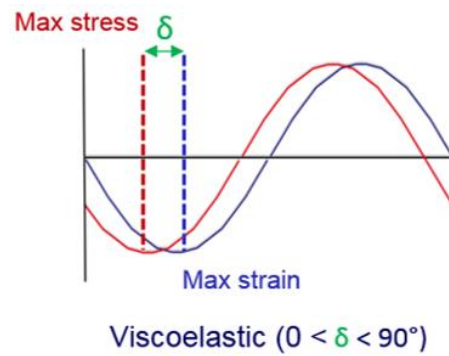
Where:

- σ_t = dynamic oscillating shear stress, Pa
- σ_0 = peak shear stress, Pa
- δ = phase angle, degree

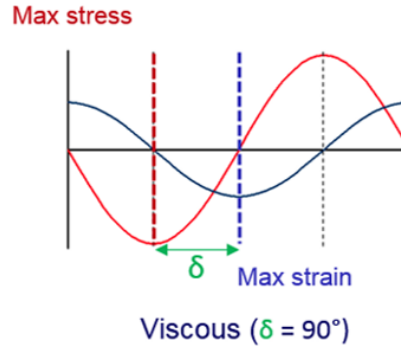
The delay between the applied load and the recorded response, in this case, is because bitumen is a viscoelastic material. In the moment of applied load, if the load is below its yielding point, a purely elastic material will respond instantaneously with no delay, thus resulting in a 0° phase angle. On the other hand, a purely viscous material will have a 90° phase angle which represents an ideal viscous flow behaviour.



(a) ideally elastic material



(b) viscoelastic material



(c) ideally viscous material

Figure 2. 23: Schematic representation of dynamic mechanical analysis (Liepsch 2016)

In a sinusoidal stress load pattern, the sinusoidal response (strain) of purely elastic, a viscoelastic, or purely viscous material can be illustrated as a non-shifting (0°), a 0° to 90° shifting graph, or 90° shifting graph next to the original load graph as illustrated in the Figure 2.23 (a), (b) and (c) respectively.

From the oscillation tests, the complex shear modulus is calculated as the ratio of the stress response to the applied strain. The complex shear modulus is the main parameter that contributes to the material's rheological or viscoelastic properties. As a viscoelastic material, bitumen's rheological response to the applied strain are highly dependent on temperature and the loading time with a large amount of delayed elasticity (Airey 1997). As defined as the ratio of the oscillation stress load to the strain response, the complex shear modulus G^* is defined as follows:

$$G^* = \frac{\sigma^*}{\gamma^*} = \left(\frac{\sigma_0}{\gamma_0} \right) \cos \delta + i \left(\frac{\sigma_0}{\gamma_0} \right) \sin \delta \quad \text{Eq. 2. 6}$$

With the $\left(\frac{\sigma_0}{\gamma_0} \right)$ is the absolute value or the norm of the complex shear modulus or complex modulus, which is defined as the ratio of the peak stress to the peak strain, $|G^*|$, Pa.

The components of the complex shear modulus, i.e. storage modulus and loss modulus, can be described as the following equations and definitions (Airey 1997):

- The storage modulus G' indicates the amount of energy that is stored and released elastically in each oscillation, thus also named as elastic modulus or elastic component of the complex modulus, that can be expressed as:

$$G' = |G^*| \cos \delta \quad \text{Eq. 2. 7}$$

- The loss modulus G'' also named as viscous modulus or viscous component of the complex modulus, is the imaginary part or out-of-phase component of the complex modulus that can be calculated as follows:

$$G'' = |G^*| \sin \delta \quad \text{Eq. 2. 8}$$

The magnitude of the norm of the complex modulus is defined as the square root of the sum of the square of loss modulus G'' and storage modulus G' or can be expressed as follows:

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \quad \text{Eq. 2. 9}$$

Figure 2.24 illustrates the trigonometrical concept of complex modulus G^* and its components: elastic modulus G' and viscous modulus G'' .

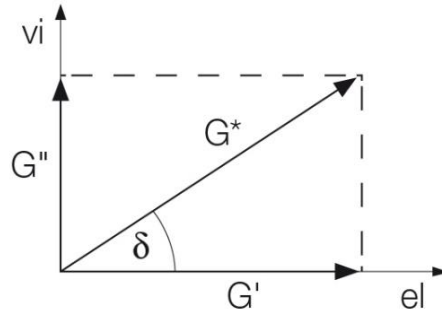


Figure 2. 24: Complex shear modulus and its components

The ratio of the loss modulus (viscous component) to the storage modulus (elastic component) of the complex modulus is known as the tangent of the phase angle. The trigonometrical correlation between the parameter results equation below:

$$\tan \delta = \frac{G''}{G'} \quad \text{Eq. 2. 10. Therefore} \quad \delta = \tan^{-1} \left(\frac{G''}{G'} \right) \quad \text{Eq. 2. 11}$$

Bitumen rheological behaviour is subject to temperatures and loading frequencies. At a very low temperature and high loading frequency, bitumen behaves like a solid or the elastic component is dominant. At this point, the measured phase angle will be low and tend to approach the Figure 2.23 (a) condition. On the other hand, at high temperatures and low frequencies, the viscous component is dominant. At this condition, the bitumen phase angle will be measured high, and the bitumen will behave like a viscous fluid.

2.4.2.1. Linear Viscoelastic (LVE) Region

To ensure the dynamic viscoelastic response of the tested bitumen are influenced only by temperature and loading time, not by the magnitude of the applied strain, the dynamic

test must be performed within the linear viscoelastic (LVE) region. The linear viscoelastic region is a small strain limit that can be identified by using strain sweep tests, where the complex modulus is higher than 95% or its initial or maximum value, according to SHRP. Different bitumen stiffness results in a different range in this region, as the increasing stiffness of the bitumen decreases the strain limit. As the bitumen stiffness increases at a lower temperature, small strain boundaries must be applied and vice versa for higher temperature tests.

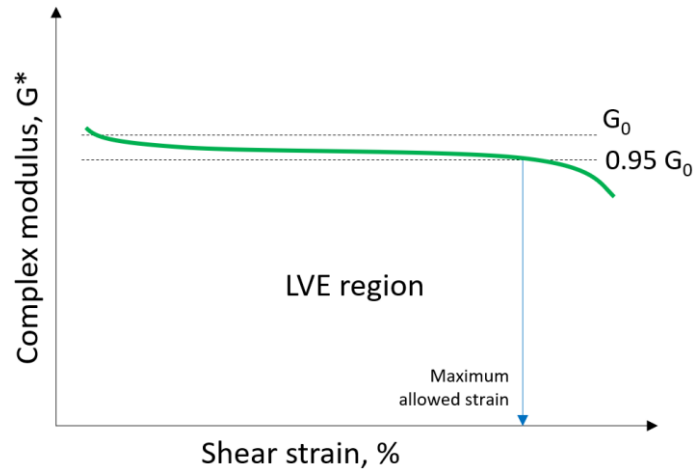


Figure 2. 25: The LVE region from the strain sweep test

The typical LVE region from the strain sweep test, where the complex modulus is slowly decreased as the strain amplitude is gradually increased at the fixed frequency, is shown in Figure 2.25. Regarding the SHRP definition, the graph shows the 95% complex modulus decrease is defined as the boundary of the LVE region. SHRP also suggested the LVE stress and strain limits for neat bitumen as a function of complex modulus as following equations:

$$\gamma = 12.0/(G^*)^{0.29} \quad \text{Eq. 2. 12}$$

$$\tau = 0.12 (G^*)^{0.71} \quad \text{Eq. 2. 13}$$

(Airey and Rahimzadeh, 2004) used five different bitumen to measure the complex modulus and added the LVE strain limit criterion based on the SHRP equation to the complex modulus vs LVE strain limit, as shown in Figure 2.26. From the plot, it can be stated that a maximum of 1% of strain level is assured to be within the LVE region.

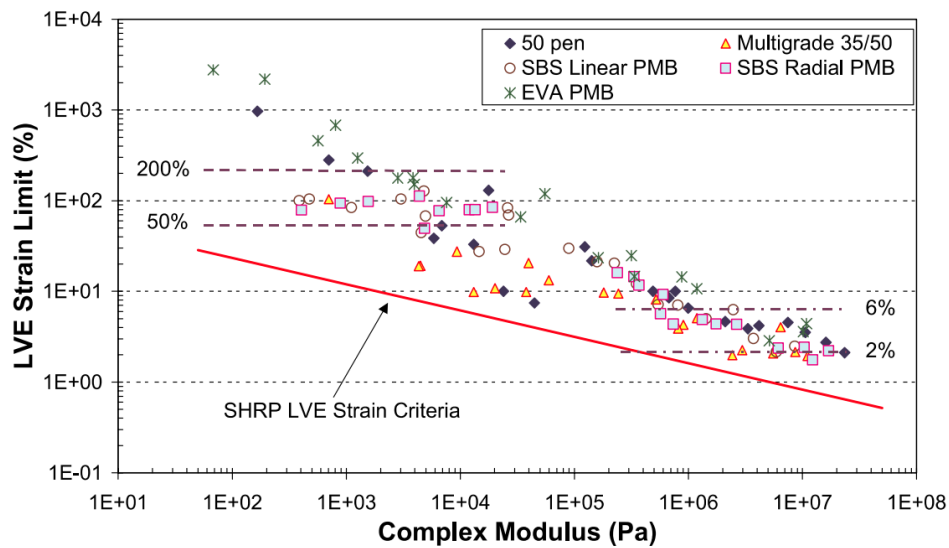


Figure 2. 26: Linear viscoelastic strain limits as a function of complex modulus (Airey and Rahimzadeh 2004b)

2.4.2.2. Representation of the DMA results

The dynamic tests of the bitumen in dynamic shear rheometer generate a large amount of valuable data that can be presented in plots or diagrams for further analysis and interpretation. Diagram and data plotting that are generally represented are:

- Isochronal plots

Bitumen viscoelastic behaviour is a function of temperature and time. Isochronal plots present viscoelastic data, such as complex modulus, over a range of temperatures at a fixed frequency. By using this plot, the bitumen viscoelastic behaviour's susceptibility to temperature can be interpreted by comparing of phase angle or complex modulus at different temperatures and fixed loading frequency.

- Isothermal plots

An isothermal plot is a plot of a viscoelastic parameter, such as complex modulus or phase angle, in the function of frequency at a fixed testing temperature. In this plot, by comparing the complex modulus or phase angle to loading frequency at the specific temperature, the bitumen's viscoelastic behaviour dependencies to time or loading frequency can be analysed. However, the dynamic tests of the bitumen are usually only undertaken over a limited time range. For further analysis over a wider range of loading time, Time-Temperature Superposition (TTSP) method is usually used.

- Cole-Cole diagram

Cole-Cole diagram is simply a plot of bitumen the loss (viscous) modulus G'' versus storage (elastic) modulus G' . This graph represents the viscoelastic balance of the bitumen without incorporating frequency and/or temperature into consideration.

- Black diagram

The Black diagram is a plot of complex modulus versus phase angle. This diagram plots the viscoelastic data over a wide range of frequencies and temperatures. In this diagram, the frequency and/or temperature are not presented, the TTSP method is not required, and all dynamic test data can be plotted in one graph. Many useful interpretations can be obtained from the Black diagram, such as the time-temperature equivalency on a smooth curve, a disjointed curve as an indication of a breakdown on the TTSP, the presence of high polymer modification, a high asphaltene structured bitumen, or a high wax content bitumen (Airey 1997).

- Master curves

A master curve is a representation of shifted complex modulus or phase angle data at different temperatures with logarithmic frequency at the axis to form a smooth continuous curve. In the case of structural changes with the temperature of the bitumen due to the presence of waxy, highly structured 'GEL' type, or polymer-modified bitumen, there might be a break of smoothness of the master curves (Airey 1997). Master curves are very useful representations, as the viscoelastic behaviour of the bitumen can be studied over an expanded range of loading frequencies obtained from the shifted isothermal plots. The TTSP method is usually used in constructing the master curves.

2.4.2.3. Time-Temperature Superposition (TTSP)

Time-Temperature Superposition principles were introduced after studies on viscoelastic properties of bitumen have concluded that there are interrelationships between temperature and loading time or frequency. Because the viscous response of bitumen is strongly temperature dependent, while elastic behaviour has an insignificant temperature effect, the influence of frequency and temperature can be separated using the time-temperature superposition principle (Airey 1997). By multiplying the loading times by a shift factor, the viscoelastic behaviour of binders at a specified temperature over a range of loading times can be equivalent to its behaviour tested at different temperatures. Therefore, viscoelastic measurements such as complex modulus G^* and phase angle δ from different testing temperatures can be shifted to a reference temperature to produce

a continuous curve at a reduced frequency or time scale known as a master curve. Bitumen are termed thermo-rheologically simple when their viscoelastic response over a range of temperatures and frequencies can be reduced to a smooth master curve (Airey 1997).

At low temperatures and high frequencies, bitumen stiffness approaches a horizontal asymptote, as illustrated in Figure 2.27. The graph illustrates how the increase in temperature from T_0 to T_1 produces a lower viscosity by a factor of $\log a(T)$. The viscous asymptote from new temperature T_1 lies below T_0 at an amount of $\log a(T)$, while the elastic asymptote is negligibly changed during the temperature rise. This results in a pair of a curve that has a distance of horizontal shift at an amount of $\log a(T)$, along the log frequency axis. In the condition where the changes in temperature cause a shift of the modulus curve and its asymptote at the same distance of $\log a(T)$, as illustrated in Figure 2.20, the bitumen is termed thermo-rheologically simple (Airey 1997).

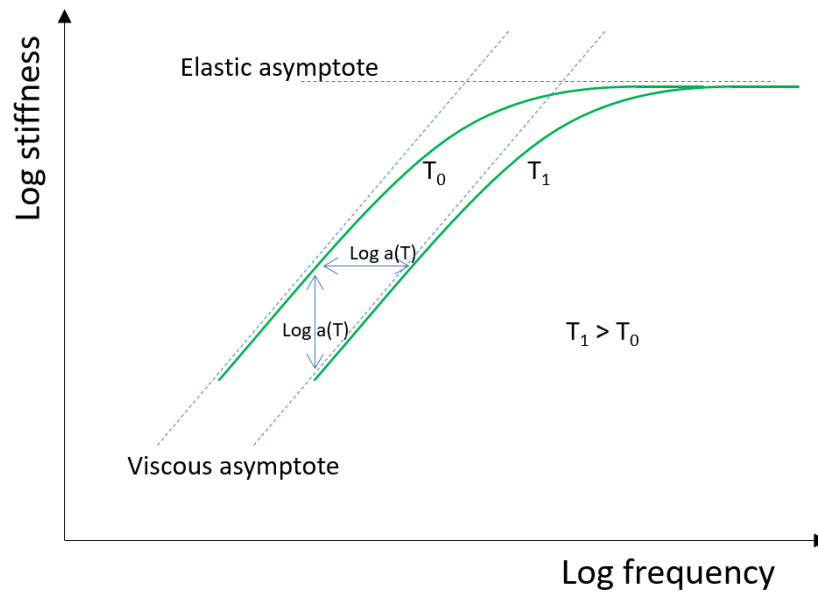


Figure 2. 27: Time-temperature superposition principle (Airey 1997)

This shifting procedure firstly requires a reference temperature to be chosen, and the next modulus curve shifted horizontally to coincide with the reference curve. Then, this procedure is repeated for a wider range of temperatures to produce a continuous smooth modulus plot called a master curve. In the constructed master curve, the extended time or frequency scale is referred as the reduced time or reduced frequency scale, defined as:

$$\log f_r = \log f + \log a(T) \quad \text{Eq. 2. 14}$$

Where:

f_r = reduced frequency, Hz

f = frequency, Hz

$a(T)$ = shift factor

The Williams, Landel and Ferry (WLF) equation has been widely used to describe the relationship between shift factor $a(T)$ and the temperature. The WLF equation is:

$$\log a(T) = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)} \quad \text{Eq. 2. 15}$$

Where:

$a(T)$ = shift factor at temperature T

C_1, C_2 = coefficient to be determined

T, T_r = temperature, reference temperature

C_1, C_2 and T_r are the constants to be determined in the WLF equation. The constants C_1 and C_2 can be calculated from the slope and intercept of the linear form of the WLF equation with respect to the reference temperature T_r (Airey 1997):

$$-\frac{T - T_r}{\log a(T)} = \frac{C_2}{C_1} + \frac{1}{C_1}(T - T_r) \quad \text{Eq. 2. 16}$$

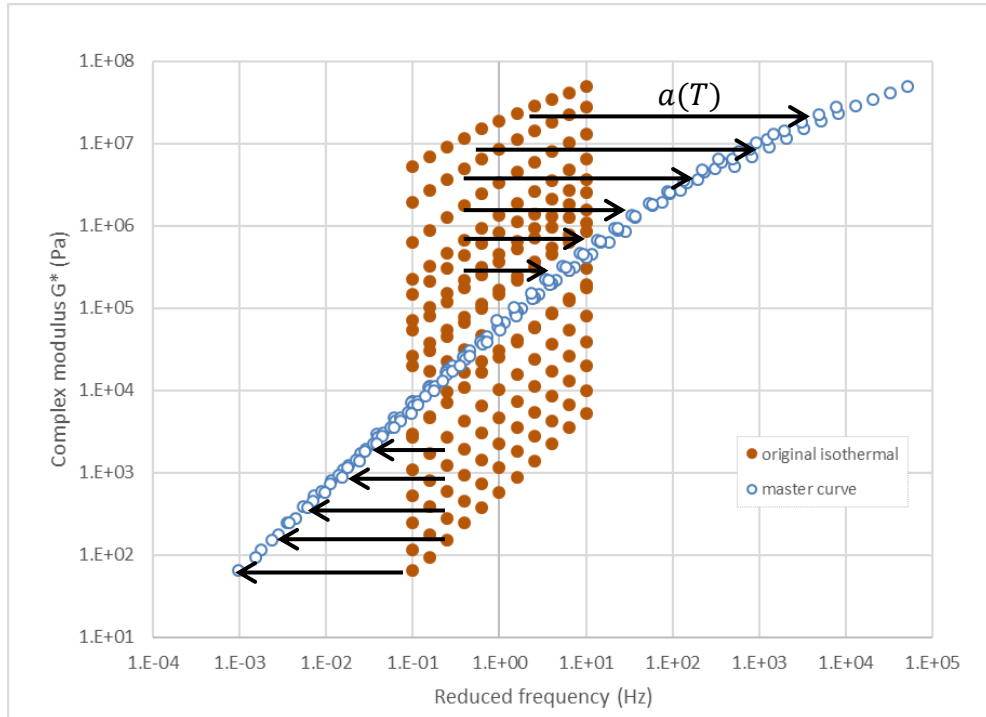


Figure 2. 28: The illustration of shifting procedure to obtain master curve

There are several proposed values of C_1 and C_2 coefficients in the above equation. (Williams, Landel, and Ferry 1955) suggested C_1 and C_2 universal values of 8.86 and 101.6 respectively, while (Anderson et al. 1991) proposed C_1 and C_2 value of 19 and 92 that suitable for aged and unaged bitumen that also assured by (Jongepier et al. 1969). The constant coefficients C_1 and C_2 can also be obtained by using help of optimization function in spreadsheet program such as Solver in MS Excel. Figure 2.28 shows the illustrative process of shifting the isothermal plot to produce a complex modulus master curve.

2.5.3. Rutting resistance

Rutting or permanent deformation occurs on flexible pavement due to slow-moving traffic and/or high-temperature environment that soften the pavement's bitumen, resulting in non-recoverable plastic deformation. In this deterioration, the viscous component of the bitumen is the main factor in the rheological response at extended loading time and high temperatures, which is responsible for the unrecoverable deformation (Anderson et al. 1991).

The importance of the rutting parameter leads to the long development of bitumen tests and characterisation to predict the permanent deformation of the asphalt mixture. The Superpave high-temperature parameters ($G^*/\sin \delta$) were considerably the early specification to correlate the bitumen and asphalt performance. However, this method's parameters are measured and calculated within the linear viscoelastic region of the bitumen at fixed frequency and temperature, which causes many simplifications and neglects, especially for modified bitumen (D'Angelo 2009). There has been reported by many studies a poor correlation between the Superpave $G^*/\sin \delta$ parameter and the corresponding asphalt mixtures (Shenoy 2001), (D'Angelo 2009).

The continuous development of rutting parameter study leads to multiple stress creep and recovery (MSCR) tests. This test is based on well-recognised recoverable (or non-recoverable) characteristics of bitumen that play an important role in pavement rutting performance. The better characterisation of bitumen at high-temperature performance to their asphalt mixtures rutting resistance compared to Superpave $G^*/\sin \delta$ parameter has been assured by many researchers (D'Angelo, Dongre, and Reinke 2006), (D'Angelo 2009).

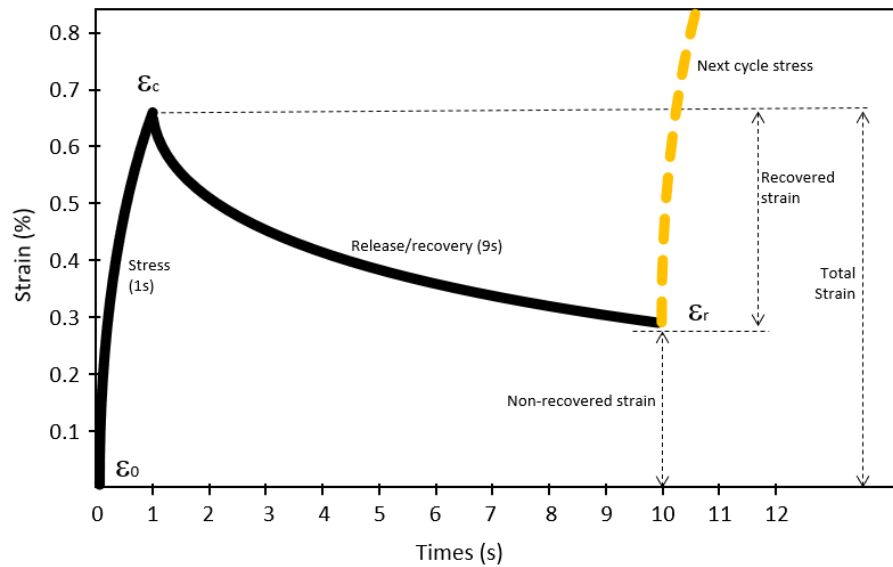


Figure 2. 29: Typical Creep – Recovery cycle of the MSCR test

The MSCR test consists of a loading and unloading pattern applied for ten continuous repetitions. The stress loading of 100 Pa is applied for 1 second, and the unloading (release) for recovery is 9 seconds. This pattern is repeated for ten cycles, and the other set of bitumen cycles is performed for different stress levels, usually 3200 Pa. The test can be performed on unaged or short-aged (RTFO) bitumen by using a 25mm spindle of Dynamic Shear Rheometer. The typical MSCR test result for one cycle is shown in Figure 2.29, and the ten cycles are shown in Figure 2.30.

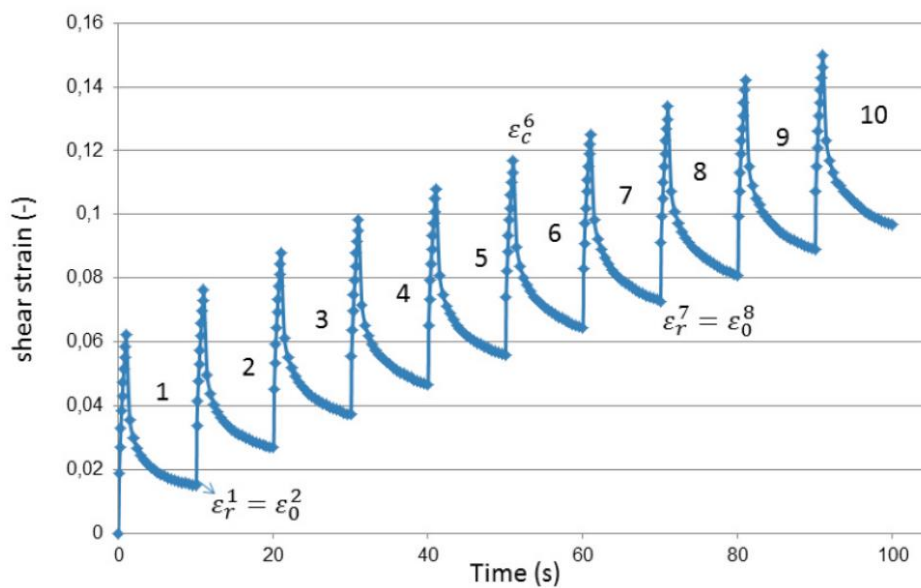


Figure 2. 30: Typical ten cycles curve of creep – recovery test (BS EN)

These are the parameters that can be retrieved from the MSCR tests after ten cycles of creep and recovery:

1) Average percent recovery (%R) at 100 or 3200 Pa (%)
$$\%R = \frac{1}{10} \times \sum_{n=1}^{10} \left(\frac{\epsilon_{recovered}^n}{\epsilon_{total}^n} \right) \times 100$$
 Eq. 2. 17

2) The unrecoverable creep compliance (Jnr) at 100 or 3200 Pa (1/kPa)
$$Jnr\ 0.1 = \frac{1}{10} \times \sum_{n=1}^{10} (\epsilon_{non-recovered}^n / 0.1)$$
 Eq. 2. 18

$$Jnr\ 3.2 = \frac{1}{10} \times \sum_{n=1}^{10} (\epsilon_{non-recovered}^n / 3.2)$$
 Eq. 2. 19

3) Difference in percent recovery (R.diff) between 100 and 3200 Pa (%)
$$R.diff.\ \% = \left(\frac{\%R_{100Pa} - \%R_{3200Pa}}{\%R_{100Pa}} \right) \times 100$$
 Eq. 2. 20

4) Difference in non-recoverable (Jnr-diff) between 100 and 3200 Pa (%)
$$Jnr.diff.\ \% = \left(\frac{Jnr_{3200Pa} - Jnr_{100Pa}}{Jnr_{100Pa}} \right) \times 100$$
 Eq. 2. 21

The average per cent recovery %R parameter indicates the bitumen's recoverability, which correlates to the bitumen's resistance to permanent deformation. %R is calculated from the average strain recovery of the 10 cycles of 100 Pa or 3200 Pa. $\epsilon_{recovered}^n$ is the recovered strain at n cycles, ϵ_{total}^n is the total strain or creep strain at the end of 1 second of the stress at n cycles. $\epsilon_{non-recovered}$ is the permanent deformation (un-recoverable strain) after 9 seconds of recovery. The unrecoverable creep compliance Jnr parameter is defined as the amount of residual strain left in the bitumen after repeated creep and recovery of 100 or 3200 Pa (Hossain et al. 2016). Jnr can predict the improvement of modified bitumen, and this parameter is suitable for unmodified or modified bitumen. Jnr is thus considerably better as the alternative to the Superpave $G^*/\sin \delta$ parameter (D'Angelo 2009). A bitumen with a high %R and low Jnr is desirable for the characterisation of rutting performance.

2.5.4. Fatigue resistance

Fatigue resistance of bitumen exhibits its ability to prevent fatigue deterioration when applied in the asphalt mixture. Fatigue failure is generally defined within the intermediate or pavement's service temperature of 10 to 35°C. At this temperature range, the pavement is subjected to repetitive loading by the traffic, while the pavement is relatively in an elastic state. In this condition, the excessive repetitive stress loads are dissipated through crack initiation and, eventually, crack propagation (Subhy 2017). As the asphalt mixture fatigue resistance is well recognised to be significantly related to their bitumen, the fatigue resistance characterization of the bitumen is crucial and has been continuously discussed for years. However, despite the lengthy discussions about fatigue cracking studies, there is no consensus about the specified control of bitumen properties or parameters that affect fatigue cracking in asphalt (Paliukaite, Verigin, and Hesp 2015a). Early discussion about pavement cracking performance and how it is related to bitumen property was provided by Kandhal (1977). He assured that bitumen with low ductility at low temperatures is likely to have poor pavement performance. The author suggested temperature limits in ductility tests to predict distresses, including loss of fines, ravelling thermal cracking and widespread cracking. However, the author could not clearly understand the fundamental property behind the ductility test results. Further studies about bitumen low-temperature ductility were presented by Van Gooswilligen, G., de Bats, F.Th. & Harrison (1989). The author concluded the ability of low-temperature ductility tests to distinguish a good and a poor bitumen binding performance.

SHRP proposed another method regarding the fatigue parameter of pavement by using bitumen loss modulus ($G^* \sin \delta$) as the control parameter. The main principle was that the energy dissipation during the dynamic load represents the sustained damage amount, thus proposed as the fatigue life performance parameter. Lower complex modulus G^* gives better energy dissipation without developing significant stress, and a lower phase angle means the bitumen can recover with minimum dissipated energy. These produce a lower value of ($G^* \sin \delta$) which means lower dissipated energy per loading cycle and thus has a better fatigue resistance. However, a considerable number of criticisms had received from further studies that suggested the ($G^* \sin \delta$) does not accurately predict fatigue cracking (Andriescu and A 2006a; Bahia et al. 2001a; Chen and Tsai 1999; Gibson

et al. 2012a; Johnson, Hussein, and Wen 2007; Planche et al. 2004; Rowe, King, and Anderson 2014; Tsai et al. 2005; Zhou et al. 2013a).

Another method of fatigue characterization was proposed by researchers from Queen's University, namely the double-edge notched tension (DENT) test, which is based on essential work of fracture (EWF) of material in a ductile state (Andriescu, Hesp, and Youtcheff 2004a). This method is based on many studies that ensure the fatigue parameter should include the damaging process during the fracture propagation. This damaging process occurs in nonlinear viscoelastic range with high strain levels and yielding of bitumen film. The resistance properties of bitumen in this condition should be considered to develop more performance-based bitumen fatigue characterization (Andriescu, Hesp, and Youtcheff 2004b; Paliukaite, Verigin, and Hesp 2015b). A further comparison of this method with fatigue cracking in the accelerated loading facility (ALF) demonstrated a strong correlation and was identical to the push-pull asphalt mix fatigue test (Gibson et al. 2012b; Zhou et al. 2013b).

A more recent and popular fatigue characterisation method utilizing a dynamic shear rheometer was proposed by Johnson et al. (2010) and Hintz et al. (2011), namely Linear Amplitude Sweep (LAS) test. LAS is a considerably good performance-related test, easy to conduct and requires a relatively short time. A concept, namely viscoelastic continuum damage (VECD), is used in this method. The fatigue life equation is derived from complex mathematical formulations and statistical fitting. The following sub-chapters will discuss further the Linear Amplitude Sweep (LAS) and Double-Edge Notched Tension (DENT) test.

2.4.4.1. Linear Amplitude Sweep (LAS) method

Linear Amplitude Sweep (LAS) is conducted to understand the fatigue resistance of the bitumen. The test is carried out according to AASHTO TP 101-12-UL to evaluate the ability of bitumen to resist fatigue damage by employing cyclic loading at increasing amplitudes in order to accelerate damage. The rate of damage accumulation in the material exhibits the measured characteristics. These characteristics can be used to indicate the fatigue performance of the bitumen given pavement structural conditions or the expected amount of traffic loading using predictive modelling techniques.

This testing procedure implements two steps. The first is a frequency sweep test to obtain information about bitumen's rheological properties, and the second is an amplitude sweep test to measure the damage characteristics of the material.

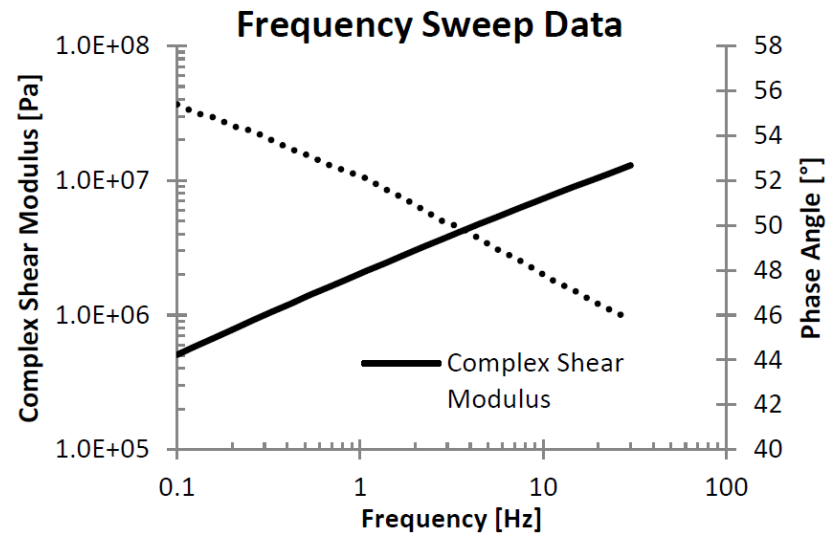


Figure 2.31: Example output of frequency sweep test (AASHTO TP 101)

The frequency sweep test is conducted to determine 'alpha', the damage analysis parameter, by employing an applied load of 0.1 % strain at a selected temperature over 12 unique frequencies of 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 20, and 30 Hz. At each frequency, the complex shear modulus $|G^*|$, Pa, and phase angle δ , degrees, are recorded as shown in Figure 2.31.

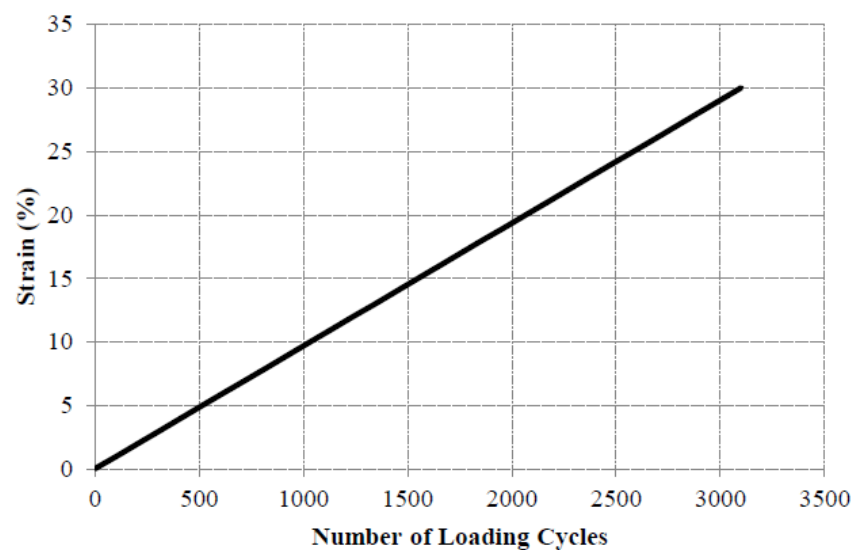


Figure 2.32: The loading scheme of the amplitude sweep test (AASHTO TP 101)

The second test, the amplitude sweep test, is conducted at the selected temperature using oscillatory shear at a frequency of 10 Hz in strain control mode. The oscillatory strain sweeps in increased from 0.1 to 30% over the course of 3100 cycle of loading within 310 seconds of total test time as shown in Figure 2.32. Every 10 load cycles (1 sec), the peak shear strain, the peak shear stress, complex shear modulus $|G^*|$, Pa and phase angle δ , degree, are recorded.

Steps of calculations are performed in further analysis and results interpretation. The damage accumulation of the specimen is calculated by using the following equation.

$$D(t) \cong \sum_{i=1}^N [\pi \gamma_0^2 (C_{i-1} - C_i)]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{\alpha}{1+\alpha}} \quad \text{Eq. 2. 22}$$

Where:

$$C(t) = \frac{|G^*|(t)}{|G^*|_{initial}}$$

γ_0 = applied strain for a given data point, percent

$|G^*|$ = complex shear modulus, MPa

α = obtained value from frequency sweep test

t = testing time, second

The bitumen fatigue performance parameter N_f is calculated by using Equation 10, where γ_{max} is the maximum expected bitumen strain for a given pavement structure, %.

$$N_f = A_{35}(\gamma_{max})^{-B} \quad \text{Eq. 2. 23}$$

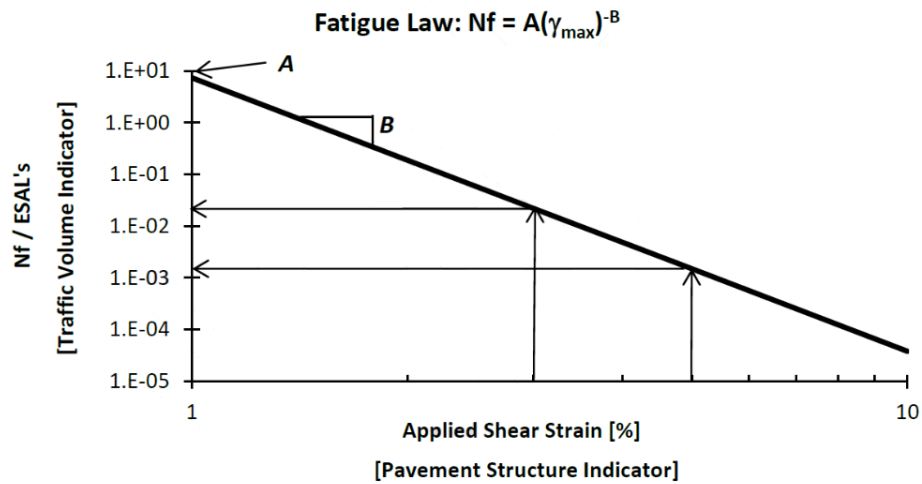


Figure 2. 33: The plot of fatigue parameter N_f versus applied shear strain (AASHTO TP 101)

Figure 2.33 shows the plot of N_f (normalized to 1 million ESALs) versus applied shear strain. The arrows indicate the allowable fatigue life can be determined for a given strain amplitude.

2.4.4.2. Essential Work of Fracture (EWF) method by using DENT

The Essential Work of Fracture tries to propose a better fatigue control parameter of bitumen, as the SHRP concept was not good enough to correlate the asphalt fracture properties to the bitumen fatigue parameter according to many studies.

In the bitumen fatigue study, the DENT (double-edged notched tension) in Ductilometer equipment is used in the EWF method using a notched bitumen sample. In the EWF concept, it is proposed that two main energy parts are required to fracture the sample: the essential work (W_E) in the inner process zone of the progressing crack, and the plastic work (W_P) or non-essential work in the outer plastic zone (Wu and Mai 1996). The essential work (W_E) is the dissipated energy in the fracture region that is needed to create two new fracture surfaces. This energy is considered as a constant material property (Wu and Mai 1996). The other part of the main energy is the non-essential or plastic work (W_P) energy, which defined as the energy dissipated in ductility, plasticity, and tearing. The essential work of fracture (W_E) is proportional to the specimen (ligament) cross-section area $A \times B$, while the plastic work (W_P) is related to the plastic zone volume ($A^2 \times B$) multiplied by β . The DENT testing specimen and the schematic fracture concept are shown in Figure 2.34.

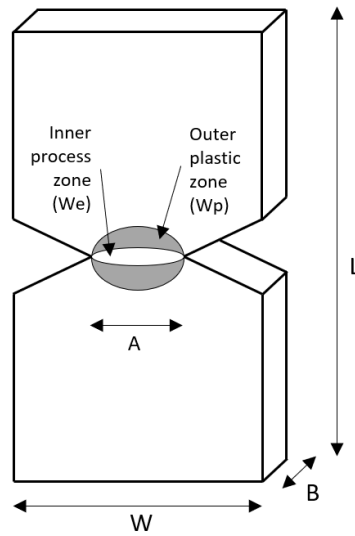


Figure 2. 34: DENT testing specimen and the schematic ductile fracture

The total work of fracture (W_T) is determined by the following equation:

$$W_T = W_E + W_P = w_e \cdot A \cdot B + \beta \cdot w_p \cdot A^2 \cdot B \quad \text{Eq. 2. 24}$$

The equation above can be written in specific terms by dividing with a sectional area ($A \times B$):

$$w_t = w_e + \beta \cdot w_p \cdot A \quad \text{Eq. 2. 25}$$

Where:

W_T, W_E & W_P	= total work, essential work & plastic work of fracture (J)
w_t	= specific total work of fracture (J/m ²)
w_e	= specific essential work of fracture (J/m ²)
w_p	= specific plastic work of fracture (J/m ²)
β	= slope of specific plastic work w_p
B	= sample thickness (m)
A	= ligament length (M)

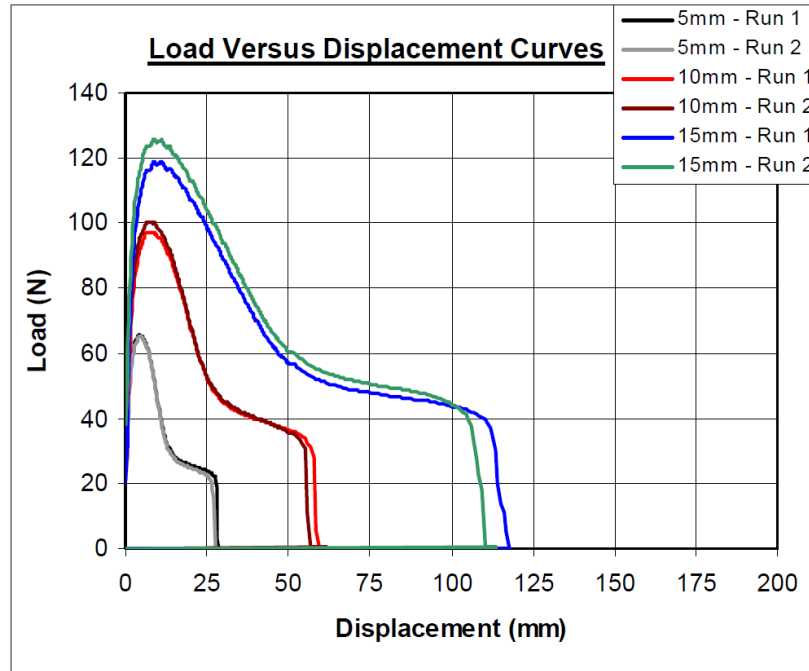


Figure 2. 35: Typical force vs displacement data from DENT

The total work of fracture (W_T) in the DENT test can be defined as the area under the force-displacement curve (J), as seen in Figure 2.35. The total specific work of fracture is then calculated by dividing the total work by the ligament cross-section area ($A \times B$). The specific total work of fracture (w_t) can be plotted versus ligament length (A) by adding the intercept of w_e and the increasing slope represented from $\beta \cdot w_p$ as shown in Figures 2.36 and 2.37.

According to Andriescu et al. (2004b) and Subhy (2017) the yielding of the smallest DENT specimen provides a reasonable approximation for the tensile yield stress. For this reason, the parameter is used as the net section stress is used to calculate the critical top opening displacement (CTOD) by the following equation:

$$\delta_t = \frac{w_e}{\sigma_n} \quad \text{Eq. 2. 26}$$

Where δ_t is the critical crack tip opening displacement (m) and σ_n is the net section stress (N/mm^2) that used as replacement for tensile yield stress. CTOD represents the strain tolerance, or the ability of bitumen to stretch in a confined space in the presence of a crack at the ductile state under severe tensile stress. For a better fatigue resistance of pavement, a higher value of CTOD is desirable as it represents the ability of the bitumen to bend before cracks initiate. The CTOD parameter also provides a good result in ranking

the bitumen fatigue performance at different temperatures and loading rates (Andriescu et al. 2004b; Gibson et al. 2012b; Zhou et al. 2013c).

Some assumptions and conditions that need to be met in the DENT test of EWF, as recommended by many references and literature (Andriescu et al. 2004b; Bárány, Czigány, and Karger-Kocsis 2010; Martinez et al. 2009; Subhy 2017) are:

- (1) The ligament must be fully yielded before the cracking initiates
- (2) Load-displacement diagrams for all ligament lengths should be similar in appearance to verify the common fracture geometries
- (3) The sample must be yielded in pure plane stress of tension

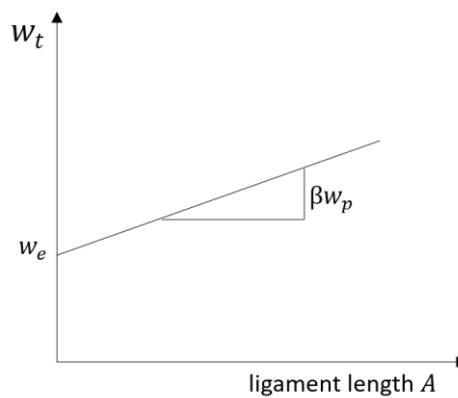


Figure 2. 36: Schematic sketch of w_t and ligament length (A) relationship

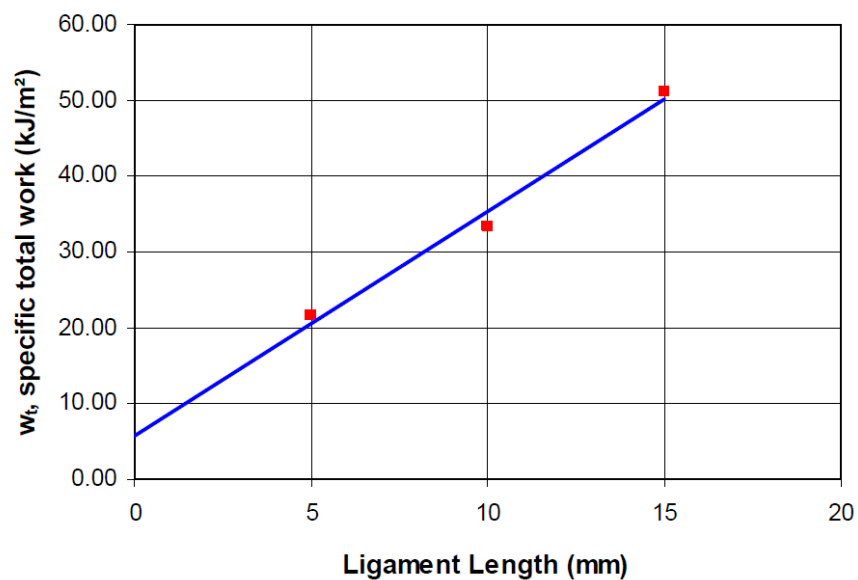


Figure 2. 37: The example of w_t versus ligament length (A) plot

The DENT moulds consist of three ligament lengths of 5, 10 and 15 mm, as shown in Figure 2.38. For each ligament length, two testing specimens are required; thus, a total of six moulds are used for each bitumen.

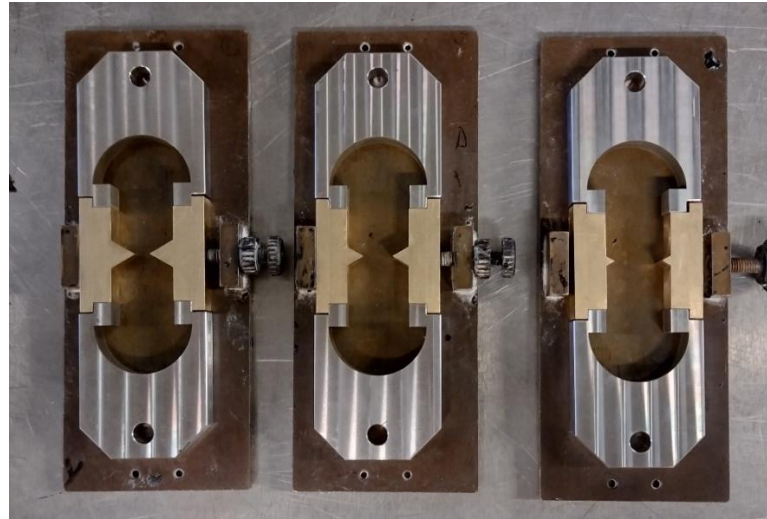


Figure 2. 38: DENT test moulds of 15, 10 and 5mm notches

2.5.4. FTIR (Fourier transform infrared spectroscopy) and bitumen ageing

The ageing of bitumen is a natural phenomenon affecting the pavement's overall performance. The principal cause of the ageing of bituminous binders in their service life is the oxidation of specific molecules in the bitumen by oxygen from the air, resulting in the formation of highly polar and strongly interacting oxygen-containing functional groups (Mouillet et al. 2008).

Based on the molecule weight and chemistry structure, asphalt can be divided into four generic components of asphaltenes, naphthene-aromatics (aromatics), polar-aromatics (resins) and saturates (Corbett 1969). The term SARA for the bitumen components is stated by Read and Whiteoak (1993), and the properties are shown in Table 2.5. In the ageing process, specific generic components of asphalt are volatilized under the oxidation procedure, resulting in stiffer behaviour and reducing the low-temperature resistance. A similar oxidation procedure can be artificially produced in the laboratory, and infrared spectroscopy can be used to quantify and analyse the change in the spectral data of aliphaticity, aromaticity and oxygenation that represents the ageing degree of the asphalt (Lamontagne et al. 2001) (Hou et al. 2018) (Nivitha et al. 2016).

Table 2. 5: Main components of bitumen

Fractions	Proportion (Corbett 1969)	Properties and particle size (Van den bergh 2011b)
Asphaltenes	5 – 25%	The main structure (5 – 30 nm), viscosity behaviour (4 – 10 nm)
Resins (polar-aromatics)	30 – 45%	Dispersion or peptizers of asphaltenes (1 – 5 nm)
Aromatics	30 – 45%	Oily components
Saturates	5 – 15%	Oily components

Fourier transform infrared spectroscopy (FTIR) offers a convenient and reliable method to analyse the bitumen in a molecular level by identifying the absorption spectrum differences of the components representing the contents and the functional groups of the bitumen (Van den bergh 2011b). Furthermore, the influence of ageing on the interaction mechanism of different modified bitumen can be studied by recording and differentiating the spectra of the neat and modified bitumen at other ageing conditions (Nivitha et al. 2016), which helps a significant understanding of the modification mechanism (Hou et al. 2018).

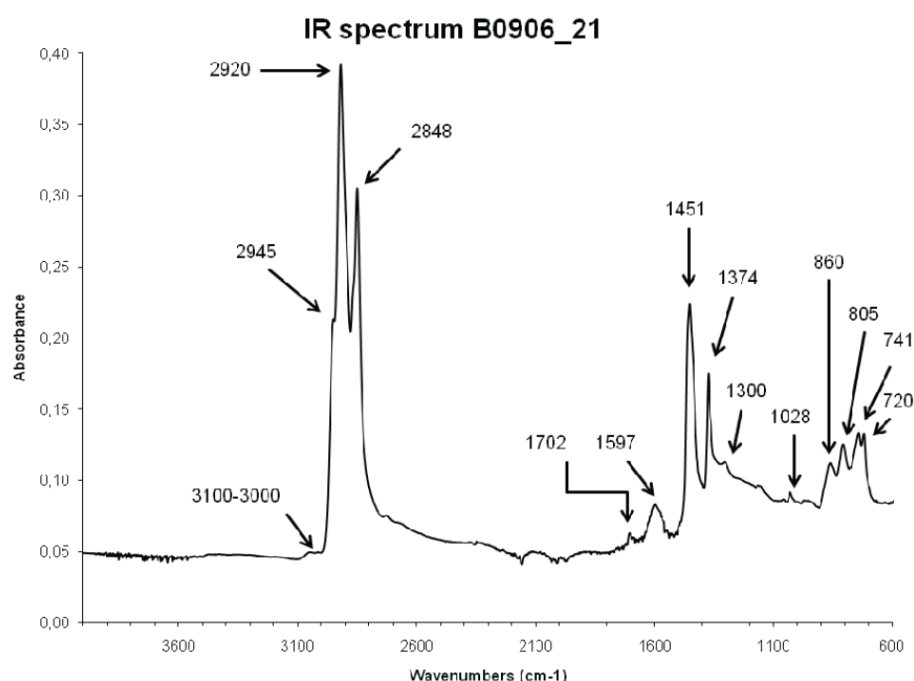


Figure 2. 39: Common IR spectrum of a random bitumen (Van den bergh 2011a)

For bituminous binders, the ATR (attenuated total reflectance) FTIR is commonly selected for quantitative analysis. This analysis provides quick and reliable information on aliphaticity, aromaticity, sulphur components and oxidation rate (Lamontagne et al. 2001). The FTIR test results are primarily expressed as a graph with the x-axis representing

the wave number and the y-axis illustrating the absorbance or transmittance, as shown in Figure 2.39. The wave numbers and absorbance vary depending on the tested material, which is represented in different graphical results. However, every specific material, for example, bitumen, will have a similar pattern of graphic shape with commonly observed peaks.

For simple quantitative analyses, the mid-infrared region between 4000 and 400 cm^{-1} is selected as a standard spectrum in bituminous material for pavement (Van den bergh 2011b). The region 1800 – 600 cm^{-1} gives information about the presence of functional groups such as oxidation groups of ketones C=O in 1700 cm^{-1} and sulfoxides S=O in 1030 cm^{-1} . Other detailed peak positions of commonly used functional groups in the bitumen are shown in Table 2.6.

Table 2. 6: Peak positions of bitumen common functional groups (Hou et al. 2018)

Peak position (area)	Functional groups	Details
727	–CH ₂	Rocking
910 & 990	–CH=CH ₂	Wagging
1000–1300	C–O	Ester; stretching
1031	S=O	Stretching
1210–1320	C–O	Carbonyl acid; stretching
1375	CH ₃	Aliphatic; plan deformation
1458	CH ₃ & CH ₂	Aliphatic; deformation
1550–1640	N–H	Amide; bending;
1580 & 1600	C=C	Conjugated ring vibration
1620–1680	C=C	Stretching
1640–1690	C=O	Amide; stretching
1675	C=O	α,βunsaturated ketone; stretching
1700–1725	C=O	Carbonyl acid; stretching
1715	C=O	Saturated ketone; stretching
1720–1740	C=O	Aldehyde; stretching
1735–1750	C=O	Ester; stretching
1740–1775 & 1800–1830	C=O	Anhydride; stretching
2500–3300	O–H	Carbonyl acid; stretching
2820–2850 & 2720–2750	=C–H	Aldehyde; stretching
2850	C–H	Aliphatic hydrogen; CH ₂ ; symmetric stretching
2870	C–H	Aliphatic hydrogen; CH ₃ ; symmetric stretching
2923	C–H	Aliphatic hydrogen; CH ₃ & CH ₂ ; asymmetric stretching
2955	C–H	Aliphatic hydrogen; CH ₃ ; asymmetric stretching
3100–3500	N–H	Amide; stretching
3400	N–H	Primary amine; asymmetric stretching
3500	N–H	Primary amine; symmetric stretching

2.4.3.1. Ageing of bitumen under FTIR observation

The bitumen molecules oxidation is primarily assigned as the ageing phenomenon in the bitumen. Therefore, in the FTIR, oxygen-containing groups are essential for detecting ageing. Studies have suggested the spectrum bands of the bitumen in the regions of 1030 cm⁻¹ (S=O, sulfoxide) and 1730 cm⁻¹ (C=O, carbonyl) could be used as the ageing indicator

of the bitumen (Van den bergh 2011b; Lamontagne et al. 2001; Mouillet et al. 2008). Table 2.7 summarizes the chemical structures of the bitumen, the wave number and which are affected or not affected by ageing.

Table 2. 7: Specific functional groups of bitumen related to ageing (Pieri *et al.*, 1996, (Van den bergh, 2011))

Type of vibration bands in FTIR	Wave number (cm ⁻¹) (integrated zones)	Affected by Ageing
C-H stretching		
=C-H stretching (aromatic)	3100-3000	No
CH sp ² and 3	2953, 2923, 2862 (3100-2700)	
Symmetric (CH ₂ , CH ₃) sp ³	2862 (2880-2823)	
Asymmetric. (CH ₂ ,CH ₃) sp ³	2953, 2923 (2997-2880)	
C=O stretching	1700 (1753-1635)	Yes
Aliphatic ester	1750-1730	
Aliphatic aldehyde	1740-1720	
Aromatic ester	1730-1705	
Aliphatic ketone	1730-1700	
Aromatic aldehyde	1720-1680	
Aromatic ketone	1700-1680	
Carboxylic acid	1700	
C=C stretching	1600 (1635-1538)	
C-H bending		
CH ₃ asymmetric	1460	No
CH ₂ scissors	1465 (1538-1399)	
CH ₃ symmetric bend	1376 (1399-1349)	
SO ₂ asymmetric stretch	1390-1290	Yes
S=O stretching	1030 (1082-980)	
SO ₂ symmetric stretching	1140 (1190-1120)	
C-H out of plane bending	900-600	No
C=CH- 1H singlet	864 (910-837)	
C=CH -2-3H adjacent	800 (837-780)	
C=CH -3-4H adjacent	743 (775-731)	
(CH ₂) _n Rock (n >=4)	722 (731-705)	

2.4.3.2. Quantitative analysis of FTIR data

In bitumen observation, FTIR quantitative analysis of the spectrum can be utilized for several purposes: comparing bitumen and its modifications, observing solvents and fillers' presence, and tracking the ageing process. The two main procedures in the quantitative analysis are band height (peak ratio) and band area ratio evaluation, with the latter method preferable in the bitumen analysis (Van den bergh 2011b).

In the FTIR quantitative analysis of the bitumen, the functional and structural indexes are calculated from the measured band areas from valley to valley of the obtained spectrum graph (Lamontagne et al. 2001). Figure 2.40 shows (a) the obtained spectrum bands from FTIR and the band areas quantification (Lamontagne et al. 2001) and (b) the wave number from the same graph (Van den bergh, 2011).

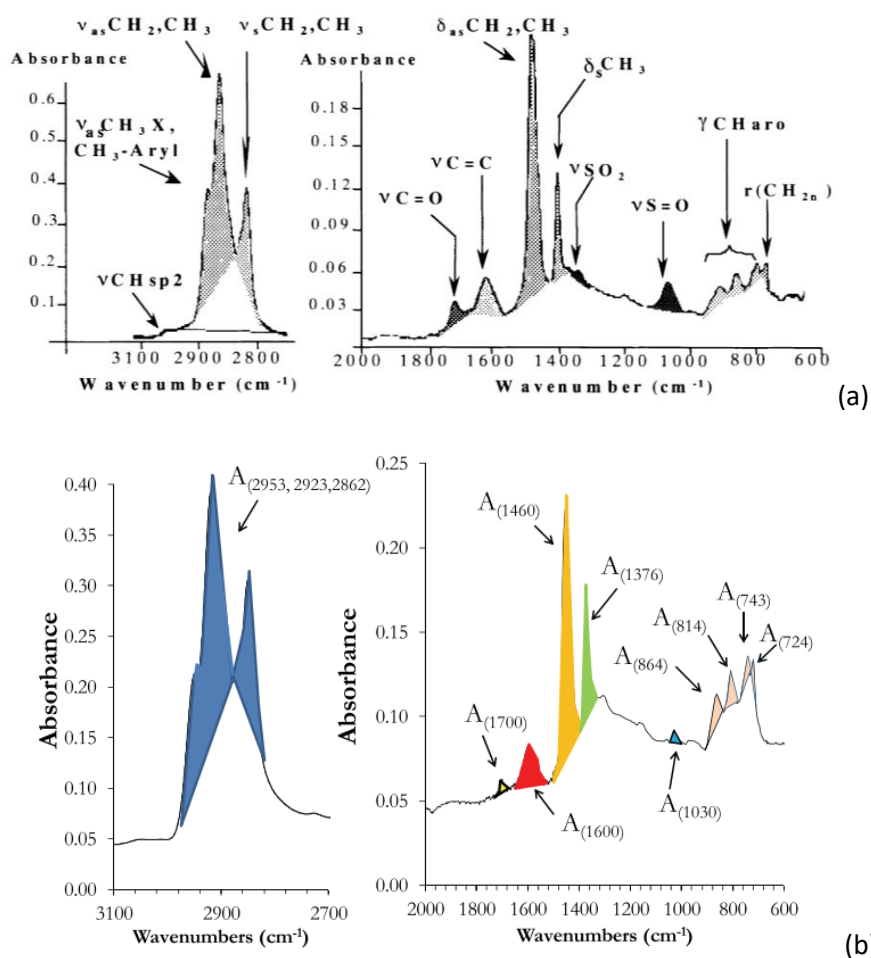


Figure 2. 40: FTIR spectrum and visualization of band area measurement (Lamontagne et al. 2001)

From the spectra, band areas are quantified with the approach by Mouillet et al. (2008), and the functional and structural indices are derived:

- Aromatic structures (aromaticity index) $\frac{A_{1600}}{\sum A}$
- aliphatic structures (aliphatic index) $\frac{A_{1460} + A_{1376}}{\sum A}$
- branched aliphatic structures $\frac{A_{1376}}{A_{1376} + A_{1460}}$
- long chains $\frac{A_{724}}{A_{1376} + A_{1460}}$
- oxygenated functions (carbonyl index) $\frac{A_{1700}}{\sum A}$
- sulfoxide index $\frac{A_{1030}}{\sum A}$
- the sum of the areas, $\sum A$ $A_{(2953,2923,2862)} + A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724}$

By quantifying the functional and structural indices of the observed bitumen, the changes or differences that represent the bitumen modification can be determined. A further study can be conducted to correlate the observed changes under FTIR to the bitumen rheological properties and bitumen performance in asphalt mixture.

To track bitumen ageing, a semi-quantitative analysis method can be used to analyse the band areas of carbonyl (C=O) at 1700 and sulfoxide (S=O) at 1030. In this analysis method, the ageing indicator areas (the C=O and S=O) are divided by the sum of two areas that are believed not to be affected by the ageing: the ethylene groups (CH₂) at 1460 cm⁻¹ and methyl (CH₃) at 1375 cm⁻¹ (Van den bergh 2011b; Mouillet et al. 2008).

2.6. Asphalt mixture performance characterisation

Asphalt or asphalt mixture is one of the major materials used in construction around the globe. Asphalt mixtures are made of aggregate particles mixed and cemented with bitumen that make a bound of sturdy material and are widely used worldwide as road

pavements. Asphalt or flexible road pavement typically consists of bituminous layers including (1) surface or wearing course, (2) binder course, (3) base course, and foundation course, i.e. (4) sub-base course from granular material, and (5) subgrade commonly from compacted existing soil. Figure 2.41 illustrates the typical flexible pavement layers. While the foundation layer has a vital role, as its name is the ‘foundation’, the upper layers play equally important roles in the pavement structure. The top bituminous layer: the surface or wearing course is the layer that directly contacts the loads, i.e. tyres, and transfers them to the lower layer, the binder course. The wearing course is also the layer that degrades mainly in the pavement service life by the tyre loads, weather, water, temperature and other environmental factors. From the wearing course, the binder course transfers and spreads the loads to the base course, which acts as the main structural load-bearing layer (Rahman 2004).

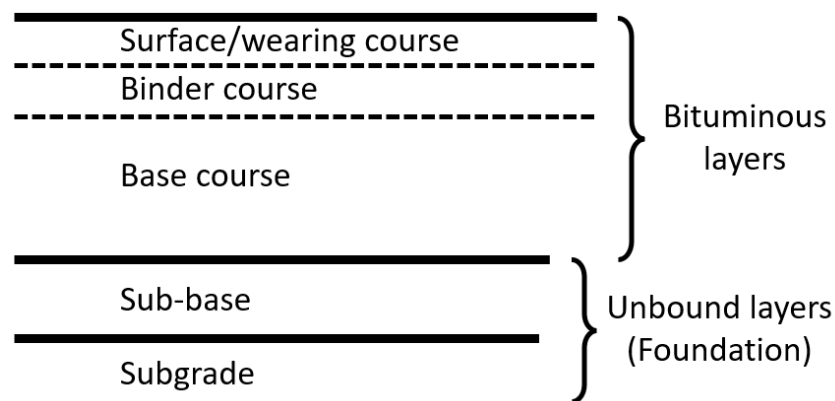


Figure 2. 41: Typical flexible pavement layers

To support the traffic loads and for safe and comfortable riding for years of their life, flexible pavements need to have essential requirements in mechanical properties (Rahman 2004):

- High elastic stiffness to provide a good load-spreading ability
- high fatigue strength to prevent fatigue initiation and propagation of cracks due to repeated traffic loading or environmental factors
- high resistance of permanent deformation to prevent surface rutting
- adequate skid resistance for safe and comfortable vehicle ride in wet or other weather conditions

With its importance of end product quality, asphalt mixture must be carefully prepared to ensure it meets the construction requirements and specifications. Asphalt preparation

starts with the material choice, the mix design: aggregate gradation, weighting and bitumen content, and the compaction method. Then, the standardised preparations are conducted to ensure the pavement can last with high quality as designed and to prevent any early asphalt failures or deterioration. The two main asphalt failures studied in this research are rutting and fatigue cracking.

2.6.1. Aggregate gradation

Three types of aggregate gradation are generally used in hot mix asphalt (HMA):

- Dense or well-graded. This is the most common gradation in HMA. In this type of gradation, the particles are well distributed from the higher sieve (bigger particle size) to the smallest particle size to give a dense pack of particles. The main goal of this gradation type is to obtain maximum stability and density.
- Open-graded mixes. This gradation contains a relatively small percentage of fine particles and a higher percentage in the mid-size range of particles. The distribution curve of this gradation is flat or near zero in small size and rising in mid to large particle size. This distribution of particles gives a bigger air void due to insufficient small particle size to fill in between the bigger aggregates. The gradation generally has a lower binder content, and the bigger air voids between the coarse aggregate allow the use of rubber, fibre or other additives in the mixture.
- Gap-graded. This gradation is prepared with a small percentage of the mid-size range of particles; thus, the distribution curve is flat in the mid-size range. This gradation is widely used in Britain and European countries on heavily trafficked roads, with hot rolled asphalt (HRA) and stone mastic asphalt (SMA) being the typical implementation of this gradation. Stone mastic asphalt (SMA) is a coarse aggregate skeleton filled with a high bitumen/filler mortar and is well-recognised for its durability and stability. The coarse aggregate consists of a stone-to-stone aggregate skeleton that provides excellent rutting resistance, while the bitumen/filler mortar offers a durable and high fatigue resistance mixture. Figure 2.42 illustrates the common types of gradation used in asphalt mixture.

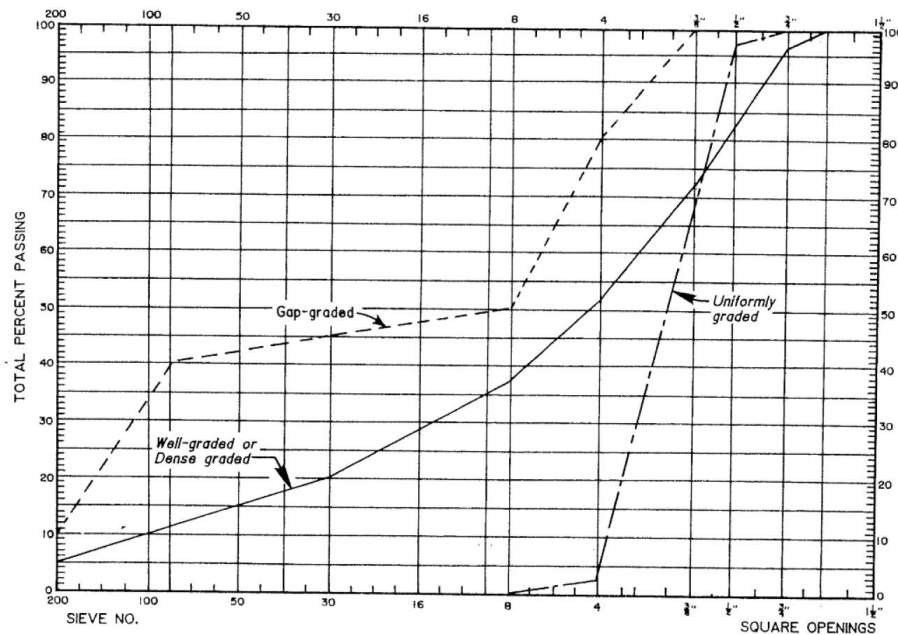


Figure 2. 42: Typical terms used to identify aggregate gradations (Brown et al. 2009)

2.6.2. Bitumen content

Bitumen or binder content is important in asphalt mixture (HMA) final mechanical properties. An optimum binder content in HMA ensures the complete coating of aggregates' surface, leading to easy compaction for optimum strength and durability and preventing any permeability or water susceptibility issues. Studies have proposed a range of approximately 4-5% in bitumen content for various aggregates and different asphalt mixtures. However, the optimum bitumen content generally varies depending on the aggregates, gradation, mixture type, or other requirements.

2.6.3. Laboratory compaction

Compaction is conducted to reduce the mixture mass volume, thus resulting in a dense asphalt mixture material. Compaction is conducted at a high temperature, generally slightly lower than the mixing temperature, by compressing the aggregates (in various methods) and reducing the mixture's air voids. The compacted asphalt mixtures ensure the aggregates are locked and bound by the bitumen. This results in an asphalt mixture material resisting permanent deformation, providing stability and durability.

Bitumen's viscoelastic behaviour make it stiff at lower temperature and become more fluid at a higher temperature. To ensure the optimum compaction process, the bitumen

must be prepared to be sufficiently fluid and thus have good workability with the aggregates during the mixing process and then the compaction process. HMA is generally prepared at 160°C, a temperature where the bitumen's viscosity is low and has good fluidity to ensure it will coat all the aggregates' surfaces. Different bitumen will exhibit different viscosity at some temperatures, depending on its pen number or its additional contents, i.e. modified bitumen. The handy guide for ideal bitumen viscosity can be referred to Shell Bitumen Handbook, as shown in Figure 2.43, which is a range of 0.2 – 0.5 Pas. Bitumen with various viscoelastic characteristics (softer or stiffer bitumen) should be prepared to have a similar 'ideal' viscosity as this reference by adjusting its temperature. Another approximate viscosity number for good bitumen workability with aggregates is mentioned in BS EN 12697-35 at a viscosity range of 0.17 – 0.28 Pas.

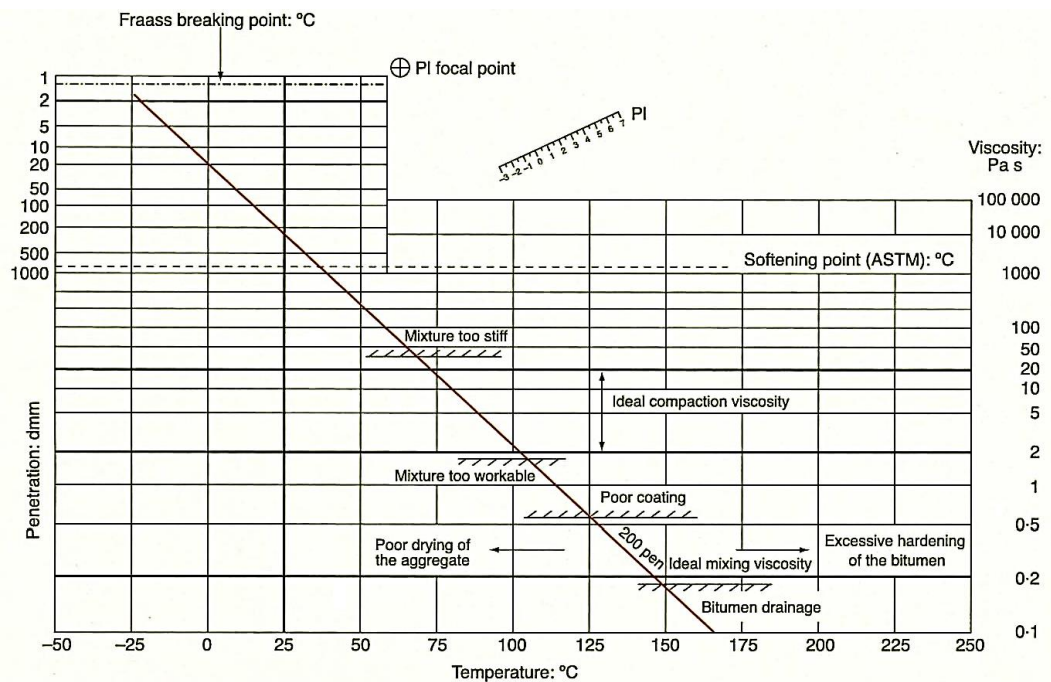


Figure 2. 43: The ideal mixing viscosity according to the Shell bitumen test data chart
(Read and Whiteoak 2003)

Laboratory compaction can be conducted in various methods, with the most commonly used are: (1) the impact compactor (Marshall compaction), which utilizes a standardised vertically falling hammer with a specific height and weight on the moulded specimen for a specified number of blows (BS EN 12697-30:2018), (2) the gyratory compaction which uses moulded mixture with rotary compaction on top of the specimen (BS EN 12697-

31:2019), (3) the roller compaction which generally works on slab shape of asphalt mixture specimen (BS EN 12697-33:2019).

2.6.4. Asphalt stiffness modulus

A pavement's stiffness (or elastic stiffness) modulus indicates the pavement material's ability to distribute the traffic loads to a larger area within the layers. The stiffness of asphalt mixtures is an important performance indicator in road pavement, particularly for the binder and base layer. In pavement design, the stiffness of a bituminous material can be used to calculate the required layer thickness. Depending on the temperature and frequency of loading, a mixture with high elastic stiffness can spread the load over a larger area. A better distribution of loads ensures the reduction of the strain level experienced by the pavement structure layers.

Bitumen and asphalt mixtures are viscoelastic materials whose stress and strain response of the material does not as 'simple' as an elastic-approached material. However, for pavement design purposes, the elastic relationship has been found reliable when some boundary conditions are applied. Therefore, there are different methods to measure the stiffness modulus of the asphalt mixture. According to BS EN 12697-26, the stiffness modulus tests methods are including:

- Sinusoidal bending tests can be applied on 2-point bending on a trapezoidal specimen, 2-point bending on a prismatic specimen, and 3-point bending test on a prismatic specimen.
- Indirect tensile test (pulse or cyclic) consists of options: indirect tension to cylindrical specimens, and cyclic indirect tension to cylindrical specimens
- Cyclic or monotonous uniaxial tests can be conducted on: cyclic tension-compression to cylindrical specimens, monotonous direct tension to cylindrical specimens, and monotonous direct tension to prismatic specimens.

The indirect tensile stiffness modulus test is currently the most convenient laboratory among other methods because it is relatively simple, non-destructive, and can be performed under static or repeated loading conditions. In addition, this test can provide tensile strength, modulus of elasticity, Poisson's ratio, fatigue, and permanent deformation characteristics.

The Nottingham Asphalt Tester (NAT) or NU14 in the University of Nottingham is widely recognised and used in the UK and across the world for asphalt research. NAT is one of the equipment that can perform the standardised requirements in the BS EN 12697-26:2019 to test the stiffness modulus by using the indirect tensile testing mode. This test is commonly known as the Indirect Tensile Stiffness Test (ITST). In ITST the mixture specimen is tested with the indirect impulse load to induce a small horizontal strain that being measured by the Linear Variable Differential Transformers (LVDT). Figure 2.44 (a) shows the ITST configuration. The ITST requires some assumptions as follows (Hudson et al., 1968) (Rahman 2004):

- The material is homogenous and behaves in an isotropic manner
- The material behaves linear elastic
- The specimen is subjected to plane stress conditions ($\sigma_z = 0$)
- The force (P) is applied as a line loading
- The material's Poisson ratio (ν) is known

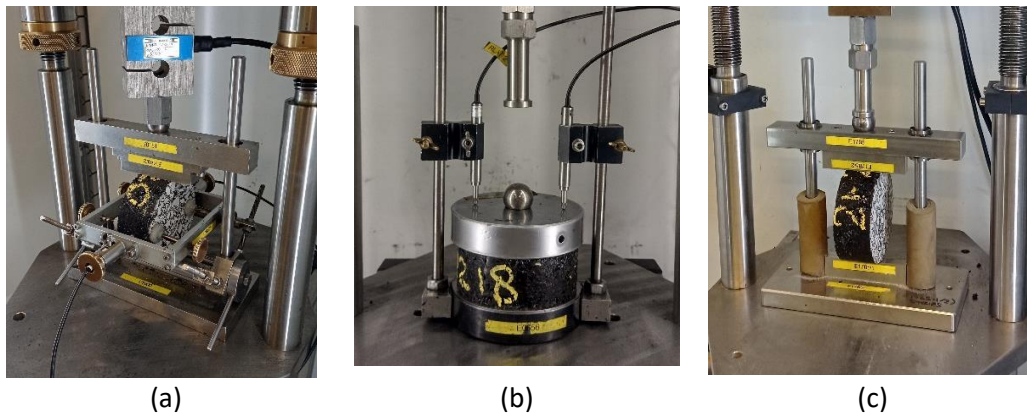


Figure 2. 44: NAT configuration: (a) stiffness, (b) permanent deformation, (c) fatigue

The NU14 monitors the specimen's transient horizontal diametric deformation by applying pulse stress. This monitoring or measurement uses two LVDTs mounted opposite one another at the specimen's horizontal diameter in a rigid frame clamped to the sample. The general term of stiffness is defined as the ratio between the maximum stress and the maximum strain:

$$E = \frac{\sigma}{\varepsilon} \quad \text{Eq. 2. 27}$$

Where:

E	= elastic stiffness (MPa)
σ	= applied stress (N/ mm ²)
ε	= resultant strain

In the ITST, the elastic deformation curve from the stress pulses can be illustrated in Figure 2.45. 'z' (in mm) is the amplitude of the resilient horizontal deformation obtained during the load cycle.

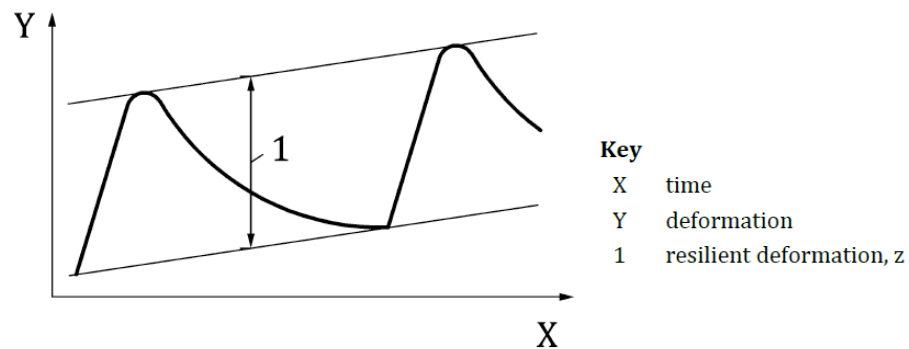


Figure 2. 45: The ITST elastic deformation curve

According to EN 12697-26, the modulus elasticity can be expressed as:

$$E = \gamma \frac{F}{z} \sin \varphi \quad \text{Eq. 2. 28}$$

With the indirect cylindrical specimen configuration, γ is suggested as $\frac{1}{b}(\nu + 0.27)$ with the applied load is $\varphi = 90^\circ$ from the strain measurement, thus results in the stiffness modulus of the specimen can be expressed as:

$$E = \frac{F(\nu + 0.27)}{z \cdot h} \quad \text{Eq. 2. 29}$$

Where:

ν	= Poisson's ratio
z	= amplitude of the resilient horizontal deformation (mm)
h	= specimen height (mm)

2.6.5. Asphalt rutting resistance

Rutting or permanent deformation resistance of asphalt mixture explains the ability of asphalt mixture to resist permanent damage generally caused by slow, heavy traffic loading and often occurs even more at a high-temperature asphalt or environment. Rutting can occur on one or more layers between the bituminous layers, the granular base

layer or the subgrade layer. This phenomenon is caused by a combination of densification of the layers due to the decrease in volume and shear deformation (Sousa, Craus, and Monismith 1991). It is also concluded that rutting is mainly caused by deformation flow without volume changing (Eisenmann and Hilmer, 1987). The greatest deformation occurs near the loaded surface and decreases gradually at lower layers (Hofstra and Klomp, 1972). Most pavement rutting occurs on the bituminous layer (HRB, 1962).

NAT in the University of Nottingham can be used in the asphalt mixture rutting resistance testing by implementing the Repeated Load Axial Test (RLAT) method. Firstly, the prepared asphalt mixture sample is tested in direct (vertical) mode, and the load pulse is applied. Then, the accumulated vertical permanent deformation is measured using the 2 LVDTs applied on top of the specimen. Figure 2.44 (b) shows the configuration of the permanent deformation testing using NAT.

In RLAT, the asphalt mixture specimen is loaded with a block pulse of axial stress of 100 ± 2 kPa. The load duration is 1 second, followed by 1 second rest, with the load pulse should be within 5% of theoretical 100kPa loading, i.e. between 95 to 105 kPa. In the testing process, a preload of 10kPa is commonly used for 600 ± 6 seconds (10 minutes), allowing the specimen to rest and be conditioned before the 100kPa stress loading. A minimum stress of 2kPa due to the top loading plate weight is also continuously applied during the test. The diagrammatic pulse load and the strain are shown in Figure 2.46 (BS EN).

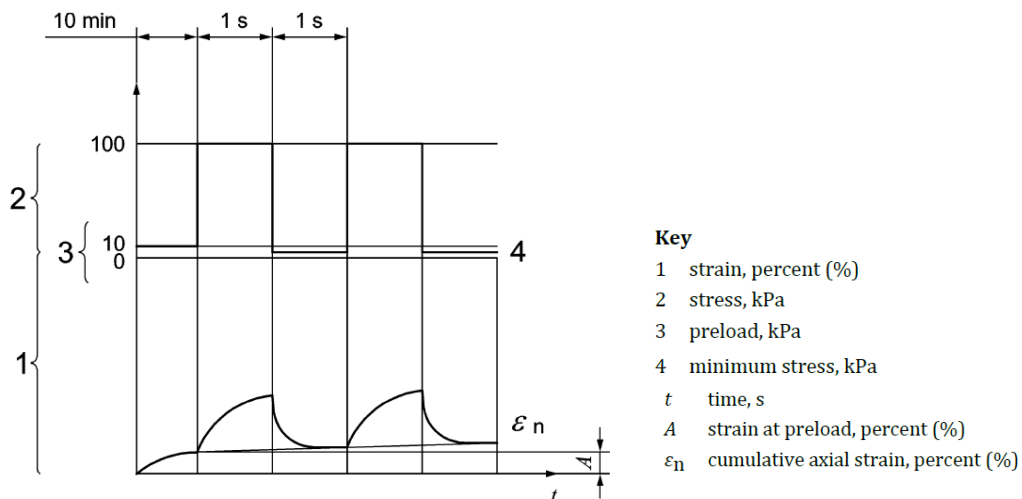


Figure 2. 46: Stress and strain curve in rectangular pulse loading RLAT (BS EN)

In RLAT, the block (rectangular) loading pulse is required to meet the minimum 'rectangular' shape as illustrated in Figure 2.47.

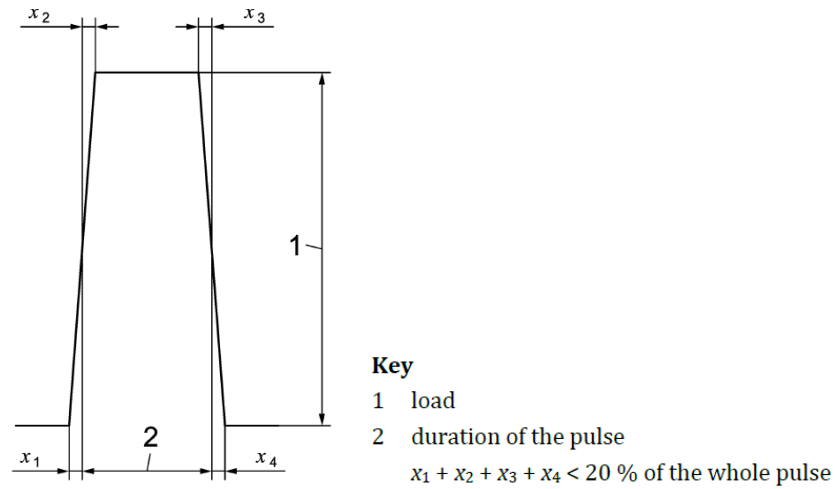


Figure 2. 47: The block loading pulse (BS EN)

Every single block load in RLAT resulted in an axial strain in the bitumen, as illustrated in Figure 2.47. With repeated loads, this axial strain accumulates and produces a permanent deformation generally visualised in the creep curve, as shown in Figure 2.48. This curve consists of three stages demonstrating the permanent deformation steps before the asphalt mixture failure.

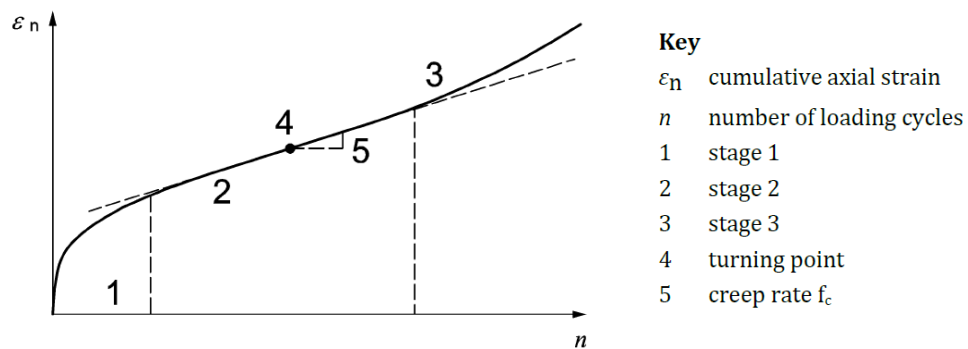


Figure 2. 48: Creep curve stages of repeated axial load (BS EN)

Stage 1 is the early permanent deformation where the rapid increase of the axial strain is shown. Stage 2 is when the axial strain increase is lower than stage 1, with the increasing proportion being relatively the same as the number of cycle loads. Stage 3 is the final stage, when the axial strain rapidly increases due to material failure. Depending on the asphalt mixture property, one or two stages may be absent in this creep curve of RLAT.

2.6.6. Asphalt fatigue resistance

Fatigue failure is a common asphalt mixture distress that occurs as a form of cracks due to the minor repeated stress that is generally less than the material's tensile strength.

Fatigue cracks come from generated tensile strains that occur because of repeated traffic loading and temperature fluctuation. This crack consists of two main phases: crack initiation and crack propagation.

Van Dijk (1975) used a wheel tracking test to study the fatigue characteristics of asphalt mixtures and discovered that fatigue-cracking development consists of a three-stage process:

- The first stage is when the hairline crack starts to appear. This stage is known as the crack initiation, which is only a small part of the fatigue life.
- In the second stage, tensile strain causes hairline cracks to widen and form a network of cracks, which is then called crack propagation. The number of load repetitions required to reach this stage is four times that of the first.
- Stage three is when the real cracks are clearly formed and visible. This stage requires more than 20 times greater load repetitions compared to reaching the first stage.

The asphalt mixture fatigue tests are conducted by applying loads to a specimen as alternating stress or strain and calculating the number of load repetitions required to cause the specimen to fail. The BS EN 12697-24:2018 provides several test methods to determine the dynamic stiffness and fatigue characteristics of bituminous mixtures, including:

- The 2-point bending test on trapezoidal or prismatic-shaped specimens
- The 3-point or 4-point bending test on prismatic-shaped specimens
- The indirect tensile test on cylindrical-shaped specimens
- Cyclic indirect tensile test on cylindrical-shaped specimens

Figure 2.44 (c) shows the configuration of the fatigue resistance testing by using NAT. The fatigue characteristics of tested materials are commonly presented as a fatigue line where the strains vs the number of loading cycles are presented. An example of a fatigue line is shown in Figure 2.49.

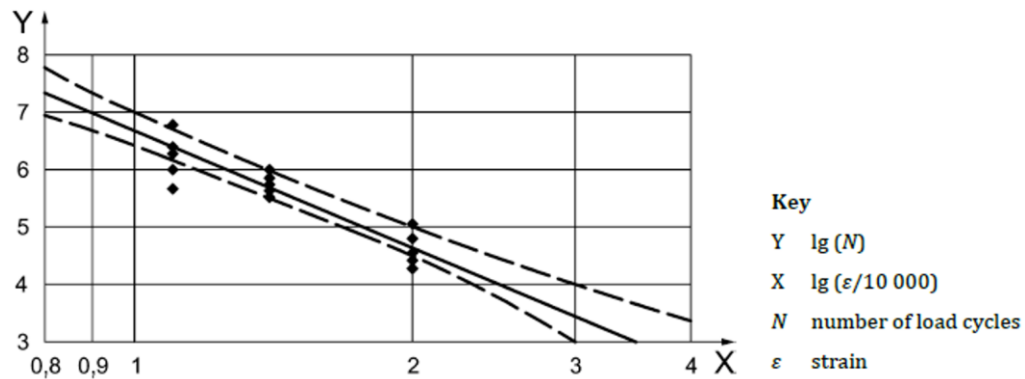


Figure 2. 49: Fatigue line example with strain vs number of loading cycles (BS EN)

The expected result of conducting this procedure, as mentioned in BS EN 12697–24:2018, are (1) understanding of the rank of bituminous mixtures based on resistance to fatigue; (2) understanding the relative performance in the pavement; (3) obtaining the prediction data of the structural behaviour of the road; and (4) the ability to judge test data according to bituminous mixtures specifications.

2.6.7. Bitumen and aggregate bonding strength

The bonding strength, affinity, or adhesion between bitumen and aggregate is the major key to affecting the performance of the asphalt mixture. The strong and durable adhesion is expected to result in a quality asphalt mixture with good stability and endurance. On the other hand, poor adhesion can lead to low endurance or even premature asphalt failure (Grönniger, Wistuba, and Renken 2010; Mulsow 2012; Riekstins, Haritonovs, and Balodis 2019). Many factors have been identified in influencing the adhesion between bitumen and aggregate. In bitumen, the chemical composition, provenance, surface tension, viscosity, and ageing resistance are likely to play a role, while in the aggregates, the porosity, surface roughness, mineralogy and chemical composition are the crucial factors to affect (Grönniger et al. 2010).

One of the widely used tests in Europe to measure the bitumen and aggregate affinity is the rolling bottle test according to BS EN 12697-11 standard. Although BS EN 12697-11 introduces three methods in bitumen and aggregates affinity tests: the rolling bottle test, static water immersion tests, and boiling water test. The rolling bottle test is considered the most suitable for asphalt mixtures test due to the applicability and reliability of the results (Grönniger et al. 2010; Nežerka and Trejbal 2020; Paliukaite et al. 2016). In this

test, a freshly made asphalt mixture is separated individually per aggregate, resulting in individual bitumen-coated aggregates. After 12 hours of room temperature conditioning, the specific amount of bitumen-coated aggregates are tested in the rolling bottle, with the condition of being immersed in distilled water. The coating condition (bitumen % coverage) after 6, 24, 48 and 64 hours of the test is recorded and measured. Figure 2.50 shows the reference of the bitumen coverage estimation.

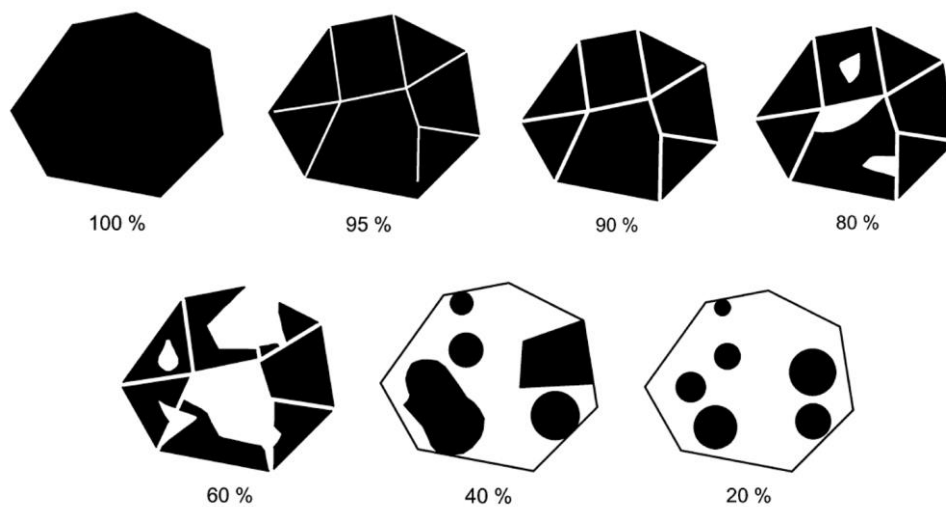


Figure 2. 50: Estimation of bitumen coverage (BS EN)

The bitumen coverage changes between the hours of testing should be tracked and presented in the plotting graph, as in Figure 2.51, for easy comparison and evaluation between specimens or bitumen types.

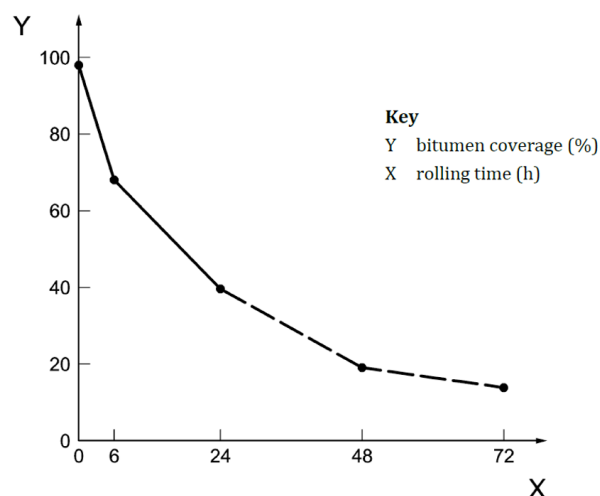


Figure 2. 51: Example of graphical presentation of bitumen coverage changes (BS EN)

2.7. Summary

This chapter has reviewed studies regarding bitumen modification, plastic-modified bitumen, the method of the modification, plastic as a polymer, ageing in plastic, and bitumen and asphalt mixtures performance tests. Based on this literature review, some conclusions can be stated as follows:

1. Studies on plastic-modified bitumen have been conducted for more than two decades and commonly resulted in better bitumen performance in the mixtures' rutting resistance and high-temperature properties. Polyethylene, including LDPE, LLDPE and HDPE, are widely studied plastic types as bitumen or asphalt mixture modifiers. In addition, these polyethylenes have been studied as virgin (pure) material or recycled material from waste plastics.
2. The dry and wet mixing methods of plastic modification have resulted in general agreement of higher stiffness, better-rutting resistance and some disagreement regarding fatigue resistance. These results are the same trend regardless of the plastic type. Therefore, this study is expected to produce similar results in rutting and fatigue.
3. The dry method is considered simpler in the application than the wet method. However, the wet method generally results in more homogenous mixtures and better performance at the same level of modification. In addition, the dry method generally requires plastic >10% of bitumen weight for good aggregate coating, whilst the wet method at 4-8% produces an improved bitumen property with proper viscosity.
4. Similar to previous studies, adding virgin or recycled LDPE as a bitumen modifier in this study is expected to improve bitumen's rheological properties and better asphalt mixture performances, especially rutting resistance.
5. For bitumen modification with LDPEs, low or high-shear mixing can be used at approximately 170°C. The high-shear mixing required a shorter blending time than low-shear mixing. Some studies stated that approximately 30 minutes high-shear mixing of polyethylene would result in homogenous blends. A more extended period will not result in any significant differences. Therefore, the 30-minute mixing duration will be used in this study.
6. Recycled LDPE is produced from previously used LDPE plastic undergoing various ageing and deterioration factors (lifetime degradation). Although some additives can be used in the recycling process to restore the material's properties, recycled

products will always have different properties than virgin. Therefore, in this study, the recycled and virgin LDPE are hypothesised to produce a different performance of modified bitumen.

7. Understanding the differences between virgin and recycled LDPEs can be done through FTIR spectroscopy and DSC thermal analysis. These methods can also be done to analyse the correlation between the unmodified and the modified bitumen, the ageing effect during the modification process, and the polymer's property changes.
8. Observing modified bitumen's microstructure or polymer dispersion can be done through optical microscopy to understand the modification effect and its correlation to modified bitumen's properties. Therefore, optical microscopy will be used in this study.
9. The asphalt mixture performance is highly related to bitumen and aggregates bonding strength. Therefore, measuring and differentiating the affinity of unmodified and modified bitumen to aggregates can help understand the changes or improvements in the asphalt mixture performance.

CHAPTER III: EXPERIMENTAL PROGRAMME

Experimental laboratory works consisting of two main phases were conducted to achieve this study's aim. The first phase is the work regarding the bitumen. This phase started with the bitumen preparation (modification process), the standard tests, the rheological tests, the Ductilometer tests, the ageing process and analysis, and microscopy works. Further tests were conducted on the bitumen and the selected aggregates for the asphalt mixture in this phase. The second phase is the asphalt mixture-related tests, including the mixture manufacture, compaction, permanent deformation, and fatigue resistance tests. This chapter explains the detailed experimental programme of this study.

3.1. Experiment Phase I

This phase focuses on sample preparation, including the neat bitumen and the virgin and recycled LDPE-modified bitumen. The bitumen used in this study is 50/70 pen bitumen as the middle range in Penetration Grade bitumen according to BS EN 12591:2009. As a widely used bitumen, this pen number has also been used for LDPE modification by Celauro et al. (2019) and Roman et al. (2016). The other consideration in choosing this pen number is, among the Penetration Grade bitumen according to BS EN 12591:2009, 50/70 bitumen is the closest penetration number to 60/70, the most commonly used pen number in Indonesia (Sihombing et al. 2020). The LDPE modifiers are the virgin LDPE from Sigma-Aldrich laboratory/chemical company and the recycled LDPE from B&J Parr recycling company.

3.1.1. Bitumen preparation

The modified bitumen was prepared by blending the 50/70 pen neat bitumen with the targeted amount of modifier by using specified methods. The blending process requires 1700-1800 mL of total blends, consisting of bitumen and modifier for each batch, using a high shear mixer of 5000 rpm at 160-170°C for 30±5 minutes. This procedure was chosen based on studies by Dalhat and Al-Abdul Wahhab (2017), who produced HDPE, LDPE, and PP-modified bitumen. The study found that the 4%wt LDPE modified bitumen required approximately 30 minutes in 5000 rpm at 160°C high shear mixing. Furthermore, the study stated that an extended period of high shear mixing was unnecessary as it produced insignificant changes in viscosity (Dalhat and Al-Abdul Wahhab 2017a).

This study uses 11 bitumen, including one unmodified bitumen (50/70 pen) as the control, five LDPE modified bitumen, and five recycled LDPE modified bitumen. The five modifications were chosen to understand the effect of different LDPE dosages on the bitumen. The 10% limit was determined based on studies that stated PE higher than 10% produces high viscosity and low workability for asphalt mixing (Punith and Veeraragavan 2007). Figure 3.1 shows the high-shear mixer.

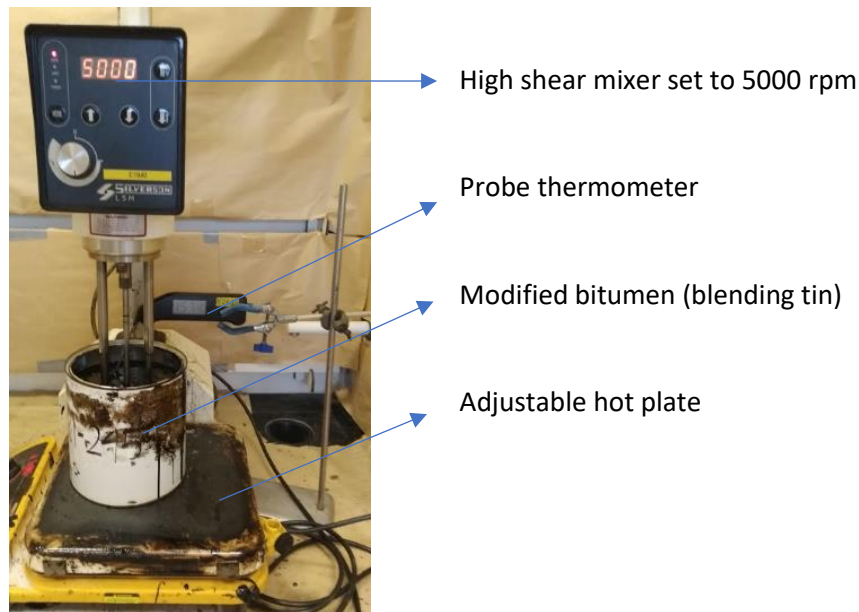


Figure 3. 1: Silverson L5M High shear mixer

The details of the procedure are as follows:

- (1) The neat bitumen was heated to 160°C until all the needed amount of the bitumen reached the desired viscosity for blending.
- (2) While the bitumen was heated, the blending tins were prepared and labelled with the sample number corresponding to the modification dosage.
- (3) The heated bitumen was transferred to a blending tin ($\pm 1700\text{mL}$) and weighed. Based on the bitumen weight, the targeted amount of LDPE was prepared.
- (4) The tin was placed on the heating plate under the high-shear mixer. The mixer head was immersed into the bitumen and run at a low shear rate ($\pm 250\text{ rpm}$). The LDPE was then transferred gradually to the bitumen at $\pm 20\text{ grams/min}$.
- (5) After the LDPE was fully transferred to the bitumen, the mixer was set to 5000rpm and started the 30 minutes blending process.

- (6) During the high shear mixer process, the bitumen temperature was monitored by using a probe thermometer and maintained at $165 \pm 5^\circ\text{C}$.
- (7) After 30 ± 5 minutes of mixing, the bitumen modification process was considered complete, and the bitumen was then transferred to smaller tins or vials for further tests. The virgin LDPE-modified bitumen is called 'LDPE modified', whilst the recycled LDPE modified bitumen is named 'rLDPE modified' bitumen.

The diagrammatic illustration of the modification procedure is shown in Figure 3.2.

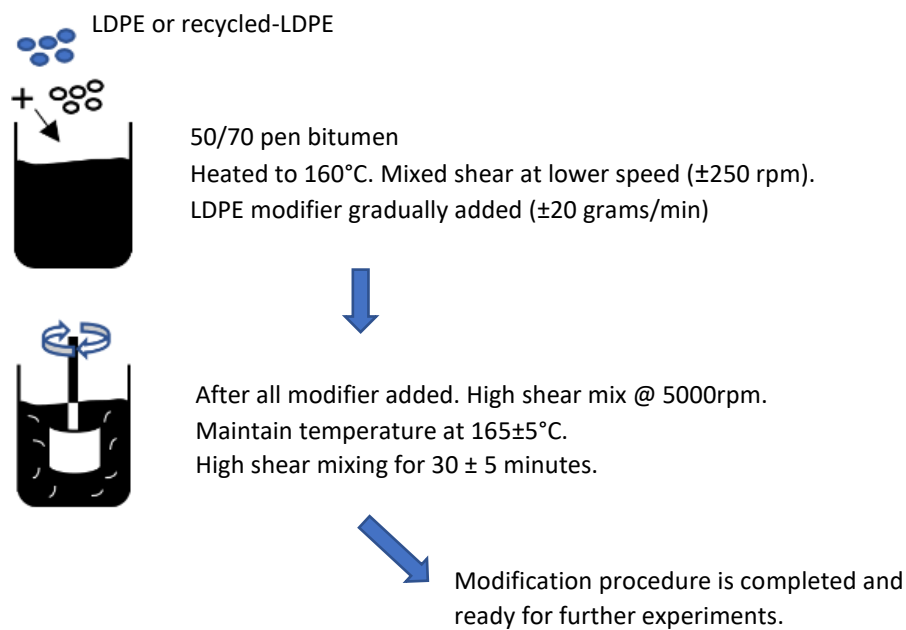


Figure 3. 2: Bitumen modification procedures

3.1.2. Viscosity, penetration number and softening point

3.1.2.1. Viscosity

Viscosity is one of the most important bitumen physical characteristics to optimize the preparation temperature of an asphalt mixture. According to BS EN 12697-35:2016, bitumen must have a viscosity of 0.17 ± 0.02 Pa.s to ensure the easy mixing process with aggregates and the optimal compaction of the freshly-made mixes. The Brookfield DV-II+ Pro rotational viscometer was used to test the viscosity due to the temperature changes of the unmodified and the modified bitumen by following the BS EN 13302:2018 standard. With the ability to perform the tests at a wide range of temperatures, rotational viscosity is considered the most practical means of measuring bitumen viscosity compared to other

testing methods (Brown et al. 2009). By using a standard S34 spindle size the bitumen viscosity was tested at 120°C, 135°C, 150°C, 165°C, 180°C and 200°C. Figure 3.3 shows the Brookfield rotational viscometer apparatus sets with the temperature controller and temperature chamber.

The procedures of the test were:

- (1) Approximately 100-gram bitumen was prepared in the oven at 160-170°C for unmodified bitumen and 170-180°C for modified bitumen. The prepared bitumen were poured into the testing cylinder. Gentle stirs were applied to homogenise the blends before the pouring process.
- (2) Meanwhile, the Brookfield viscometer was turned on and prepared at the lowest testing temperature (100°C).
- (3) The amount of 9.5 g of bitumen was poured into the testing cylinder and put the cylinder into the Brookfield temperature chamber.
- (4) The test was started after approximately 30 minutes of bitumen in the testing chamber.
- (5) After the testing at the desired temperature, the temperature was raised to the next higher temperature and repeated step (4).
- (6) In the case of highly modified bitumen, to minimize the effect of polymer separation, the test was taken once per target temperature per cylinder specimen, without the 'temperature rise and retest' as described in step (5)

3.1.2.2. The standard penetration tests

The standard penetration tests were carried out on all bitumen using the standard needle penetration test apparatus following BS EN 1426:2015. Setamatic penetrometer supplied by Stanhope-Seta was used in the bitumen penetration test. Each sample was prepared in an approximately 80 mL container and 60 minutes of 25°C water conditioning before the test. Then, the 97.5±0.05 grams of needle and mass weight were applied to the sample for 5 seconds. The penetration test apparatus is shown in Figure 3.4.

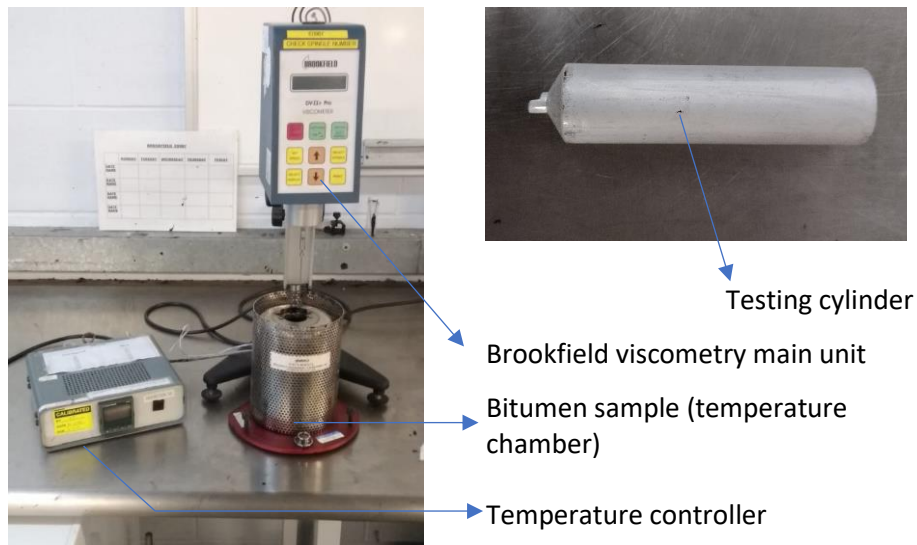


Figure 3. 3: Brookfield rotational viscometer apparatus

The penetration test procedures were:

- (1) The bitumen was heated in the oven at 160-170°C for unmodified bitumen and 170-180°C for modified bitumen. Then it was poured into the testing tin (± 80 mL) after a gentle stir to homogenise the modified blends.
- (2) The bitumen was cooled for 60 minutes at room temperature and then immersed in the water bath at a testing temperature of 25°C for another 60 minutes.
- (3) Put the tin into the testing jar filled with water from the water bath.
- (4) Put the tip of the needle slightly touch on top of the bitumen surface.
- (5) The testing procedure was started. The test was repeated on the same sample for the other two points, thus resulting in three pen readings per sample.

3.1.2.3. Softening point

The bitumen softening point observation was carried out using the standard ring and ball (R&B) test. For unmodified bitumen, a water-based bath was used. For a higher percentage of LDPE-modified bitumen, which is expected to have softening point $>80^{\circ}\text{C}$, a glycerol bath was used on the pair of the sample test. The RB365G tester by ISL was used for water-based testing configuration, while for glycerol-based immersion testing, the Petrotest RXA5 R&B tester was used. Figure 3.5 shows the R&B test apparatus.

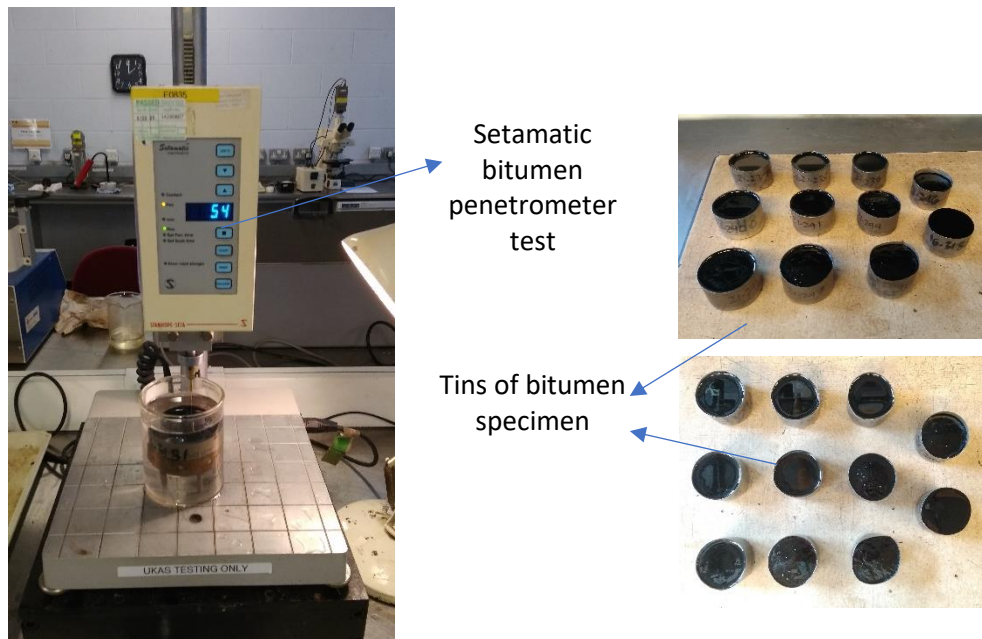


Figure 3. 4: Bitumen needle penetration test and the testing specimens

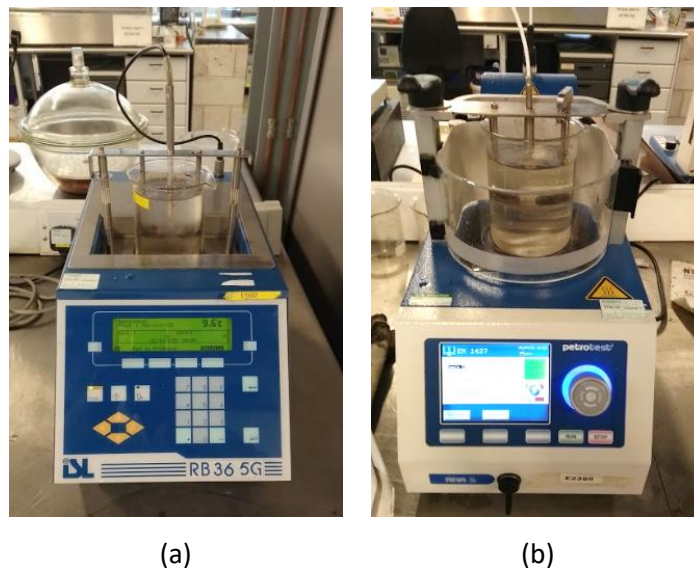


Figure 3. 5: (a) ISL RB365G for water-based bath softening point test, (b) Petrotest RXA5 for glycerol bath softening point test

The R&B test procedures were:

- (1) A small amount of bitumen (± 50 mL) was heated in the oven at 160-170°C for unmodified bitumen and 170-180°C for modified bitumen until liquid enough to be poured into R&B rings. A gentle stir was applied to the modified bitumen to homogenise the blends before pouring.

- (2) The rings were heated to not more than 100°C and then put on the pouring table that had been greased.
- (3) The bitumen was poured until there was a slight excess on top of the rings
- (4) The bitumen was cooled for 30 minutes at room temperature, and then cut the excess with the heated knife until the bitumen surface flat to the rings' top
- (5) The rings were assembled with the apparatus, put in the water bath, and stored in a cold room until they reached 5°C and maintained for 15-20 minutes. For modified bitumen, the assembled apparatus was put of glycerol at 30°C.
- (6) The balls were put on top of the specimen when ready to test. The tests were started at 5°C for the water-based bath and 30°C for the glycerol-based bath.
- (7) The test was started by initiating the temperature increase and the recording process.

3.1.3. Amplitude and Frequency sweep tests

The sets of dynamic mechanical analysis (DMA) tests were carried out using Gemini and CVO DSR by Bohlin Instruments. Amplitude sweep is the earliest test carried out in this stage to determine the bitumen's linear viscoelastic (LVE) region. Understanding the LVE ensures that further frequency tests of the bitumen will be carried on within these regions. Testing in the LVE region produces viscoelastic responses of the bitumen that are influenced by temperature and loading time and not the magnitude of the applied load (strain). Therefore, the loads (strain) were applied to increase gradually at a controlled frequency in this test. Tests were conducted using a 25 mm geometry set, with a minimum strain of 0.1% and a maximum strain of 10% at the temperature of 40°C. The amplitude sweeps tests showed that 0.3% of strain is within the LVE for all tested bitumen. This strain level was then used in the frequency sweep test.



Figure 3. 6: (a) Gemini, and (b) CVO Dynamic Shear Rheometer

The frequency sweep tests were carried out afterwards in two phases. For 25°C to 70°C with 5°C increments, the test used a 25mm spindle and base plate set, 1 mm gap, with 0.3% strain. The temperature of 10°C to 45°C with 5°C increments used 8 mm geometry set and 2 mm gap, 0.3% strain level. The tests were conducted on unaged bitumen at a minimum frequency of 0.1 Hz and a maximum frequency of 10 Hz. A thermal equilibrium time of 900 seconds was applied between the temperature changes. The loading temperature of the modified bitumen was at 70°C for any temperature tests. This temperature was chosen to ensure the bitumen was not suddenly cooled down after pouring and firmly applied and adhered to the top and the bottom plate before the test. The used Gemini and CVO DSR in this test are shown in Figure 3.6.

3.1.4. MSCR (multiple stress creep recovery) tests

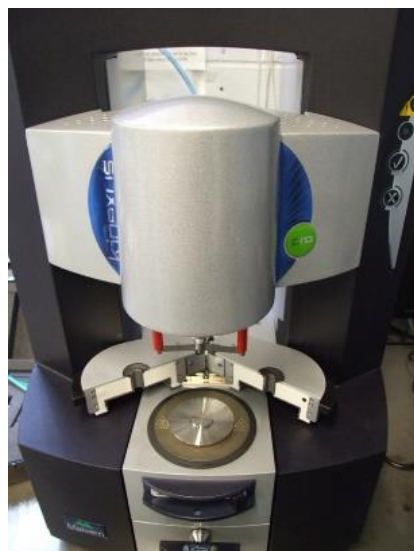
The Multiple Stress Creep Recovery (MSCR) test procedure is according to BS EN 16659:2015. This test was carried out by using a 25 mm geometry set and 1 mm gap at 50°C, 60°C, 70°C and 80°C temperatures. The tests were conducted by 1-second stress creep loading, followed by 9 seconds of zero stress recovery. This pattern was repeated another nine times to have a total of ten creeps and recoveries for each stress level and twenty creeps and recoveries data for all stress levels. The testing stress levels were at 100 Pa and 3200 Pa, running simultaneously with no rest period between them. The test was run once at every temperature; thus, after two simultaneous stress levels, the specimen was discarded, and a new bitumen sample was prepared for another testing temperature. The loading temperature also needed to be near the softening point, and the spindle was also heated during the bitumen application to ensure the bitumen

adhered properly. The 900 seconds equilibrium time was also applied before the test, which was counted after the temperature reached the loading temperature to the specified testing temperature.

In addition to the normal unaged bitumen, the MSCR tests were also conducted on the short-aged specimen from the rolling thin film oven (RTFO) to understand the short ageing effect on the rutting parameter of the bitumen. The Gemini and CVO DSR were used in this test.

3.1.5. LAS (linear amplitude sweep) tests

The linear amplitude sweep tests were carried out to evaluate the bitumen fatigue resistance by using the Kinexus DSR by Malvern Instruments Ltd. The short aged (RTFO) bitumen resistance to cyclic loading damage will be used to understand the modification effect on fatigue cracking based on AASHTO TP 101-12-UL. The tests were carried out in two main phases, the frequency sweep and the amplitude sweep. The frequency sweeps were applied on 0,1% strain at 20°C on 12 unique frequencies of 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 20, and 30 Hz. The amplitude sweeps were conducted at a frequency of 10 Hz in strain control mode. The strains were applied increasingly from 0.1 to 30% on the 3100 cycles of loading within 310 seconds of total test time. The 8mm spindle with a 2mm gap was used in this test.



8 mm specimen

Figure 3. 7: Kinexus Dynamic Shear Rheometer (DSR) and the specimen

3.1.6. DENT (double-edge-notched tension test)

The double-edge-notched tension test was conducted to measure the fracture resistance of the bitumen due to fatigue based on the LS-299 standard. This approach is based on the concept of essential work of fracture (EWF) of materials. The Ductilometer with three DENT moulds for each specimen was used in this test. The testing procedures of the DENT tests were:

- (1) The bitumen used in this test was the PAV-aged bitumen.
- (2) The bitumen was heated in the oven at 160-170°C for unmodified bitumen and 170-180°C for LDPE and rLDPE modified bitumen. A gentle stir to homogenise the blends was applied to the modified bitumen.
- (3) The DENT moulds were prepared by applying grease on the notches' surfaces to prevent adherence to the bitumen and ease of its extraction.
- (4) The bitumen was then poured into the DENT testing moulds with little excess on the top surface.
- (5) Two moulds per notches size were prepared; thus, a total of six moulds (six specimens) were prepared per bitumen type
- (6) The moulded bitumen was cooled for 30 minutes at room temperature and then was trimmed on the surface excess by using a hot knife.
- (7) The trimmed specimen was then immersed in the water bath at a testing temperature of 20°C for 90 minutes.
- (8) After the water bath conditioning, the notches then were taken off prior to the testing, and the test was conducted on every pair (two moulds) of the notches size.
- (9) After the first notch size, the tests were repeated on two other sizes. A total of three tests were conducted per bitumen.

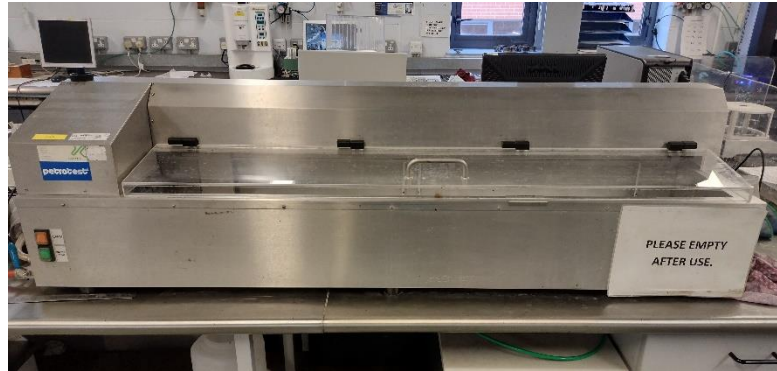


Figure 3. 8: The Ductilometer to perform the bitumen's DENT

3.1.7. Ageing procedure on bitumen

Bitumen ageing was conducted as a requirement for frequency sweep tests, MSCR tests, FTIR spectroscopy, LAS, and DENT tests. Two ageing procedures were used: short-term ageing by RTFO (Rolling Thin Film Oven) and long-term ageing by PAV (Pressure Ageing Vessel). RTFO test incorporates air flow to the heated bitumen film at 163°C for 75 minutes. PAV uses a pressure vessel for 20 hours with 100°C constant heating to the RTFO-ed bitumen specimens. Figure 3.9 shows the RTFO oven and PAV instrument.

The RTFO procedures were:

- (1) The bitumen was heated in the oven at 160-170°C for unmodified bitumen and 170-180°C for modified bitumen. A gentle stir was applied to the modified bitumen to homogenise the blends.
- (2) The RTFO oven was also turned on to reach the ageing temperature of 163°C
- (3) Eight different bitumen can be run simultaneously with a total capacity of eight bottles in the RTFO oven. One RTFO bottle amounts to 35±0.5 g of bitumen. One type of bitumen can also run on multiple bottles to have more samples for further tests.
- (4) 35±0.5 g of bitumen was poured into the RTFO bottle and labelled accordingly.
- (5) The bottles were put into the RTFO at the testing temperature (163°C). During this process, the oven temperature commonly dropped to lower than 163°C. The rotation and the air flow were then started.
- (6) The 75 minutes counting was started when the temperature reached back to 163°C.

- (7) The tests (ageing) procedure was stopped after 75 minutes, and the bitumen was poured out from the bottles into small tins for further testing purposes
- (8) For long-term (PAV) ageing, the bitumen was poured from the bottles to the PAV trays for further PAV procedures.



Figure 3. 9: RTFO Oven and PAV instrument

For specified bitumen test that requires long-term ageing, such as the DENT and the FTIR, the PAV procedures were conducted on the RTFO bitumen. The procedures of the PAV were:

- (1) 50.0 ± 0.5 grams of RTFO bitumen was poured into the PAV trays. The poured bitumen thickness was about 3.2 mm
- (2) The PAV were run at 100°C with (2.1 ± 0.1) MPa of pressure for 20 hours
- (3) After the ageing finished, the bitumen was transferred to the vacuum oven (170 ± 5) $^{\circ}\text{C}$ for (30 ± 1) minutes to release the trapped gas in the bitumen
- (4) The PAV-aged bitumen was ready for further tests.

3.1.9. Microscopy observation

The microscopy observation will be conducted to understand the bitumen morphology in the presence of LDPE modifiers. This work tends to know how the LDPE were dispersed in the bitumen and capture the polymer network phase in the blends. Based on the fluorescent microscopy observation, Polacco et al. (2005a) stated the dispersed LDPE phases in bitumen are spherical with no linkages with the bitumen. Thus, the LDPE polymers are immiscible, and there is very low interfacial adhesion between the two

phases, as shown in Figure 3.10 (a). There was an insignificant increase of ring and ball softening point (TR&B) that, according to Polacco et al. (2005a), indicated the minor enhancement of the modification. However, no further rheological tests were carried out by the author on this LDPE-modified bitumen. Adding reactive polymer (compatibilizer) to the LDPE blends helped the better polymer-rich formation, as shown in Figure 3.10 (b). The author also used LLDPE (linear low-density polyethylene) modified bitumen that showed a different result as shown in Figure 3.10 (c).

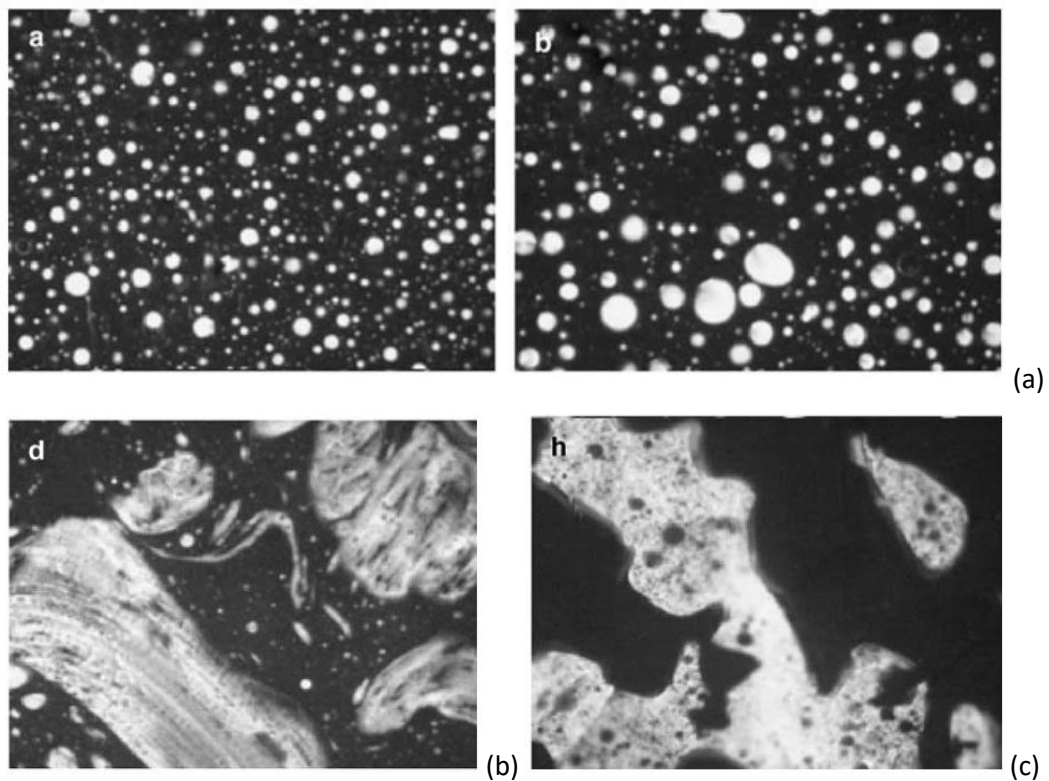


Figure 3. 10: Polyethylene dispersions in bitumen (Polacco et al. 2005a)

According to Polacco et al. (2005a), the TR&B can be used to measure the compatibility of the polymer blends, where the higher result of softening point represents a better blend of modification. Many studies have resulted in the higher softening point of LDPE modified bitumen, which is also represented in changes in rheological properties. This study will use microscopic works for the LDPE-modified blend observation to better understand any bitumen morphology changes affecting the bitumen's properties.

The microscopy tests will be conducted to understand the bitumen morphology, polymer dispersion, or polymer network changes in the presence of LDPEs. Different LDPE contents and types (virgin and recycled LDPE) will also be the observation variables. The bitumen will be heated to 160°C – 180°C, dropped on a heated glass slide, and the top glass squeezes the bitumen to get a thin glass slide specimen. The OPTIKA IM-3 microscope with ImageJ analysis software will be used in this work, as shown in Figure 3.11. The detailed microscopy specimen preparation and testing procedures are:

- (1) The bitumen was heated in the oven at 160-170°C for unmodified bitumen and 170-180°C for modified bitumen.
- (2) The hot plate specialized for glass preparation was turned on and set the temperature to 160-180°C.
- (3) Before the bitumen drop application, the glass slide was preheated on top of the hot plate to prevent sudden thermal changes that might cause cracks.
- (4) A tiny bitumen was dropped on the glass. And immediately, the top glass (cover) was put on the drop to squeeze the bitumen into a thin and slightly transparent.
- (5) After the bitumen had cooled down, the glass is ready to be observed under microscopy.
- (6) Two specimens were made per bitumen type as a precaution for glass braking.
- (7) The observations were made on the OPTIKA IM-3 with trials of 15 to 40x magnifications. Image capturing was done by the microscope's software.
- (8) The image analysis was done using ImageJ software.

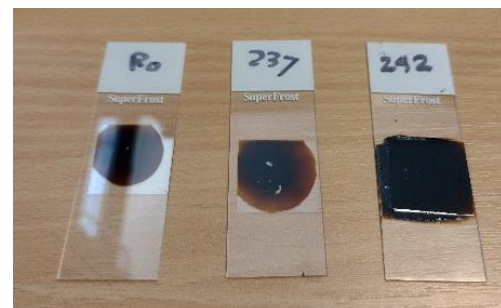
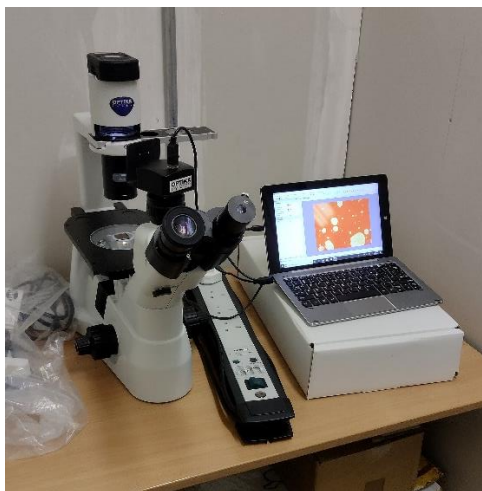


Figure 3. 11: OPTIKA IM-3 microscope and the glass slides of bitumen

3.1.10. Differential Scanning Calorimeter (DSC) tests on LDPE and rLDPE

The bitumen modifiers, i.e., LDPE and rLDPE were tested in Differential Scanning Calorimeter to measure their heat capacity and to understand their structural changes due to changes in the temperature. By conducting this test, the LDPE and rLDPE are expected to be distinguished in their temperature-changing behaviour. The structural transition data, such as melting point and glass transition, are expected in this test. The test also observed the consistency for several samples. Even though they come from different sources, both materials are expected to have relatively the same characteristic as LDPE. The results of this test might also be helpful to correlate the LDPE's temperature changes behaviour in affecting the modified bitumen rheological performance.

The testing procedures were:

- (1) A small amount of LDPE and recycled LDPE were prepared (± 20 mg) as the testing specimen
- (2) The specimens were put in the testing cup and closed with the lid
- (3) The testing was carried out with starting temperature of 60°C with linear increments up to 180°C
- (4) The test is completed once the top temperature is reached and the thermal characteristic data can be retrieved from the instrument software.

The test was carried out on Q2000 TA Instruments, as shown in Figure 3.12.



Figure 3. 12: Q2000 TA Instruments

3.1.11. FTIR test of bitumen

FTIR spectroscopy of bitumen was used to understand the ageing of bitumen and the functional group changes in the presence of LDPE. The test was carried out on unmodified bitumen, LDPE-modified bitumen and rLDPE-modified bitumen for unaged, RTFO-aged, and PAV aged. The Bruker Tensor 27 IR Spectrometry was used to measure the FTIR spectra of the bitumen. The spectra were acquired from $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} , with each measurement averaging 64 scans. Three trials of each bitumen sample were conducted at each RTFO and PAV ageing condition. The statistical coefficient of variation was used in the three trials to understand the data reliability. Van den bergh (2011) stated the coefficient of variation $<5\%$ obtained from FTIR data represents good results for further analysis. The Bruker instrument is shown in Figure 3.13.

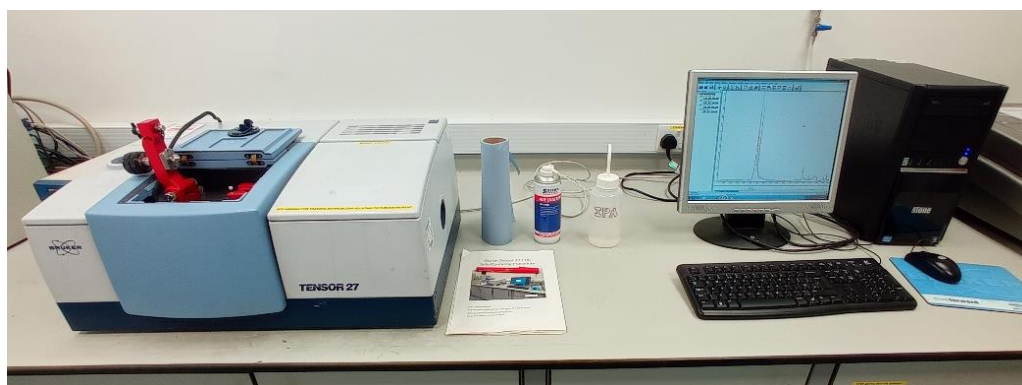


Figure 3. 13: Bruker Tensor 27 FTIR instrument

The testing procedures are:

- (1) The PC with the analysis software and the FTIR instrument was turned on.
- (2) The top mounter of the instrument was opened, and the diamond/bottom mounter was cleaned with isopropyl alcohol.
- (3) After the isopropyl alcohol was completely dried, the bitumen was prepared by scooping it from the prepared vials, cut it into small pieces ($\pm 3 \times 3 \times 2\text{ mm}$), and put on top of the instrument's diamond.
- (4) The top of the bitumen specimen was shielded with small paper, followed by closing the top mounter.

- (5) The tests were carried out on unmodified, 6% of LDPE-modified bitumen and 6% recycled LDPE-modified bitumen. In addition, those bitumen's RTFO and PAV ageing were tested, resulting in 9 bitumen types.

3.2. Experiment Phase II

Manufacturing and conducting tests on asphalt mixtures is the main aim of this phase. This phase consists of aggregate sieving or gradation preparation, asphalt mixture batching and gyratory compaction, specimen test on stiffness modulus, resistance to permanent deformation and fatigue resistance, and the rolling bottle test to identify the bitumen and aggregates affinity. The asphalt mixtures consisted of 5 types (1 unmodified and 4 modified bitumen). The four modified bitumen consisted of two LDPE-modified bitumen and two recycled LDPE-modified bitumen. The asphalt mixtures in this study only used one type of aggregate: limestone. This selection is based on literature stating that limestone minerals have higher polarity, are hydrophobic, have more adhesion, and are less susceptible to moisture damage than granite minerals (Haider et al. 2020). Therefore, the asphalt mixture tests tend to confirm the bitumen-increasing performance and measure the same parameters on the respective mixtures.

3.2.1. Mixing and compaction

Asphalt mixture fabrication was conducted by manual hand mixing according to BS EN 12697-35, followed by gyratory compaction in accordance with BS EN 12697-31. The manual hand mixing started with weighing (batching) the aggregates and oven both the aggregates and bitumen to reach 185°C for modified bitumen and 170°C for unmodified bitumen. After the pre-heating of the mixing bowl to the designed mixing temperature, the aggregates containing all the sieving sizes were poured and mixed well, followed by pouring the bitumen in a precise quantity. The mixing was started immediately afterwards with a duration of approximately 5 minutes. This mixing was done until the aggregates were coated entirely with the bitumen. The specimen was made one by one, and each mixing was done according to the mix design to reach the targeted dimension and density. For the asphalt mixture tests that include stiffness modulus, repeated load axial test, and indirect tensile fatigue test, cylindrical specimens were fabricated with 100mm diameter and 60mm height dimension by the gyratory compaction.



Figure 3. 14: (a) NU-14 (Nottingham Asphalt Tester), indirect configuration for (b) ITST/stiffness and (c) ITFT/fatigue

The asphalt specimen from gyratory compaction usually has bumpy or non-flat surfaces due to the nature of the aggregates. Therefore, the cuttings were done to the bottom and top of the specimens to obtain perfectly flat surfaces and reach the final dimension of 40mm height x 100mm diameter. This dimension is according to the tests' specifications. The gyratory compactions were done at 150°C, with binder content and mixture target density designed as 5.5% and 5%.

3.2.2. Asphalt mixture stiffness modulus

Asphalt mixture stiffness is one of the important properties of asphalt. It represents the ability of the asphalt to withstand the applied load and spread and distribute it to a wider

area of the material. The stiffness test is non-destructive; thus, the tests were carried out on all gyro specimens used on the permanent deformation and fatigue test. Sixty-five gyro specimens were tested with a diameter of 100 ± 1 mm and height of 40 ± 2 mm. The NU-14 or NAT (Nottingham Asphalt Tester), as shown in Figure 3.14, were used in all mixture tests, including the stiffness, permanent deformation, and fatigue resistance tests.

3.2.3. RLAT (Repeated Load Axial Test) of the mixture

The asphalt mixture's permanent deformation or rutting resistance was tested using RLAT (EN 12697-25:2016 Method A1) for five mixture types. Three gyratories (EN 12697-31) compacted specimens were prepared for each asphalt type. Table 3.1 shows the testing design and the NU-14 equipment.

3.2.4. ITFT (Indirect Tensile Fatigue Test) of the mixture

The asphalt mixture fatigue resistance was tested using the indirect tensile test (BS EN 12697-24:2018 IT-CY). Identical to the RLAT test specimen, three cylindrical-shaped asphalt specimens were prepared with a diameter of (100 ± 1) mm and height of (40 ± 1) mm for each asphalt type. This test also used NU-14 as the testing equipment. The number of specimens for fatigue, permanent deformation and stiffness tests are shown in Table 3.1.

Table 3. 1: Stiffness, RLAT and ITFT plan

	Test	Testing Plan/Specimens
1	Indirect Tensile Stiffness Test (ITST)	▪ 1 R0 bitumen x 13 ▪ 2 LDPE bitumen x 13 ▪ 2 rLDPE bitumen x 13 Total: 65 gyro specimens
2	Repeated Load Axial Test (RLAT) for resistance to permanent deformation	▪ 1 R0 bitumen x 3 ▪ 2 LDPE bitumen x 3 ▪ 2 rLDPE bitumen x 3 Total: 15 gyro specimens
3	Indirect Tensile Fatigue Test (ITFT)	▪ 1 R0 bitumen x 10 ▪ 2 LDPE bitumen x 10 ▪ 2 rLDPE bitumen x 10 Total: 50 gyro specimens

By conducting the asphalt tests, the conclusion on differences between rLDPE and LDPE-modified bitumen in rutting and fatigue resistance of asphalt mixtures are expected to obtain.

3.2.5. Rolling bottle test for bitumen – aggregate affinity

The rolling bottle test was conducted to qualify the bitumen and aggregate bond strength or affinity. This test was conducted in conform of BS EN 12697-11 (rolling bottle test part) on three types of bitumen: unmodified bitumen, 6% virgin LDPE modified bitumen and 6% recycled LDPE modified bitumen.

The procedures of this test are:

- (1) For each bitumen type test, approximately 600 grams aggregate of 6.3 mm to 10 mm fraction were prepared, washed with water, and dried at 110°C overnight oven.
- (2) On the day of mixture preparation, the mixing bowl was preheated to the designed mixing temperature (160°C for unmodified and 180°C for modified bitumen)
- (3) From the dried aggregate, 510 ± 2 grams of them were mixed intensively with 17.0 ± 0.2 grams of bitumen using a spatula in the mixing bowl until all the aggregates were thoroughly coated.
- (4) The mixes were then immediately spread onto flat metal or silicon-coated paper, with each of the aggregates separated individually/loosely spread and avoided any lumps as can be seen in Figure 3.15(a).
- (5) The mixes were then stored for 12 h for next-day testing.
- (6) After storage, the mixes were split into three parts of samples, each weighing 150 ± 2 grams.
- (7) The split portion was put into the testing bottle one by one particle (after the bottle was filled with distilled water). After all the mixes particles were in the bottle, the bottles were filled up and ready for the test.
- (8) The test was carried out by rolling the bottles with 60 rotation/min speed. Figure 3.15(b) shows the RBT test apparatus.

- (9) At 6, 24, 48, and 72 hours, the test was paused and the particle coating was read visually by taking out the particles from the bottle. After the reading the particles were put back into the bottle to continue the testing.



(a)



(b)

Figure 3. 15: a) Individually spread aggregate mixes for RBT, (b) the RBT settings

3.3. Summary

The experimental programme consists of preparations, tests and experiments on the LDPE modifiers, bitumen and asphalt mixtures. The summary of this chapter can be listed as follows:

1. Differentiating the virgin and recycled LDPE as the modifier is important for further analysis of the modified bitumen and mixtures. For this purpose, ATR-FTIR spectroscopy and DSC thermal analysis were done to differentiate the LDPEs' physical or chemical properties.
2. LDPE-modified bitumen preparation was done based on previous literature and studies. High shear mixing on 5000 rpm, 160-170°C, and 30 minutes duration were the selected method.

3. Bitumen's rheological properties were observed by DSR. Dynamic mechanical analyses were done on unmodified and LDPE-modified bitumen. The MSCR test observed bitumen's rutting resistance, while LAS tested fatigue resistance. In addition to LAS test, bitumen's resistance to fatigue cracking was also tested by Ductilometer's DENT.
4. The 30 minutes of high shear mixing at 160°C for modification could potentially age the bitumen. Therefore, ATR-FTIR spectroscopy was done on all modified bitumen to understand the ageing degree of this bitumen.
5. The microscopy analysis of the LDPE-modified bitumen was done to analyse the polymer dispersion that affects the bitumen's properties.
6. The bonding strength analysis of bitumen and aggregates that influence mixtures' fatigue and rutting properties was conducted on the rolling bottle method.
7. The asphalt mixture specimens were prepared by gyratory compaction based on BS EN, and the rutting and fatigue resistance tests of the asphalt mixture were conducted on the Nottingham Asphalt Tester (NU14).

CHAPTER IV: MODIFIER CHARACTERISTIC AND BITUMEN BLENDING RESULTS

This chapter elaborates on the LDPE-modified-bitumen general properties, including the standard bitumen penetration, softening point and viscosity tests. Because this study focused on two types of LDPE modifiers, i.e., virgin LDPE and recycled LDPE, to better understand the differences between the two materials, this chapter is started with a discussion of modifiers' characteristics.

4.1. Modifier characteristic

This study used two types of LDPEs as bitumen modifiers: virgin LDPE and recycled LDPE. The virgin LDPE is purely made LDPE granules for laboratory purposes produced by Sigma-Aldrich (Merck). The virgin LDPE comes in the form of round pellets with a diameter of 3-4 mm in white/opaque colour. The other material is the recycled LDPE produced and supplied by BJ Parr recycling company. This material has a mix of light to dark blue in the form of round flat pellets with a diameter of 4-5 mm, slightly bigger than the virgin LDPE. The general descriptions of the two LDPEs are shown in Table 4.1.

Table 4. 1: LDPE descriptions

Samples	General properties	Photo description
1. Virgin LDPE	Produced by Sigma-Aldrich (Merck) Diameter: 3-4 mm Form: round pellets Colour: white/opaque Melting point: 112°C	 A photograph showing a clear plastic jar filled with white, round pellets. To the left of the jar, several pellets are placed on a ruler for scale. The ruler shows markings from 0 to 4 cm. The text 'Sigma Aldrich - LDPE' is printed above the pellets.
2. Recycled LDPE	Produced by BJ Parr recycling company Diameter: 4-5 mm Form: round – flat pellets Colour: mixed, light to dark blue Melting point: 120°C	 A photograph showing a clear plastic jar filled with blue, round pellets. To the left of the jar, several pellets are placed on a ruler for scale. The ruler shows markings from 0 to 4 cm. The text 'BJ Parr - recycled LDPE' is printed above the pellets.

4.1.1. Modifier thermal changes characteristics test

This test was conducted to verify that the recycled and virgin LDPE satisfy the generally known low-density polyethylene thermal properties. Both LDPEs were tested in the Q2500 TA Instruments Differential Scanning Calorimeters (DSC) for thermal changes behaviour analysis. Two samples of 5.4 and 5.1 mg of LDPEs, and two recycled LDPEs with the weight of 5.9 and 3.9 mg were tested with the increasing ramp temperature method at a constant rate of 10°C/minute. The tests were carried out using one empty pan as a reference and the tested LDPE specimen pan, resulting in the DSC measurements as shown in Figure 4.1.

The tests were conducted in temperature cycles. The temperature cycle started from the initial room temperature of 25°C, raised to 200°C, turned down back to 50°C, raised to 200°C, cooled back to 50°C, raised to 200°C, and finally turned down back to room temperature. In addition, the DSC cycles and the range temperature were selected for two primary purposes. Firstly, the temperature range was chosen to understand the LDPE thermal characteristic at the mixing temperature with bitumen at 160-180°C. Secondly, in plastics studies, the standard operating procedure of DSC requires a heat-cool-heat cycle run. The first heating and cooling are to fulfil the requirement of the standard heat history of the material, which plays an essential role in the material's properties. The second and further heating allows the observation to produce a satisfactory output of the thermal characteristics (PerkinElmer 2010).

The DSC graph states that both materials have different melting points (T_m). The virgin LDPE has a melting point of 110°C, whilst the recycled LDPE has a slightly higher T_m of 123°C. The virgin LDPE shows the typical LDPE melting temperature result that corresponds to previous studies and literature, which vary from 106 to 112°C (Mohsen Mohammadi, Ali Akbar Yousefi 2010; Prasad 1998). The recycled LDPE, on the other hand, based on the wider melting valley and the higher melting point, suggests several indications as follows:

- 1) The material (recycled LDPE) has the potential partial miscibility of a meagre amount of other material, e.g. HDPE (Mohsen Mohammadi, Ali Akbar Yousefi 2010). This condition could occur during the recycling process that used various sources of plastic materials, which were probably contaminated by or in-deliberately included a higher density polyethylene material.

- 2) The material probably has lost or reduced its molecular chain branches. The lower chain branches resulted in a more compact and higher density LDPE with a higher melting point than virgin LDPE. This condition is either due to previous life usage or during recycling.
- 3) The material has increased its density due to the rise of oxygen content during its life ageing (Komitov et al. 1989). The higher content of weighty oxygen molecules increases the materials' density.
- 4) However, the LDPE's more compact form is less than high-density polyethylene (HDPE) with a melting point of 130°C.

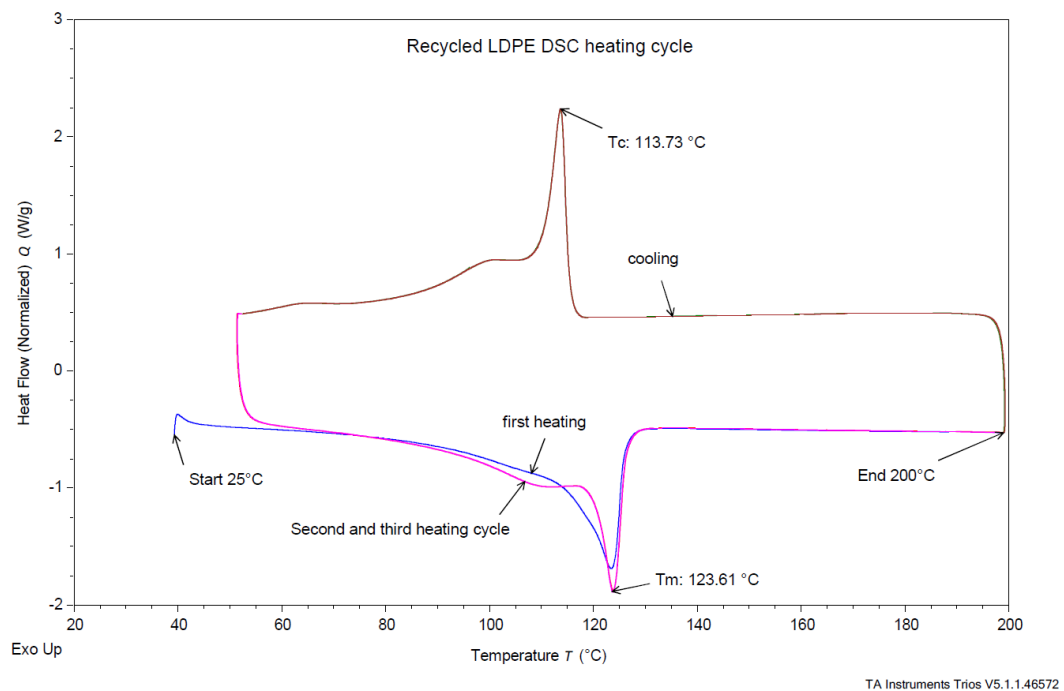
This type of polyethylene is commonly categorised as linear low-density polyethylene (LLDPE). LLDPE is a form of polyethylene with lower molecular branches than the LDPE, with a slightly higher melting point at approximately 120°C. Compared to LDPE, the linear LDPE has better thermal and mechanical properties such as stiffness, puncture and elongation but is more difficult to process (Prasad 1998).

The DSC thermal graph suggests that, although both materials have relatively the same T_m starting point (approximately 75°C), there are differences between the two materials in terms of the valley area shape and, consequently, the valley peak, i.e. the melting point, T_m . The recycled LDPE requires higher endotherm (heat absorption) heat flow changes than the virgin LDPE. The two virgin LDPE specimens have $T_m = 110.96$ and 110.30°C and total endotherm energy of 39.24 and 33.35 (W/g)°C. The melting valley of this material shows an instantaneous fall at around 106°C before peaking at 110°C as the melting point. The recycled LDPE has shown a different valley shape. Starting at approximately the same temperature, 75°C, the valley slope decreased and flattened at 110°C. The curve continued to increase at around 115°C until reaching the peak of 123°C. The recycled LDPE specimens have T_m of 123.45 and 123.77°C, with the total required melting energy of 44.04 and 46.69 (W/g)°C.

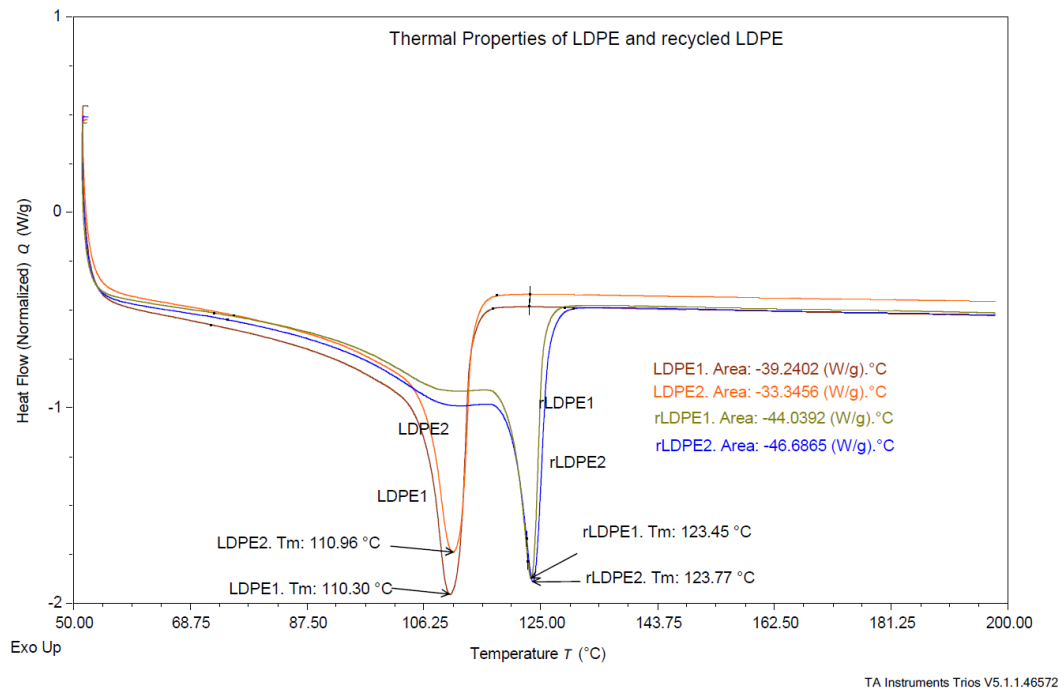
The relatively same slope of the endotherm heat flow that started at approximately 75°C suggests that these materials share the same fundamental molecules of polyethylene (Mohsen Mohammadi, Ali Akbar Yousefi 2010). The slope changes in the recycled LDPE at around 110°C (become flat) are probably due to the partial miscible of higher density of polyethylene particles that increase the material's thermal property. These thermal property changes allow the material to absorb the heat to raise the temperature other

than to melt its body. After the contributing higher density polyethylene has reached its heat absorption limit, the whole material started melting and peaks at 123°C as the melting point.

A similar endothermal starting slope might describe the two materials' close principal properties. However, there are differences in the endotherm valley shapes; the total endotherm energy for both materials to melt; and ultimately, the melting point. Moreover, the larger width of the melting valley of recycled LDPE explains the higher dispersity (Komitov et al. 1989), representing the potential presence of other molecules (Mohsen Mohammadi, Ali Akbar Yousefi 2010). With these differences, the two materials present two different properties of polyethylene. Based on their melting point, according to the literature, the virgin LDPE can be categorised as LDPE, whilst the recycled LDPE is more likely to be Linear LDPE.



(a)



(b)

Figure 4. 1: DSC test results: (a) heating cycle of rLDPE and (b) melting point of virgin and recycled LDPE

4.1.2. Modifier's FTIR results

The chosen band for polyethylene analysis under the FTIR method are the regions 3000–2800, 1550–1400 and 750–650 cm^{-1} (Gulmine et al. 2002). Two samples of each LDPE type (virgin and recycled) were tested for FTIR spectra by ATR from 4000–600 cm^{-1} wavenumbers. The samples were thin sheets from a cut of the LDPE granule. Without further sample preparation, the ATR method obtains the spectra directly and relatively quickly from the LDPE cut sheet (Gulmine et al. 2002). The FTIR test on all LDPEs, as shown in Figure 4.2, exhibits the same typical peaks region as expected, as described in Table 4.2. Variations of intensity were recorded at specified polyethylene area as shown in Figure 4.3.(a) for 3000–2800 cm^{-1} , Figure 4.3.(b) for 1550–1400 cm^{-1} , and Figure 4.3.(c) for 750–650 cm^{-1} . Still, all remain at the same fundamental vibration frequency. The intensity variation is generally caused by the thickness differences between the tested specimen and accepted as the same chemical functional group as long as at the same band number.

Table 4. 2: Band assignments and qualitative analysis of polyethylene (Gulmine et al. 2002)

Band (cm^{-1})	Assignment	Intensity
2919	CH_2 asymmetric stretching	Strong
2851	CH_2 symmetric stretching	Strong
1473	Bending deformation	Strong
1377	CH_3 symmetric deformation	Weak
720	Rocking formation	Medium

Figure 4.3.(a) shows the double peaks at the wavenumber region of 3000–2800 cm^{-1} , which is 2850 cm^{-1} and 2920 cm^{-1} , representing the strong intensity of CH_2 asymmetric and symmetric stretching. Both are the typical peaks of band absorption in polyethylene with solid intensity, thus described in the clear spikes in both wavenumbers. Another clear sign of IR band absorption in polyethylene is at 1470 cm^{-1} , assigned as bending deformation in strong intensity, and at 1377 cm^{-1} as a weak intensity of CH_3 deformation as shown in Figure 4.3.(b). There is also a rocking deformation at the medium intensity in the 720 cm^{-1} , as shown in Figure 4.3.(c).

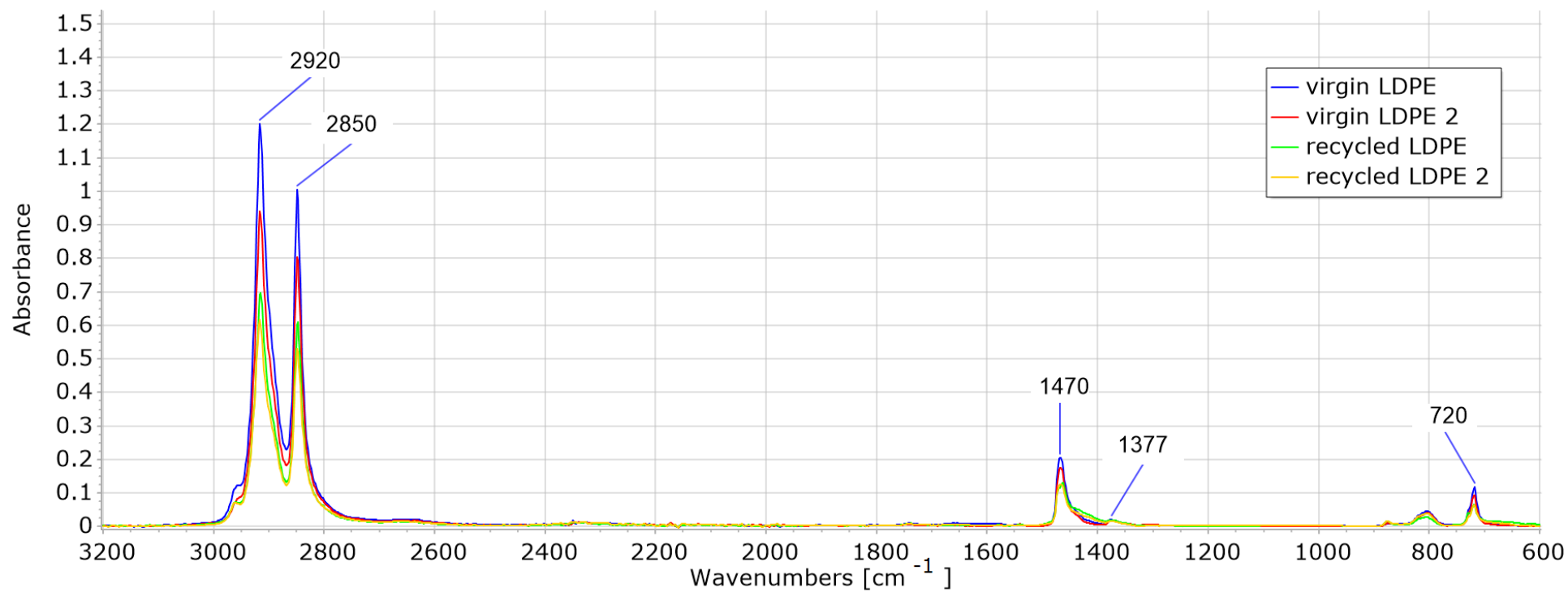
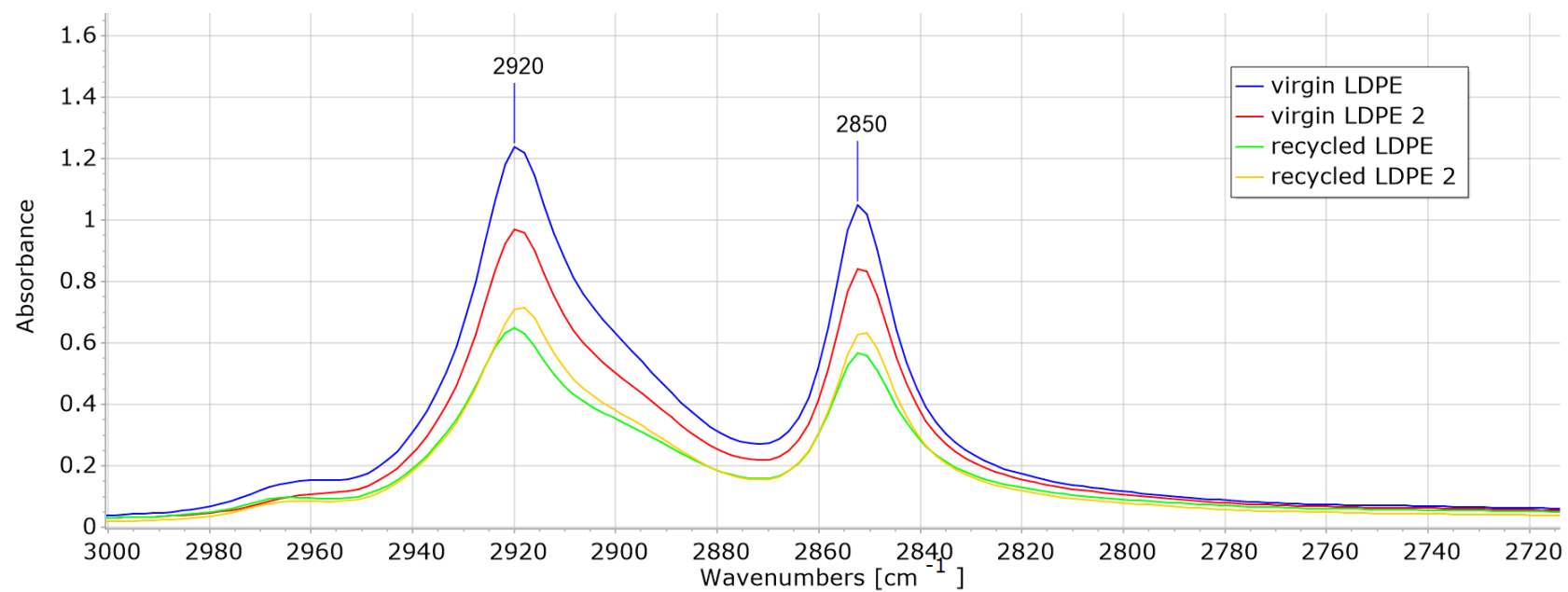
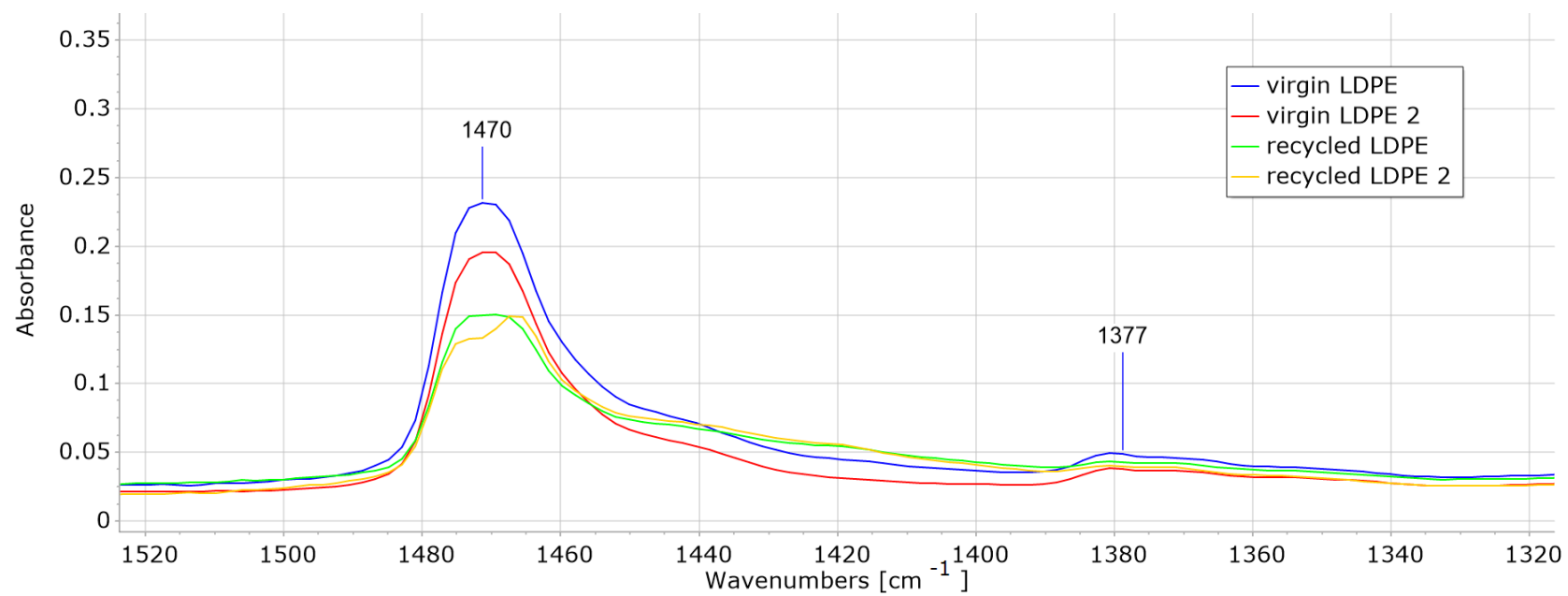


Figure 4. 2: FTIR spectra of virgin and recycled LDPEs

(a) Detail LDPE spectra at region 3000-2800 cm^{-1}



(b) Detail LDPE spectra at region 1550-1400 cm^{-1}



(c) Detail LDPE spectra at region 750-650 cm^{-1}

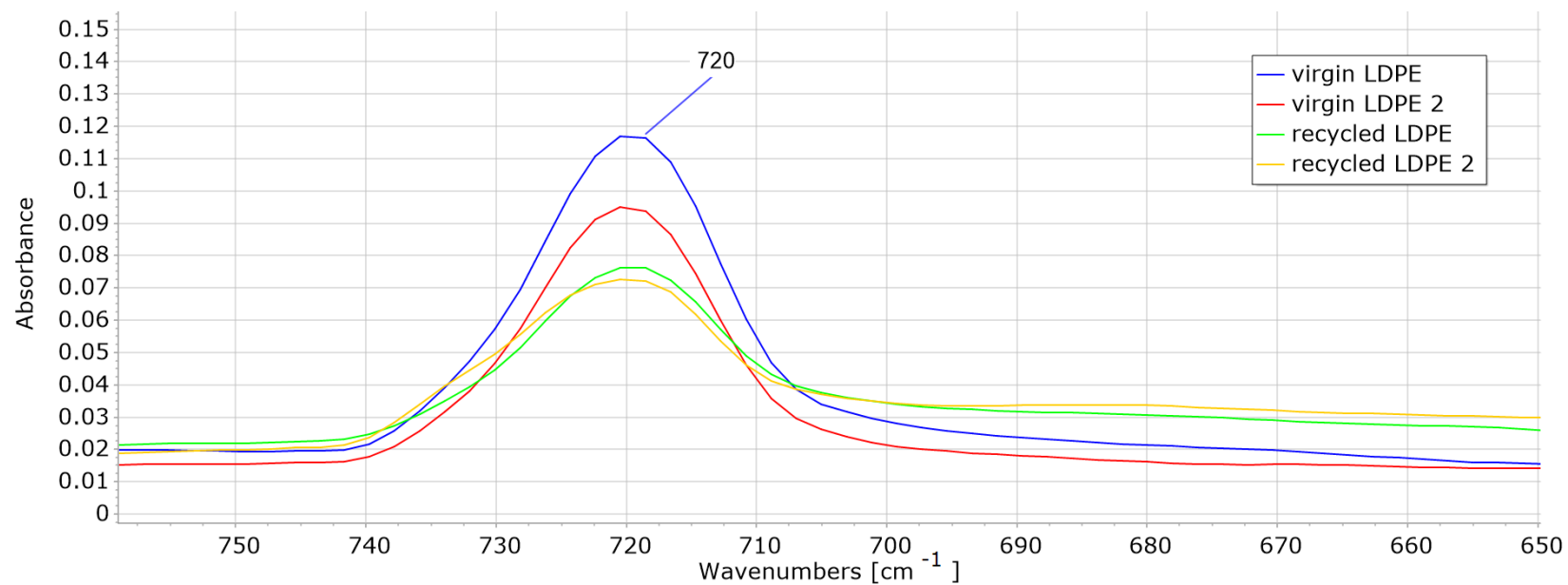


Figure 4. 3: Detailed FTIR spectra of LDPE modifier at region of (a) 3000-2800 cm^{-1} , (b) 1550-1400 cm^{-1} and (c) 750-650 cm^{-1}

The FTIR results of the LDPEs that correspond to previous studies (Gulmine et al. 2002; J. Haslam, H.A. Willis 1983; Zbinden 1964) explain that both materials are LDPEs as expected, either as a virgin products or recycled material. The variance intensity of peaks can be attributed to differences in sample thickness in the preparation process (Gulmine et al. 2002). Nonetheless, according to the common peak absorbances, all samples satisfy the typical FTIR result of polyethylene.

However, it should be noted that from the DSC test, the two distinguishable melting valleys and peaks revealed that the materials are essentially different. The virgin LDPE has the general properties of LDPE, while the recycled LDPE can be categorised as LLDPE. This finding shows that the ATR FTIR procedure could not clearly distinguish the two LDPEs. Therefore, several points might be concluded from the test:

- (1) The used ATR FTIR procedure can be used to recognise the generally known polyethylene functional groups (Gulmine et al. 2002; J. Haslam, H.A. Willis 1983; Zbinden 1964)
- (2) However, the ATR FTIR procedure was unable to distinguish the density differences of the polyethylene molecular chains clearly,
- (3) From the observed functional groups, both used materials (virgin and recycled LDPE) can be confirmed as polyethylene polymers.

4.2. Bitumen modification procedures and results

The high shear mixing modification for each bitumen batch was carried out in a mixing tin with a total volume of 2000mL. The modification was started by preparing approximately 2000 grams of bitumen and an amount of LDPE modifier as targeted. The modification was started by heating the neat 50/70 pen bitumen to $160\pm5^{\circ}\text{C}$ as the targeted blending temperature. After being heated to the designed temperature, the bitumen was carefully poured into the mixing tin to a net weight of 1700 ± 25 grams. The amount of LDPE or recycled LDPE were then calculated based on the bitumen weight, followed by gently pouring into the bitumen at approximately 20 grams/minute. The mixing was set at a lower speed of 200-250 rpm during this LDPE pouring. After all the modifiers were added to the bitumen, the blending speed was turned up to the designed procedure of 5000 rpm. The high shear mixing with the duration of 30 ± 5 minutes was carried out while maintaining the bitumen blends temperature at $160\pm5^{\circ}\text{C}$. To maintain the temperature,

a probe thermometer was installed, immersed in the bitumen, and continuously monitored during the mixing. The hot plate temperature controller has adjusted accordingly to the temperature changes of the bitumen blend.

Table 4. 3: Modification composition

No	Composition Name	%wt LDPE modifier	
		Virgin	Recycled
1	R0 (unmodified)	-	-
2	VL1	2	-
3	VL2	4	-
4	VL3	6	-
5	VL4	8	-
6	VL5	10	-
7	RL1	-	2
8	RL2	-	4
9	RL3	-	6
10	RL4	-	8
11	RL5	-	10

By visual observation, the end of the mixing procedure showed that the LDPE modifiers were dispersed homogenously in the bitumen blend. This result was as expected and similar to previous studies. Also, to this result, the modification procedure was considered satisfying the planned program; therefore, no further period was added to the modification process. Shorten the modification as a precaution to prevent risks of oxidations and bitumen ageing. Moreover, the visually satisfactory result corresponds to previous study that stated no further significant changes in the LDPE-modified bitumen viscosity were observed after a more extended period of high shear mixing (Dalhat and Al-Abdul Wahhab 2017a).

After each mixing process on the designed duration had been completed, the bitumen was separated into smaller containers for further tests. The bitumen modification was carried out on 10 (ten) different variations with a total of 11 types of bitumen to test, as shown in Table 4.3. The bitumen names were then assigned to each type with the unmodified 50/70 bitumen named R0, the recycled LDPE modified bitumen named RLs, and the virgin modified bitumen named VLs. RL1 to RL5 and VL1 to VL5 correspond to the degree of modification as explained in the table.

4.3. Bitumen softening point and penetration number

Bitumen was tested on the standard needle penetration number and the ring and ball softening point. The unmodified bitumen has a penetration number of 54 at the 25°C test, according to BS EN 1426 2015. This result was expected as the bitumen is recognised as a 50/70 pen grade number. The modified bitumen test resulted in a pen number decrease at 25°C. The reductions of the penetration number were increasing in line with the modification rate of the blend. On the exact dosage of modification, however, the recycled LDPE produced more reduction (lower) in the penetration number compared to virgin LDPE, especially for more than a 4% modification rate.

The softening point test was conducted based on BS EN 1427 2015. Two liquid baths were used in this test, i.e. water and glycerol. For highly modified bitumen whose softening point reached >80°C, the test was stopped and repeated using the glycerol bath. Table 4.4 shows the results of the test. On a low modification rate (2% and 4%), there are no significant differences in softening point between the virgin LDPE and recycled LDPE. The significant softening point jump occurred on 6% of recycled LDPE-modified bitumen, reaching 109°C compared to 60°C for virgin LDPE. The softening point increased even more at 8% and 10% rates of recycled LDPE-modified bitumen. The virgin LDPE had a similar significant softening point leap on 10% of modification, even at a lower increasing rate than the recycled LDPE.

Table 4. 4: Bitumen softening point and penetration number

Bitumen	Pen number at 25°C	Softening point °C
R0	54	54.0
VL1	42	55.2
VL2	39	58.9
VL3	33	60.0
VL4	33	66.8
VL5	26	94.3
RL1	41	54.9
RL2	32	59.9
RL3	28	109.0
RL4	23	113.0
RL5	15	121.0

The penetration and softening point tests resulted in a relatively consistent pattern where a lower modification rate (2 and 4%) produces the same rate of changes for both recycled

LDPE and virgin LDPE. However, the more evident difference in the modification effect can be recognised at a 6% and higher modification rate, where the recycled LDPE produced a noticeably lower pen number than virgin LDPE at the same modification rate. Similar trends were also observed in the softening point test result, where the recycled LDPE produced a drastically higher softening point than virgin LDPE. Figure 4.4 visualises the test result.

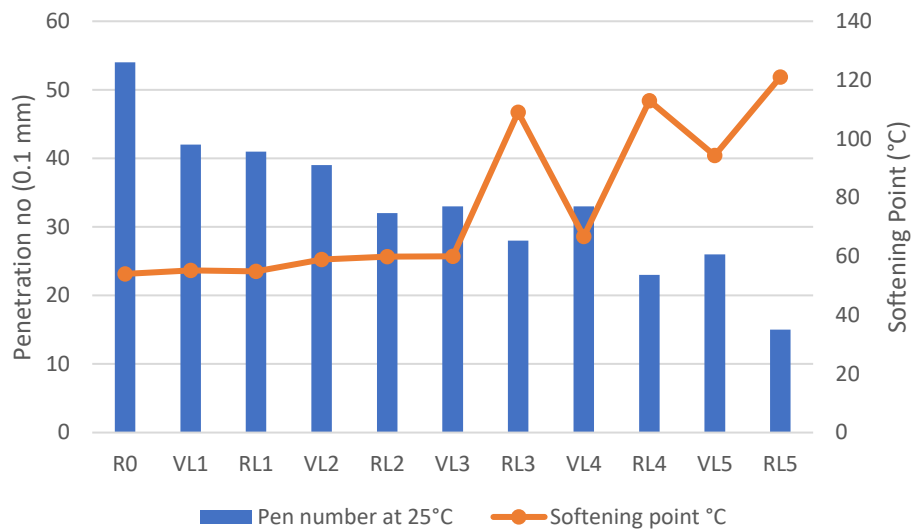


Figure 4. 4: Bitumen pen number at 25°C and softening point

A higher softening point, viscosity, and lower penetration number can be associated with a higher asphaltene component of the bitumen. In addition, the breakdown during heating and reform on the cooling of the asphaltene component also affects bitumen stiffness properties. However, changes in the asphaltene component that affected the bitumen's standard test results were not the case because they were using the same base bitumen, the same testing temperature, and the same and carefully taken modification (high shear mixing) duration.

Therefore, this result can refer to the successful modification of the recycled LDPE to the bitumen. In other words, this can be directed to the better ability of recycled LDPE to change the microstructural shape of the bitumen compared to the virgin LDPE.

At a lower modification, the microstructural changes are insignificant for both bitumen to affect the bulk bitumen's properties. However, at higher modification, the structural changes are strong enough to affect the bitumen properties, especially for the recycled

LDPE. This phenomenon has been captured in the standard tests of pen number and softening point. The microstructural changes will also affect the rheological properties of the bitumen. Later in the following chapters, the differences in the rheological properties of virgin and recycled modified bitumen will be observed and elaborated. Furthermore, the microscopy analysis will also help to explain the phenomenon.

4.4. Bitumen viscosity

Table 4.5 shows the result of the Brookfield viscosity test on the 11 bitumen combinations. The test result clearly states that the LDPE modifier increases the bitumen's viscosity, which is in line with the increase of softening point and the reduction of penetration number.

According to BS EN 12697-35, the viscosity range of 0.17 – 0.28 Pa.s is required for good workability for bitumen mixing with aggregates and the asphalt compaction process. According to this guidance, Figure 4.6 shows unmodified bitumen R0 starts to have good workability at 145°C. Meanwhile, the modified bitumen VL1 and RL1 have good workability at 150-153°C, VL2 and RL2 at 160°C, while VL3 and RL3 start at 180°C. The higher modification rate bitumen (≥ 8 %wt) shows a significantly higher viscosity. VL4 requires $>185^\circ\text{C}$ to have viscosity under 0.30 Pa.s, while RL4, VL5, and RL5 require $>200^\circ\text{C}$. These results show that the feasible modification rate for virgin and recycled LDPE is lower than 8%wt bitumen. The viscosity test result confirmed the difficulties experienced during the bitumen preparation for an 8% and higher LDPE modification.

Hot asphalt mixtures are commonly prepared at 160°C or slightly higher for modified bitumen in the mixing process with aggregates. From the test result, the range of viscosity 0.17 – 0.28 Pa.s for good workability is practically impossible to reach for the highly modified bitumen at average hot mixing temperature. The highly modified bitumen requires a temperature higher than 200°C to reach the viscosity range for reasonable workability. The test result shown in Figure 4.6 explains how the highly modified bitumen (RL4, RL5, VL4 and VL5) have high viscosity even though at a temperature of 180°C. This temperature is considered an unreliable and unfeasible preparation temperature for asphalt mixing.

Based on this result, the VL4, VL5, RL4 and RL5 are considered impractical for further use. Furthermore, the workability concern of highly plastic-modified bitumen was also stated

in previous studies (Almeida et al. 2020a; Hu et al. 2018a; Movilla-Quesada et al. 2019b). Therefore, based on this result, some of the planned tests on VL4, VL5, RL4 and RL5 will not be conducted on the following chapters' bitumen tests, and there will also be no further work on the asphalt mixture tests.

Table 4. 5: Bitumen viscosity test results

Bitumen		Viscosity (Pa.s)					
		120°C	135°C	150°C	165°C	180°C	200°C
R0	Unmodified 50/70	1.50	0.43	0.24	0.12	0.07	0.05
VL1	2% LDPE	1.48	0.61	0.31	0.17	0.10	0.08
VL2	4% LDPE	2.03	0.84	0.42	0.22	0.15	0.08
VL3	6% LDPE	3.45	1.38	0.71	0.42	0.27	0.16
VL4	8% LDPE	3.80	1.76	0.96	0.56	0.33	0.21
VL5	10% LDPE	6.45	3.71	1.87	0.92	0.62	0.35
RL1	2% rLDPE	1.72	0.60	0.33	0.19	0.12	0.09
RL2	4% rLDPE	3.01	0.92	0.42	0.23	0.14	0.11
RL3	6% rLDPE	5.08	1.75	0.85	0.49	0.28	0.16
RL4	8% rLDPE	32.39	10.02	4.35	2.24	1.53	0.81
RL5	10% rLDPE	N/A	13.16	7.86	4.21	2.21	1.17

The high viscosity at high temperatures on the modified bitumen is in line with previous results of low penetration and high softening point tests. This phenomenon can also refer to the presence of a polymer network that forms in the bitumen structure that affects the physical properties of the bitumen.

Figure 4.5 shows the changes in viscosity in the changes of temperature and modification percentage. The graph demonstrates the precise viscosity reduction pattern with the temperature increase. This trend is shown for all bitumen, including the unmodified, virgin LDPE and rLDPE modified bitumen. The graph also exhibits a consistent viscosity increase in the addition of LDPE modifiers, with a noticeably higher rise for rLDPE compared to the virgin LDPE-modified bitumen.

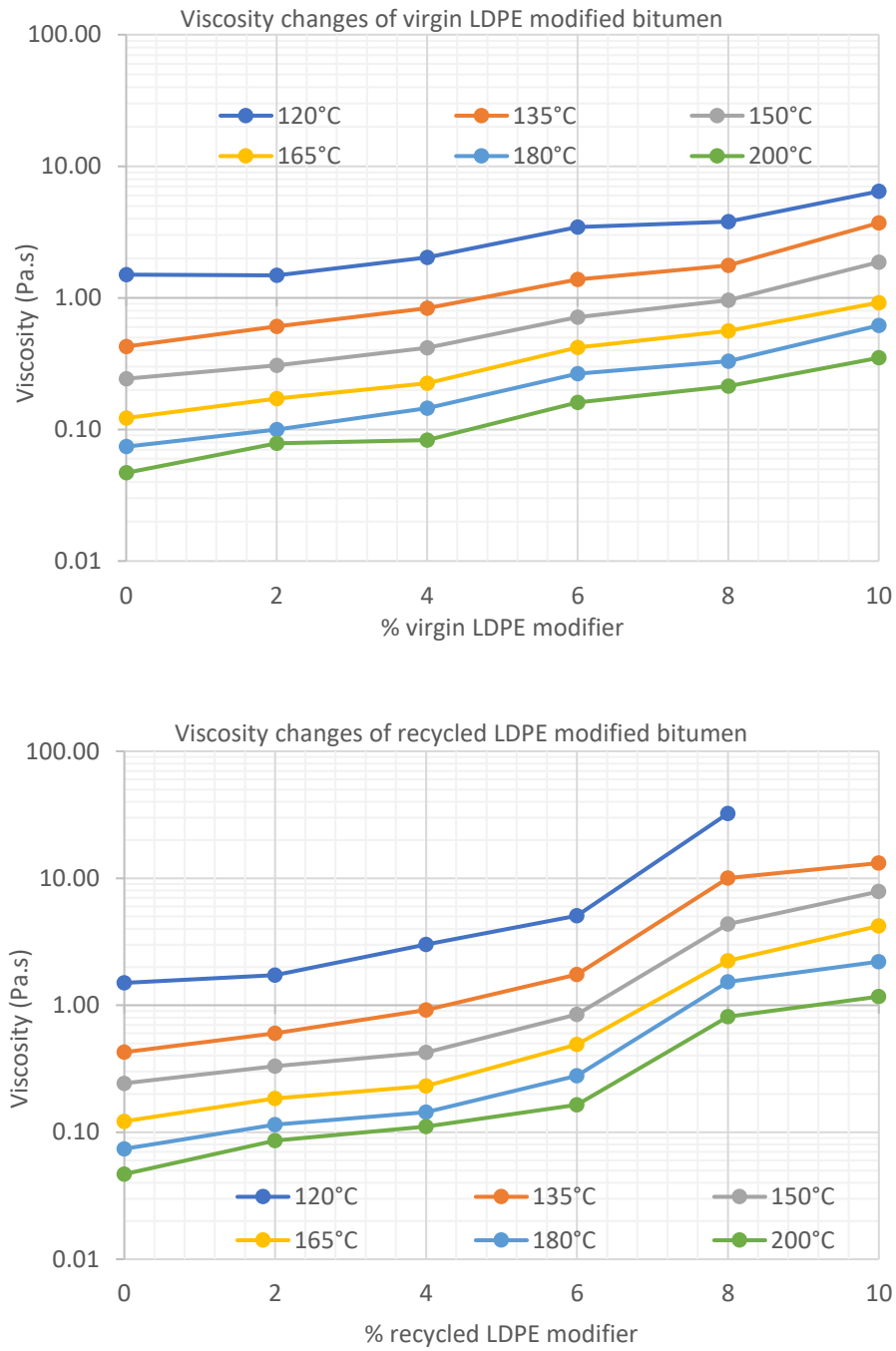


Figure 4. 5: Viscosity changes trend due to temperature and %modifier

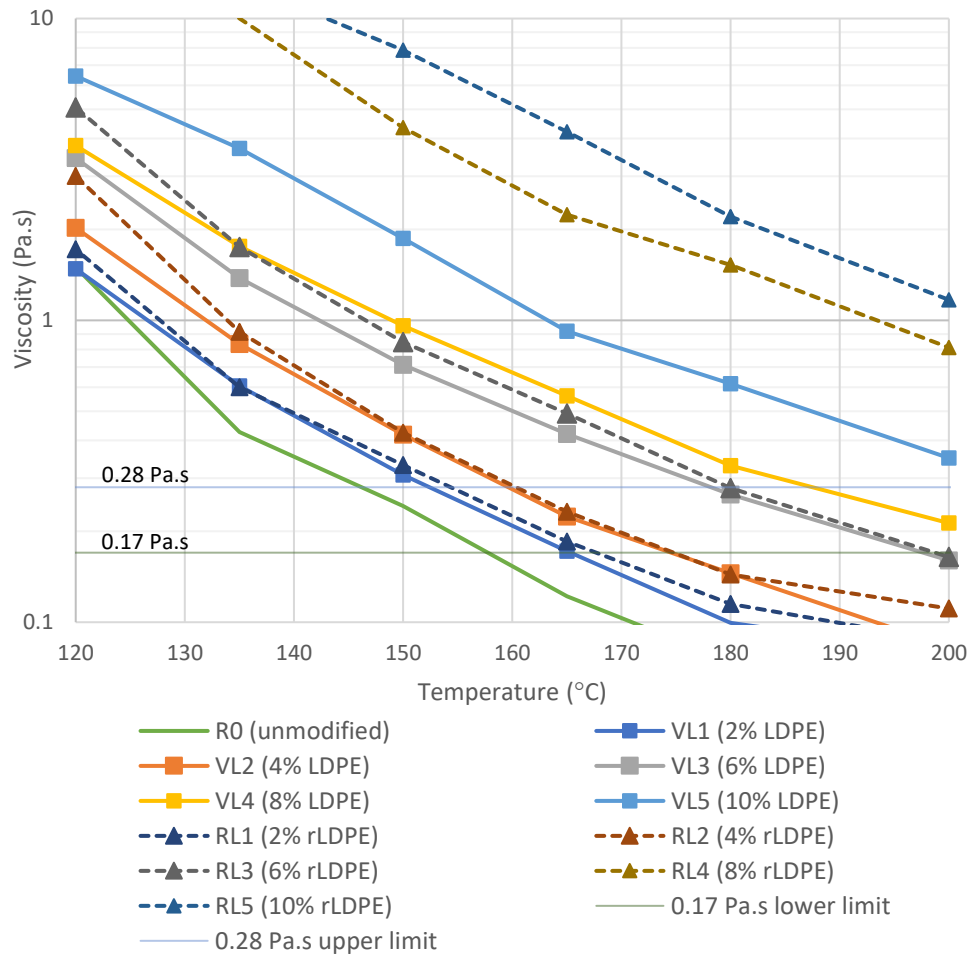


Figure 4. 6: Bitumen viscosity changes

4.5. Summary

This chapter presents the differentiation of the modifiers, followed by the blending (high shear mixing) procedure on the modified bitumen manufacture and the standard tests on bitumen. In the overall research objectives, results in this chapter show the successful differentiation of used modifiers (recycled and virgin LDPEs), the importance of modification procedure to successfully produce modified bitumen, and the possible range of bitumen modification by using LDPEs. This result is carried out to the further stages of this research. In details, some conclusions can be drawn as follows:

1. The ATR-FTIR and DSC tests were conducted to differentiate the virgin and recycled LDPE. The ATR-FTIR resulted in relatively insignificant differences between the two

materials. In fact, both materials presented typical band peaks of polyethylene, as stated by (Gulmine et al. 2002; J. Haslam, H.A. Willis 1983; Zbinden 1964). Meanwhile, the DSC test resulted in different thermal behaviour that explains the differences between the two materials. As expected, the $T_m=110^{\circ}\text{C}$ from the virgin LDPE's DSC test revealed that this material is a common LDPE. Meanwhile, the recycled LDPE has a slightly higher melting point $T_m=123^{\circ}\text{C}$ that commonly observed in Linear LDPE (LLDPE).

2. The 30 minutes, 5000 rpm high shear mixing at $160\pm 5^{\circ}\text{C}$ on both LDPEs produced satisfactory results with visually homogenous blends of LDPE and recycled LDPE modified bitumen. This result corresponds to previous studies and literature by (Dalhat and Al-Abdul Wahhab 2017b).
3. The modification has increased the bitumen stiffness, seen from the rising softening point and the lower penetration number. At a low modification rate (2% and 4%), relatively the same softening point between virgin and recycled LDPE was observed. Meanwhile, the higher modification (6% to 10%) resulted in dramatic differences. The recycled LDPE modifier affected the penetration and the softening point more significantly than the virgin LDPE modifier.
4. The viscosity test by Brookfield resulted in an apparent potential use of LDPE and rLDPE modification at 2% to 6% of bitumen weight. However, 8% and 10% modifications resulted in poor workability due to stiffness. Therefore, based on the viscosity test, only 2% to 6% LDPE and rLDPE modified bitumen will be used in the following bitumen and asphalt mixture tests.

CHAPTER V: LDPE-MODIFIED BITUMEN PERFORMANCE

This chapter discusses the results of bitumen dynamic mechanical analysis, the rutting resistance from the Multiple Stress Creep Recovery (MSCR) tests, fatigue resistance through the Linear Amplitude Sweep (LAS) test and Double Edge Notched Test (DENT). The ageing factor that affects bitumen properties is also presented in this chapter. Artificial ageing of the bitumen use RTFO and PAV. The analysis was conducted in Fourier Transform Infra-Red (FTIR) spectroscopy. The bitumen polymer dispersion through microscopy observation is also presented in this chapter.

5.1. Bitumen rheological properties (dynamic mechanical analysis)

The viscosity test in the previous chapter concluded the experimental plan not to include the very stiff 8% and 10% modified bitumen in further tests. However, the dynamic mechanical analysis was tried on all bitumen, including these, to fully observe the trend from unmodified to highly modified bitumen of both modifiers (virgin and recycled LDPEs).

Before conducting the frequency sweep test, an amplitude sweep test was carried out to determine the bitumen's linear viscoelastic (LVE) region to ensure the further tests will be taken on these limits. The test was carried out using a 25mm geometry set, minimum strain 0.1%, maximum strain 10%, at the temperature of 40°C.

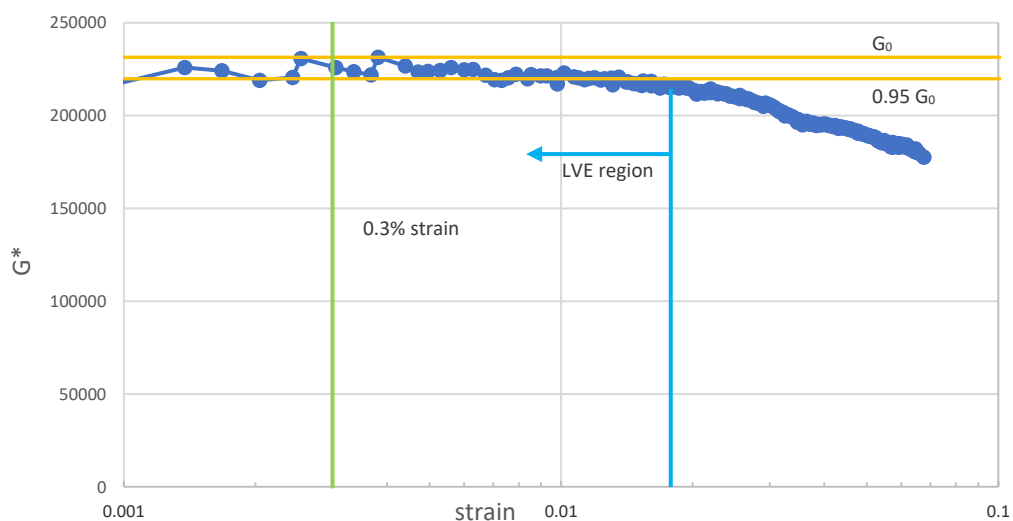


Figure 5. 1: Amplitude sweep test result of RL3 (6% rLDPE)

Figure 5.1 shows the amplitude sweep test result of RL3 or 6% recycled LDPE-modified bitumen. By adopting the criterion of LVE according to SHRP, where the LVE limit is when the strain occurs at the complex modulus higher than 95% of its initial or maximum value, the LVE region can be illustrated in the figure. This result shows that the maximum allowable strain for the LVE region is 0.02 or 2%; thus, the planned 0.3% strain limit in the further tests is safely within the LVE region. This result also confirms that the bitumen strain limit of no more than 1% is ensured to be within the LVE region (Airey and Rahimzadeh 2004b).

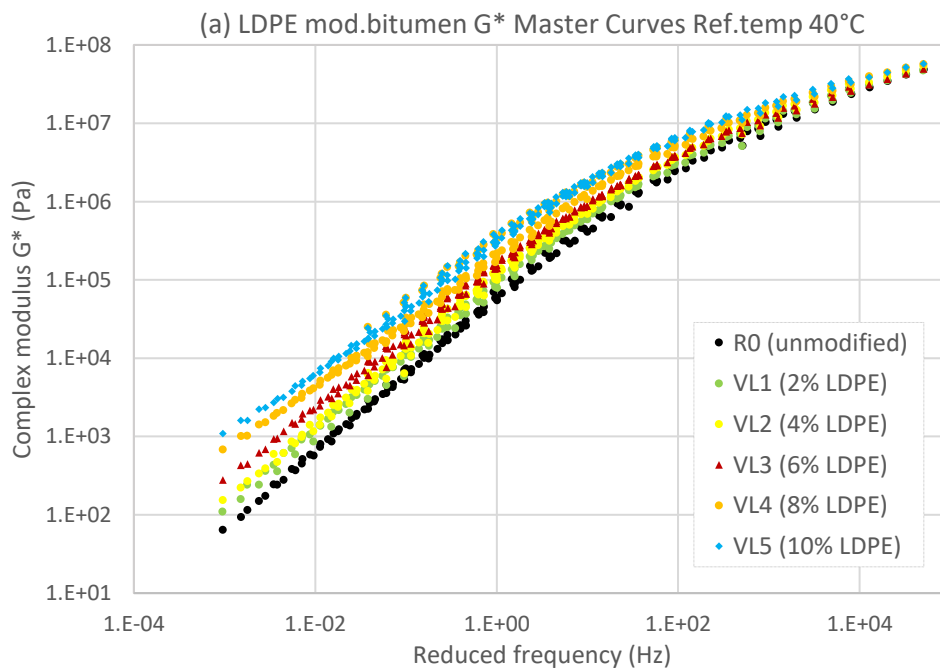
Following the amplitude-sweep tests are the frequency sweep tests carried out in two phases. The first phase tests the specimen for 10 to 45°C with 5°C increments. The test used an 8 mm geometry spindle set for this temperature range with a 2 mm gap and 0.3% strain level. The second phase is for the temperature range of 25°C to 70°C with 5°C increments, using a 25 mm geometry spindle set, 1 mm gap and the same 0.3% strain. Bitumen's important rheological data can be obtained from frequency sweep tests, including complex modulus and phase angle.

5.1.1. Master curves

From complex modulus, phase angle, and temperature data from the frequency sweep test, master curves were constructed by the time and temperature superposition (TTSP) principle. This method horizontally shifts the complex modulus G^* versus frequency plot data to obtain the curve. By using the Williams Landel and Ferry (WLF) equation and universal values for C constants of 8.86 and 101.6, as also proposed by Williams Landel and Ferry (Airey 1997), the shifting factor at selected 40°C temperature were calculated and produced the master curves for complex modulus and phase angles. Figures 5.2 and 5.3 show complex modulus and phase angle master curves from R0, VLs and RLs bitumen. The curves exhibit the increasing complex modulus of modified bitumen in the presence of both virgins and recycled LDPE modifiers, especially at the lower frequency that corresponds to high temperature. For both modifier types, the trends are identical, where the higher modifier content increases the complex modulus number. However, the increasing rate is different where at the same amount of modifier, recycled LDPE improves better bitumen performance than the virgin LDPE. The curves are also different in both modifier types. The virgin LDPE-modified bitumen shows relatively smooth and

continuous curves that can be referred to as a 'thermo-rheologically simple' condition (Airey 1997).

Meanwhile, the recycled LDPE-modified bitumen shows relatively spreading and disjointed in some isothermal plots. The addition of 2% of virgin LDPE increases approximately 25% of G^* at a lower reduced frequency. Adding 4, 6, 8 to 10% increases the LDPE modified bitumen complex modulus to about 2.4 times, 4.31 times, 10.58 times and 16.84 times of unmodified bitumen complex modulus, respectively. Significant differences in the increase rate of complex modulus were observed for recycled LDPE modified bitumen where the 2 to 10% modification resulted in 2.13 times, 6.7 times, 48.63 times, 233 times and 1217 times higher complex modulus, respectively, compared to unmodified bitumen at a lower frequency.



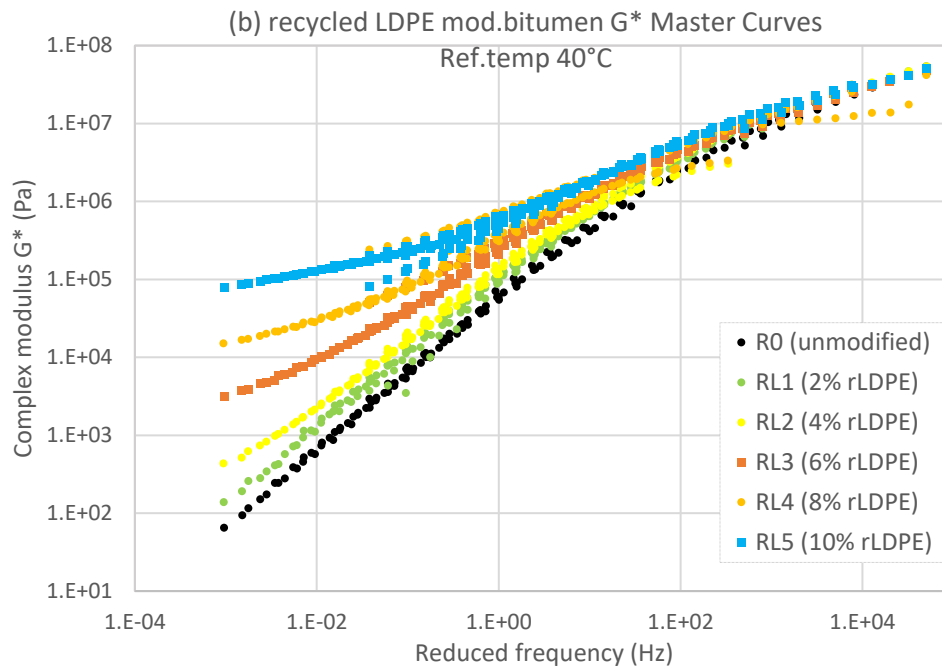


Figure 5. 2: Complex modulus master curves (a) R0 and virgin LDPE, (b) R0 and rLDPE

The visible increasing complex modulus at a lower frequency or higher temperature happens due to at high temperature, the low viscosity of the bitumen makes the elastic network of the polymer influence the mechanical properties of the modified bitumen dominantly (Airey 2003) (Goodrich, 1991). A similar result had explained that the modulus of the polymeric modifier is higher than the base bitumen; thus, incorporating it into base bitumen increases the bitumen blend's complex modulus (Da Silva et al. 2004). This result can be attributed to the molecular interaction of bitumen and the modifier, which includes dispersion or swelling between bitumen and modifier, and the compatibility factor between bitumen and modifier (Airey 2003; Asgharzadeh and Tabatabaee 2013). While the polymer networks are the main factor in influencing the bitumen properties at a higher temperature, the merging part of the curves at higher frequency (low temperature) explains the bitumen dominance over the polymer network. The relatively same complex modulus of all bitumen (unmodified, LDPE modified, or recycled LDPE modified bitumen) in this low temperature is the proof and the clear explanation of this phenomenon.

Similar to the complex modulus, the changes in phase angles are visible in the phase angle master curves. The 'thermo-rheological complexity' is relatively more apparent than the complex modulus master curves, especially for the recycled LDPE-modified bitumen. The disjointed curve of the recycled LDPE-modified bitumen occurred at almost all modification percentages except for the RL1 (2% rLDPE), which produced a relatively smooth and continuous curve, as shown in Figure 5.3(b). The RL2 (4% rLDPE) to RL5 (10% rLDPE) show the thermo-rheological complex condition that indicates the modification produced a 'highly modified' bitumen. This condition was not obtained on the virgin LDPE-modified bitumen even though made with the same procedure and the same level of modification.

The significant phase angle changes at lower frequencies (high temperature) are due to the modifier becoming the main contribution to the rheological behaviour of the binders. This condition improves the viscoelastic characteristics of the binder at higher temperatures (Pérez-Lepe, Martínez Boza, and Gallegos 2005). On the contrary, at higher frequencies (low temperature), the merging graph shows that the modifier's effect on the bitumen blends decreases. This condition is due to the stiffness increase of the bitumen dominating the polymer network, so the base bitumen characteristic becomes the dominant factor of the whole material (Airey 2003). The trends in the master curves of LDPE-modified bitumen correspond to the previous study (Vargas et al. 2013b), indicating the potential better rutting resistance of the modified bitumen at high temperatures.

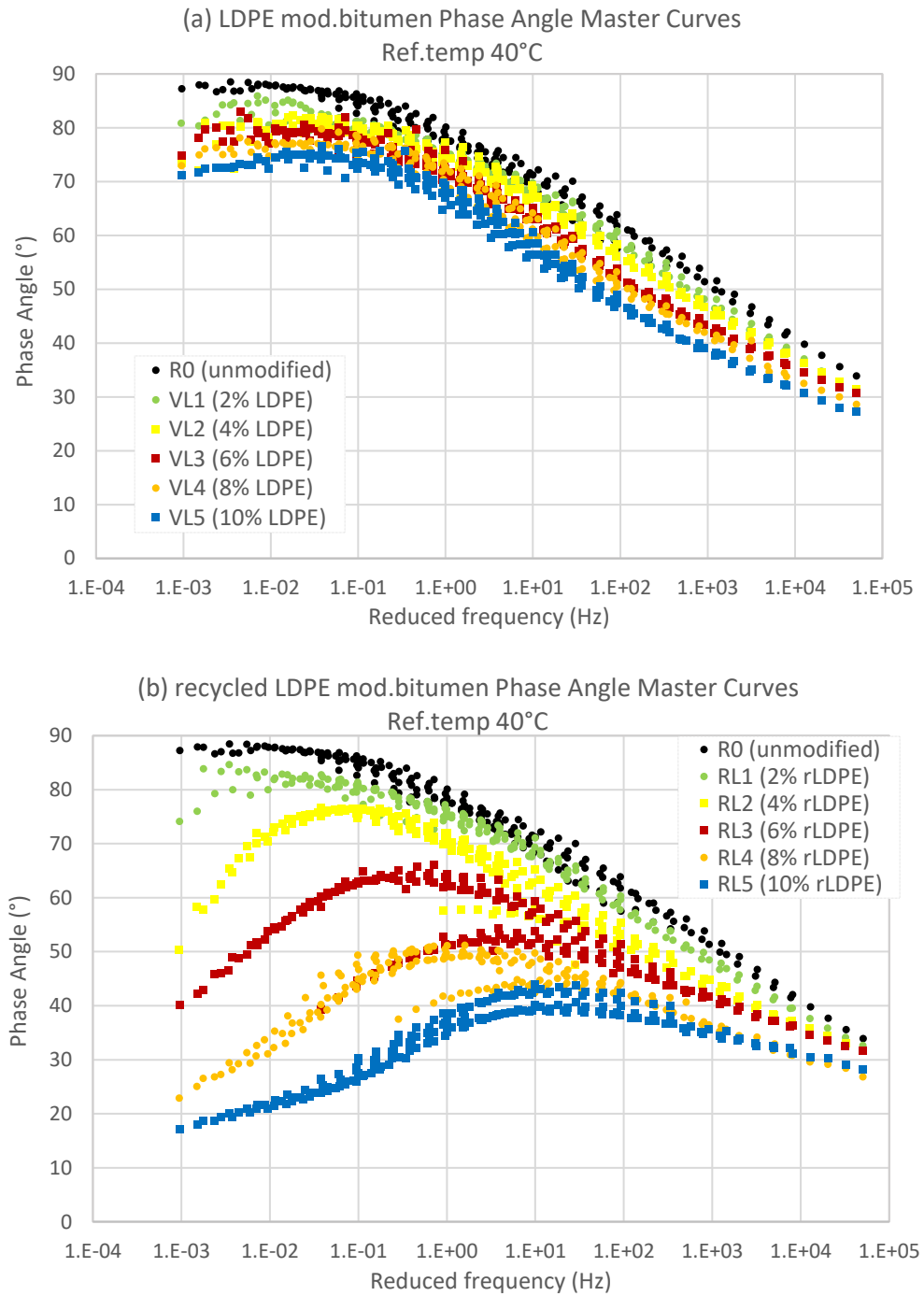


Figure 5. 3: Phase angle master curves (a) R0 and virgin LDPE, (b) R0 and rLDPE

5.1.2. The Black diagram

Figure 5.4 shows the Black diagram of the unmodified and both LDPE-modified bitumen. The Black diagram also observed a consistent result regarding the thermo-rheological aspect of the unmodified and virgin LDPE-modified bitumen. The unmodified and the virgin LDPE-modified bitumen have a smooth curve of complex modulus versus phase angle, representing a time-temperature equivalency or thermo-rheologically simple condition observed in the master curves. On the other hand, the recycled LDPE, especially at a high modification rate, shows a disjointed curve expected from highly polymer-modified bitumen.

For virgin LDPE-modified bitumen, it can be seen from the black diagram the slight shift of phase angle curves to a lower number. This result indicates the improved elastic response of the bitumen, even though relatively minor. The complex modulus is also slightly shifting higher, especially for highly modified bitumen (VL3, VL4 and VL5).

On the other hand, a relatively different phenomenon can be seen in the case of recycled LDPE-modified bitumen, which shows the 'complexity' of the curves. The complexity of the black curves of this bitumen indicates the phase angle sensitivity due to the microstructural changes in the presence of LDPE polymer in the bitumen (Subhy 2017). The phase angle shifts in this bitumen are visible for almost all modification rates except for RL1 or 2% recycled LDPE. The significant changes in phase angle in recycled LDPE compared to LDPE at the same modification rate can be attributed to the ability of the recycled LDPE to form a better polymer network within the bitumen phase compared to the virgin LDPE. This polymer network tends to dominate the properties of the entire bitumen bulk. The higher amount of recycled LDPE modifier significantly changes into higher phase angles, suggesting the polymer is even more dominant in determining the bitumen properties. These changes also occur to the bitumen's complex modulus.

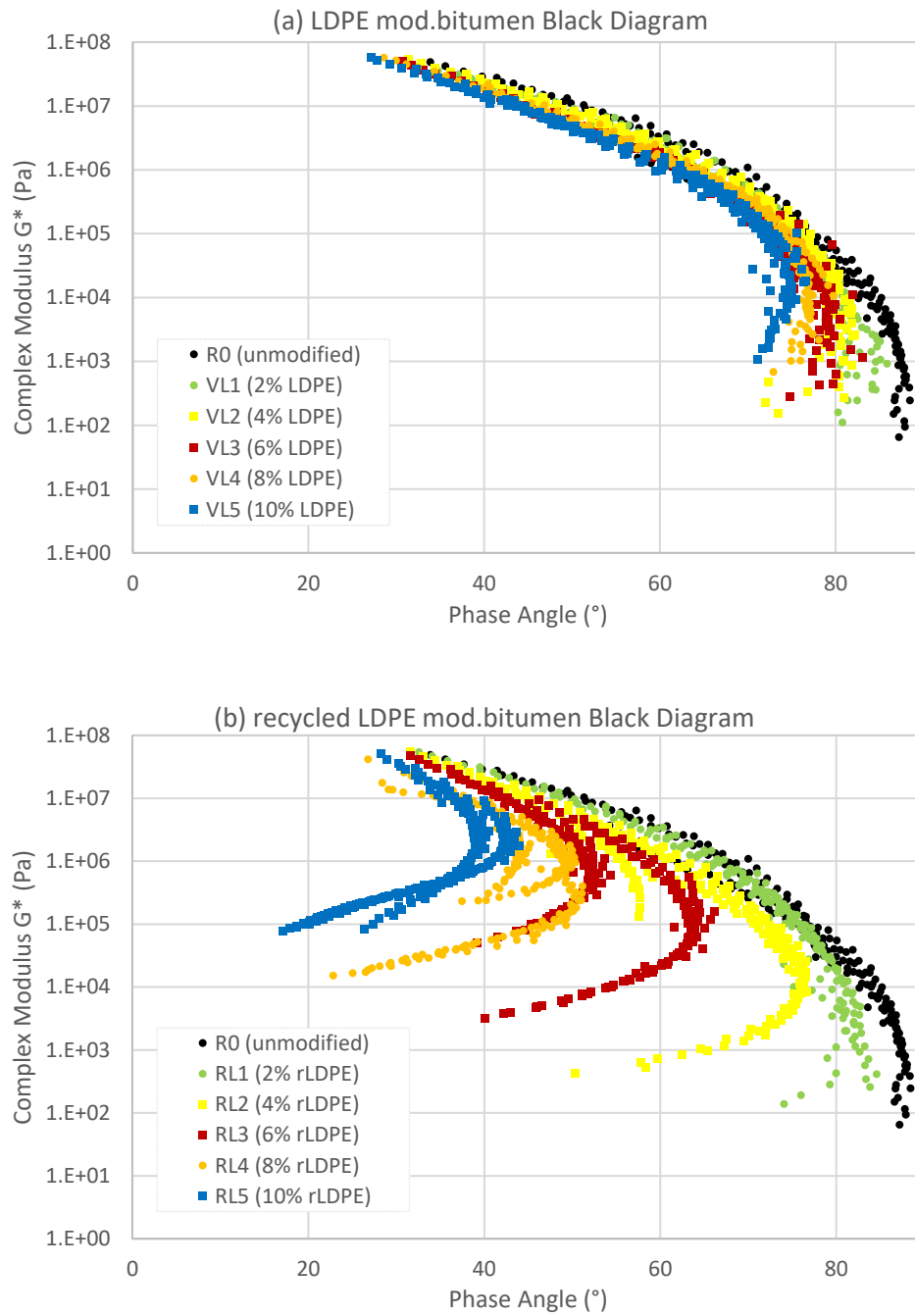


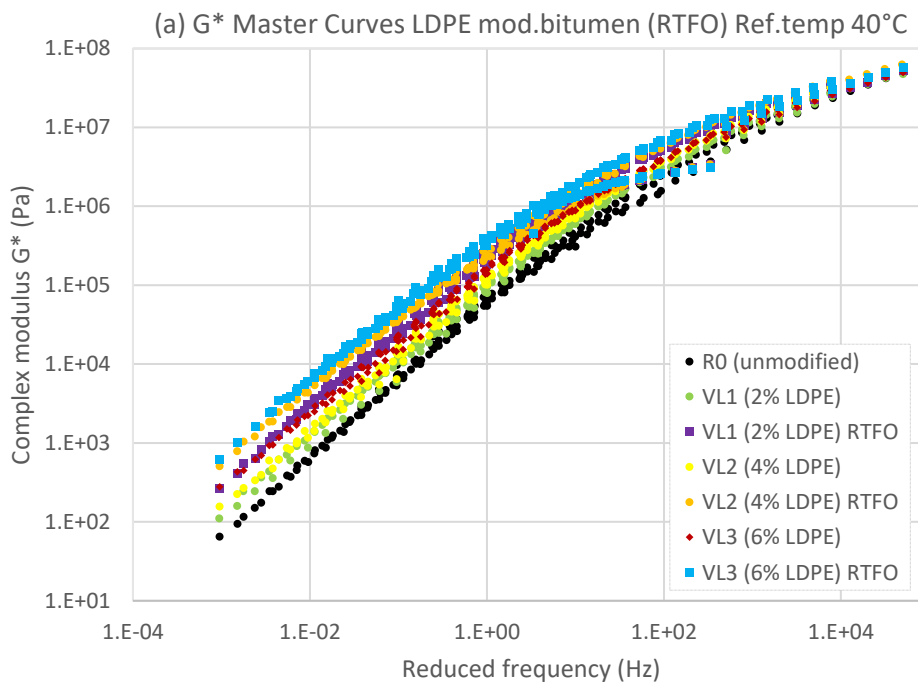
Figure 5. 4: Black diagram of (a) R0 and virgin LDPE, (b) R0 and rLDPE

5.1.3. Ageing effect on the rheological properties

Short-term artificial ageing was conducted by Rolling Thin Film Oven (RTFO) test on the bitumen to understand its effect on the rheological properties. According to BS EN, RTFO can be considered a simulation of ageing during bitumen preparation in an asphalt mixing plant. Therefore, by conducting this test, the bitumen is expected to have a certain degree of hardening due to ageing, simulating an early pavement age in road application. The detailed RTFO procedures are described in chapter 3.

The tested bitumen in this section are the R0, VL1, VL2, VL3, RL1, RL2 and RL3. Based on the viscosity test results regarding the bitumen's workability, no RTFO and rheological tests were conducted on 8% and 10% of modifications (VL4, VL5, RL4 and RL5).

The frequency sweep tests were conducted on the RTFO bitumen. Complex modulus and phase angle master curves, as well as the Black diagram, were made to understand the effect of ageing on rheology. Similar to the previously presented unaged bitumen, a reference temperature of 40°C was chosen.



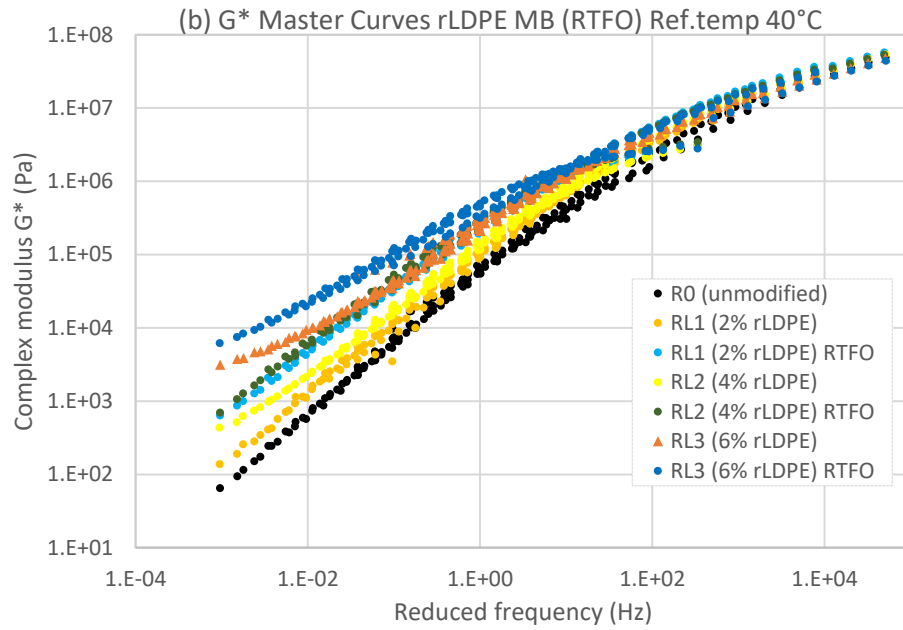
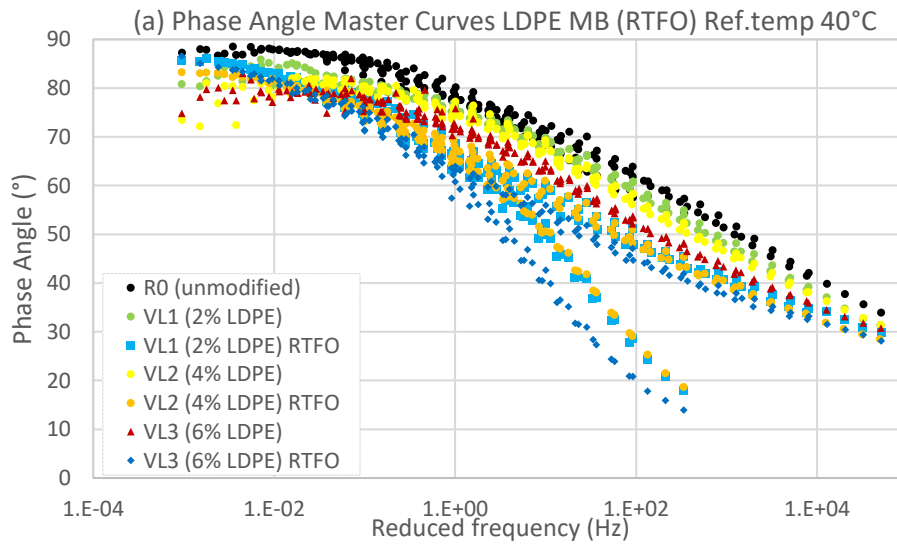


Figure 5. 5: Complex modulus master curves (RTFO) (a) virgin LDPE, (b) recycled LDPE



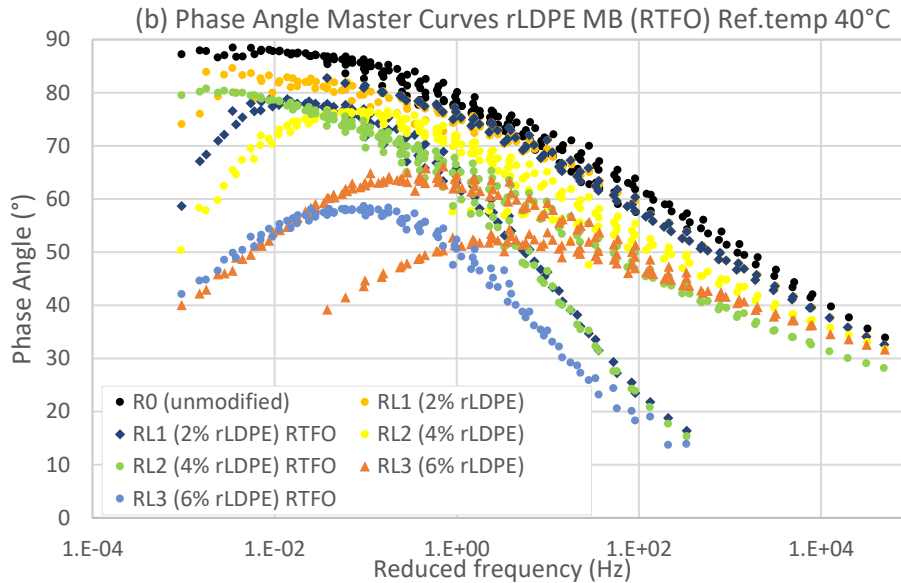


Figure 5. 6: Phase angle master curves (RTFO) (a) virgin LDPE, (b) recycled LDPE

Each master curve was built from rheological data obtained from two spindles, i.e. 8mm and 25mm. The 8mm is used for low bitumen temperatures of 10 to 40°C, whilst the 25mm is used for high temperatures from 25 to 70°C. In using two spindles in the frequency sweep test, the overlapping temperatures should result in similar rheological data from the two spindles. In this case, however, different results seemingly occurred, forming different 'curve paths' or disjointed curves, as shown in Figure 5.7. This phenomenon is an inconsistency condition (Airey, 2002) that could occur on modified bitumen and can also be observed from the Black diagram. The phenomenon happened on all RTFO-aged modified bitumen and all modification percentage (RTFO of VL1, VL2, VL3, RL1, RL2 and RL3).

Based on these results, it is concluded that the short artificial ageing (RTFO) resulted in a more obvious sign of a disjointed curve in master curves from two spindles of frequency sweep test. This phenomenon signifies a more 'thermo-rheologically complex' behaviour of modified bitumen after the ageing process. This condition can also be translated as the modification effect of the LDPE and rLDPE being higher when the modified bitumen is experiencing ageing.

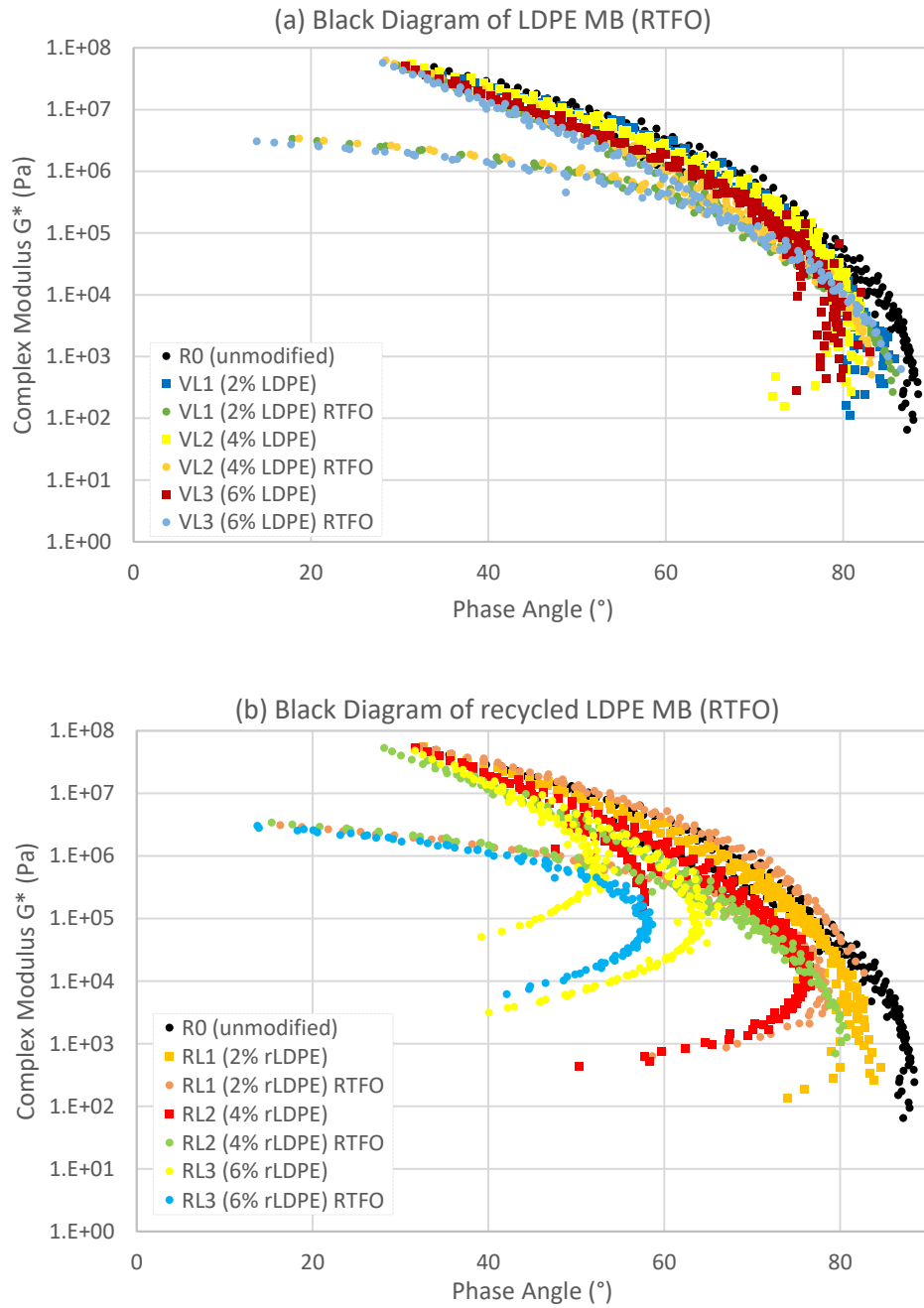


Figure 5. 7: Black diagram (RTFO) (a) virgin LDPE, (b) recycled LDPE

5.2. Bitumen resistance to rutting

Multiple stress creep recovery (MSCR) tests were conducted to understand the rutting resistance performance of the bitumen. Even though the potential rutting resistance can be concluded from the complex modulus master curves in the dynamic mechanical analysis in the previous sections, the DSR tests in those tests were conducted in the

bitumen's LVE region, i.e. very low strain level. Meanwhile, the MSCR test is performed at a higher stress level beyond the LVE regions to better understand the bitumen rutting resistance. Eleven types of bitumen which are unmodified bitumen, five virgin LDPE modified bitumen and five recycled LDPE modified bitumen, were tested on 50°C, 60°C, 70°C and 80°C on 0.1 kPa and 3.2 kPa stress levels with ten cycles for each stress level.

5.2.1. Percentage of recovery (%R)

Percentage recovery (%R) explains the ability of the bitumen to reform back to its original shape after being loaded with loads contributed by the elastic property of the bitumen. The %R is calculated from the average of 10 cycles at specified stress levels and temperatures. Figure 5.8(a) and 5.8(b) show the recovery percentage (%R) results of the virgin LDPE and recycled LDPE modified bitumen, respectively, compared to unmodified bitumen at 60°C with 100 Pa and 3200 Pa stress level.

The virgin LDPE modified bitumen %R performance, as shown in Figure 5.8(a), is increasing as more LDPE is blended in the bitumen. Even though the virgin LDPE-modified bitumen can demonstrate good recoverability at 100 Pa stress, this ability is considerably lower at higher stress levels (%R at 3200Pa is almost half of 100Pa), especially for a 2% to 8% modification rate. This result is harmonious with the rutting resistance improvement concluded from the complex modulus master curves.

The recycled LDPE-modified bitumen demonstrates a higher percentage recovery than the virgin LDPE. At only a 2% addition of recycled LDPE, the bitumen %R reached 44.32% for 100 Pa stress and 12.52% for 3200 Pa stress. The trends of increasing per cent recovery at higher modification rates are visible in Figure 5.8(b). The per cent recovery of recycled LDPE modifier bitumen is considerably higher at an average of four times at the same modification rate compared to virgin LDPE. The %R that reached 68% at only 4% modification and 91% at 10% of modification rate explain that the recycled LDPE is noticeably improving the rutting resistance of the bitumen. The calculated per cent recovery of virgin LDPE and recycled LDPE modified bitumen concludes that both materials demonstrated a better rutting resistance than the unmodified bitumen.

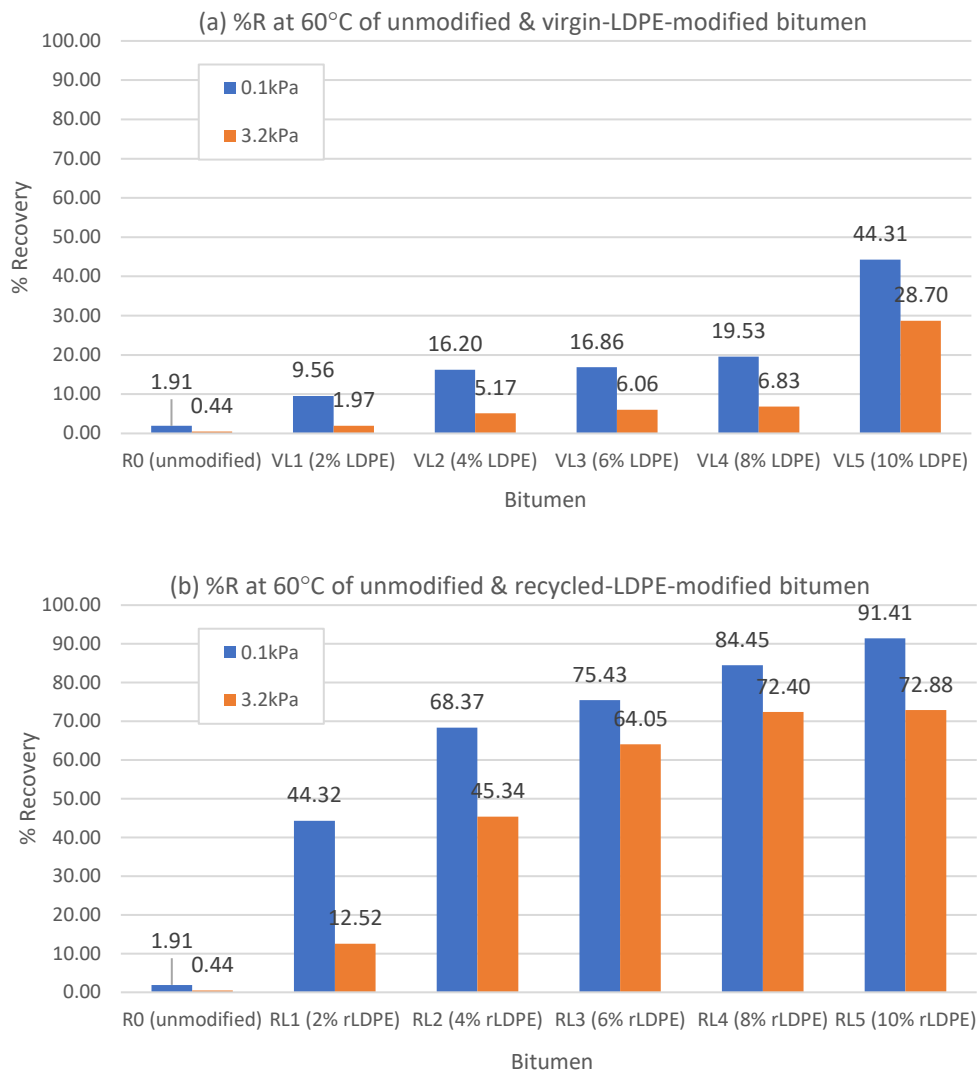


Figure 5. 8: %R at 60°C of (a) virgin LDPE and (b) recycled LDPE modified bitumen

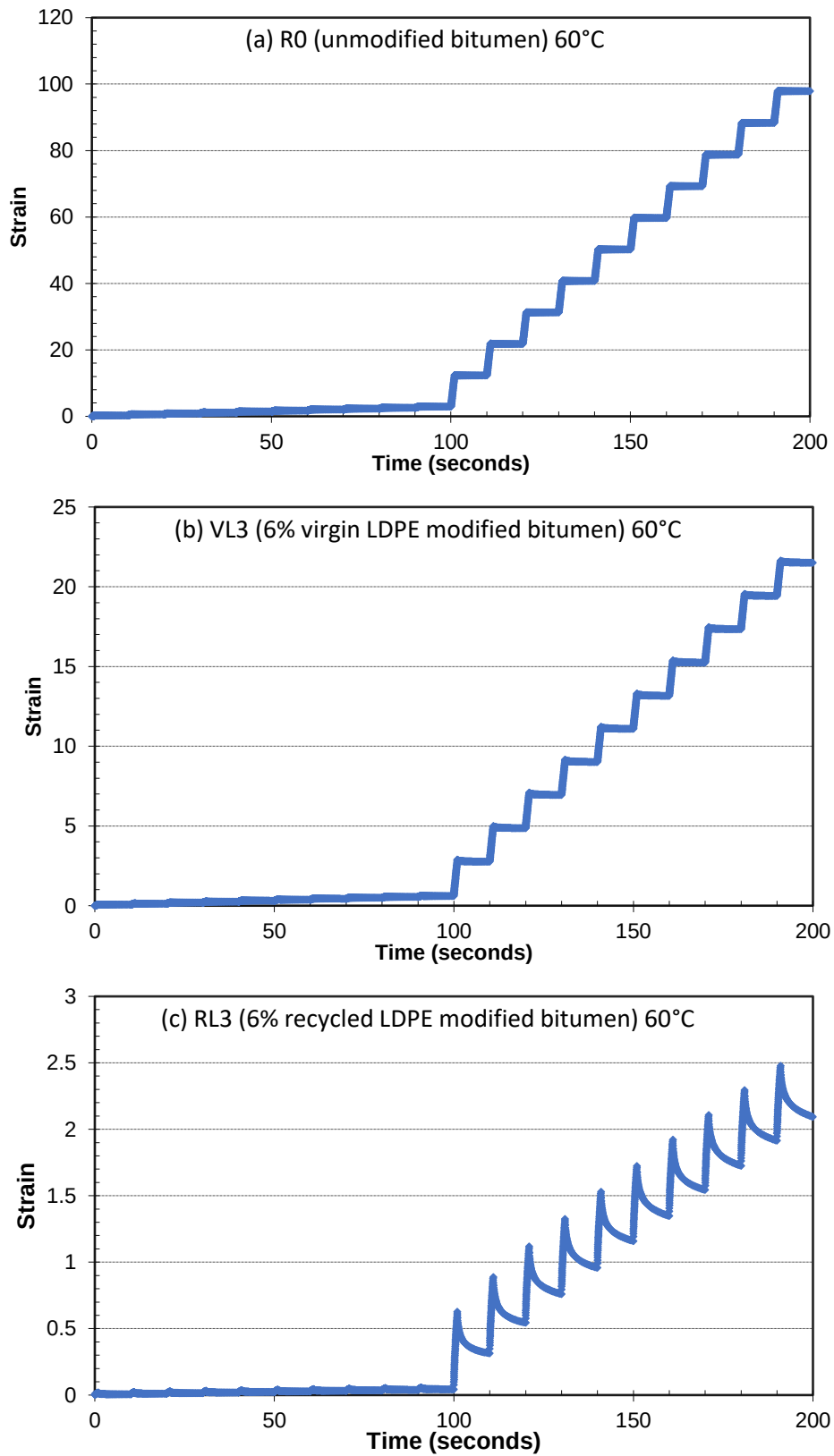


Figure 5. 9: MSCRT Creep-recovery cycles at 0.1kPa and 3.2kPa

The creep-recovery graphs in Figure 5.9 show the ability of modified bitumen at a 6% modification rate to perform elastic recovery at 60°C testing temperature. Figure 5.9.(a) shows how the unmodified 50/70 bitumen performed repeated stress load-release cycles 2x10 times of 100 Pa and 3200 Pa. The high strain and a very low recovery were recorded at an average of 1.91% from 100 Pa and 0.44% from 3200 Pa stress level.

Figure 5.9.(b) shows how the virgin LDPE is improving the ability of the bitumen to recover from repeated load cycles. An average of 16.86% and 6.06% were recorded from 100 Pa and 3200 Pa stress. This value is considerably better compared to unmodified bitumen. Lastly, for recycled LDPE-modified bitumen, as shown in Figure 5.9.(c), the recorded average recovery was significantly higher than other bitumen at 75.43% for 100 Pa and 64.05% for 3200 Pa. This graph also illustrates how the strain was considerably lower than the other two. Based on these results, overall, in terms of rutting resistance, the virgin LDPE performs better than the unmodified bitumen, whilst the recycled LDPE is superior to all bitumen.

Some results of the test showed negative values of %R, which are the 3.2kPa at 80°C for unmodified bitumen and 2% virgin LDPE modified bitumen. These are non-ideal conditions where the lowest %R should theoretically be zero. These conditions might happen due to some rheometers being unable to unload applied stress quickly enough at the end of the loading cycle, thus resulting in a slight increase of strain curve in the unloading phase. This condition can occur in a low %R ability bitumen with high temperature, high-stress levels, and large strains (Zakaria 2019).

5.2.2. Non-recoverable creep compliance (Jnr)

Following the higher %R, the lower Jnr values were obtained in the modified bitumen, as graphically exhibited in Figure 5.10 for the case of 100 Pa and 3200 Pa stress levels at 60°C temperature. Figure 5.10(a) shows decreasing number of Jnr in the higher percentages of virgin LDPE. A similar trend with a higher magnitude of changes is shown in the recycled LDPE, as depicted in Figure 5.10(b). The recycled LDPE-modified bitumens have a very low number of Jnr starting at RL2, indicating that at this percentage of modification (4%), significant property changes have occurred, which matches the obtained %R values. From both graphs, it can also be clearly seen that there are insignificant differences in Jnr between the 100 Pa and 3200 Pa stress levels, except for the case of 2% and 4% of recycled

LDPE. This result explains that the J_{nr} of LDPE-modified bitumen is relatively stable and less stress-dependent.

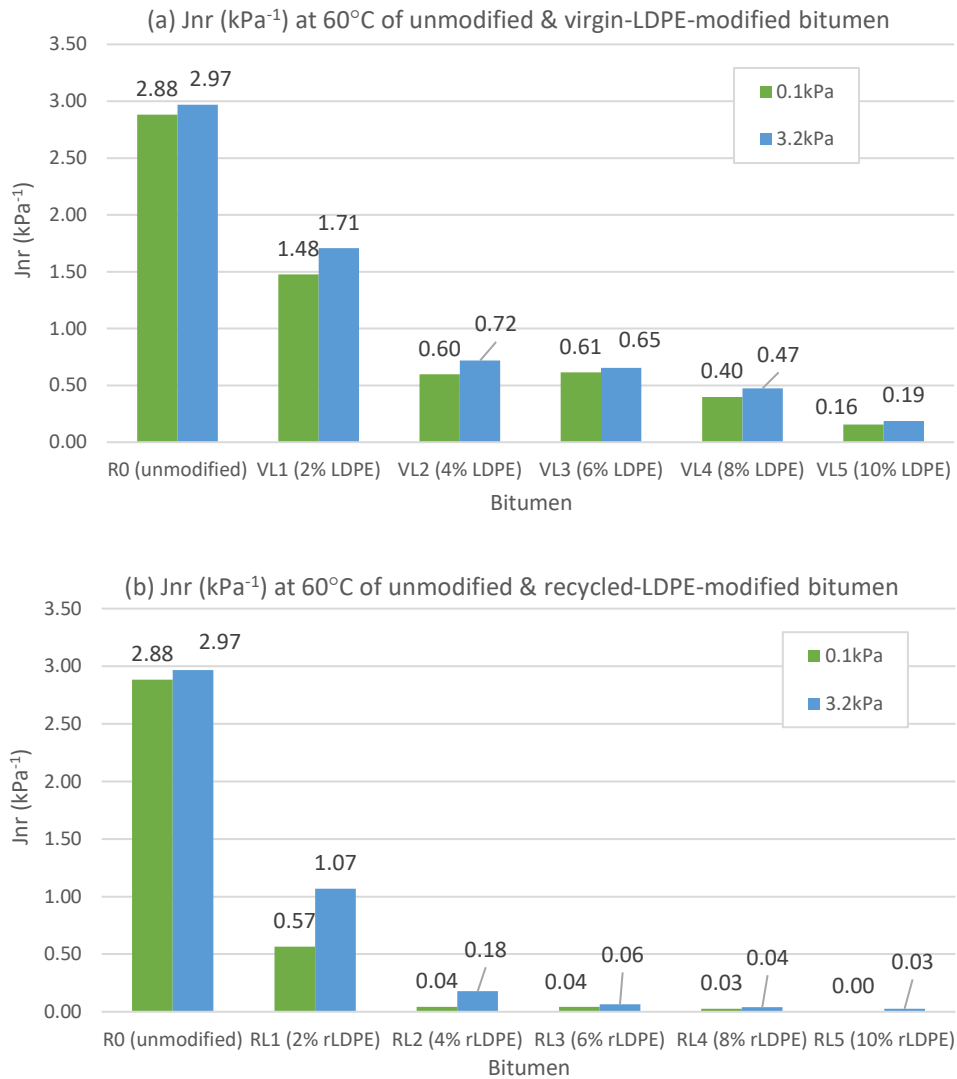


Figure 5. 10: Unrecoverable creep compliance, J_{nr} (kPa^{-1}) at 60°C of (a) virgin LDPE and (b) recycled LDPE-modified bitumen

The lower number of J_{nr} and the higher %R in the LDPE-modified bitumen are the expected results and correspond to the previous studies by (Nuñez, Domingos, and Faxina 2014). The presence of LDPE modifies the physical properties of bitumen, and the lower J_{nr} and higher %R represent the higher resistance to rutting of the modified bitumen as described by (García-Morales et al. 2006b), (Vargas et al. 2013b), (Nuñez et al. 2014) (Roman et al. 2016). The J_{nr} and %R results of the MSCR test from 50°C to 80°C are shown in Table 5.1.

Table 5. 1: MSCR test results

	50°C				60°C			
	Jnr		%R		Jnr		%R	
	100Pa	3.2kPa	100Pa	3.2kPa	100Pa	3.2kPa	100Pa	3.2kPa
R0	0.64	0.64	5.25	4.06	2.88	2.97	1.91	0.44
VL1	0.33	0.33	10.87	8.62	1.48	1.71	9.56	1.97
VL2	0.17	0.20	17.32	11.23	0.60	0.72	16.20	5.17
VL3	0.15	0.17	21.18	13.33	0.61	0.65	16.86	6.06
VL4	0.09	0.11	26.30	16.50	0.40	0.47	19.53	6.83
VL5	0.02	0.02	47.03	41.94	0.16	0.19	44.31	28.70
RL1	0.31	0.28	47.26	15.61	0.57	1.07	44.32	12.52
RL2	0.03	0.05	72.36	66.18	0.04	0.18	68.37	45.34
RL3	0.02	0.02	84.45	73.27	0.04	0.06	75.43	64.05
RL4	0.01	0.01	86.41	79.86	0.03	0.04	84.45	72.40
RL5	0.00	0.01	91.57	69.19	0.00	0.03	91.41	72.88
	70°C				80°C			
	Jnr		%R		Jnr		%R	
	100Pa	3.2kPa	100Pa	3.2kPa	100Pa	3.2kPa	100Pa	3.2kPa
R0	11.56	12.00	1.05	0.80	24.42	37.51	0.88	-1.32
VL1	3.90	4.75	7.61	0.24	22.85	28.11	4.50	-0.27
VL2	1.97	3.22	11.63	1.76	5.44	8.45	8.70	0.18
VL3	0.79	2.45	13.10	5.24	3.84	5.49	11.47	0.47
VL4	1.77	2.28	13.29	0.98	3.32	0.12	12.35	2.98
VL5	0.33	0.73	34.30	10.17	1.59	2.25	24.15	1.92
RL1	0.91	3.30	34.19	5.36	0.29	2.05	28.83	6.21
RL2	0.20	1.08	62.06	22.21	0.13	2.60	53.58	8.53
RL3	0.18	1.14	64.46	24.69	0.63	2.83	61.10	12.71
RL4	0.07	0.34	66.05	35.81	0.09	1.10	62.76	23.66
RL5	0.02	0.08	84.85	59.27	0.10	0.63	81.26	34.85

The different magnitude of changes of %R and Jnr between the recycled LDPE and virgin LDPE can be attributed to the superiority of the recycled LDPE compared to virgin LDPE in forming a polymer network in the bitumen phase at the same modification rate. The polymer network is dominant in affecting the bitumen properties; thus, a better-forming polymer network results in more significant improvements in bitumen properties, including rutting resistance. The later microscopy analysis in the following chapters will be provided to confirm and underline this statement.

5.3. Bitumen resistance to fatigue failure

Fatigue cracking is a common pavement distress due to repeated loading for a long time. Therefore, research has been conducted to understand the ability of bitumen to resist fatigue failure. The Linear Amplitude Sweep (LAS) test using DSR and Double Edge Notched Tension test (DENT) in Ductilometer are two standard methods for this purpose. This chapter presents the LAS and the DENT test results of unmodified bitumen, the 2%, 4% and 6% of virgin and recycled LDPE modified bitumen. The 8% and 10% of modifications were not tested as mentioned in the previous (viscosity test) chapter since these bitumens are very stiff and have low workability. In addition, the LAS and DENT tests require the bitumen to be artificially aged with RTFO or PAV before testing, which increases the stiffness of the bitumen and is thus considered impractical to conduct.

5.3.1. Linear Amplitude Sweep (LAS) test

The LAS test evaluates the fatigue resistance of bitumen according to standard AASHTO T 391-8. This test consists of two main steps: the frequency sweep test and the amplitude sweep test. The frequency sweep test was performed on 12 unique frequencies over the range of 0.2 to 30 Hz at a fixed 0.1% of strain load. From this test, the complex shear modulus and phase angle were recorded at each frequency. The amplitude sweep test was performed at a frequency of 10 Hz at 31 strain levels starting from 0.1% to 30%, whereas each loading strain consisted of 10 cycles for a duration of 1 second. Every ten cycles (1 second), the current cycle's peak shear stress and strain were recorded. The bitumen was RTFO-aged before being tested in LAS, and the test was conducted at 20°C.

5.3.1.1. Stress-strain curve

The stress and strain data obtained from the amplitude sweep tests can be used to analyse the failure behaviour of the bitumen. The increasing shear stress when the loading strain was increasingly applied demonstrates the damage resistance of the bitumen. In this test, all bitumen from unmodified to 6% LDPE and rLDPE modified bitumen performed similar trends and curve shapes with slightly different magnitudes of shear stress. The unmodified bitumen (R0) showed the lowest shear stress, and the higher modification resulted in a higher peak of shear stress. VL1 and RL1, which are 2% of virgin LDPE and recycled LDPE modified bitumen have relatively the same shear stress vs strain curve where the same trend also showed for VL2, RL2 and VL3.

The highest shear stress was performed by RL3 or 6% recycled LDPE-modified bitumen, as shown in the highest peak. This peak is defined as bitumen's yield threshold or failure starting point when subjected to an increasing load (Masad et al. 2001; Xue et al. 2017). In other definition, when the shear stress response is still increasing, the bitumen would not experience any damage (Jafari, Babazadeh, and Rahi 2017; Johnson 2010). Thus, the highest peak of RL3 explains the ability of the bitumen to respond to the applied strain at the highest stress level compared to other bitumen. The trend also states that the higher modification resulted in a higher shear stress peak.

Figure 5.11 also explains that all bitumens were performing the same shear strain level in the peak of the shear stress curve, which is approximately at 9% strain level. This number indicates that even though each bitumen responds differently to strain load, all bitumens have the same strain degradation or failure point. This phenomenon could also be translated as the higher modified bitumen requiring higher stress to accumulate the same strain level, indicating potentially better fatigue resistance.

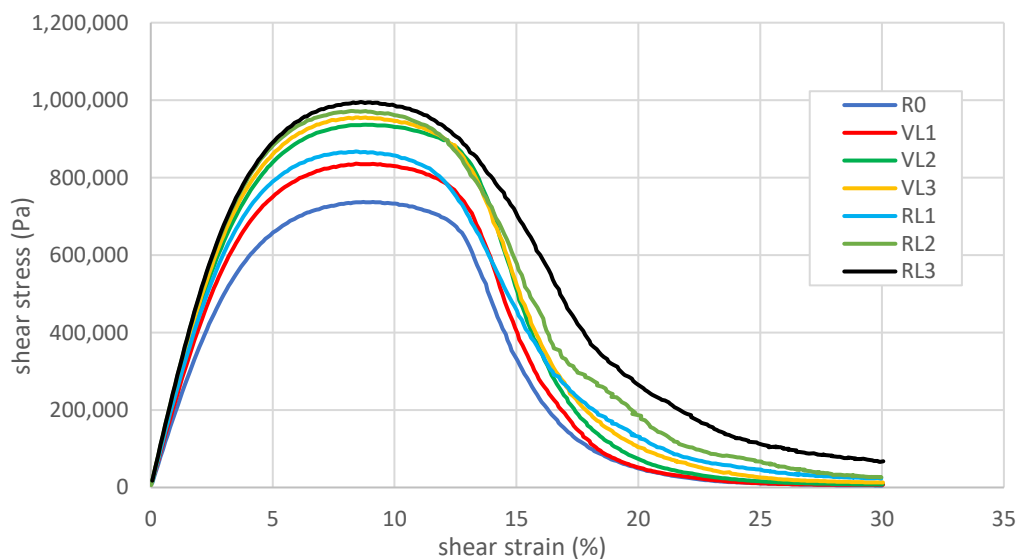


Figure 5. 11: Stress vs strain curve at 20°C

The different slope gradients after the peak can also be translated to different degradation behaviour of the bitumen (Zakaria 2019). For example, the unmodified bitumen R0 shows a slightly steeper fall curve compared to other bitumen, while the VL1, VL2, RL1 and RL2 have relatively the same slope gradient. Meanwhile, the RL3 has the lowest slope gradient, which means that at a higher strain level, this bitumen exhibits the

lowest decrease in shear stress response. This result can be translated as the RL3 having the slightest damage or being more resistant to fatigue.

Overall the stress vs strain curve of the bitumen explains that the LDPE-modified bitumens have a potentially better fatigue resistance compared to unmodified bitumen. However, the similar slope gradient of VL1, RL1, VL2 and RL2 demonstrate that fatigue resistance improvement depends on the modification rate rather than the modifier type.

5.3.1.2. Damage and failure analysis

The damage intensity curve can be used to understand the bitumen resistance to fatigue failure. The material integrity C explains the changes (reduction) of bitumen complex modulus due to repeated strain load in the LAS test. C is the ratio of G^* at a specified time ($t=n$) to initial G^* ($t=0$). The lower complex modulus changes indicate the bitumen's lower strain susceptibility or better resistance to fatigue damage (Jafari and Babazadeh 2016; Jafari et al. 2017). Figure 5.12 shows the material integrity C as a function of damage intensity D for all bitumen.

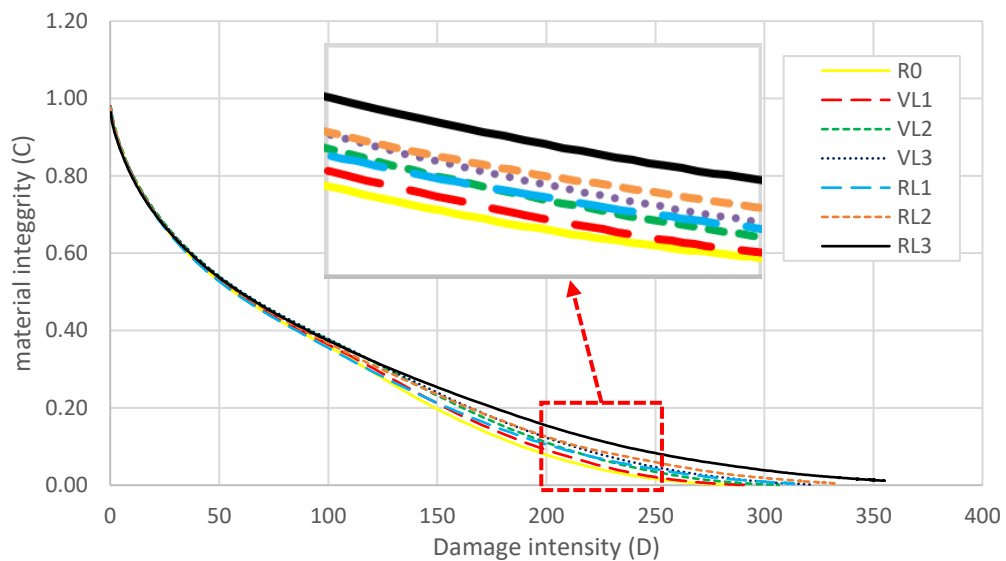


Figure 5. 12: Damage intensity curve

The graph shows decreasing material integrity occurs on all bitumen at increasing damage intensity. The decreasing C is relatively at the same rate for all bitumen at lower damage intensity. At higher damage intensity or D at approximately 100, the material integrity slightly differs between bitumen. The inset picture clearly shows the differences, where the unmodified bitumen R0 has the lowest material integrity, while RL3 has the highest. This condition is matched with the stress-strain curve where the curve is

relatively parallel at lower strain, and then different curve slopes occur at the higher strain level. The curves between the R0 and RL3 show the gradual change in the material integrity, indicating the higher modification of LDPE and recycled LDPE produce better fatigue resistance.

5.3.1.3. Coefficient of fatigue

The 'A' and 'B' parameters derived from the LAS test are also important indicators of the fatigue performance of bitumen. Parameter 'A' is the damage resistance parameter representing the material's ability to keep its integrity during the loading, while parameter 'B' represents the sensitivity of bitumen to strain level change (Nejad, Naderi, and Zarroodi 2017). Under the same testing condition and temperature, the higher number of parameters 'A' represents the lower number of initiated cracks damage on the material. In other words, the material has better fatigue resistance. Meanwhile, parameter 'B' is the slope of the fatigue line which means the higher the absolute number of this parameter, the higher susceptibility of the material to strain amplitude changes. This means the fatigue life of material with a higher parameter 'B' decreases at a higher rate (Zakaria 2019). By this definition, under the same testing conditions, materials that have higher parameter 'A' and lower absolute parameter 'B' is favourable to have a better fatigue resistance.

Figure 5.13 shows the fatigue parameter 'A' of unmodified bitumen R0, virgin LDPE-modified bitumen VL and recycled LDPE-modified bitumen RL at 2%, 4% and 6%. This figure states that the unmodified bitumen has the highest propagated cracks due to the lowest 'A' parameter. On the other hand, VL3 and RL3, which are 6% of LDPEs, have a better fatigue resistance parameter explained in the higher 'A' parameter. The recycled LDPE (RL3) has a slightly better 'A' value than the virgin LDPE-modified bitumen (VL3). Overall, it can be stated that the addition of LDPE modifiers improves the bitumen fatigue resistance parameter, which can be seen from the increasing parameter 'A' for both LDPE types. The recycled material is slightly better in improving fatigue parameters compared to the virgin one at the same modification rate.

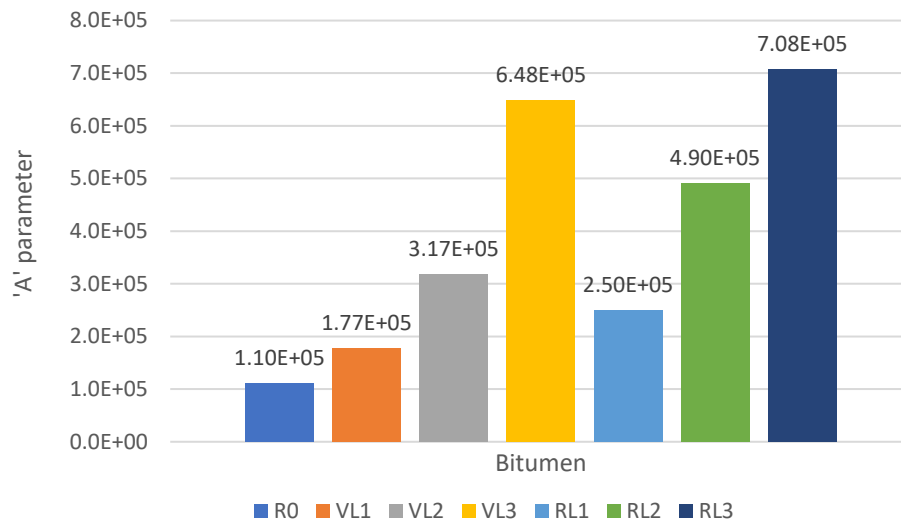


Figure 5. 13: Fatigue 'A' parameter

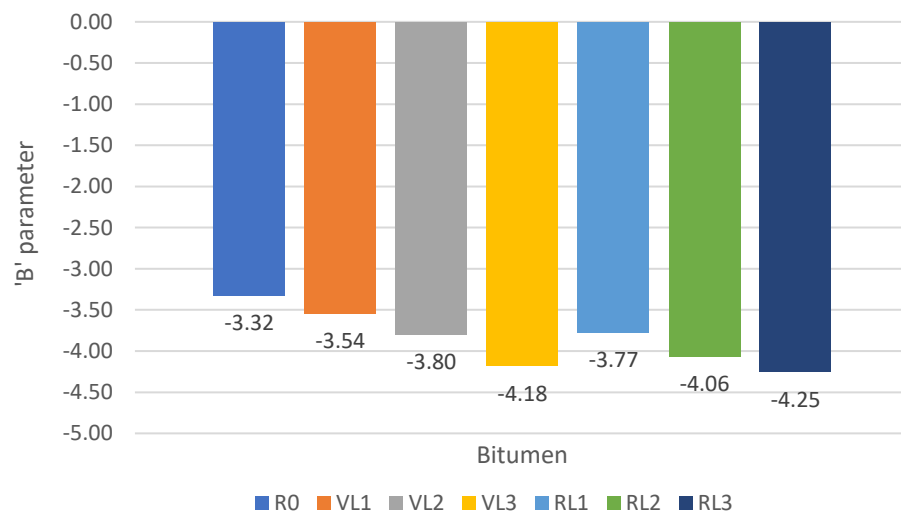


Figure 5. 14: Fatigue 'B' parameter

On the other hand, Parameter 'B' shows a better performance for unmodified bitumen than modified bitumen. The lower absolute 'B' value of the unmodified bitumen means the lower fatigue life decrease of the material compared to the modified bitumen. Figure 5.14 shows that the unmodified bitumen R0 has the highest number or lower absolute value of parameter 'B', indicating a lower rate of fatigue life degradation. Similar to the parameter 'A', the higher modification leads to a greater change in the parameter 'B'. However, the parameter 'B' changes go in the negative direction, representing a higher strain amplitude susceptibility. Therefore, the recycled LDPE shows a higher susceptibility

than the virgin LDPE-modified bitumen at the same modification rate. This result concludes that the VL3 and RL3 have a potentially higher fatigue life degradation rate than all bitumen. Since fatigue life is a function of parameters 'A' and 'B', the opposite trend of this parameter in these bitumen resulted in the need to plot and analyse the 'fatigue life versus strain' graph to conclude which bitumen is performing a better fatigue resistance. The mentioned graph is presented in the following sub-chapters.

5.3.1.4. Fatigue life prediction of bitumen

This section describes the number of cycles with two strain levels of distress, 2.5% and 5%. The determined strain levels are based on the asphalt pavement specification and the expected or allowed deformation limit. Generally, a 2.5% strain level is determined for strong and thick asphalt layer pavements where a low strain deformation is expected. Meanwhile, a higher strain deformation limit of 5% can be expected for a thinner asphalt layer (Jafari and Babazadeh 2016). Figure 5.15 shows the number of cycles (N_f) to failure at a 2.5% strain level, while Figure 5.16 shows the 5% strain level.

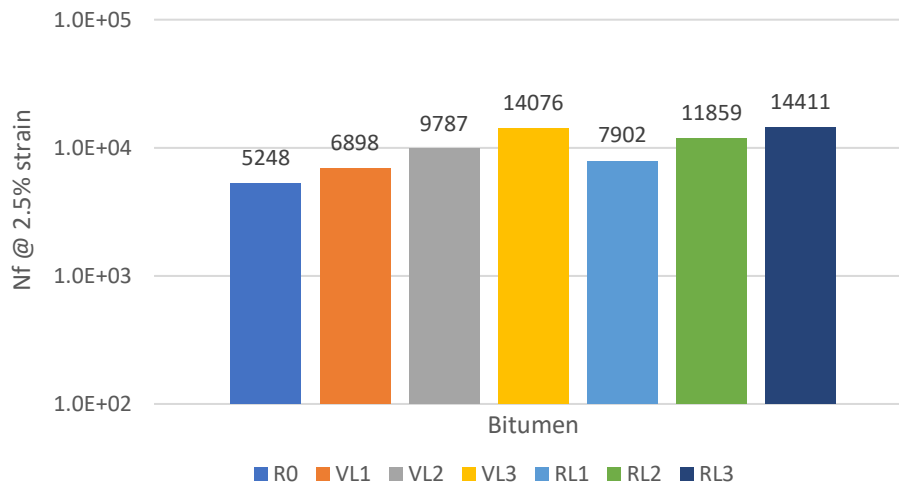


Figure 5. 15: Number of cycles to failure at 2.5% strain level

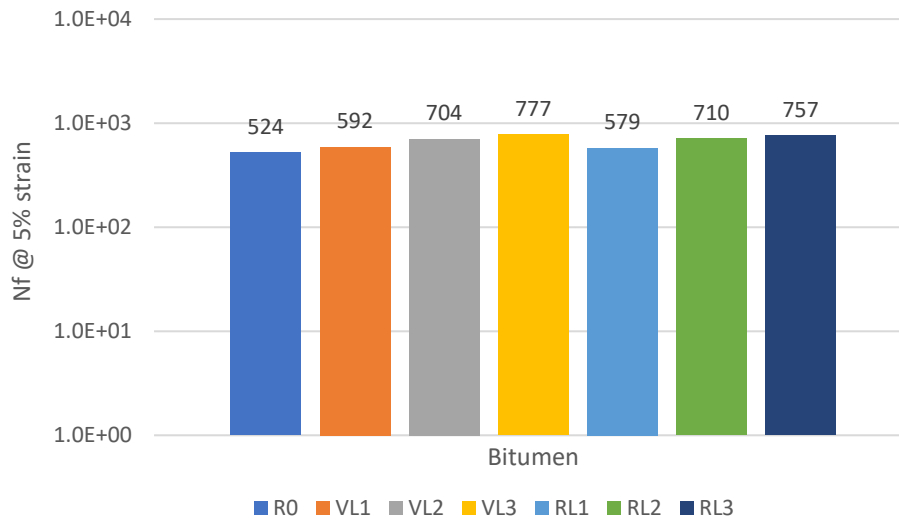


Figure 5. 16: Number of cycles to failure at 5% strain level

Based on Figures 5.15 and 5.16, the higher modification resulted in a higher number of cycles to produce a failure for both 2.5% and 5% strain levels, indicating the longer life of the LDPE-modified bitumen compared to unmodified bitumen. At a 2.5% strain level, the recycled LDPE-modified bitumen performed better at all modification rates compared to the virgin ones. At a 5% strain level, however, the virgin LDPE-modified bitumen performed slightly better at all modification rates. The critical factor of this condition is the different fatigue life slopes that determine the fatigue degradation rate. The recycled LDPE-modified bitumen tends to have a slightly shorter fatigue life at a higher strain level limit. This result indicates that for an excellent thick pavement with a low strain level limit of 2.5%, recycled LDPE-modified bitumen will perform better compared to virgin LDPE or unmodified bitumen. However, a virgin LDPE-modified bitumen, especially at 6% modification, will perform better compared to the recycled one at a thin asphalt layer at a strain level limit of 5%. The same trend is not exhibited at 2% and 4% of modification rates, where at this level, the recycled LDPE modified bitumen is still better than the virgin one. A better visualization of this condition is presented in the fatigue line graph in Figure 5.17.

The unmodified R0 performs the least at a low strain, while RL3 and VL3 are relatively comparable to have the best fatigue life. This condition is changed at a higher strain level. At a 3% strain, the RL3 curve overlaps the VL3, indicating that both have the same Nf. Meanwhile, at 5%, the RL3 is positioned completely under VL3. Visually, it can be stated

that at the 7% strain, all bitumens have the same fatigue life, and they are starting to turn over where the highly modified bitumen tends to have a lower fatigue life afterwards while the least modified and the unmodified bitumen have slightly better fatigue life. This condition is matched with the 'parameter B' that the highly modified bitumen is more susceptible to strain, which, consequently, the fatigue life is affected at high strain levels, as seen in the fatigue line.

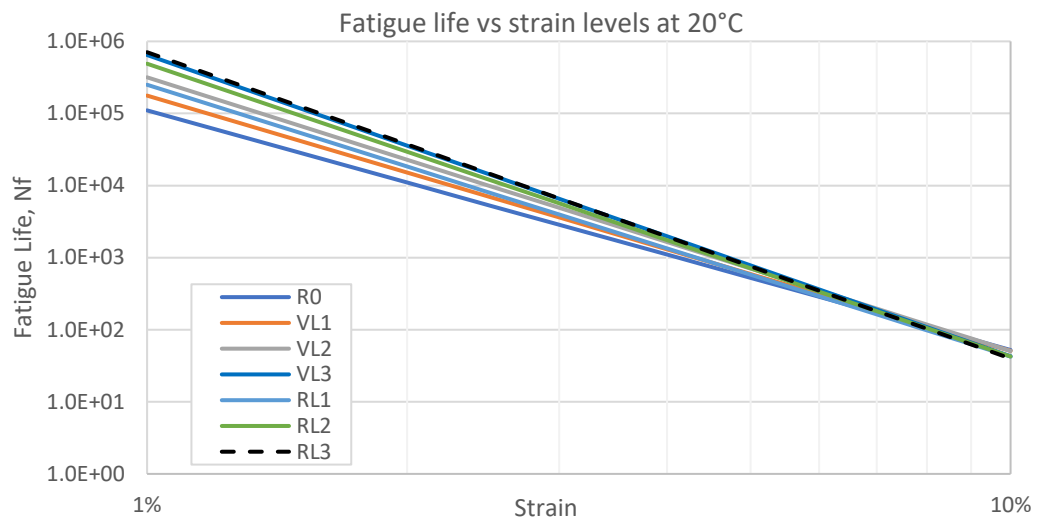


Figure 5. 17: Fatigue line of bitumen at 20°C

From the LAS test, it can be concluded that, in general, the LDPE-modified bitumen is slightly improving the fatigue life performance of the bitumen. The Nf graph at 2.5% and 5% strain levels demonstrate this improvement, especially at lower strain levels up to approximately 5%. The improvement is more prominent at the higher than at the lower modification rate. The 6% of LDPEs exhibited the best fatigue resistance. At the same modification level, the recycled LDPE-modified bitumen performs better than the virgin one.

5.3.2. Double-edge-notched tension (DENT) test

Complementary to the LAS test, the DENT test was used to understand the resistance of the bitumen to fatigue through the essential work of fracture (EWF) method by evaluating the energy needed to fracture the bitumen in its ductile state. The bitumen was artificially aged with RTFO and 20 hours of 100°C PAV before being tested by this method. Three mould types that represent three ligament lengths were used in this test. The test was

conducted in two repetitions per mould type, with six samples tested per bitumen type at the temperature of 20°C.

The essential work of fracture (EWF) method suggests three conditions to meet. Firstly, the ligament must be fully yielded prior to the cracking initiates. Secondly, the load-displacement diagrams should appear similar for all ligament lengths and thirdly, the sample must be yielded in pure plane stress.

For the first condition, the fully yielded ligament can be seen on all bitumen, as presented in load vs displacement curves in Figure 5.18. The peak of the curve explains the yielding point which occurred on all bitumen at all ligament lengths and repetitions, followed by a dropping curve that indicates the tearing process. The clear presence of the peaks on all curves indicates that the first condition is fulfilled.

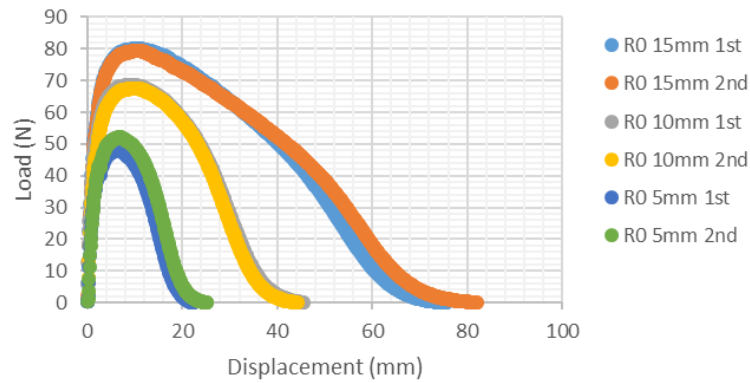
The similar shape of the curves for each ligament length can also be seen on all bitumen. The shape of the curves can be divided into three steps which represent the fracture process of the bitumen: (1) the stretching that demonstrated the increasing curve from zero to the maximum peak, (2) the yielding process that occurred on top of the curve as a turning point, and (3) the tearing process which indicated by the dropping curve after the peak. This similarity also explains that the test produced excellent repeatability, and the bitumen failure mechanism was similar. This result also confirms that the second condition is fulfilled.

For the third condition of pure plane stress yielding of bitumen to be fulfilled (Andriescu et al. 2004b; Subhy 2017; Subhy, Lo Presti, and Airey 2017) stated that the bitumen net section stress needs to be decreased with the increase of ligament length. Net section stress is the stress obtained from the average peak load from the smallest ligament length of the tested samples. The plot of net section stress as a function of ligament length for all bitumen is presented in Figure 5.19. This figure shows the decreasing net section stress of all bitumen at all ligament lengths, confirming that the third condition is fulfilled.

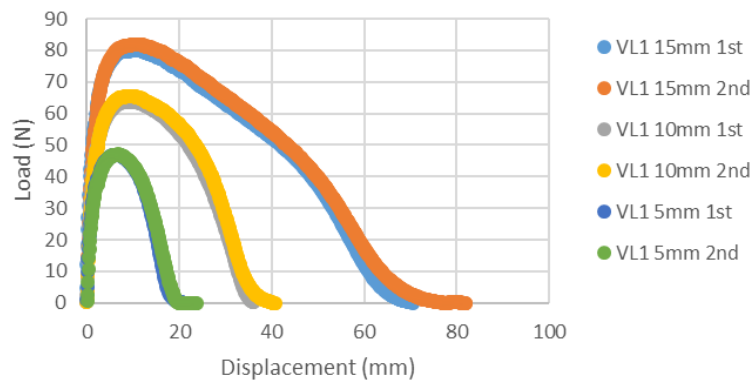
5.3.2.1. Load vs displacement curve of bitumen

The load versus displacement of the bitumen is presented in Figure 5.18. All bitumen shows a similar curve shape, representing the test's good repeatability. The graph also reveals that the increasing level of modification resulted in a higher load peak of the curves. This condition explains that the higher modification rate resulted in the ability of the bitumen to withstand higher stress prior to yielding.

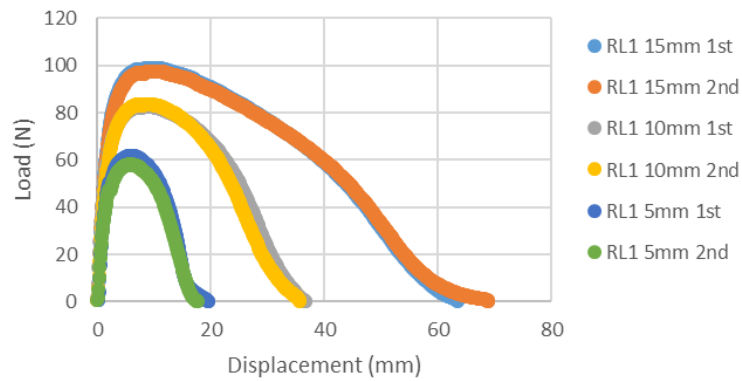
(a) Load vs Displacement Curves of R0



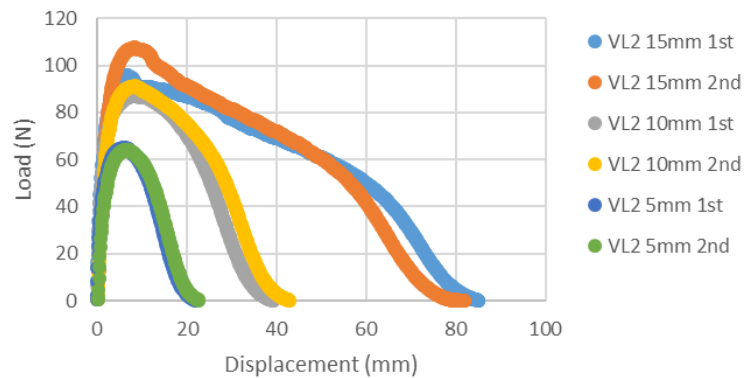
(b) Load vs Displacement Curves of VL1



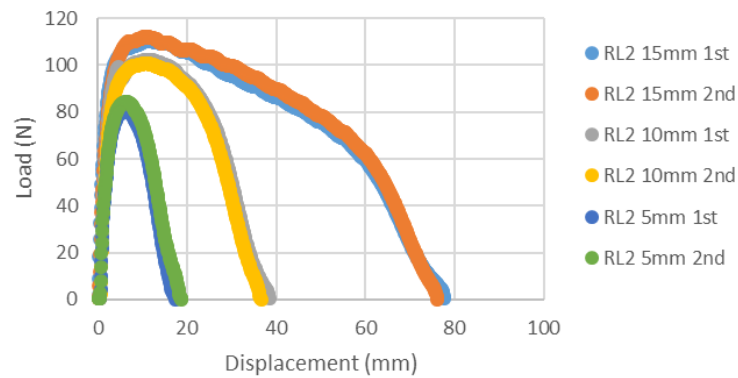
(c) Load vs Displacement Curves of RL1



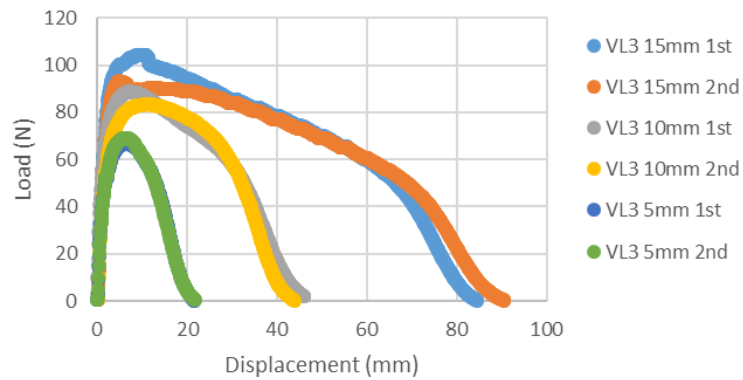
(d) Load vs Displacement Curves of VL2



(e) Load vs Displacement Curves of RL2



(f) Load vs Displacement Curves of VL3



(g) Load vs Displacement Curves of RL3

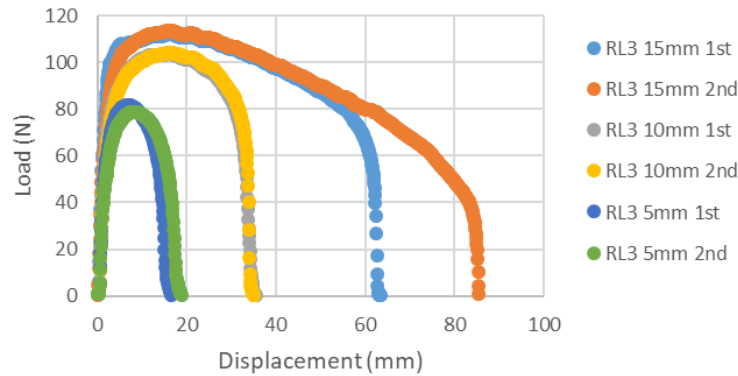


Figure 5. 18: Load vs displacement curve of bitumen

As shown in Figure 5.18(a), the unmodified bitumen demonstrated 5mm, 10mm and 15mm ligament average peak loads of 50.05 N, 68.1 N and 79.75 N, respectively. At the same ligament length, VL3 exhibited an average of 68 N, 86.15 N, and 98.75 N, while RL3 resulted at 80.15 N, 103.85 N and 112.95 N, as shown in Figure 5.18(f) and 5.18(g). This condition is due to the increasing stiffness of the bitumen by the presence of the LDPE

modifier. The recycled LDPE-modified bitumen resisted a higher maximum load at the same modification rate than the virgin LDPE-modified bitumen.

While the modification rate is increasing the maximum load, this parameter is relatively insignificant in affecting the total displacement of the bitumen. For example, the unmodified bitumen R0 at 5mm ligament length samples had a total displacement of 20mm. The approximately same number of displacements were recorded on all bitumen, including the highly LDPE-modified bitumen of VL3 and RL3. However, this condition is favourable where the stiffer characteristic of the modified bitumen is not followed by a significant brittle behaviour as previously resulted by Zakaria (2019), which used 160/220pen-based recycled LDPE modified bitumen.

The load versus displacement curve states that the bitumen modification produced a higher maximum stress with a higher percentage of LDPE modifier, while no significant changes were recorded in the maximum displacements. This condition can be translated as the modified bitumen can withstand higher stress compared to unmodified bitumen while maintaining flexibility and preventing early fracture.

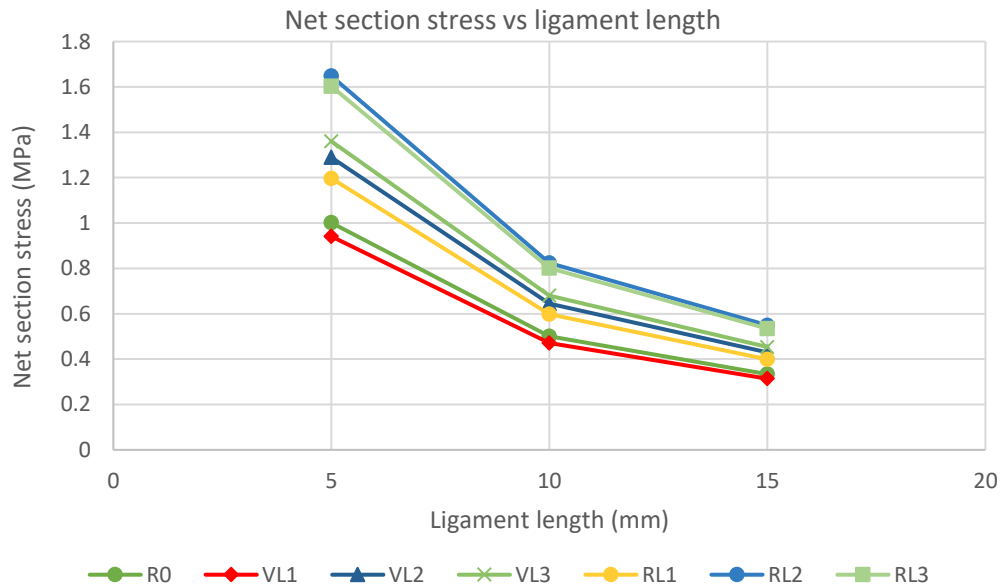


Figure 5. 19: Net section stress vs ligament length of bitumen

5.3.2.2. Total work of fracture

The total work of fracture is the area under the load vs displacement curve proposed to explain the fatigue failure resistance of bitumen. Figure 5.20 shows the specific total work of fracture, which is the total work of fracture per unit area of the bitumen section. Figure

5.20(a) shows the specific total work of fracture of unmodified bitumen and virgin LDPE-modified bitumen, while Figure 5.20(b) shows the same profile for unmodified bitumen and recycled LDPE-modified bitumen.

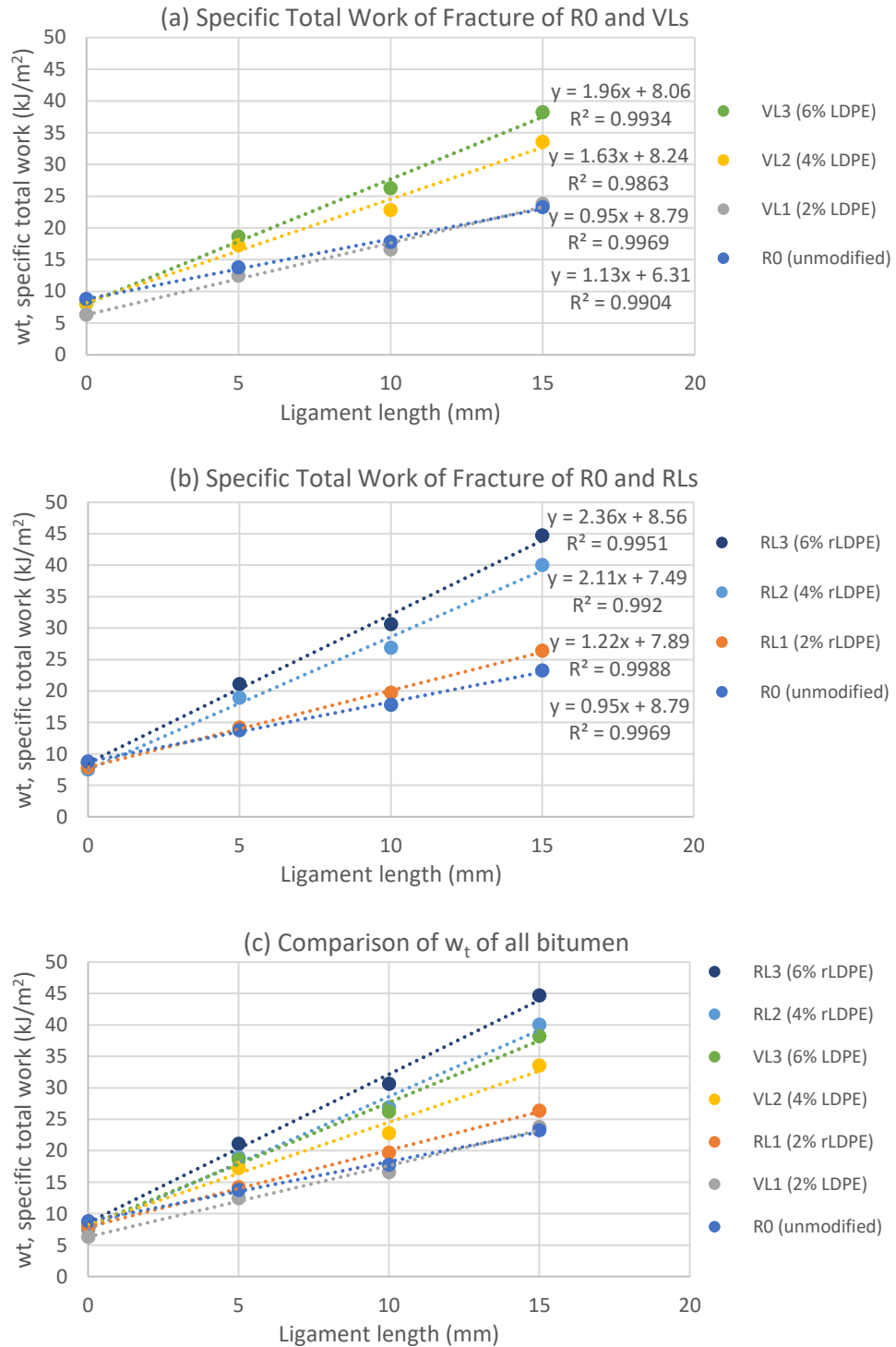


Figure 5. 20: Specific total work of fracture (w_t) of bitumen

By calculating the area under the load vs displacement curves and dividing them with the bitumen specimen cross-section, the specific total work of fracture (w_t) were obtained for all ligament length and all bitumen. The graph demonstrates that the increasing modification rate resulted in a higher w_t . The high coefficient of correlation R^2 for these curves (all >90%) indicates that the linear fitting procedure is acceptable and the assumptions of the essential work of fracture method are satisfied (Bahia et al. 2001b; Jafari and Babazadeh 2016). Figure 5.20(c) shows the rank order from the highest to the lowest specific total work of fracture from all tested bitumen. This figure shows that the recycled LDPE-modified bitumen (RLs) has higher w_t than virgin LDPEs (VLs), especially at 4% and 6% modification. Moreover, the figure explains that the modified bitumen generally has higher w_t than the unmodified bitumen.

The linear regression of the specific total work of fracture resulted in the equation as shown in Figure 5.20 (a) and (b) that represents the specific essential work (w_e) from the intercept and the specific plastic work of fracture (βw_p) from the slope coefficient. The recapitulation of these parameters is presented in Figure 5.21.

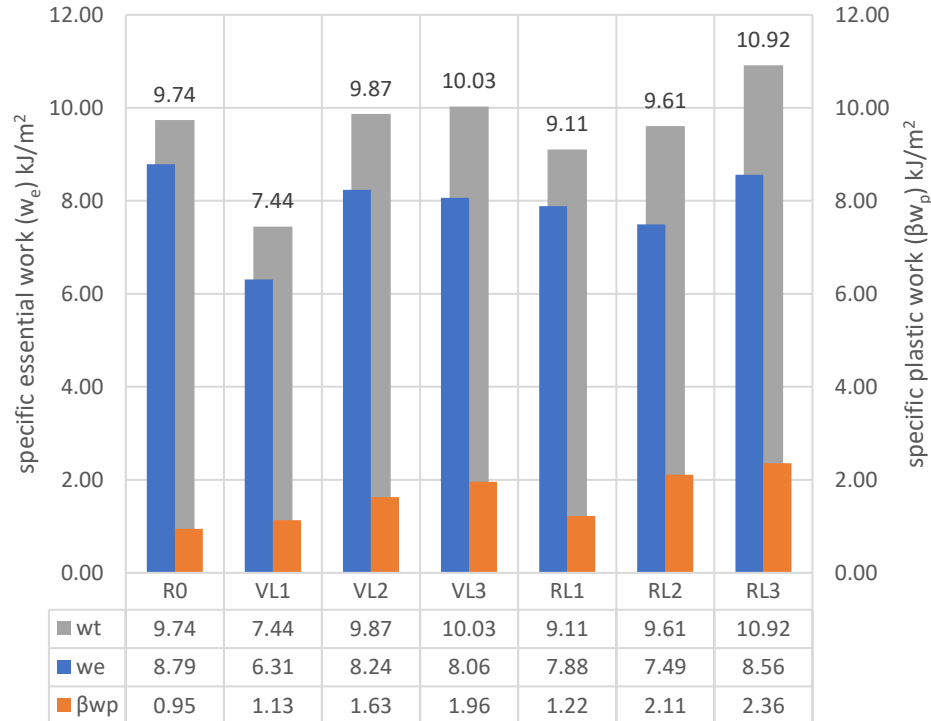


Figure 5. 21: The specific essential work (w_e), plastic work (βw_p), and total work of fracture (w_t) of bitumen

The parameter that relates to the damage process and is critical in defining fatigue cracking property is the specific essential work (w_e) (Bahia et al. 1999; Jafari and Babazadeh 2016; Schapery and Park 1999; Zhou et al. 2013c), while the parameter that affects additional deformation outside the fracture zone of the material thus less critical to fatigue cracking property is the plastic work (βw_p) (Schapery and Park 1999). However, both parameters are necessary in defining the material property and in the case of equal specific essential work of bitumen, a higher βw_p will define the overall fatigue properties (Andriescu and A 2006b), or in other words, a higher value of both will resulting better fatigue cracking resistance of the bitumen (Schapery and Park 1999).

Figure 5.21 shows the specific essential work decreased for all bitumen with VL2, VL3, RL1, RL2 and RL3 decreasing relatively slightly compared to the VL1. Meanwhile, the βw_p parameter was recorded as increasing for all modified bitumen. The combination of these two parameters resulted in a relatively similar value of specific total work of fracture for all bitumen except for the VL1 (decrease) and RL3 (significant increase). This result can be translated as the LDPE modification produced relatively unchanged fatigue resistance properties of the bitumen apart from the slight decrease of VL1 and increase of RL3.

5.3.2.3. The Critical Tip Opening Displacement (CTOD)

The critical tip opening displacement (CTOD) values of bitumen are presented in Figure 5.22, along with the specific essential work of fracture. CTOD is one of the parameters from the DENT test that demonstrates the bitumen's strain tolerance in the presence of a crack while loaded with stress during the ductile regime. This definition also means that the CTOD states the bitumen's ability to sustain the total elongation after the cracks have propagated (Subhy 2017). Therefore, CTOD is considered a good fatigue resistance indicator of bitumen.

Figure 5.22 shows that the presence of LDPE modifiers reduces the CTOD value. This condition has a clear trend on virgin LDPE but a relatively unspecific trend on recycled LDPE, especially the RL2, as also mentioned in the previous study by Zakaria (2019). Nevertheless, all modified bitumen shows a lower CTOD value, representing a lower fracture resistance than the unmodified bitumen. The increasing stiffness of LDPE modified might be the logical cause of the lower fracture resistance. With a higher stiffness value, the modified bitumen becomes more robust and able to withstand a higher load, as seen from the higher total work of fracture. On the other hand, their

rigidity prevents them from stretching longer than unmodified bitumen; thus, a lower CTOD has resulted.

Like CTOD, the specific essential work of fracture (w_e) of LDPE-modified bitumen, as discussed before, is slightly lower compared to unmodified bitumen. Although, there is no specific trend that can correlate w_e and the CTOD value. Figure 5.22 shows the superimposed w_e to the CTOD values.

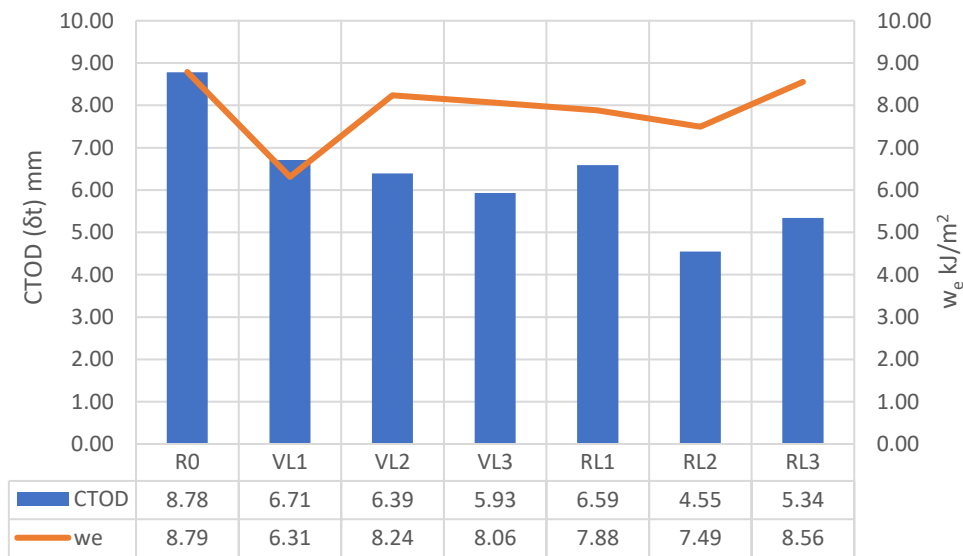


Figure 5. 22: The critical tip opening displacement (CTOD) vs specific essential work of fracture (w_e) of bitumen

The CTOD result concludes that the LDPE-modified bitumen will likely have a lower fatigue resistance than the unmodified bitumen once the initial crack is propagated. However, it is worth mentioning that the initial crack could not only be a factor of specific essential work (w_e), but also some of the material's plastic work (βw_p) (Schapery and Park 1999). In this case, while the relatively same w_e of bitumen will theoretically give similar endurance before the initial crack propagates, adding plastic work (βw_p) will provide additional strength to resist them.

It is also worth mentioning that for CTOD calculation, the net section stress was calculated from the smallest DENT sample (15mm notched specimen), approximating the bitumen tensile yield stress (Andriescu et al. 2004b; Subhy 2017). The fact that the bigger DENT specimens (10mm and 5mm notch) resulted in a larger curve area of loading vs displacement (higher total work of fracture) provides a reliable conclusion that, in general,

the modified bitumen requires a higher load to initiate the crack, or in other words more resistant to initial crack.

From overall DENT tests, several interpretations can be made regarding the fatigue resistance of the LDPE-modified bitumen compared to unmodified bitumen:

- Based on the load versus displacement curve, the LDPE-modified bitumen demonstrates a higher yield strength while maintaining flexibility, which can be translated as better resistance to fatigue.
- Based on the total work of fracture calculation, the LDPE-modified bitumen has a higher total work of fracture value that can be interpreted as better fatigue resistance.
- The critical tip opening displacement states less resistance to fatigue of the LDPE-modified bitumen due to its less ability to prevent further damage after an initial crack. This condition is because of the increased stiffness of the modified bitumen, even though it is believed that the early crack is harder to initiate on the LDPE-modified bitumen than the unmodified bitumen.

Based on these results, it is difficult to state the fatigue resistance tendencies of the LDPE-modified bitumen clearly. Besides, in the mixture system, a fatigue failure can occur due to bituminous mortar cracking (cohesion failure), the interface failure between the thin bitumen film and aggregate (adhesion), or a combination of both. To further understand this, the sets of asphalt mixture tests in the following chapters will help explain the fatigue property of the bitumen and its application in the mixtures.

5.4. Bitumen microstructure from microscopy observation

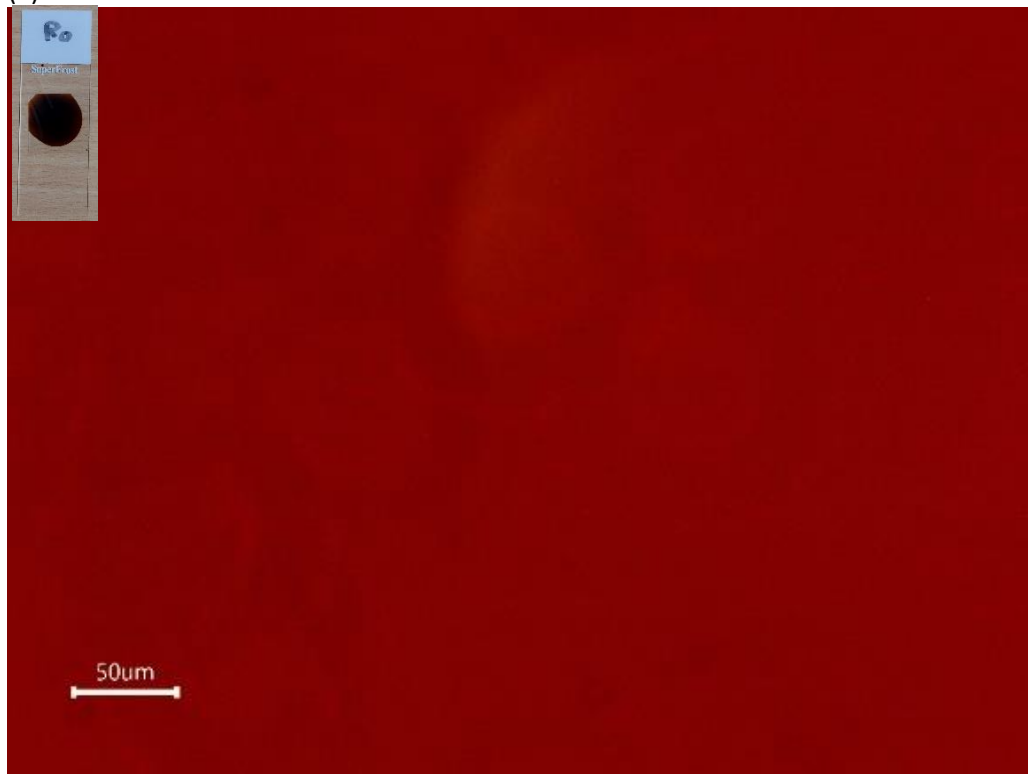
The physical properties of the neat and modified bitumen were discussed, and a clear improvement in rutting and fatigue performance has concluded. The most interesting part of the results is the major difference between the virgin LDPE and recycled LDPE in affecting or improving the bitumen properties. As has been discussed, recycled LDPE has better improvement in bitumen properties compared to virgin LDPE at the same modification rate. The recycled LDPE's better ability to disperse and interact with bitumen is believed to be the main reason for the differences with the virgin LDPE. To better understand the phenomenon, microscopy observation has been conducted on the neat

or unmodified bitumen, the virgin LDPE-modified bitumen and the recycled LDPE-modified bitumen.

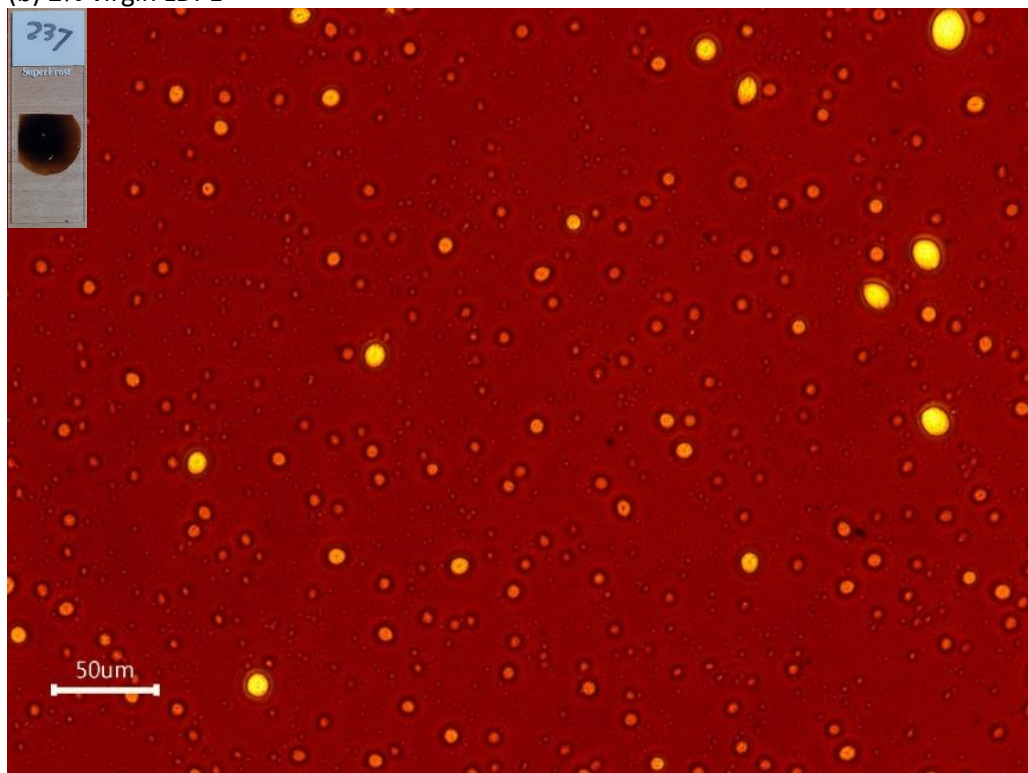
The unmodified bitumen, the 2%, 4% and 6% of recycled LDPE and virgin LDPE modified bitumen were observed under optical microscopy. The bitumen sample was prepared on top of the glass slide at 160-170°C. The bitumen sample layer must be very thin and translucent under bright light, ensuring it will be visible under optical microscopy. To acquire this, a tiny amount of bitumen (approximately 2-3 tips of a needle) was prepared per sample. The detailed procedure of the sample preparation is presented in Chapter 3. Figure 5.23 (a) shows the results of microscopy image capture of the bitumen at 20x magnification. The unmodified bitumen shows a clean dark red without any spot of impurities or modification. This result is reasonable and expected from optical microscopy of unmodified bitumen. Figure 5.23 (b) depicts the 2% virgin LDPE-modified bitumen, which shows the LDPE particle in the form of droplets in the bitumen. The individually separated droplet indicates the immiscibility of the LDPE-polymer-based phase in the dark bitumen phase (Polacco et al. 2005a) with very low interfacial adhesion between them. Similar results are presented in Figure 5.23 (f), where bitumen was blended with 6% of the LDPE modifier without additional compatibilizer or reactant. The same condition can be seen in Figure 5.23 (d). Figure 5.23 (f) depicts a slightly different appearance where the LDPE particle sizes are larger than the 2% and 4% of modifications. The bigger particles are probably due to the partial bitumen and polymer merging or swelling. Some of the polymer droplets show dark dots inside that indicate the presence of swollen bitumen in the polymer. This condition results in bigger droplet size with the biggest of 1197 μm^2 and a polymer coverage area of 19%. This result significantly increases compared to the particle size and polymer coverage in 2% and 4% of modifications.

Nevertheless, the droplets of the LDPE-polymer-rich phase remains individually separated and dispersed in the bitumen phase without any form of polymer network or linkages. In this condition, rather than as a polymer network, the virgin LDPE simply acts as a filler (Airey 1997). This condition leads to low changes in bitumen properties or insignificant rheologically polymer-dominant systems (Airey 1997).

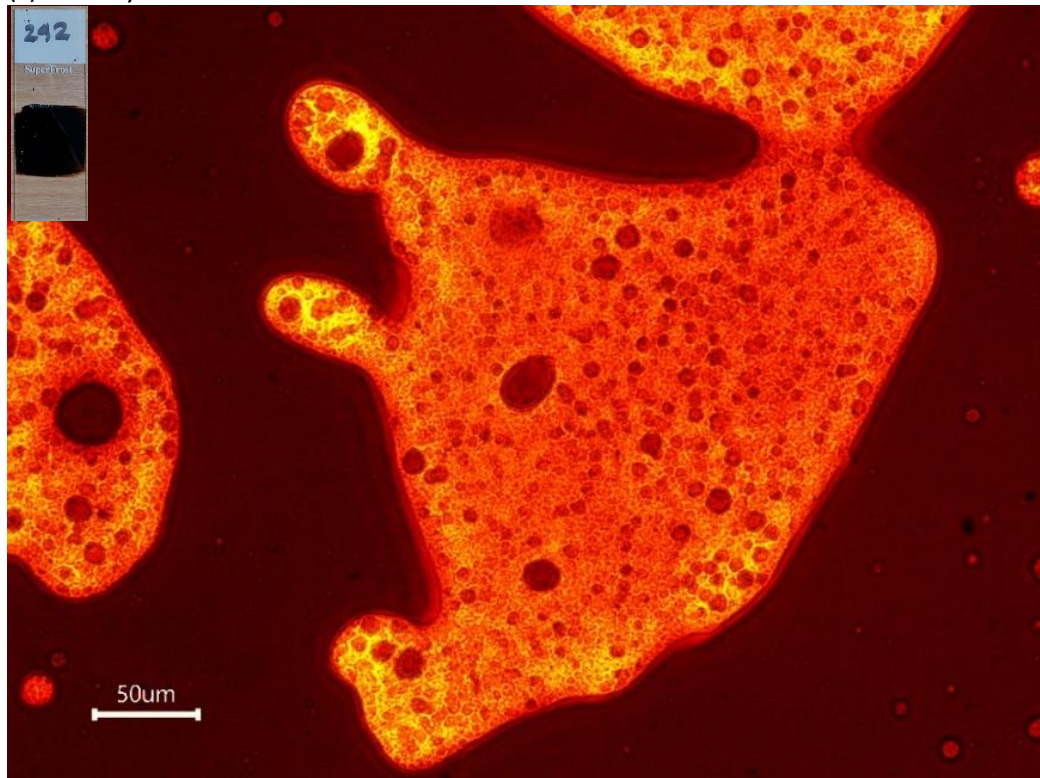
(a) Unmodified bitumen



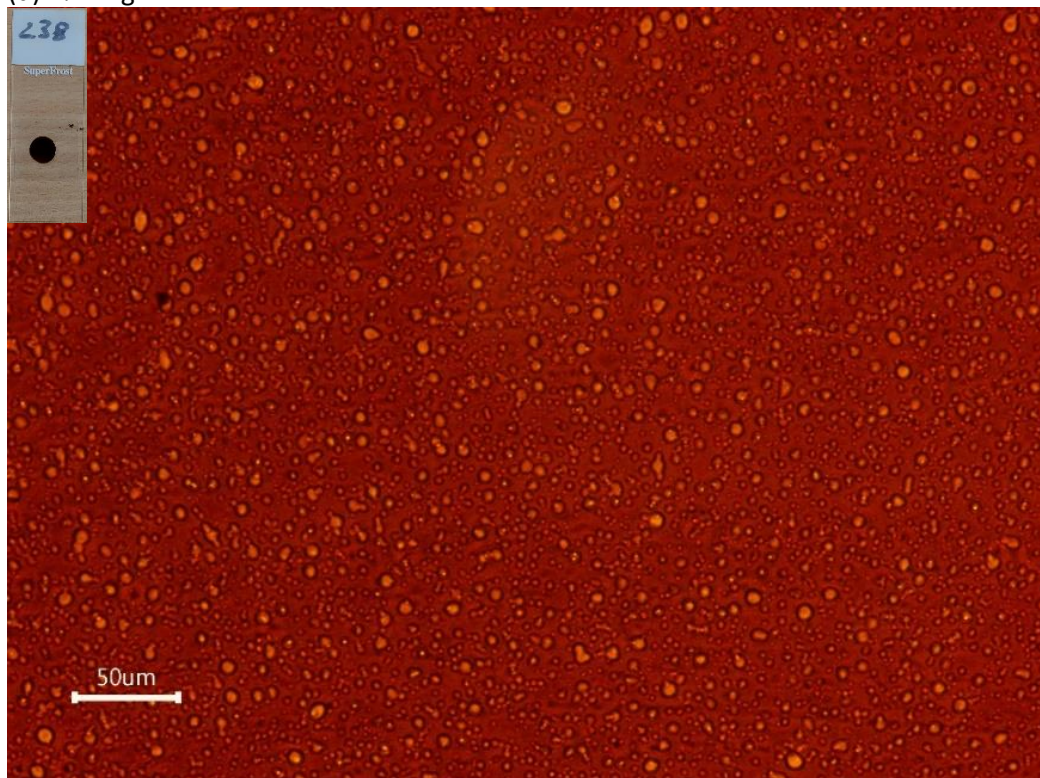
(b) 2% virgin LDPE



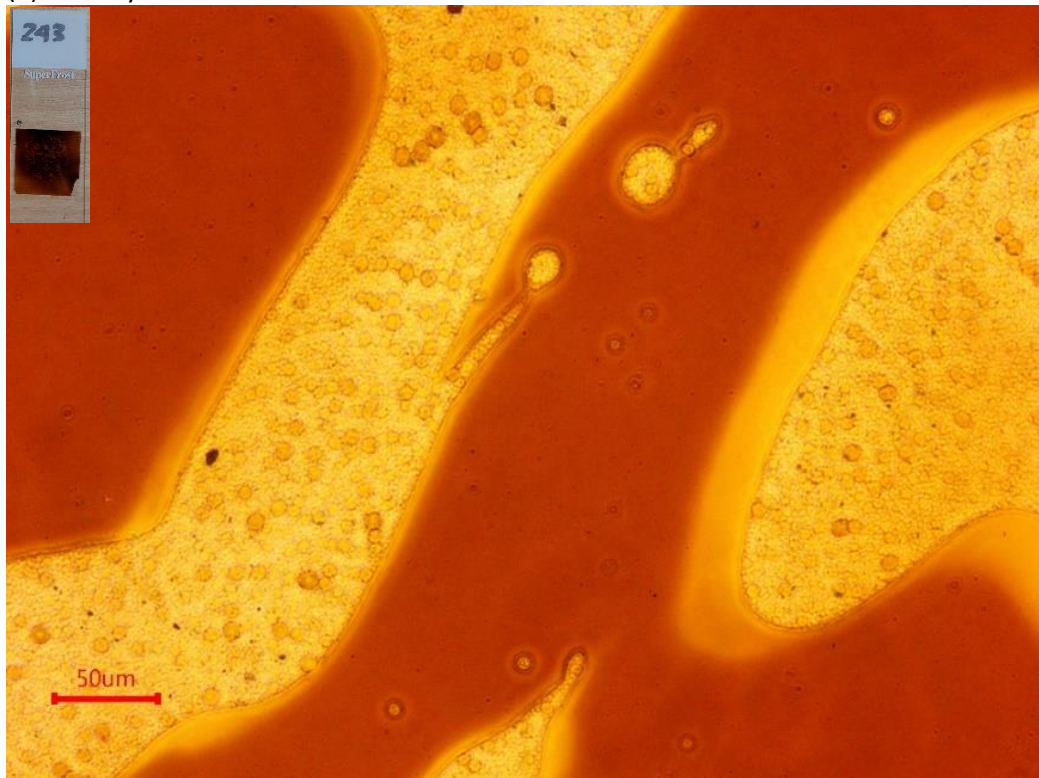
(c) 2% recycled LDPE



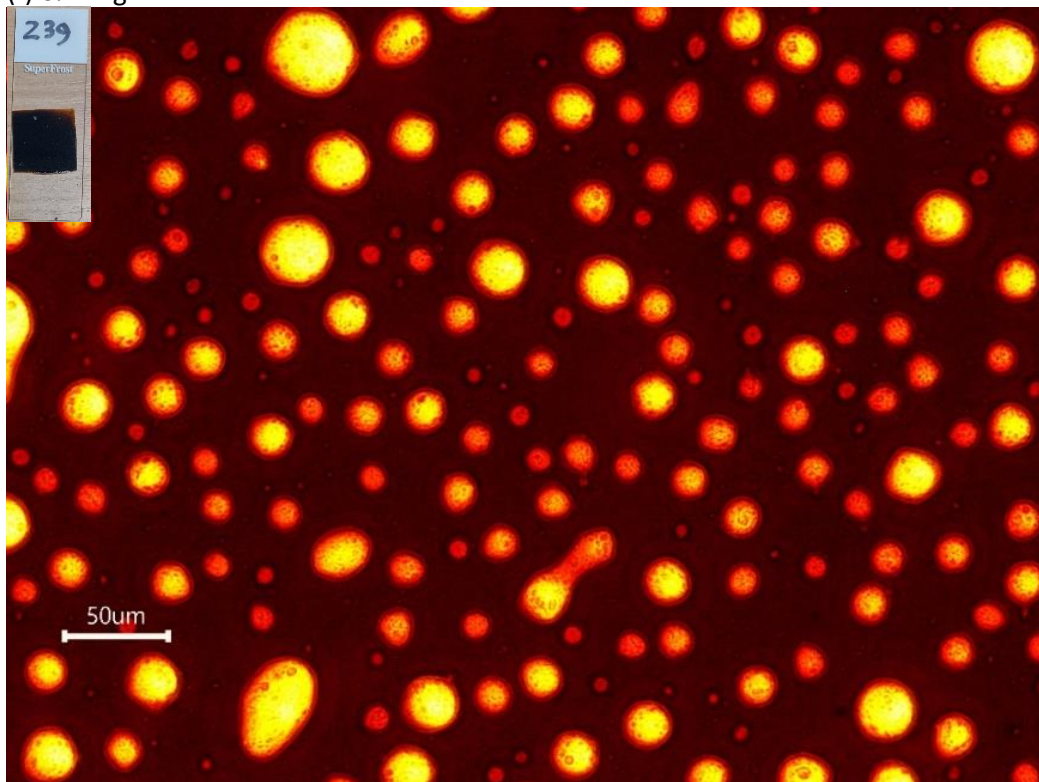
(d) 4% virgin LDPE



(e) 4% recycled LDPE



(f) 6% virgin LDPE



(g) 6% recycled LDPE

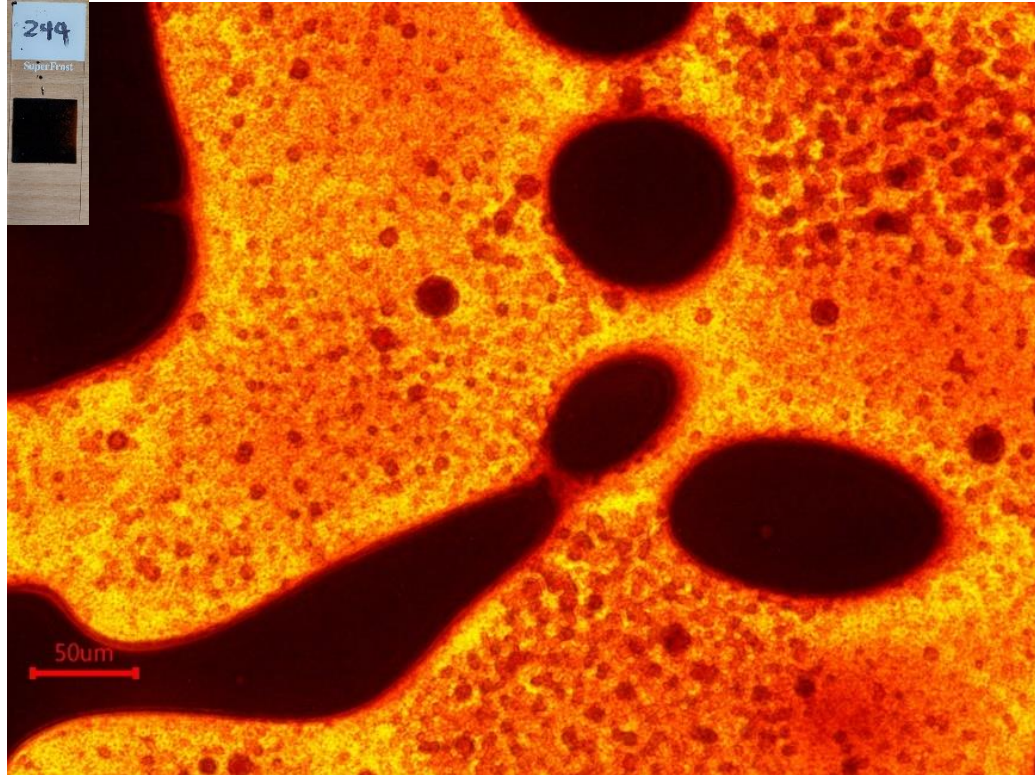


Figure 5. 23: Bitumen under optical microscopy

A noticeably different condition is shown in the recycled LDPE-modified bitumen. Figure 5.23 (c), (e) and (g) show the utterly different morphology of polymer dispersion compared to the virgin LDPE-modified bitumen at the same modification rate. In the recycled LDPE-modified bitumen, the modifier forms a polymer network that accumulates in the shape of interconnected islands. These island formations represent the polymer-rich phases that were dispersed in the bitumen-rich phase (Polacco et al. 2005a), as shown in Figures 5.24 (b) and (c). It can also be seen that inside the islands, dark spots represent the swollen bitumen and the intimate mixing between the bitumen and the modifier. The intimate mixing is believed to be because of the aliphatic groups' diffusion and absorption into the polymer (Upadhyay et al. 2008). This interaction results in a significant increase in the polymer-rich phase area, as shown in Figures 5.23 (c), (e) and (g). As a result, the measured polymer coverage area exhibits a significant leap, as in Table 5.2.

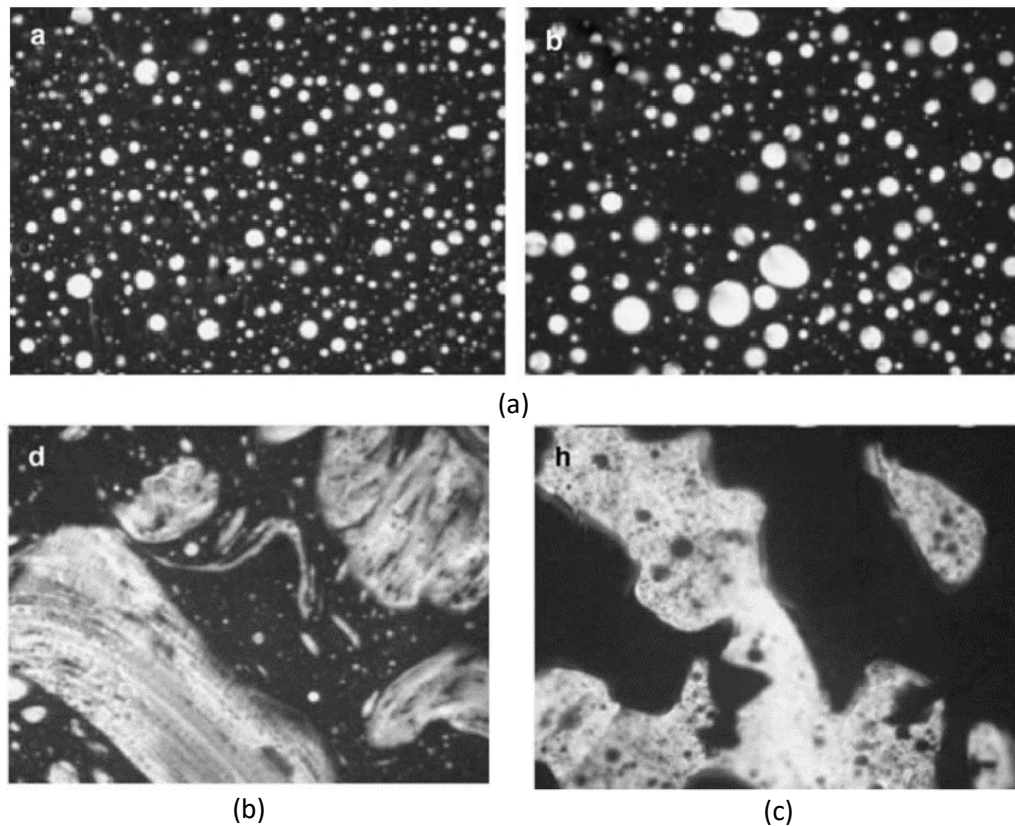


Figure 5. 24: Various PE-based modifiers (a) 6% Riblene LDPE, (b) 6% of Riblene & Lotader (reactant), (c) 6% Flexirene LLDPE (Polacco et al. 2005a)

It can be visually witnessed that the recycled LDPE-modified bitumen has modified the bitumen more dramatically than the virgin LDPE. The blend of 2% rLDPE resulted in a 49% coverage area compared to the 3% coverage area for the virgin LDPE. The 4% and 6% or rLDPE resulted in even higher coverage of 57% and 65%, incomparable to 9% and 19% of LDPE. Indeed, this is due to the different absorption mechanisms between the bitumen-LDPE and the bitumen-recycled LDPE.

Table 5. 2: Particle size and polymer coverage area of the modified bitumen

Bitumen	particle size (μm^2)		% polymer coverage area
	mean	max	
2% LDPE	5	83	3%
4% LDPE	3	39	9%
6% LDPE	124	1197	19%
2% rLDPE	-	-	49%
4% rLDPE	-	-	57%
6% rLDPE	-	-	65%

In the case of recycled LDPE and bitumen, the absorption mechanism might be referred to as dual-mode sorption (Upadhyay et al. 2008), in which some bitumen molecules normally diffuse inside the polymer while others are partly immobilised by contact with polymer molecules. By this adsorption process, the immobilised bitumen molecules are joined to microvoids with enough volume to hold several molecules simultaneously. As a result, the accumulated microvoids might cause the forming of a more extensive bitumen-polymer system that can be seen as a broad polymer coverage under microscopy.

The ability of bitumen to have contact with rLDPE polymer molecules might be because this material has typical properties of an LLDPE. Compared to LDPE, LLDPE polymer has fewer branches and is less amorphous, allowing bitumen to diffuse and interact directly with the polymer (rLDPE) molecules (Basfar and Idriss Ali 2006) and conducting the dual-mode sorption (Upadhyay et al. 2008). The dual-mode sorption occurs when there are two molecules penetration system; first: the penetrant molecules (bitumen) are diffused normally within the polymer, and second: some other bitumen molecules are partially immobilized due to interaction with polymer molecules. In some cases where the penetrant molecule is polar and capable of disrupting the polar polymer network, a chemical bond within the network could be formed (Bond and Smith 2006). However, due to the LDPE's non-polar nature, the interaction of bitumen-LDPE is merely physical without the addition of a reactant or compatibiliser. The typical phase separation in plastic-modified bitumen proves this physical-only interaction.

In the case of virgin LDPE, the highly branched structure of LDPE polymer prevents alien molecules from directly contacting the polymer through a diffusion mechanism (Basfar and Idriss Ali 2006). In bitumen and LDPE mixing, these long chain branches protect the polymer structure, causing a minimal bitumen diffusion. This condition prevents the interaction of bitumen with the polymer's main structure chains. The inability of bitumen to interact with polymers' molecules results in an immiscible particle of LDPE in the bitumen phase (Polacco et al. 2005a).

These LDPE and LLDPE findings are similar to (Polacco et al. 2005a), where the LDPE tends to have immiscible, individually separated particles with minimum bonding with the bitumen, as shown in Figure 5.24(a). Meanwhile, the LLDPE has shown a different behaviour that represented a good bonding and interaction with the bitumen, forming polymer-rich phases in the bitumen phase, as shown in Figure 5.24(c).

The microscopy observation clearly explains how the differences between the virgin LDPE and recycled LDPE-modified bitumen have occurred. The virgin LDPE acts as immiscible polymer particles in the bitumen, resulting in a relatively low effect in modifying the bitumen into desirable enhanced properties. On the other hand, the recycled LDPE have modified the bitumen into an entirely different polymer dominant system. This result explains the previously obtained findings in the softening point, needle penetration, rotary spindle viscosity, and the MSCRT's per cent of recovery (%R) and Jnr, as presented in Table 5.3.

Table 5. 3: Physical property comparison of LDPE and rLDPE

	Unmodified	6% virgin LDPE	6% recycled LDPE
Softening point (°C)	54	60	109
Pen number @25°C	54	33	28
Viscosity (Pa.s) @150°C	0.24	0.71	0.85
MSCR (%) %R @60°C 3.2kPa	0.44	6.06	64.05
MSCR Jnr (kPa ⁻¹) @60°C 3.2kPa	2.97	0.65	0.06

In general, the modification has changed the bitumen properties, with the recycled LDPE has provided more significant changes compared to the virgin material. This significance is because the recycled LDPE has the close physical property of Linear LDPE, the polymer that can bond better with bitumen than LDPE. The slight increase of R&B by 6°C in virgin LDPE indicates the polymeric phase behaves as a rigid dispersed phase, while a significant increasing softening point to 109°C in the recycled LDPE indicates a major polymer modification (Polacco et al. 2005a). In addition, the decrease in penetration and increasing viscosity were higher at recycled LDPE than virgin LDPE. The MSCR tests also explained a similar trend where the potential rutting resistance is higher at recycled LDPE compared to virgin LDPE-modified bitumen.

5.5. Functional group and ageing of LDPE-modified bitumen

Understanding the interaction between bitumen and LDPE modifiers in forming the modified bitumen will help in understanding the physical properties of the modified bitumen. This section discusses the FTIR spectroscopy observation to understand the bonding interaction of the bitumen and the LDPE modifiers.

Another discussed topic is the ageing phenomenon of bitumen. Since the LDPE-modified bitumen is a product of constant 30 minutes of 5000 rpm high shear mixing at a high temperature of 160-170°C, ageing could occur during this process.

5.5.1. The LDPE and bitumen interaction

From the FTIR spectroscopy, as discussed in the previous chapter, the characteristic peaks of LDPEs according to Gulmine et al. (2002) were captured, including the strong CH₂ asymmetric and symmetric stretching at 2920 cm⁻¹ and 2850 cm⁻¹, strong bending deformation at 1470 cm⁻¹, weak CH₃ symmetric deformation at 1377 cm⁻¹ and medium rocking formation at 720 cm⁻¹. These results were observed on both virgin LDPE and recycled LDPE. In addition, FTIR spectroscopy was also used for bitumen, resulting in the commonly observed peak, as shown in Figure 5.25.

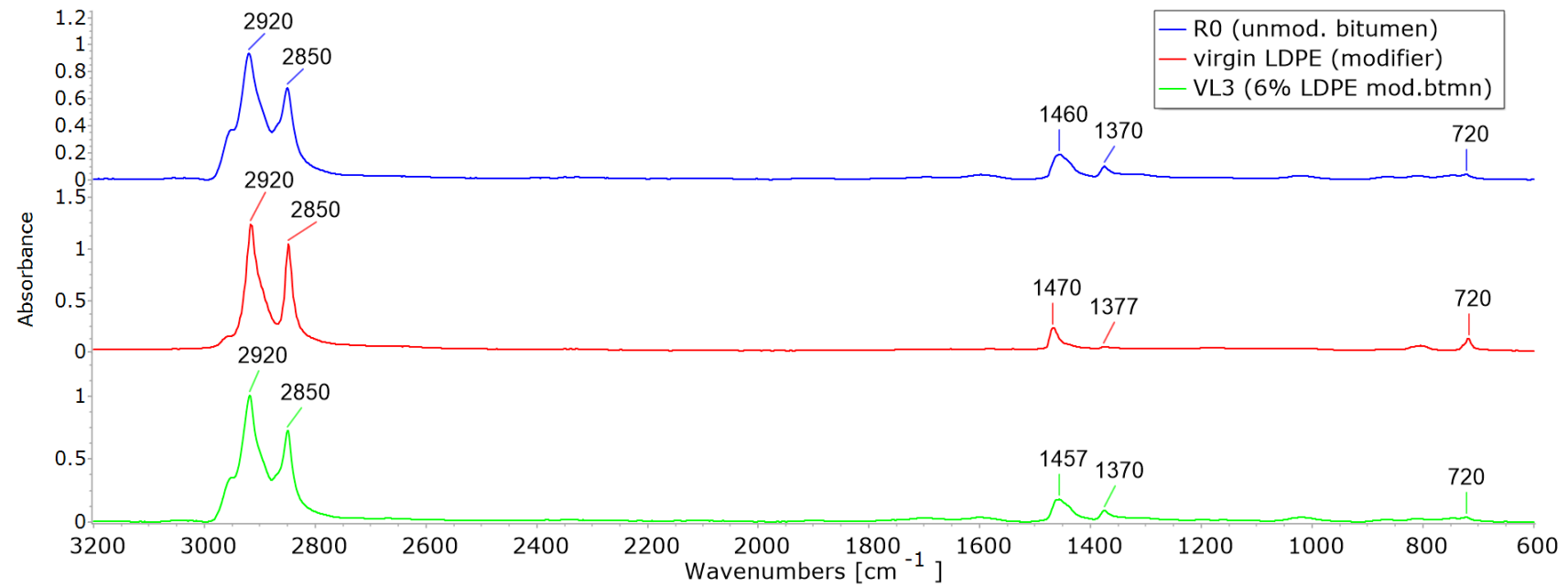
FTIR spectroscopy was also used to understand the interaction of bitumen and LDPEs in the modified bitumen. For example, in a blend of bitumen and modifier with chemical interaction or reaction, a new functional group could be formed in the bitumen and detected as a new infrared spectrum peak or a horizontal reposition of peaks in the FTIR. Meanwhile, in the case of physical interaction only, the FTIR spectra of the final product might be the combined wave numbers from each component material (Nivitha et al. 2016).

Figure 5.25 depicts the FTIR spectra stack of the unmodified bitumen, the modifier and the modified bitumen. Figure 5.25 (a) shows the unmodified bitumen, the virgin LDPE and the virgin-LDPE-modified bitumen, while Figure 5.25 (b) shows the products of recycled LDPE. From these stacked spectra, it can be stated that there is no sign of peak shifting or horizontal reposition, new peak formation, or peak deformation. This condition explains that there are no chemical changes in the modified bitumen. In other words, the interaction between bitumen and the virgin LDPE or recycled LDPE is merely physical, and the modified bitumen is the product of a physical blend of the materials. In this case, the observed spectra should consist of all characteristic peaks of both materials. However, since LDPEs and bitumen have the same major peak spectra, the modified bitumen showed relatively the same FTIR spectra as the unmodified bitumen.

The characteristic spectra of bitumen from previous studies (Bukka, Miller, and Oblad 1991; Hou et al. 2018; Lamontagne et al. 2001; Maria de Fatima A. de S. Araujo et al. 2012;

Yao, Dai, and You 2015) also consists some of the functional groups that found as the characteristic band of LDPE (Gulmine et al. 2002) (Upadhyay et al. 2008) which are 2923 cm^{-1} for CH_3 & CH_2 , 2850 cm^{-1} for C-H_2 , 1458 cm^{-1} for CH_3 & CH_2 , 1375 cm^{-1} for CH_3 , and 727 cm^{-1} for CH_2 . In addition, some of the bands have a higher intensity at bitumen than LDPE, resulting in a more obvious peak, for example, the CH_2 at 1370 cm^{-1} . Because of these identical characteristic spectra, the superposition peaks of the bitumen and the LDPE modifiers are indistinguishable.

(a) Spectra stack of unmodified, virgin LDPE, 6% LDPE modified bitumen



(b) Spectra stack of unmodified, recycled LDPE, 6% recycled LDPE modified bitumen

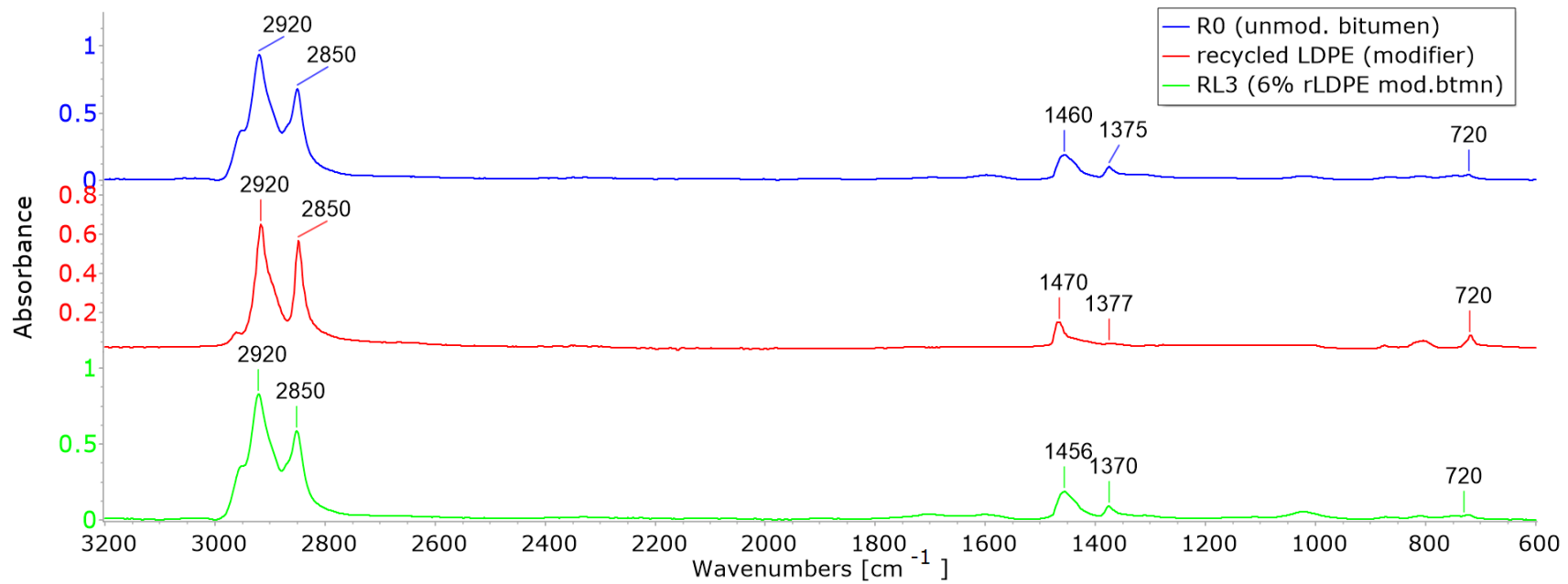


Figure 5. 25: Spectra stacks of (a) unmodified, virgin LDPE, 6% LDPE modified bitumen and (b) unmodified, recycled LDPE, 6% recycled LDPE modified bitumen

5.5.2. The ageing effect of modification

Ageing generally makes bitumen stiffer and affects other performances. This section elaborates on the modification process's effect on the ageing of the bitumen. This section also discusses the ageing degree of the bitumen, including the unmodified, the virgin LDPE and the recycled LDPE modified bitumen. To simulate the bitumen's natural ageing in asphalt preparation and long-life services, the short ageing RTFO and long ageing 20 hours 100°C PAV were conducted.

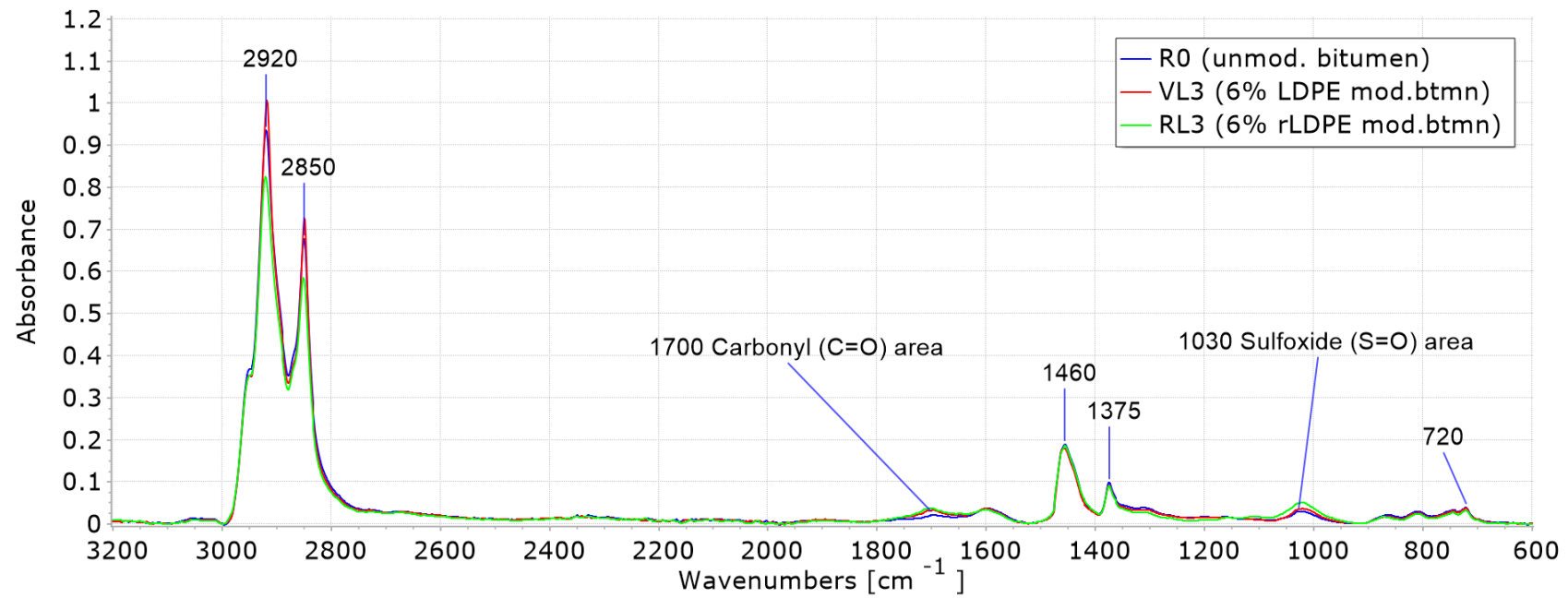
The most critical spectrum bands in the FTIR spectroscopy as the ageing indicator stand in the regions of 1000 to 1730 cm^{-1} (Van den bergh 2011b) that includes the sulfoxide or sulphur groups in the region of 1000 cm^{-1} , the carbonyl aliphatic from 1730 to 1700 cm^{-1} and carbonyl aromatic ketones in and from 1700 to 1680 cm^{-1} .

In the FTIR observation, the variation of bitumen sample thickness could influence the absorbance result. In this case, the semi-quantification method can be used in the analysis, where the simple ratio area calculation can be done without the step of curve normalization as long as the same spectrometer is used (Van den bergh 2011b). In the bitumen ageing evaluation, the combination of bands that are not to be influenced by the ageing is a reference factor and is used as the denominator of the area ratio calculation. This factor is constant in ageing for the same bitumen observed at the same FTIR spectrometer.

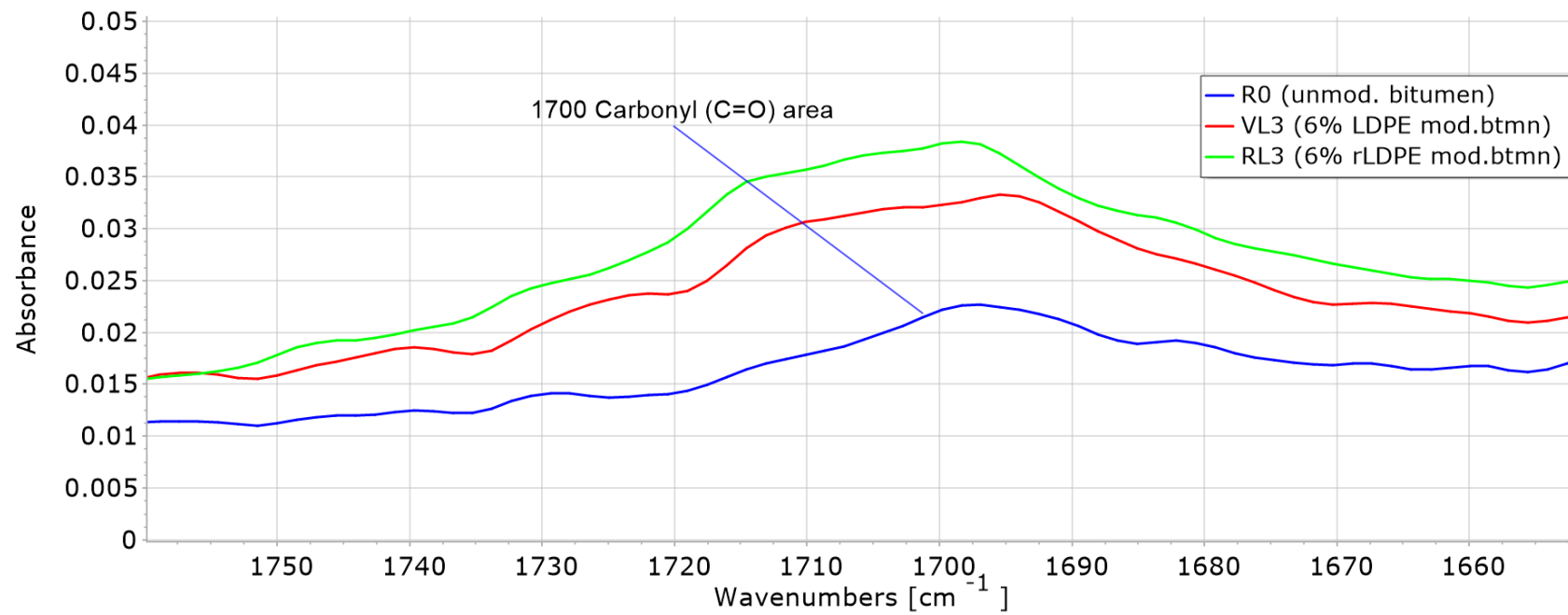
5.5.2.1. The effect of the modification process on ageing

The 30 minutes modification process with a high shear mixing of 5000 rpm was presumed to affect the ageing condition of the bitumen. The FTIR spectra of the bitumen are used to observe the presumed ageing by comparing the bitumen's known potentially oxidised functional group. Figure 5.26 (a) shows the FTIR result of unmodified bitumen, 6% LDPE-modified bitumen and 6% recycled LDPE-modified bitumen. The spectra of three bitumen in Figure 5.26 (a) show the same generally observed peaks of bitumen with slightly noticeable differences at the ageing indicator of 1700 cm^{-1} (carbonyl) and in 1030 cm^{-1} (sulfoxide) area.

(a) FTIR spectra of unmodified, 6% LDPE and 6% rLDPE bitumen



(b) Detail FTIR at 1700 carbonyl area



(c) Detail FTIR at 1030 sulfoxide area

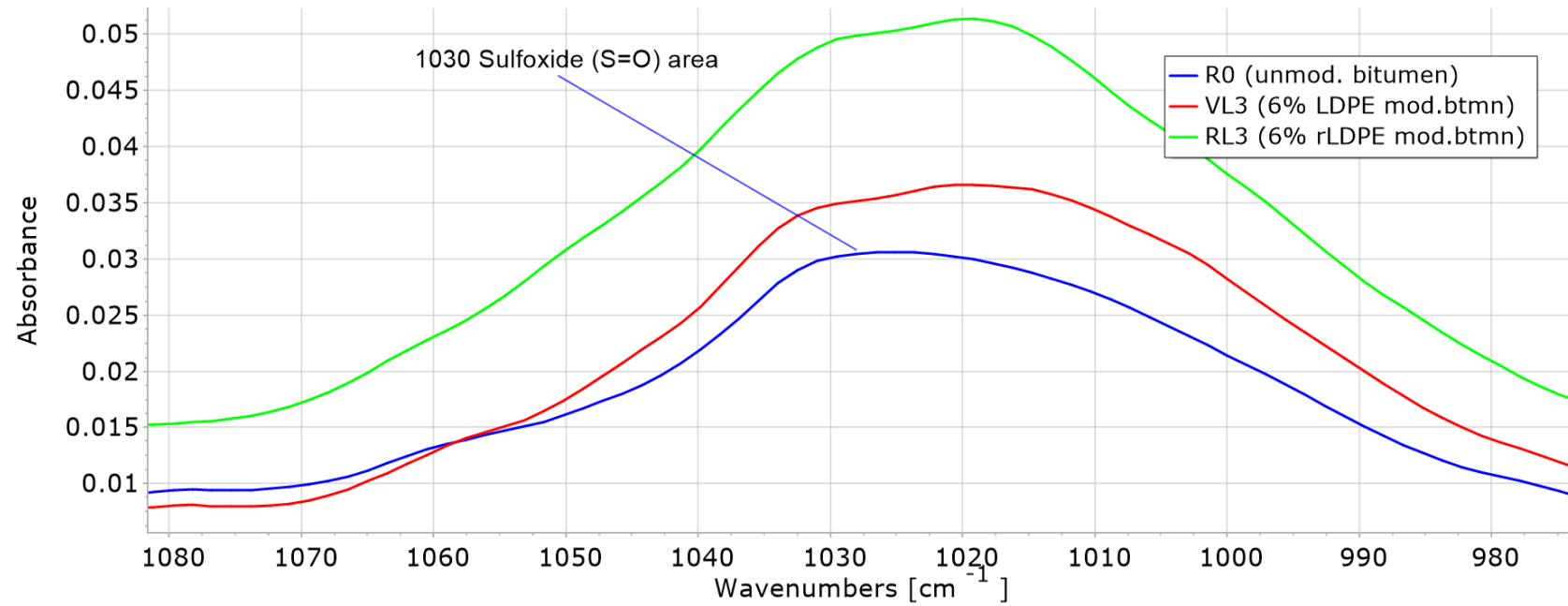


Figure 5. 26: FTIR spectra of (a) unmodified, 6% LDPE and 6% rLDPE bitumen, (b) detail at 1700 carbonyl area, (c) detail at 1030 sulfoxide area

By zoom detailing at 1700 carbonyl area (C=O), as shown in Figure 5.26 (b), there are relatively slight differences in absorbance between the three bitumen of unmodified R0 and modified bitumen RL3 and VL3. The more evident condition showed at the 1030 sulfoxide area, as shown in Figure 5.26 (c), where the three bitumen have peaks at this wavenumber, with the unmodified bitumen R0 having the lowest absorbance compared to RL3 and VL3. The absorbance differences in C=O and S=O, where the modified bitumen VL3 and RL3 have higher values than the unmodified bitumen R0 indicate that the ageing has already occurred during the 30 minutes blending process of the modification, the same phenomenon that was stated by (Zakaria 2019).

While visual comparison of the graph at the specified wavenumber indicates ageing, the semi-quantitative analysis method can provide quantitative data for a better conclusion. The method is based on the RILEM ATB-TG5 project, where the area calculation is based on band areas of 1376 and 1460, which are believed to be unaffected by ageing, and the ageing indicator wave numbers are the 1030 (sulfoxide) and 1700 (carbonyl) (Van den bergh 2011b). The detailed baseline and vertical limit of these bands are as follows:

Table 5. 4: Band areas for ageing indication

Band ID	Area 1030		A1376		A1460		A1700	
Baseline and vertical limit wave numbers	995	1047	1350	1390	1400	1525	1660	1753

The sulfoxide and the carbonyl area divided by the 1376 and 1460 waveband area resulted in the ageing sulfoxide index and ageing carbonyl index. Using Spectragryph v.1.2.16.1, the calculated band areas of the bitumen are presented in Table 5.5.

Table 5. 5: The calculated band areas of the bitumen

	R0	VL3	RL3
A1700 (carbonyl)	0.237	0.562	0.713
A1030 (sulfoxide)	0.399	0.428	0.453
A1376	1.098	1.025	1.035
A1460	6.761	6.387	6.828
Carbonyl index, CI	0.030	0.076	0.091
Sulfoxide index, SI	0.051	0.058	0.058

The calculation of the carbonyl area of R0 resulted in 0.237, which is the lowest compared to VL3 with 0.562 and RL3 with 0.713. VL3 and RL3 carbonyl area differences are 137% and 200% compared to the R0. The sulfoxide area also gives the same trend with a lower

magnitude of differences, where the VL3 and RL3 have 7% and 14% higher values than R0. Figure 5.27 (a) depicts the area calculation of carbonyl peaks and the denominator peaks.

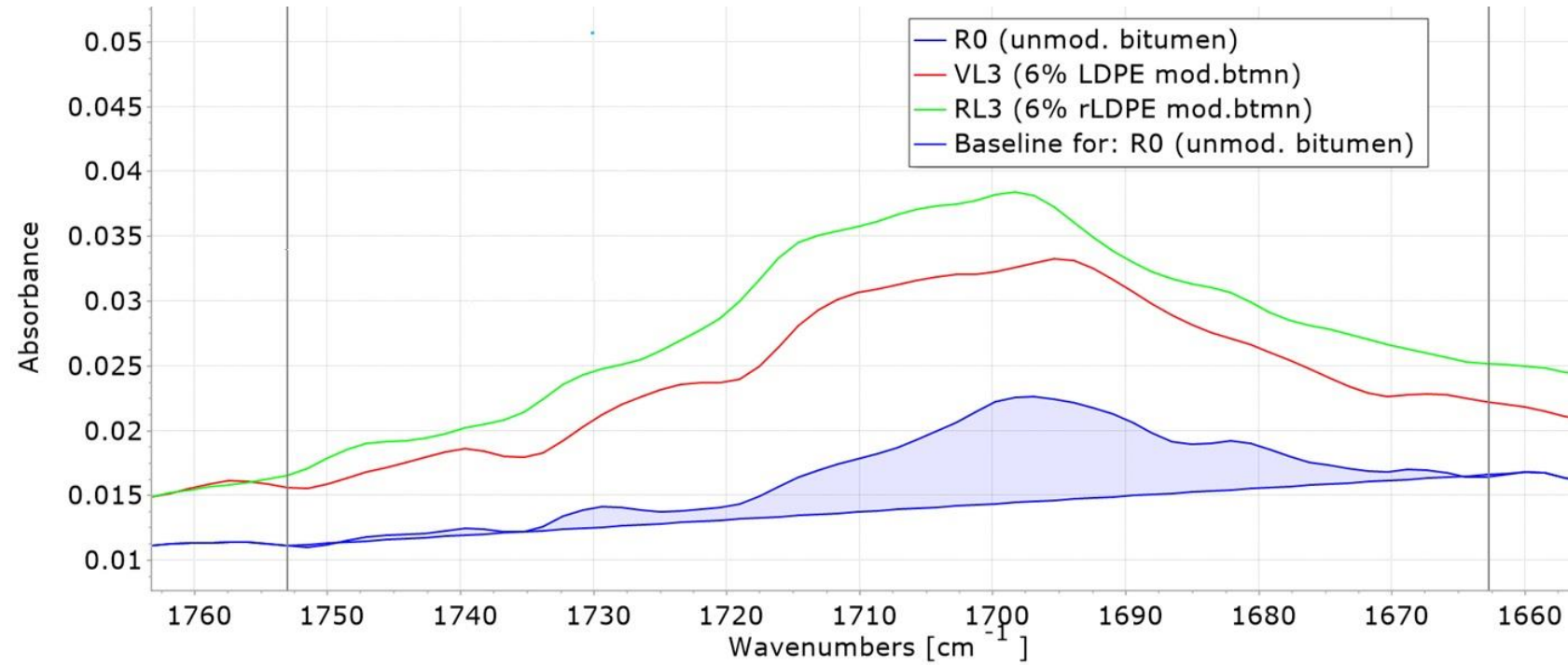
While the oxidized wavenumber area (especially the carbonyl) differences between R0, VL3 and RL3 were noticeable, the differences in the area 1376 and 1460 of the VL3 and RL3 were insignificant compared to the R0's. The coefficient of variation of the carbonyl and sulfoxide areas are 0.48 and 0.06, while both denominators' areas of 1376 and 1460 have 0.04. This low value proves that these areas are unaffected by ageing (Van den bergh 2011b). Figure 5.27 (b) shows that the three bitumen curves coincide in the 1376 and 1460 peaks, resulting in close area calculation values. Calculating the carbonyl and sulfoxide indexes gives a more precise explanation of the ageing phenomenon during the preparation of the modified bitumen. The carbonyl index of R0 is 0.030, where VL3 has 0.074, which is more than twice, while the RL3 has 0.090 or three times the R0. The sulfoxide indices also indicate the same, where VL3 and RL3 have 30% and 44% higher values. Both carbonyl and sulfoxide indices can be interpreted as the oxidation had occurred in the modified bitumen. This semi-quantification result confirms the previous method of spectra visual comparison.

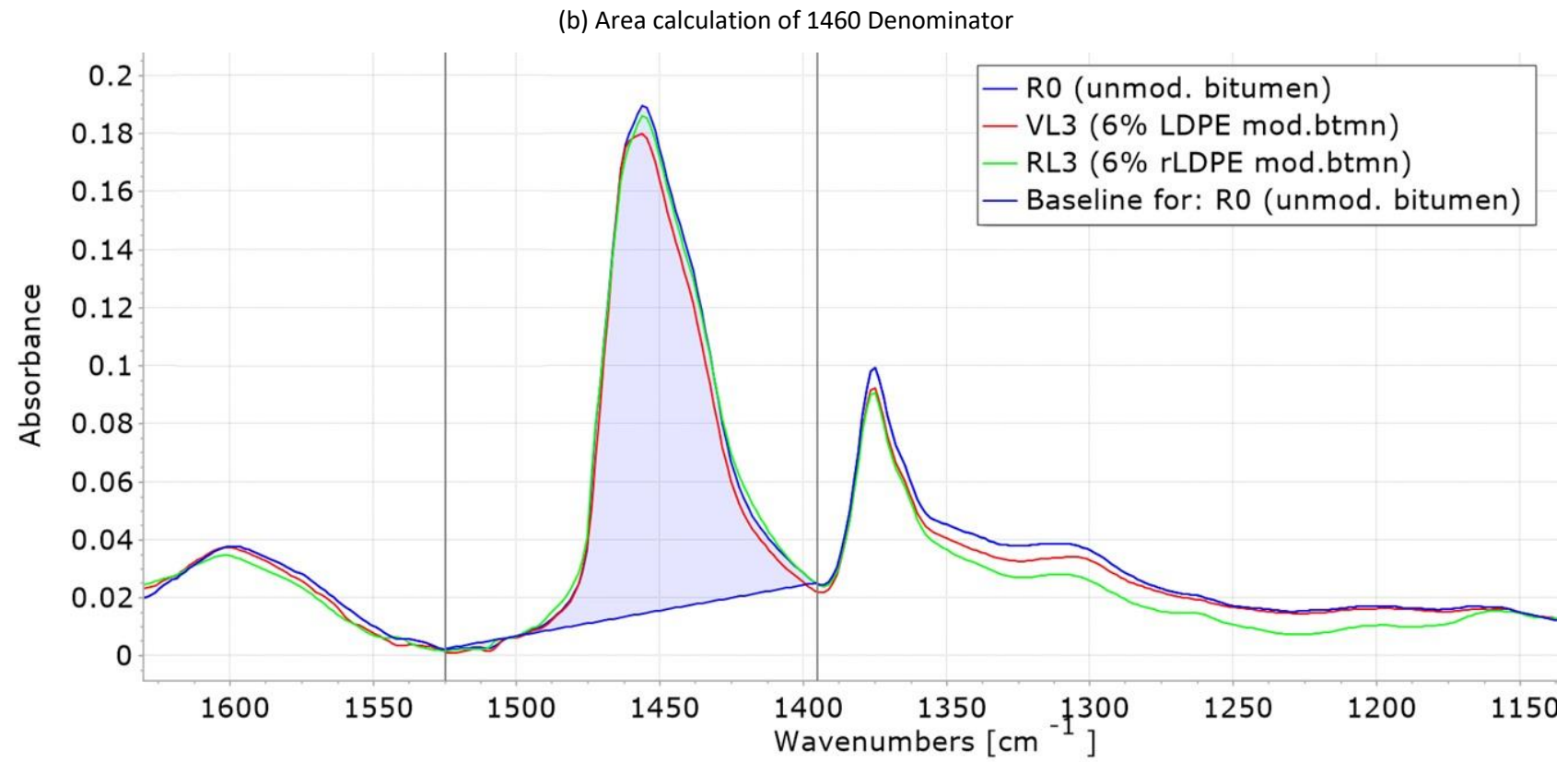
5.5.2.2. The ageing degree of LDPE-modified bitumen

The previous subchapter revealed the ageing phenomenon on the modified bitumen that occurred during the modification process. Using the same FTIR method, the ageing indicator of all bitumen (R0, VL3 and RL3) are compared in unaged, short-aged RTFO and long-term aged PAV to understand the ageing degree of the bitumen further.

Figure 5.28 shows the carbonyl and sulfoxide area of the bitumen. The figure visually explains that the unaged and unmodified R0 has the lowest absorbance value for both carbonyl and sulfoxide areas, while the aged R0 starts to blend in the curve crowd of VL3 and RL3, and complex to conclude the ageing trends. Therefore, a semi-quantification method is preferable in this case. The calculated areas of carbonyl, sulfoxide, and the denominators of the bitumen in unaged, RTFO and PAV-aged conditions, as shown in Figure 5.28, are presented in Table 5.6. Table 5.6 shows the expected different values of the carbonyl and the sulfoxide areas and relatively the same values of denominator areas of 1376 and 1460. Calculation of the coefficient of variation resulted in a noticeably high for carbonyl (0.40), sulfoxide (0.13) and a low co-var for both 1376 and 1460 areas (0.03).

(a) Area calculation of Carbonyl





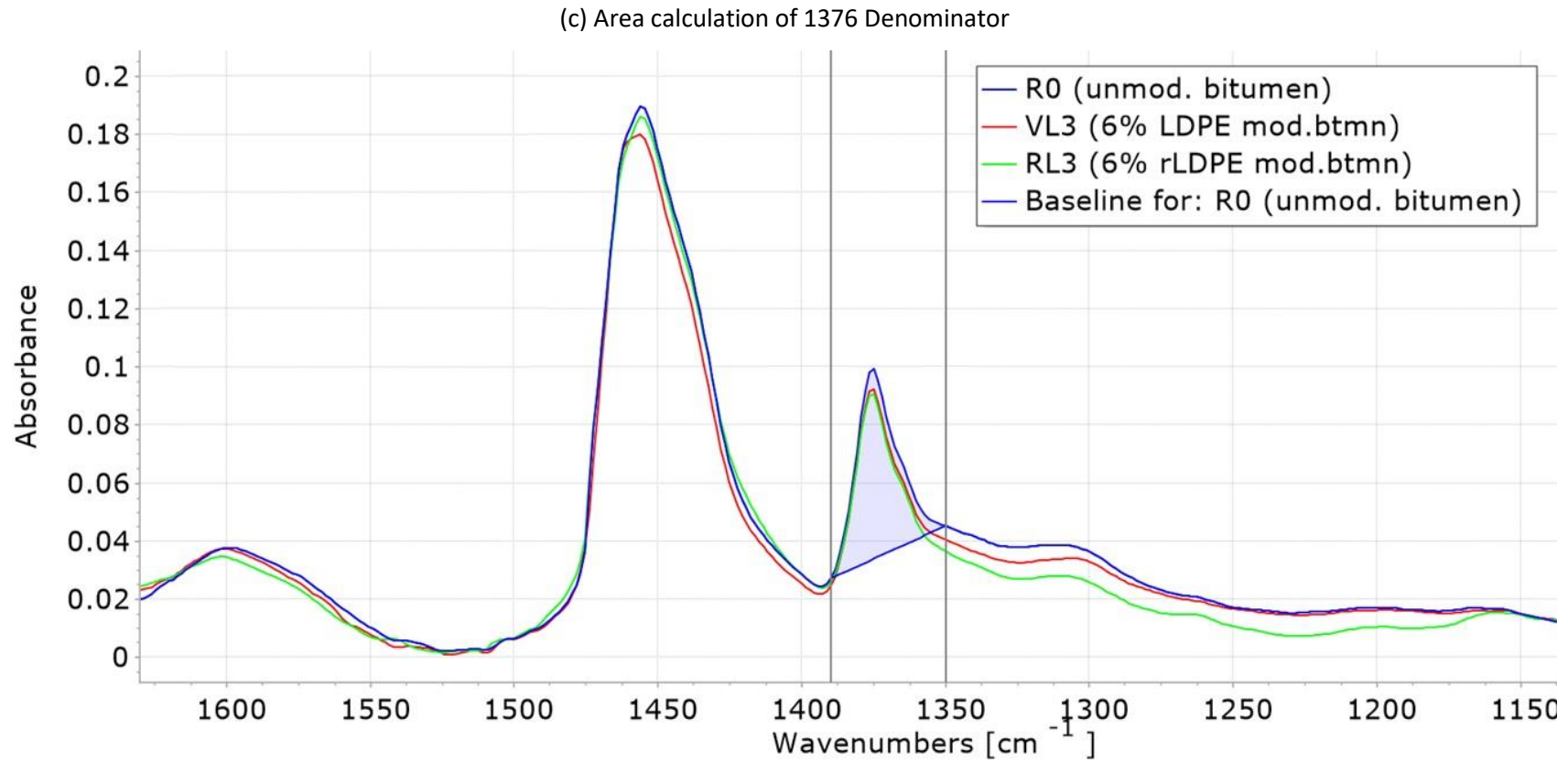


Figure 5. 27: The calculation areas of FTIR's (a) Carbonyl, (b) Denominator 1460, and (c) Denominator 1376

For the carbonyl area, the lowest value resulted from the unmodified bitumen R0 with 0.030, followed by VL3 (0.076), R0-rtfo (0.088) and RL3 (0.091). This number indicates the preparation of VL3 and RL3 was 'ageing' the bitumen at relatively the same level of short ageing (RTFO, 75 minutes of airflow at 163°C) of R0. The carbonyl indices of these bitumen also confirm the modified bitumen's (VL3 and RL3) close values to the R0-rtfo.

Similar to the carbonyl, the larger sulfoxide areas and the higher sulfoxide index (SI) also presented as an indication of the occurred bitumen ageing. The R0 has the lowest sulfoxide index of 0.051, followed by VL3 and RL3, which both have the same sulfoxide index as R0-rtfo, which is 0.058. Further ageing procedures (PAV) consistently lead to a higher SI for all bitumen.

The carbonyl and sulfoxide index calculation shows that all bitumen presents a consistent increase in CI and SI value when the artificial ageing RTFO and PAV have been applied. This result is in line with many studies that stated the successful use of carbonyl and sulfoxide index calculation to determine the ageing phenomenon in bitumen. Furthermore, the modification procedure of bitumen with LDPEs using the high shear mixer of 5000 rpm for 30 minutes at 160-170°C proves to produce aged bitumen.

Table 5. 6: The calculated band areas of unaged and aged condition

	R0	R0-rtfo	R0-pav	VL3	VL3-rtfo	VL3-pav	RL3	RL3-rtfo	RL3-pav
A1700 (carbonyl)	0.237	0.689	1.004	0.562	0.801	1.145	0.713	0.980	1.371
A1030 (sulfoxide)	0.399	0.455	0.543	0.428	0.454	0.560	0.453	0.491	0.576
A1376	1.098	1.079	1.020	1.025	1.059	1.009	1.035	1.071	1.016
A1460	6.761	6.713	6.291	6.387	6.271	6.451	6.828	6.614	6.769
Carbonyl index, CI	0.030	0.088	0.137	0.076	0.109	0.153	0.091	0.127	0.176
Sulfoxide index, SI	0.051	0.058	0.074	0.058	0.062	0.075	0.058	0.064	0.074

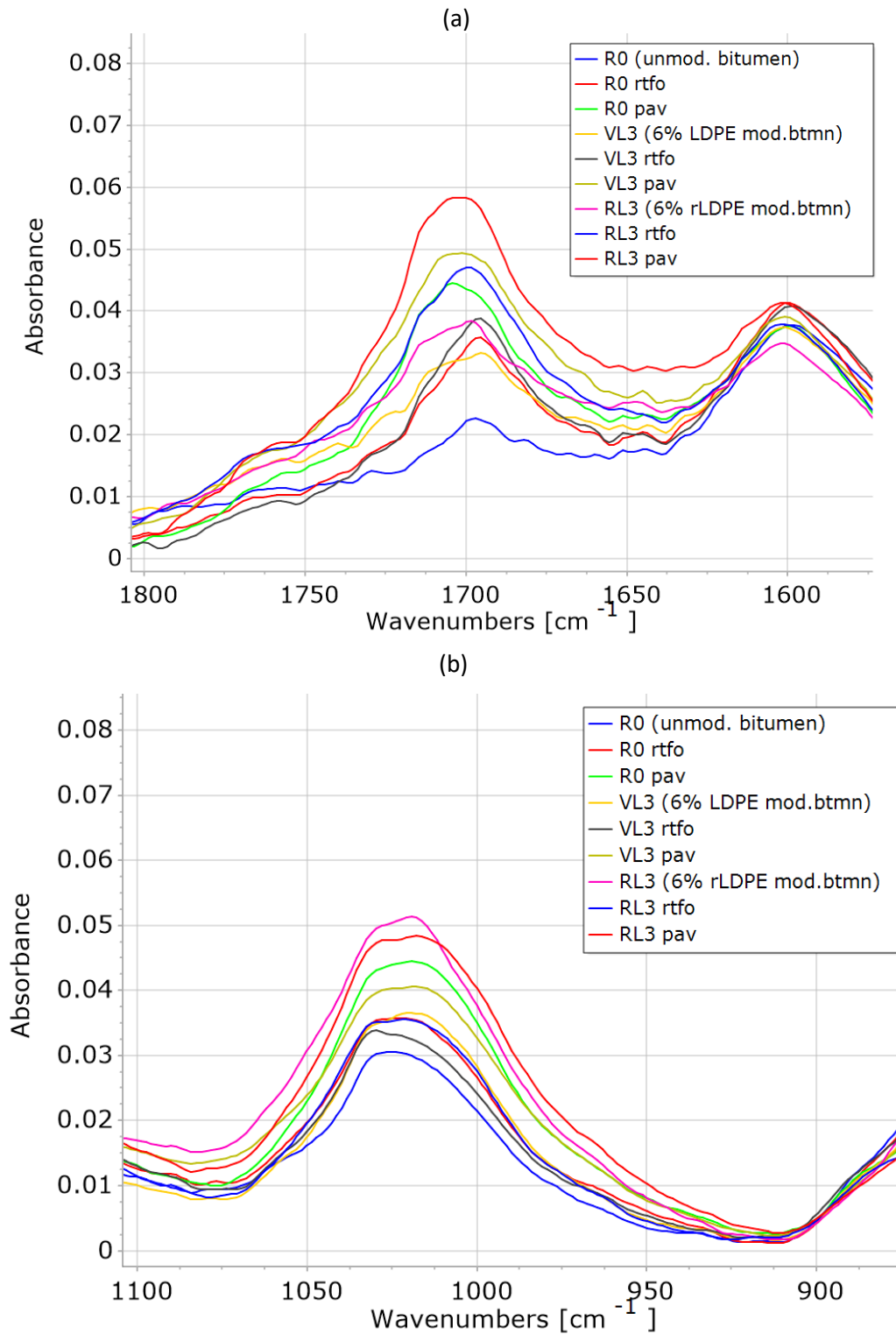


Figure 5. 28: (a) the carbonyl area, (b) the sulfoxide area of the bitumen

In addition, the consistently increasing trend of CI and SI in different aged bitumen also demonstrates the potential ability of this method to differentiate the degree of bitumen

ageing. Figure 5.29 shows the values of the bitumen's carbonyl index and sulfoxide index from unaged, RTFO, to PAV aged condition.

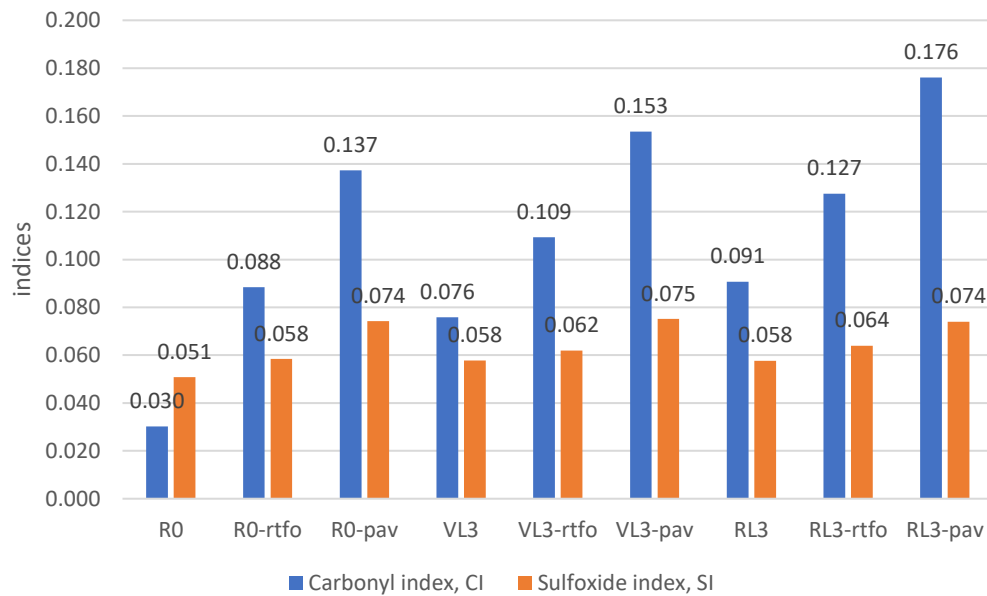


Figure 5. 29: The carbonyl and sulfoxide index of the bitumen

From the calculated CI and SI data, as shown in Figure 5.29, several conclusions can be stated as follows:

- (1) The carbonyl index (CI) and sulfoxide index (SI) are consistently increasing for all bitumen in the presence of laboratory ageing.
- (2) The CI demonstrated a more apparent and significant increase as an indication of ageing than SI. Similar trends were presented by Aguiar-Moya et al. (2017), where a PAV-aged bitumen had a 14.33 times higher carbonyl area than the neat bitumen, while the sulfoxide area had 6.3 times higher.
- (3) The LDPE modification resulted in an aged bitumen with approximately the same level of RTFO. The unaged VL3, RL3, and the R0-rtfo have CI of 0.076, 0.091, and 0.088, with a low coefficient of variation of 0.09.
- (4) Based on the CI, the rank level of ageing can be listed from the lowest to the highest aged bitumen as $R0 < VL3 < R0\text{-rtfo} < RL3 < VL3\text{-rtfo} < RL3\text{-rtfo} < VL3\text{-pav} < RL3\text{-pav}$.

5.5.2.3. The ageing implication to the rutting resistance

One of this study's aims is to compare the unmodified to the modified bitumen regarding rutting resistance. Meanwhile, aged bitumen is generally stiffer, leading to higher rutting

resistance. In this case, the CI and SI calculation becomes even more critical because the ageing phenomenon can be revealed; thus, a potentially biased understanding of the rutting resistance changes can be prevented.

Because the LDPE and rLDPE modified bitumen are basically 'slightly aged' in their neat condition (non-RTFO and non-PAV aged), the direct MSCRT results comparison to the neat bitumen can be regarded as an inaccurate result. Thus, the Jnr and %R comparison of unmodified (R0) and modified bitumen (VL3 and RL3) were completed using RTFO-aged-R0 and non-aged-VL3 and RL3.

From the comparison, the Jnr and %R of unaged VL3 and RL3 indicate a better rutting performance than the R0-rtfo. For example, the Jnr values (kPa^{-1}) of VL3 and RL3 at 60°C 100Pa are 0.61 and 0.04 compared to 1.29 of the R0-rtfo. While the %R (%) of VL3 and RL3 are 16.86 and 75.43 compared to 6.35 of the R0-rtfo at the same stress and temperature (100Pa, 60°C). These numbers clearly explain that the rutting resistance improvement of the LDPE and rLDPE-modified bitumen results from polymer modification rather than the ageing implication.

5.6. Summary

This chapter presents test results on bitumen that include dynamic mechanical analysis, MSCR (rutting), LAS (fatigue), ductilometer test (DENT), microscopy observations and ATR-FTIR tests. From these tests, some conclusions can be drawn as follows:

1. The complex modulus master curves explain the rutting resistance improvement of the modified bitumen, especially at a lower frequency or high temperature. This result proved the presence of polymer (LDPE)-dominant network within the bitumen. At higher frequencies or low temperatures, the bitumen's high viscosity disabled the polymer's effect and resulted in relatively the same property as unmodified bitumen. The higher %modification produced a higher complex modulus, and the recycled LDPE resulted in more pronounced effects on the complex modulus changes than virgin LDPE.
2. A similar trend to complex modulus is observed in phase angle master curves and the Black diagram. While the virgin LDPE-modified bitumen presented relatively slight changes, the rLDPE-modified bitumen presented significant changes in phase angles compared to unmodified bitumen. The LDPE-modified Black diagram also presents

slight changes, while the rLDPE-modified Black diagram shows noticeable differences from the unmodified bitumen.

3. The short-term aged of all bitumen (unmodified, LDPE-modified or rLDPE-modified) shows higher complex modulus and lower phase angle, depicting a stiffer behaviour or higher elastic response.
4. The MSCR test result shows that the LDPE and rLDPE modified bitumen have higher resistance to rutting, as indicated by the higher %R and lower Jnr. In addition, the higher %modification resulted in a higher rutting resistance, with the rLDPE showing a more significant increase than LDPE at the same modification rate.
5. The LAS test result shows that the modified bitumen has a higher 'A' parameter, representing higher fatigue resistance but a lower 'B' parameter, indicating a higher fatigue degradation rate. However, the modified bitumen still performs better fatigue life than the unmodified bitumen.
6. Based on the DENT test, there are indications that the modified bitumen has better fatigue resistance based on a higher load vs displacement curve and higher total work of fracture. However, the lower CTOD (critical tip opening displacement) shows higher potential cracks once an early crack has been initiated, indicating lower fatigue resistance. An asphalt mixture test on fatigue could further demonstrate the modified bitumen's fatigue behaviour.
7. Bitumen optical microscopy reveals essential information regarding the modified bitumen microstructure or polymer dispersion within the bitumen phase. The rLDPE shows an entirely different dispersion than LDPE. The higher softening point, higher complex modulus at high temperatures, and higher rutting resistance of rLDPE than LDPE are clearly due to the better interaction of rLDPE-bitumen in forming the polymer-rich phase.
8. The ATR-FTIR shows the increase in modified bitumen's carbonyl (CI) and sulfoxide (SI) indices, indicating that the ageing had occurred during the high shear mixing. The rLDPE-modified bitumen shows higher CI and SI than virgin-modified or unmodified bitumen.
9. The bitumen test results demonstrated a higher rutting resistance and relatively unclear fatigue resistance. Overall, the rLDPE-modified bitumen performs better than the LDPE-modified bitumen in improving rutting resistance and other parameters.

The microscopy work shows that the rLDPE behaves significantly differently than LDPE in interacting with the bitumen phase. A further test in bitumen-aggregate interaction (bonding strength test) and asphalt mixtures (permanent deformation and fatigue failure test) could help understand the modified bitumen behaviour in mixture application.

CHAPTER VI: LDPE MODIFIED ASPHALT MIXTURE PERFORMANCE

This chapter emphasises the LDPE-modified asphalt mixture tests results. The chapter starts with a brief description of the conducted asphalt mixture preparation, followed by the aggregate and bitumen bonding strength test. Then, the gyratory asphalt mixture compaction, stiffness test, rutting resistance test and fatigue resistance test results are presented. The finding result in this chapter is compared to the bitumen test results from the previous chapters. Based on bitumen tests in the previous stage of this study, the LDPE-modified bitumens are improving the neat bitumen performance in rutting resistance and fatigue resistance, with a consistent increase with the higher LDPE content. However, the viscosity test suggested the 2%, 4% and 6% bitumen weight are the only reasonable modification rate due to higher viscosity and low workability on higher modification rates. Since the 2% modification was relatively low in improving the bitumen performance, 4% and 6% were the percentages used in the asphalt mixtures. Five asphalt mixtures were made and tested from the bitumen R0, VL2, VL3, RL2 and RL3.

6.1. Asphalt mixture preparation characteristics

This study uses limestone aggregate from Tunstead Quarry, United Kingdom. This aggregate has an apparent particle density of 2.71 g/cm^3 , the filler has 2.78 g/cm^3 , and standard 50/70 pen grade bitumen has 1.03 g/cm^3 . The asphalt concrete (AC) with a 14mm maximum aggregate size was used in this study. The gradation table from the NTEC laboratory was used to calculate the composition of each aggregate size, resulting in the gradation that satisfies the AC mixture according to BS EN, as shown in Figure 6.1. The dark and light blue lines show the upper, lower and mid-gradation values, and the black line is the design used in this mixture. From the calculated aggregate composition (or gradation) and the particle density data, the asphalt mixture's maximum density of 2490 T/m^3 was obtained. The designed air voids of 5% resulted in the specimen's targeted density of 2366 T/m^3 . Table 6.1 shows the asphalt mixture design properties used in this study.

The gyratory compaction was used to prepare gyro specimens of five asphalt types. With 13 specimen gyros per type, a total of 65 specimens were made. The gyratory used a standard 1.25° gyration angle and 0.6 MPa compression stress. Table 6.2 shows the

number of gyratory compactions of specimens that had been done to meet the targeted density. The mean number shows that the modified bitumen of LDPE and recycled LDPE require gyratory compactions comparable to the unmodified bitumen, even though the mean value may not well-representing the actual data distribution of the number of gyrations. However, this indicates the acceptable workability of these bitumens without any noticeable compaction difficulties.

Table 6. 1: Asphalt mixture design properties

Design	Value
Binder Content (%)	5.5
Target Air Voids (%)	5
Maximum Density (kg/m ³)	2490
Target Density (kg/m ³)	2366

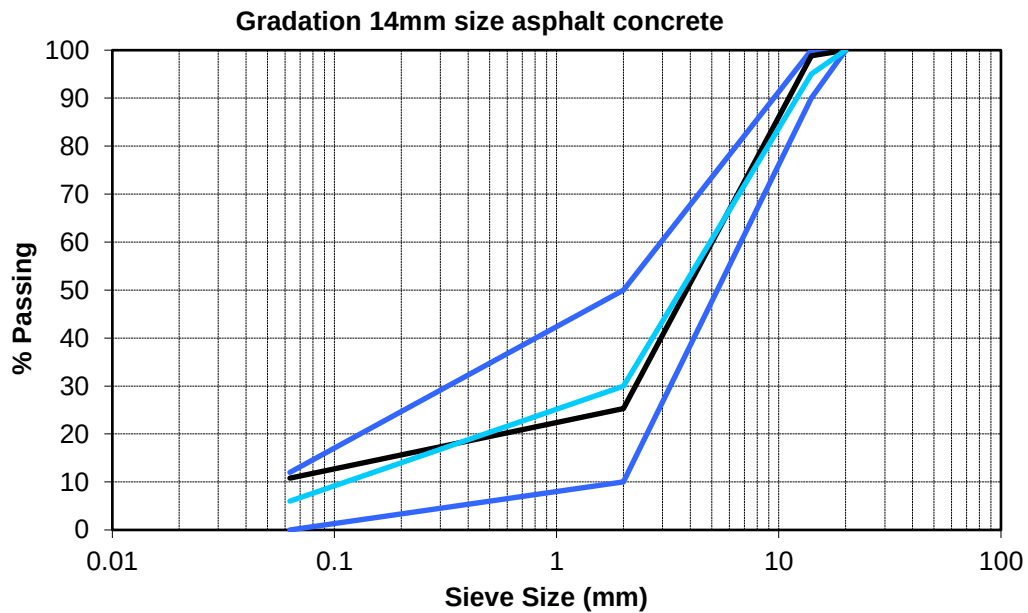


Figure 6. 1: Aggregate gradation of 14mm asphalt concrete (AC) mixtures

Table 6. 2: Gyratory numbers of specimen preparation

	R0	VL2	VL3	RL2	RL3
mean	148.9	149.9	159.3	141.8	149.0
st. dev	77.8	79.2	61.9	50.0	53.3
co. var	52%	53%	39%	35%	36%

To understand the conducted mixing and compaction, the bitumen viscosity data were plotted to the Shell Bitumen Test Data Chart for bitumen workability guidance, as shown

in Figure 6.2. According to this criteria, the ideal mixing viscosity of bitumen to have an excellent aggregate coating is between 0.2 to 0.5 Pa.s. A lower viscosity than 0.2 Pa.s will result in bitumen drainage, while a higher viscosity than 0.5 Pa.s will lead to a poor coating of aggregates. According to this criterion, the conducted mixing at 160°C for unmodified bitumen was slightly below 0.2 Pa.s, and 170°C for modified bitumen were at the ideal mixing viscosity. However, no distinct unmodified bitumen drainage was experienced. This plot explains the successful mixing of all bitumen.

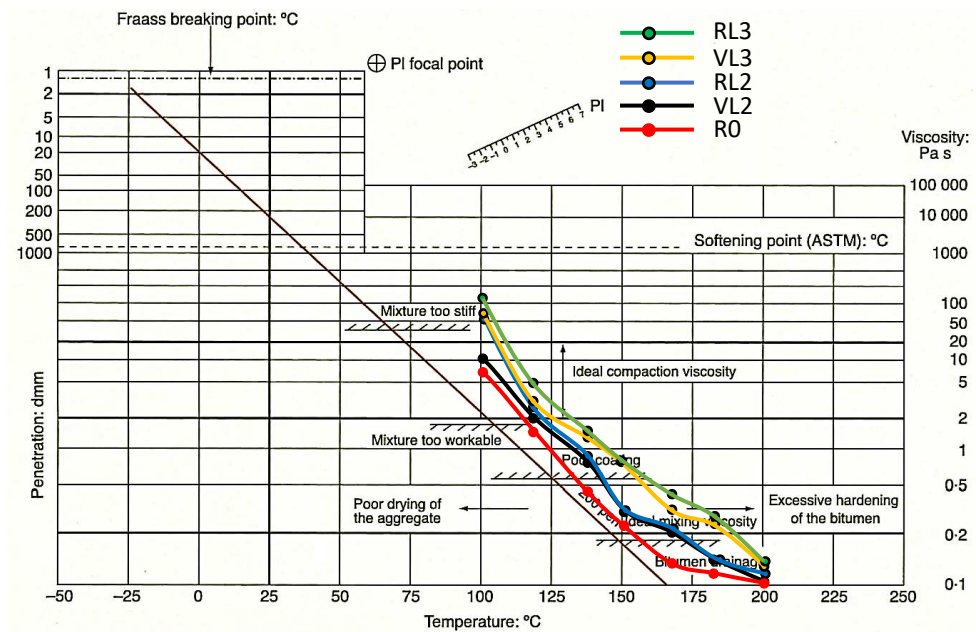


Figure 6. 2: Plots of bitumen viscosity to the Shell Bitumen Test Data chart

For mixture compaction, this guidance states the ideal bitumen viscosity to be at 2 to 20 Pa.s to prevent too stiff or too workable mixtures. The gyratory compactions were done at 120°C. According to this guidance and the data plots, all bitumens were within the ideal compaction range. Although the modified bitumen generally has higher stiffness than unmodified bitumen, the viscosity data ensures that the mixing and compaction of the bitumen remain within the ideal workability range. The combination of satisfactory-produced mixtures from 'ideal mixing viscosity', the compaction at 'ideal compaction viscosity', and the adequate compressive strength of gyratory produced satisfactory results of gyro specimens. These three factors allowed aggregates inside the mould to move, rotate, and interlock with each other in the process of gyratory compaction because of the adequate bitumen fluidity. Furthermore, during the decreasing

temperature, the modified bitumen that has an excellent adhesion slowly bonds the aggregate into a strong structure of the asphalt mixture (gyro) specimen. However, the high coefficient of variation needs to be counted into consideration. This number shows the variation of gyration numbers that imply a potential easier, or in other conditions, a more difficult compaction in actual world application.

6.2. Bitumen – aggregates mixture bonding strength

Previous chapters have elaborated that all LDPE-modified bitumens are rheologically better than unmodified bitumen. The LDPE-modified bitumen demonstrated a higher complex modulus and lower phase angles at high temperatures than neat bitumen, which was depicted in the complex modulus and phase angle master curves. This result indicates that the modified bitumen has a better rutting resistance, confirmed by the MSCR test result. The LAS and DENT tests have also demonstrated better fatigue resistance of the modified bitumen. Overall, in all studied aspects: the rutting and the fatigue resistance, the recycled LDPE-modified bitumen is superior to the virgin LDPE-modified bitumen in improving the bitumen performance.

The SI and CI calculation from FTIR analysis has answered the concern of rutting resistance inaccurate comparison. With the help of ageing indices, the %R and Jnr comparison proved that the rutting resistance improvements were the product of successful modification by the LDPEs than the ageing during the high shear mixing.

Furthermore, the microscopy work revealed the differences in the polymer-bitumen interaction and dispersion between the virgin LDPE and recycled LDPE-modified bitumen. These differences are responsible for the bitumen performance improvements. Under microscopy, the recycled LDPE showed an exceptional interaction with the bitumen by spreading and forming a polymer network, which started even with a low modification percentage. A phenomenon that was not found in the virgin LDPE-modified bitumen.

In the asphalt mixture, bitumen and aggregate bonding strength is the primary factor that affects the material's properties, including rutting and fatigue resistance. Strong adhesion with the bitumen ensures the aggregates are bound in the mixture system and produce a long-lasting asphalt mixture. On the contrary, a weak bonding of bitumen and aggregates results in premature mixture failures (Gürü et al. 2014; Haider et al. 2020; Leng, Sreeram, et al. 2018a; Santhirasegaram and Weragoda 2018). To further understand and correlate

the bitumen's to the asphalt mixture's performance, tests on bonding strength between bitumen and aggregate were carried out by rolling bottle test. This test demonstrates the affinity profile of bitumen and aggregate by differentiating the final bitumen coating on tested aggregates after being water-immersed and rolled in the testing bottle for a specific time. The rolling mechanism causes the aggregate particles to collide, resulting in the aggregate's bitumen-coating loss. The level of coating loss indicates the bonding strength between the two materials.

Two aggregate types were used in this rolling bottle test: Tunstead limestone and Mount Sorrel granite. Tunstead limestone is the aggregate used in this study's asphalt mixtures, while the Mount Sorrel granite was only used for the rolling bottle test. Mount Sorrel granite aggregates were chosen because of their infamous relatively poor properties. This aggregate performs poorly in moisture-sensitivity studies and for being susceptible to coating loss in rolling bottle tests. On the other hand, limestone aggregates are generally regarded to perform better in moisture-sensitivity properties not only in experiments but also in practices (J. Grenfell et al. 2014).

Three bitumen types were used in this test: the unmodified R0, the 6% LDPE-modified bitumen (VL3) and 6% recycled LDPE-modified bitumen (RL3). The test was started by preparing clean, washed and oven-dried 510 ± 2 grams of 6.3 mm to 10 mm aggregates. Then, the aggregates were mixed with 17.0 ± 0.2 grams of bitumen. Finally, the finished mixtures were spread or individually separated before testing on the rolling bottle the next day. The detailed testing procedure is described in Chapter 3.

A total of six mixture combinations from three bitumen and two aggregates were run in this test. BS EN 12697-11 guided three repetitions for each tested bitumen; thus, 18 testing bottles were needed for this test. The average calculation of the observations is presented in Table 6.3.

Table 6. 3: Rolling bottle test result

Test hours	Aggregates' bitumen coverage (%)					
	Tunstead limestone			Mount Sorrel granite		
	R0	VL3	RL3	R0	VL3	RL3
0	100	100	100	100	100	100
6	95	95	95	85	95	97
24	92	88	90	57	77	83
48	85	78	82	30	47	57
72	60	68	75	12	23	28

At the beginning of the test, all aggregates are fully coated and have 100% bitumen coverage. After 6 hours of rolling, the bitumen coverage started to faint and was recorded to have approximately a 5% loss. At this stage, the coverage losses were relatively low except for the case of R0 and Mount Sorrel granite, with a 15% loss. A noticeable coverage loss was started after 24 hours of running tests, with the granite's coverage loss being 20 to 40%, while the Tunstead limestones had approximately 10%. At this point, the differences between the limestone and granite's nature in bonding with bitumen started to be seen. Also, the differences between the R0, VL3 and RL3 were easily observed, especially in the case of granite.

Granites that were expected to have a poorer adhesion with bitumen helped show the bitumen's performance differences starting at 24 hours of the test. At this hour, RL3 were performing the best in coating coverage (83%), followed by VL3 (77%) and R0 (57%). The adhesion trend of modified bitumen on granites continued for 48 and 72 hours of the test, where the modified bitumen RL3 was superior to VL3 and R0 in bitumen coverage. The final 72 hours test resulted in 12% coverage of R0, 23% of VL3 and 28% of RL3 on granite bitumen. Figure 6.3 shows the graphical representation of the results.

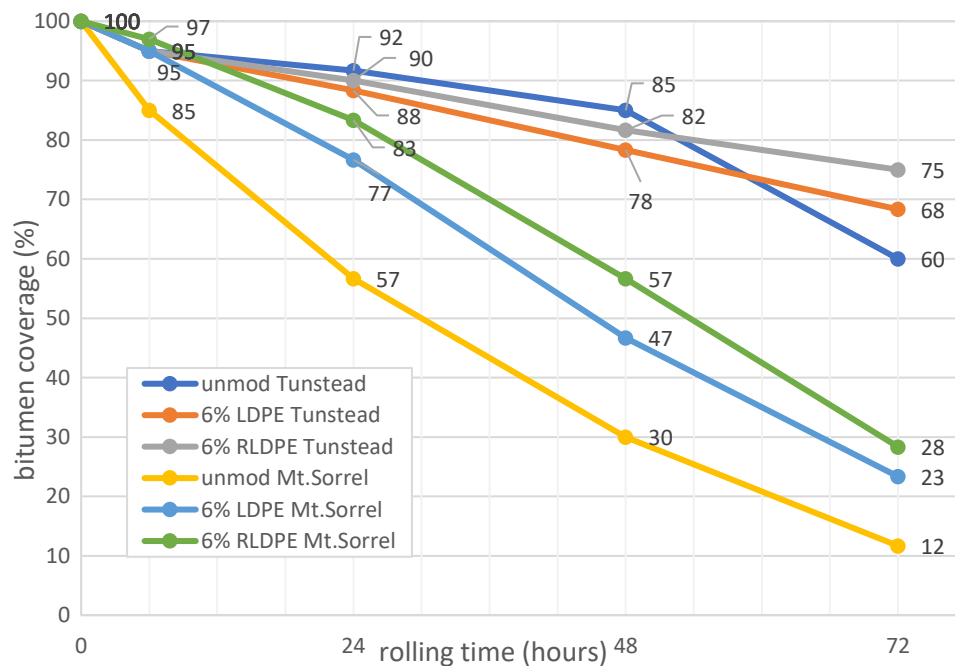


Figure 6. 3: Bitumen coverage (%) from the rolling bottle test

Compared to Mount Sorrel granite, Tunstead limestone had a better adhesion to bitumen. At 24 hours, the R0, VL3 and RL3 showed relatively the same bitumen coverage (92, 88 and 90%, respectively). After 48 hours, the test showed slightly different results, with the R0 having the higher coverage at 85%, followed by RL3 (82%) and VL3 (78%). The final testing at 72 hours resulted in a noticeable difference with 60% for R0, 68% for VL3 and 75% for RL3. At this point, the RL3 had shown its superiority over other bitumen. This trend was the same compared to the granite aggregates where RL3 is the best, and unmodified bitumen R0 showed the worst in terms of bitumen adhesion to aggregates. Figure 6.4 depicts the 72 hours rolling bottle test results.



Figure 6. 4: Results of 72 hours rolling bottle test

6.2.1. The effect of aggregate types

The variations in the bitumen and aggregate bonding test result can be addressed to the physical characteristics of the aggregate, such as surface roughness and porosity, and the nature of the aggregate as either hydrophobic (repulse water) or hydrophilic (attract water). These factors can affect the bonding strength between the adhesive layer of bitumen and the aggregate (JAKARNI 2012).

A higher surface roughness means a greater surface area, providing a more significant bond area with the bitumen and allowing better interlocking of bitumen and aggregates (Bhasin 2006). However, no surface roughness test was conducted in this study to provide further insight into observation.

The better adhesion of limestones to bitumen could also be attributed to the lower porosity of the aggregate compared to granites. Because even though a higher porosity could lead to a higher bitumen absorption, this could also attract moisture to the aggregates that induce bitumen stripping. A lower porosity prevents the aggregate and bitumen bond from being destructed by moisture during the rolling bottle test, resulting in a lower bitumen coverage loss. Similar results were presented by (J. Grenfell et al. 2014), where a higher aggregate porosity (granite) had a higher bitumen coverage loss compared to a lower aggregate porosity (limestone).

The hydrophilic or hydrophobic nature of the aggregates also plays a role in affecting adhesion to bitumen. As granite material, the Mount Sorrel aggregates are likely to be hydrophilic in nature, leading to an easier strip in bitumen coverage compared to hydrophobic Tunstead limestones. This condition is because the hydrophilic aggregates tend to better in attracting moisture than bitumen; at the same time, the common notion of bitumen as hydrophobic repels the moisturised aggregates.

These results have justified previous studies that stated granite materials commonly have lower moisture resistance than limestone. Typically, granites have a substantial fraction of certain minerals, i.e., quartz and feldspar, that affect moisture-related properties. Due to the poor adhesion between these minerals and bitumen leads to a detrimental moisture property, including interfacial failure between bitumen and aggregate (J. R. A. Grenfell et al. 2014).

6.2.2. The effect of modified bitumen

According to (Rand 2002), as opposed to the bitumen's properties, the aggregates' properties significantly influenced either the adhesive or cohesive failures. Additionally, the impact of bitumen types is essentially negligible for hydrophobic aggregates such as limestone and basalt. However, the final rolling bottle test result of Tunstead limestones with LDPE-modified bitumen had proven otherwise. VL3 and RL3 considerably affect the bitumen and aggregate adhesion by performing a better final bitumen coverage than

unmodified bitumen R0. This improvement has been proven further with the same trend on two aggregates: limestones and granites. Meanwhile, R0 has noticeably the lowest bonding strength on both aggregates.

The adhesion improvement might be caused by the presence of LDPE polymer networks that increase the material integrity of the modified bitumen film. This stronger bitumen film causes difficulties for the moisture to diffuse and soften the bitumen. The damage caused by the bitumen's softening effect due to water diffusion is commonly known as cohesive failures. This effect is driven by the loss of cohesive strength within the bitumen caused by its interaction with water. In this scenario, the water interaction causes the bitumen particles to separate each other due to spontaneous emulsification (Fromm, 1974) that ultimately leads to adhesive failure with aggregates. In other words, the LDPE and recycled LDPE modification prevent the cohesive failure that could lead to bitumen stripping.

Similarly, another factor could be referred to as the stronger modified bitumen phase provided by the LDPE polymer network. This network strengthens the bitumen and prevents moisture intrusion into the bitumen-aggregate bonding surfaces. The moisture intrusion could occur through the bitumen film destruction, which could lead to adhesion failure or stripping (Kiggundu and Roberts, 1988; Taylor and Khosla, 1983; Terrel and Al-Swailmi, 1994). This presumption is in line with the general adhesion improvement of a stiffer bitumen (JAKARNI 2012).

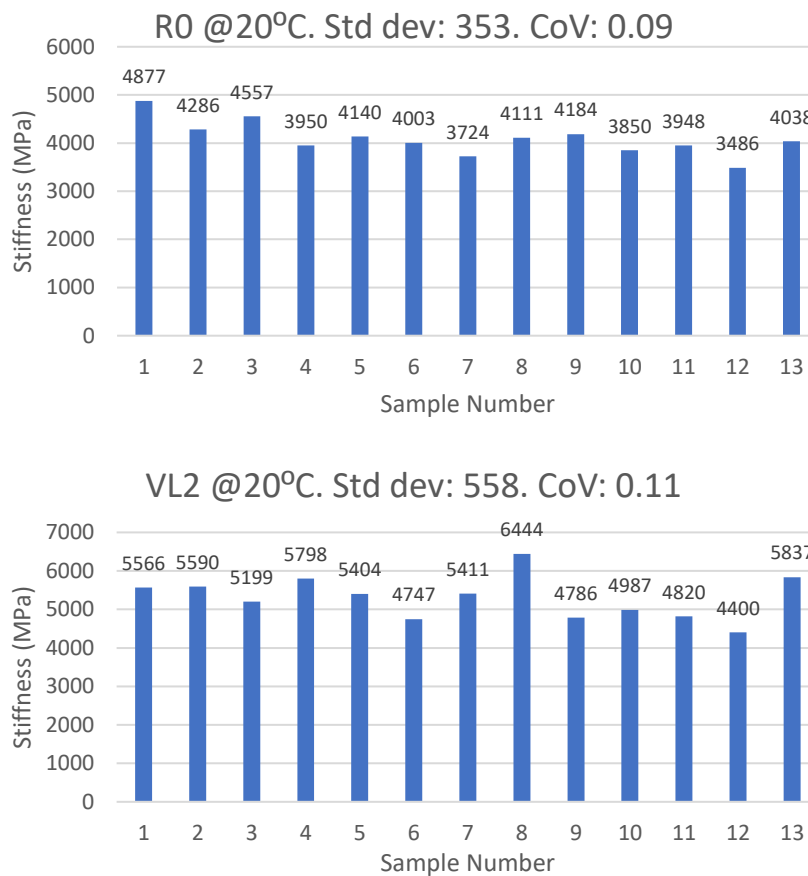
The rolling bottle test results showed the improvement of bitumen adhesion or bonding capability to aggregates, confirmed on two different aggregates: limestone and granite. The increased adhesion is believed to significantly improve the asphalt mixture properties in rutting and fatigue resistance.

6.3. Asphalt mixture stiffness

The asphalt mixture stiffness modulus was observed through the Indirect Tensile Stiffness Modulus (ITSM) test. The test was conducted on the mixture specimen from unmodified bitumen R0, 4% and 6% LDPE modified bitumen (VL2 and VL3), and recycled LDPE modified bitumen of 4% (RL2) and 6% (RL3). The test temperature was 20°C, with each sample's result data representing the average of 13 gyro specimens. ITSM is non-

destructive testing, and after this test, the specimens were used in the permanent deformation or rutting resistance, RLAT, and fatigue resistance, ITFT.

Figure 6.5 shows the stiffness of each asphalt mixture type. It can be seen from the graphics that each bitumen resulted in good repeatability, with the maximum coefficient of variations being 0.11 in the case of VL2. The lowest coefficient of variation is on RL2 and RL3, with 0.04, while VL3 and R0 are at 0.07 and 0.09. The stiffness modulus is one of the easy parameters to indicate the asphalt mixture's ability to distribute loads within its structure. The close result within the specimens reflects that the hand mixing procedure was reliable in producing a consistent 13 mixtures from separated mixes. The hand mixing method is also reliable for unmodified, LDPE, and rLDPE-modified bitumen. Also, the result indicates that the modified bitumen itself is considerably homogenous. This homogenous bitumen allows a consistent 13 mixture results even though they were separately prepared.



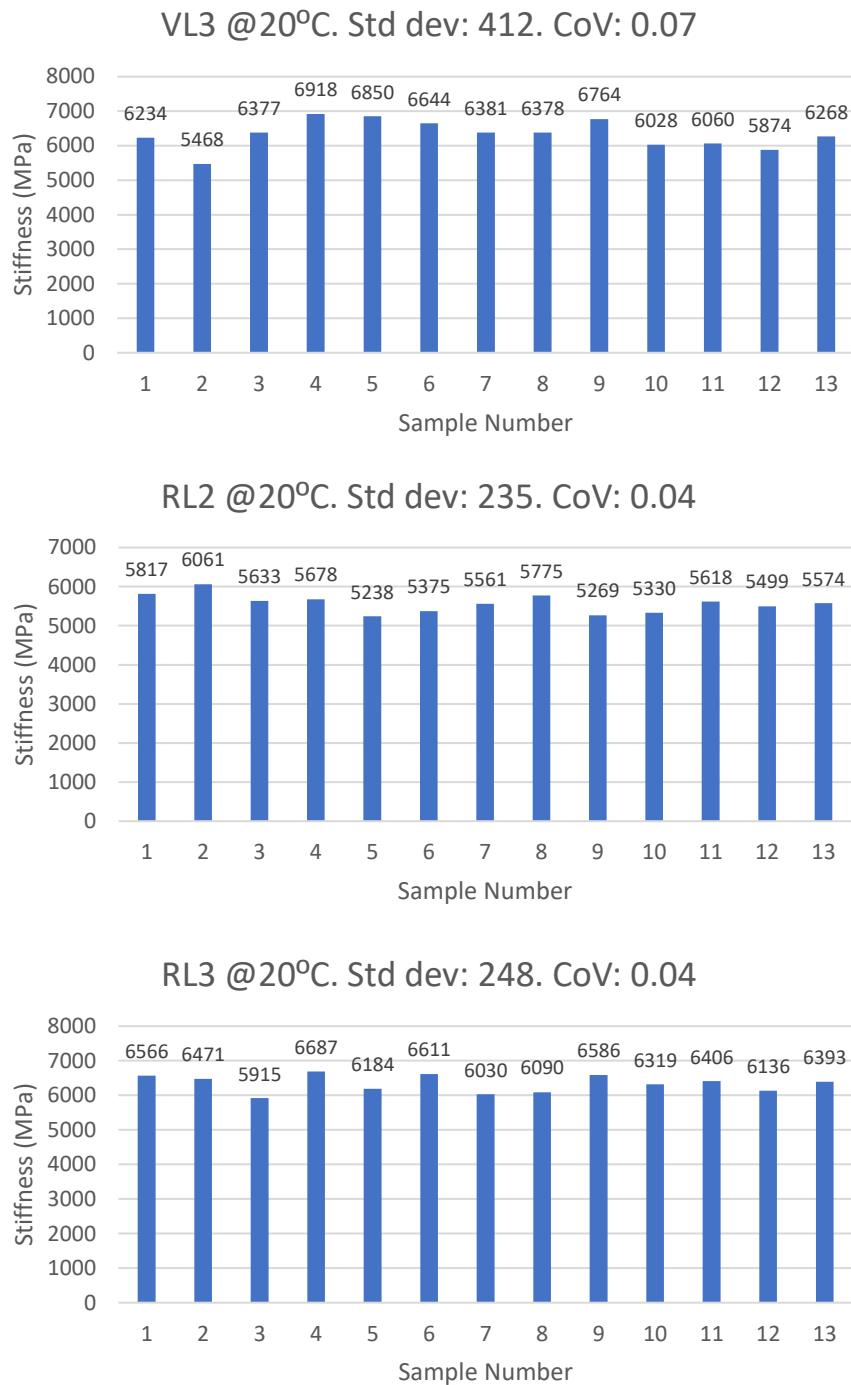


Figure 6. 5: Stiffness test results at 20°C

The average stiffness of all mixtures is presented in Figure 6.6. This figure clearly shows that the LDPE-modified bitumen is increasing the mixture stiffness or stiffness modulus. This study mainly focuses on rutting and fatigue pavement distresses. The increasing stiffness modulus indicates the better ability of the asphalt mixture to spread the load,

resulting in more resistance to distress. In the case of rutting and fatigue, better stiffness may contribute to the better ability of the mixture to prevent these damages.

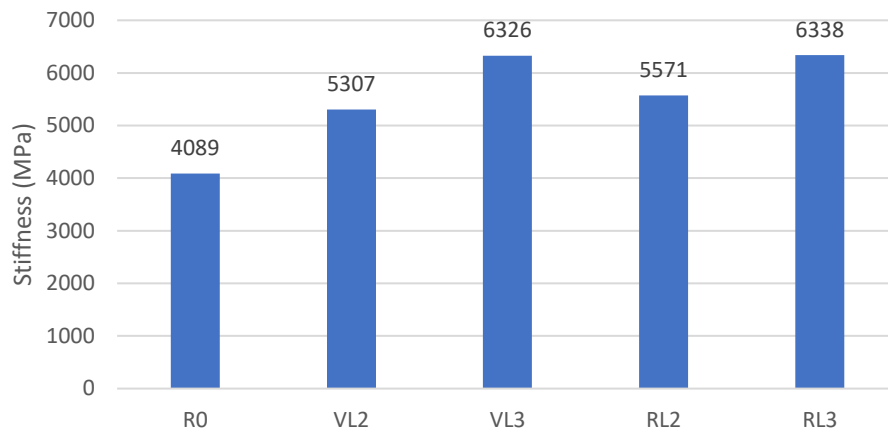


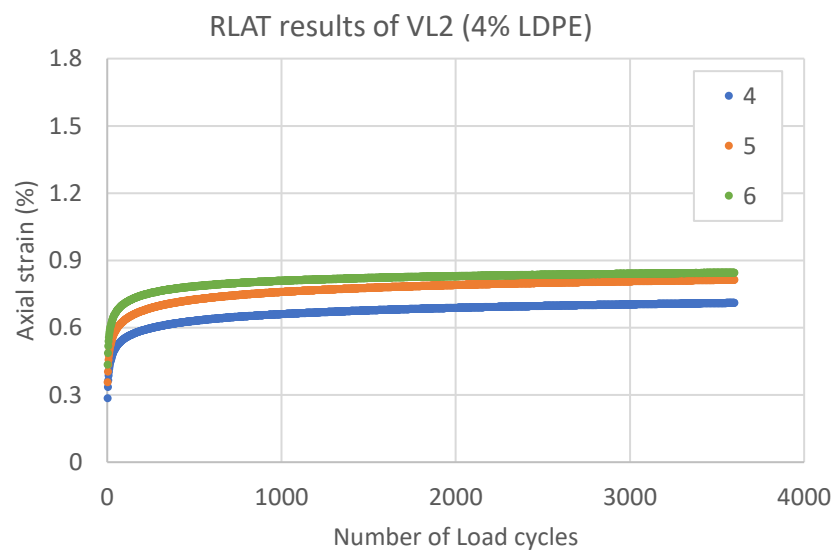
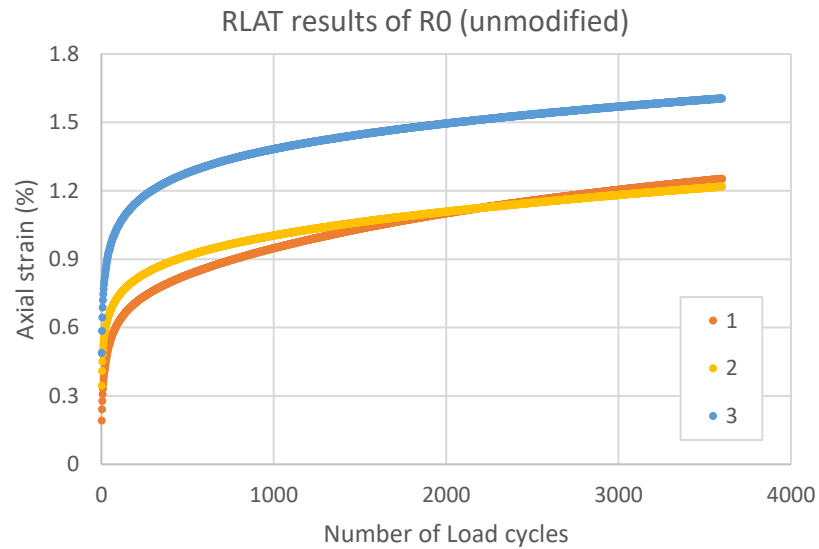
Figure 6. 6: Average stiffness test results at 20°C

6.4. Asphalt mixture rutting resistance

The repeated load axial test (RLAT) was used to observe the asphalt mixture's permanent deformation or rutting resistance. The repeated loads in RLAT accumulate the axial strain representing the mixtures' susceptibility to rutting. The RLAT graphical plot is commonly presented in the cumulative axial strain of the test specimen (%) as a function of the loading cycle number. This graphical plot, i.e., creeps curve, generally can be categorised into three stages of deformation prior to material failure. The first stage is the initial part of the creep curve. In this stage, the strain increases rapidly due to material densification and the adjustment of loading platens (Subhy 2017). This phenomenon can be recognised as a steep rising of the curve. At the end of this stage, the slope of the curve decreases with the increasing number of loading cycles. Stage 2 is the middle part of the creep curve. This stage starts when the slope of the curve shows a constant rate, commonly expressed by the creep rate, f_c . In this stage, the axial strain increases approximately at the same rate as the number of cycles. Stage 3 is the last part of the creep curve, where the slope increases with the increasing number of loading cycles, indicating the failure of the specimen. Depending on the testing conditions and the mixture properties, one or more of these stages may present or absent in the RLAT result.

Regarding the creep curve stages, none of the tested mixtures reached the third stage of the creep curve. Figures 6.7 and 6.8 show that only two stages were visualised. The

mixtures' stiffness and the 40°C testing temperature may have contributed to this result. With mixtures' stiffness property, a test at a higher temperature than 40°C might have resulted in a more apparent three stages of creep curve, as rutting susceptibility is higher at a higher temperature.



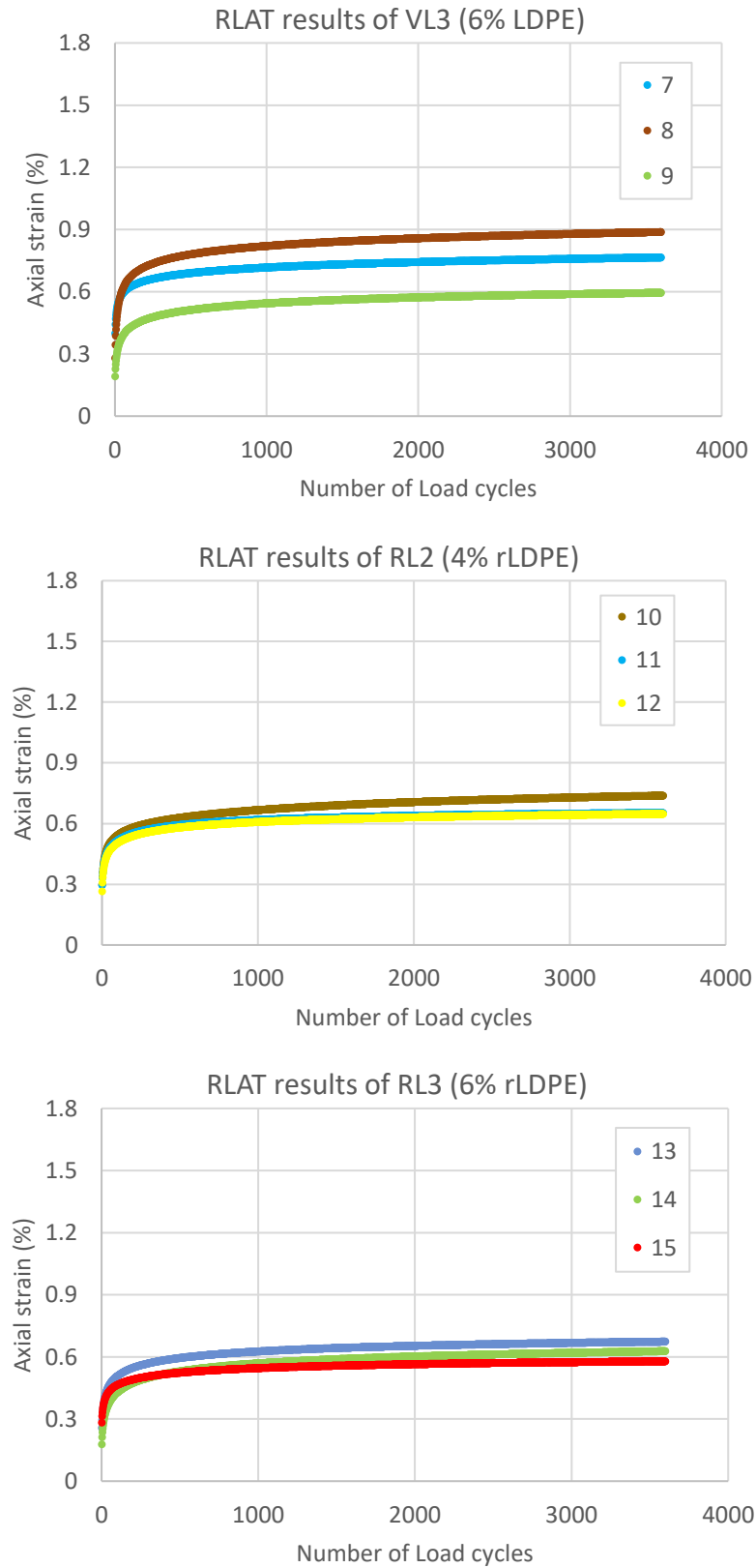


Figure 6. 7: The RLAT results of mixtures

The RLAT was conducted at 40°C on unmodified mixtures, 4% and 6% of LDPE and recycled LDPE-modified bitumen (R0, VL2, VL3, RL2 and RL3). Figure 6.7 shows the RLAT results of the mixtures. Repetition was made by testing three mixture specimens per bitumen type. Sample numbers 1 to 3 are the unmodified bitumen, 4 to 6 for VL2, and so on with the serial sample number, as seen in the figure. This axial strain vs the number of cycles plots shows that good repeatability of the RLAT result can be visually seen, especially for the modified bitumen. However, a slight variance can be seen on the unmodified bitumen and the VL3. The simplified RLAT result trend from the axial strain data's average was calculated and presented in Figure 6.8.

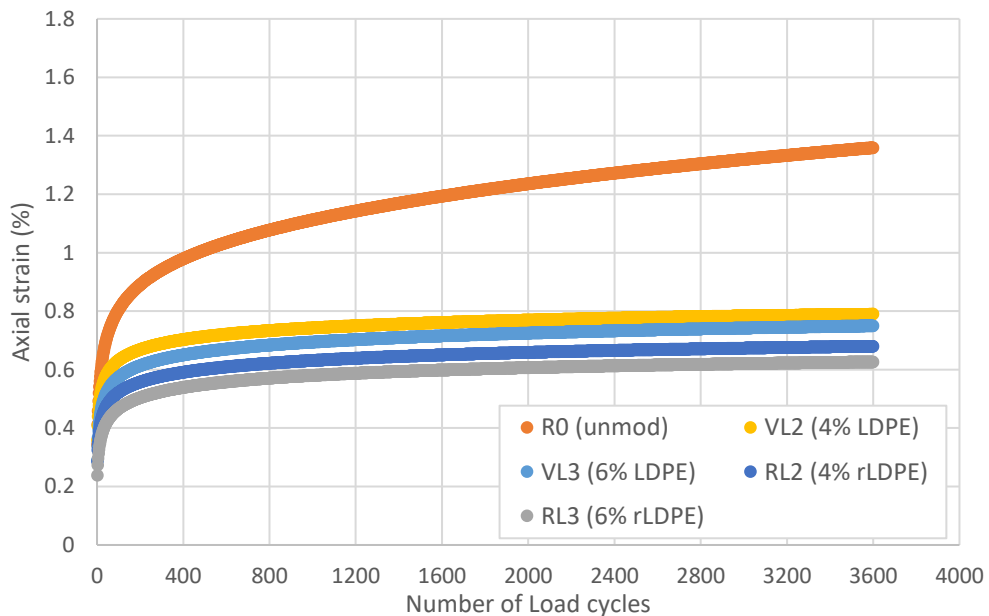


Figure 6. 8: Comparison of RLAT result of all mixtures

To classify the rutting resistance on RLAT, it is suggested the threshold of rutting susceptibility to 2% of axial strain after 3600 applications of 100kPa load at 40°C testing (Widyatmoko 2008). In other words, the sample mixture with a cumulative axial strain less than 2% is more resistant, while over 2% means the mixture has poor resistance to rutting. Meanwhile, BS EN stated that the axial strain should not exceed 4%, where the specimen should have been demolished at this strain level. As seen in Figure 6.8, none of the test's mixtures resulted in more than 2% axial strain. The relatively low axial strain was recorded with the maximum strain value of 1.7% in the case of the unmodified mixture. However, the different axial strain value between mixtures clearly states the

improvement made by the modified bitumen. Under the same repeated axial loads, the unmodified mixtures have the highest axial strain. This result represents the lower resistance to rutting compared to the LDPE-modified mixtures. The trend indicates that the higher modification rate resulted in higher rutting resistance. Among the tested mixtures, the recycled LDPE is predominant regardless of the modification rate. The RL2 (4% rLDPE) has higher rutting resistance even compared to 6% of LDPE (VL3). This result is in line with the bitumen's MSCR test that concluded the same trend, as seen in Figure 6.9. Jnr or non-recoverable creep compliance as a permanent deformation susceptibility indicator has decreased value in the presence of an LDPE modifier. Among the modified bitumen, the rLDPE has shown superior improvements in this regard.

As shown in the Figure 6.9, 4% rLDPE modified bitumen has Jnr of 0.18 kPa-1 at 3.2kPa stress level, which is better than 4% or 6% LDPE modified bitumen at 100Pa or 3.2kPa stress level. In line with the Jnr, the recovery percentage (%R) shows better rutting resistance performance in the case of LDPE-modified bitumen compared to unmodified bitumen. Among the modified bitumen, the recycled LDPE modified has shown the superiority of all, including the LDPE modified bitumen. 4% rLDPE modified bitumen (RL2) have R=68.37% (100Pa) and 45.34% (3.2kPa), which are better than LDPE modified bitumen that has 16.2% (100Pa) and 5.17% (3.2kPa) at the same modification rate. RL2 also has a better %R than 6% LDPE-modified bitumen.

The same trend for bitumen and the applied mixtures explains that the bitumen's high-performance recovery property is prominent in improving the mixtures' rutting resistance performance.

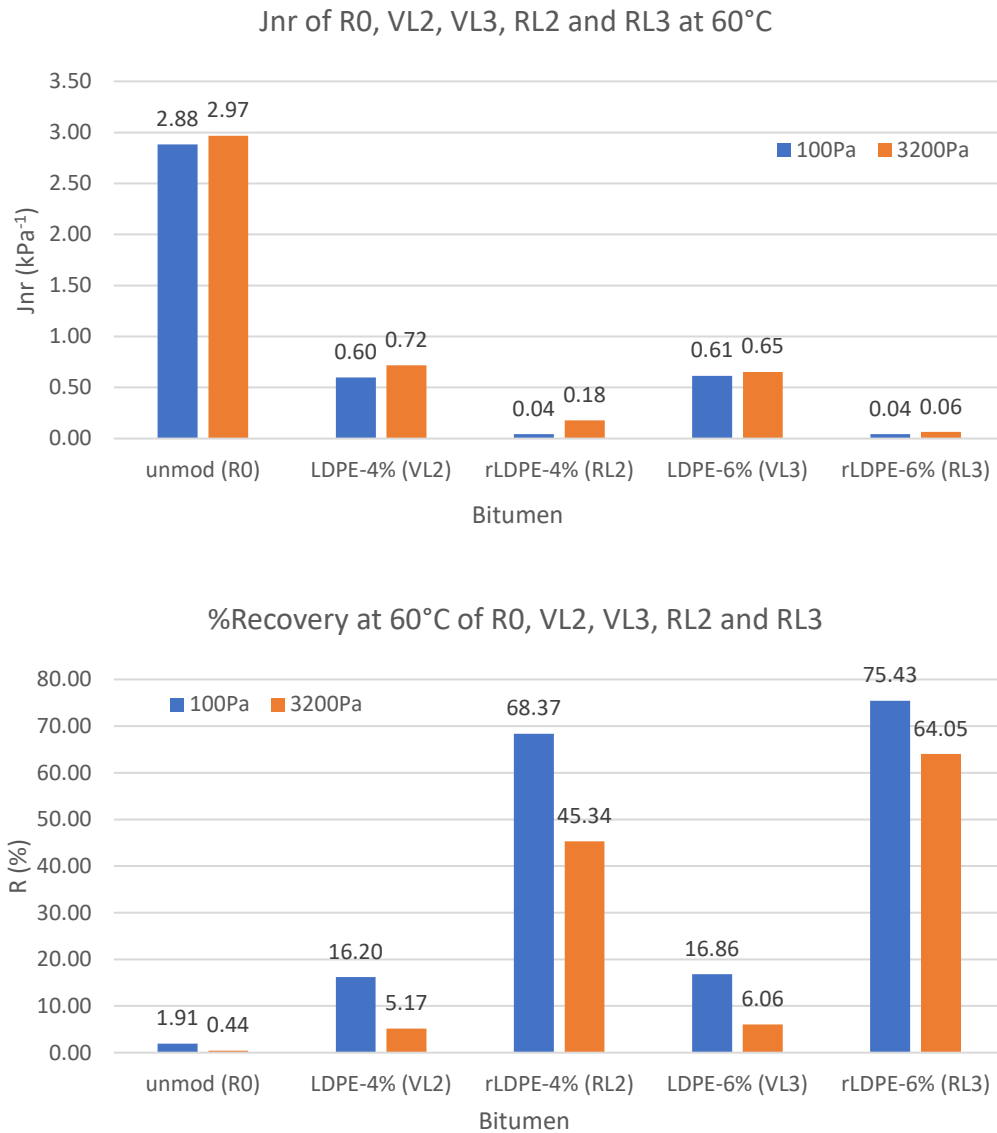


Figure 6. 9: Jnr and %R of R0, VL2, VL3, RL2 and RL3 at 60°C

The RLAT's slope of the steady state phase (second stage) has been used to distinguish the better-performing mixtures between unmodified, LDPE-modified, and rLDPE-modified bitumen. The load cycle segments between 1500 and 2500 in the second phase creep curve were selected to calculate the minimum strain rate as follows:

Table 6. 4: Minimum strain rate and total strain of mixtures

	R0	VL2	VL3	RL2	RL3
$\mu\epsilon$ at 1500 cycles	2951	1894	1778	1617	1488
$\mu\epsilon$ at 2000 cycles	3087	1921	1810	1645	1514
$\mu\epsilon/\text{cycle}$	0.27	0.05	0.06	0.06	0.05
Total strain (%)	1.36	0.79	0.75	0.68	0.63

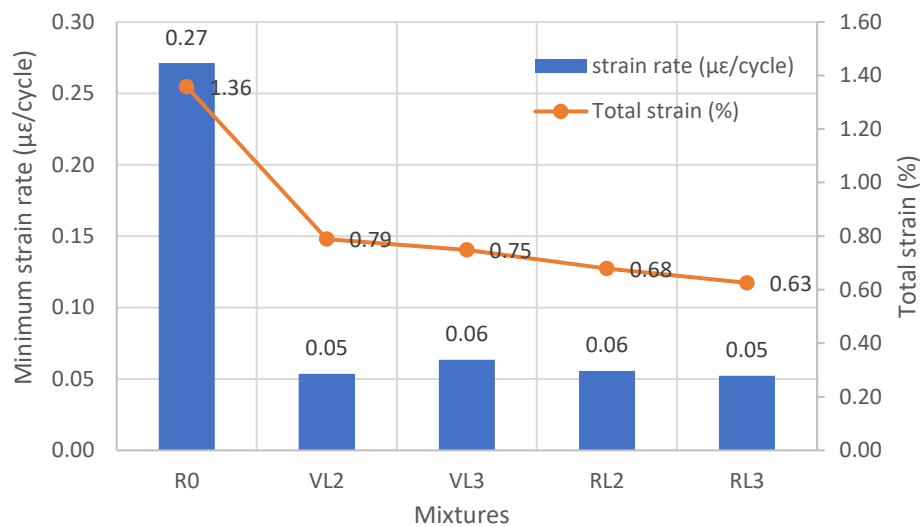


Figure 6. 10: Minimum strain rate and total strain from RLAT result

Table 6.4 and Figure 6.10 exhibit the minimum strain rate (micro strain per cycle) and the tested mixtures' total strain (%). At the steady state phase in the secondary stage of the creep curve, the minimum strain rate explains the lowest strain rate of the mixture due to the repeated axial load. The unmodified bitumen clearly shows a considerable strain that exceeds 0.25 microstrain per 100kPa axial block load cycle of the RLAT. At this stage, compared to the unmodified, the LDPE and rLDPE modified mixtures show noticeable improvement in the ability to withstand rutting per load cycle. Insignificant differences in strain rate were observed among the modified bitumen with approximately 0.05 micro strain per load cycle. Consequently, the total axial strain representing the rutting shows its superiority compared to the unmodified mixture. RL3 shows the highest resistance to rutting with a total strain of 0.63%, followed by RL2, VL3, VL2 and R0 with 0.68%, 0.75%, 0.79%, and 1.36%, respectively.

6.5. Asphalt mixture fatigue resistance

The Indirect Tensile Fatigue Test (ITFT) were used in the fatigue resistance analysis of the asphalt mixture. The test was conducted at 20°C on R0, VL2, VL3, RL2 and RL3 mixtures, with 8 specimens per asphalt mixture type. Figure 6.11 shows the ITFT results of the mixtures. The fatigue lines in this figure are plotted on the number of cycles against (micro) strain $\mu\epsilon$, as this representation is recommended and more reliable for asphalt mixture fatigue analysis (Subhy 2017). Lines in Figure 6.11 demonstrate the relatively similar values of the number of cycles versus strain data between the five tested mixtures. The densely packed and overlapping data make it difficult to interpret; thus, it can be interpreted that all the tested mixtures have relatively insignificant differences in fatigue behaviour.

To distinguish the results and have a better quantitative qualification, Table 6.5 shows the fatigue parameter data of the tested mixtures. Brown and Needham (2000) stated that flexible pavements are possibly to experience strain below 200 $\mu\epsilon$, while BS EN 12697-24 (2018) suggested the analysis of strain ranged from 70 to 400 $\mu\epsilon$. The table shows that among the mixtures, the unmodified R0 has the lowest number of cycles to suffer 100 $\mu\epsilon$ in the specimen. This value explains that the unmodified mixture R0 is the first mixture to quickly reach 100 $\mu\epsilon$ among the others. This condition can be understood because the higher mixture stiffness is one of the effects of LDPE and rLDPE modifications. Therefore, the unmodified mixture is naturally the least stiff and vulnerable to strain upon the same loads compared to the modified mixtures. However, it is worth noting that, as can be seen in Figure 6.11, the 100 micro strain lays outside several mixtures' fatigue lines and the R^2 might affect the actual value.

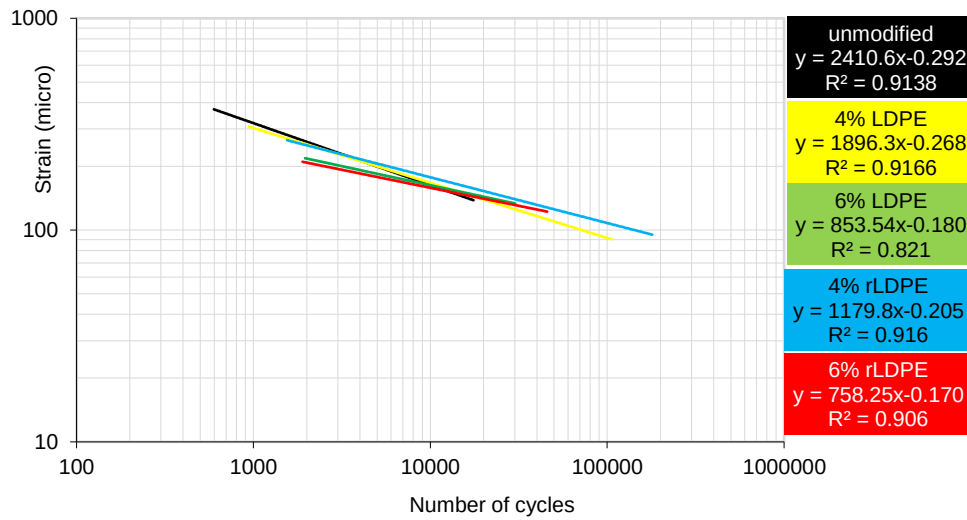


Figure 6. 11: Fatigue lines of mixtures

At slightly higher strain, i.e. 150 micro strain (N_f at $150\mu\epsilon$) as shown in Table 6.5, all mixtures demonstrated relatively the same fatigue failure performance. At $150\mu\epsilon$, all mixtures have N_f at approximately 13000-15000 cycles, with the exception of 4% rLDPE (RL2), with slightly higher value at 21833 cycles. Figure 6.12 depicts the graphical presentation of N_f at $150\mu\epsilon$.

Table 6. 5: Fatigue parameter data

	N_f at $100\mu\epsilon$	N_f at $150\mu\epsilon$	$\mu\epsilon$ at $10^6 N_f$	Fatigue Equation & coefficient of determination (R^2)	
Unmodified (R0)	54113	13497	42.67	$N_f = 7.10^{10} \cdot \epsilon^{-3.125}$	$R^2 = 0.91$
4% LDPE (VL2)	58656	12920	46.76	$N_f = 3.10^{11} \cdot \epsilon^{-3.425}$	$R^2 = 0.92$
6% LDPE (VL3)	149096	15674	70.99	$N_f = 1.10^{14} \cdot \epsilon^{-4.564}$	$R^2 = 0.82$
4% rLDPE (RL2)	142679	21833	65.67	$N_f = 6.10^{13} \cdot \epsilon^{-4.362}$	$R^2 = 0.94$
6% rLDPE (RL3)	149750	13789	72.41	$N_f = 5.10^{15} \cdot \epsilon^{-5.326}$	$R^2 = 0.91$

By comparing the material's stiffness, as shown in Figure 6.6, the higher stiffness of the group of VL2, VL3, RL2 and RL3 compared to R0 might affect the the fatigue resistance performance of the mixtures. Firstly, the higher stiffness of those groups of mixtures prevents initial strain. The lower initial strain leads to a lower chance of crack initiation and propagation, resulting in a lower potential for macro cracks. This condition can be translated as potentially a better fatigue properties of the material. Secondly, the stiffness prevents initial deformation, leading to better rutting and fatigue resistance. According to Moreno-Navarro and Rubio-Gómez (2016), permanent deformation accumulation can

make the pavement more vulnerable to cracking. This results from the strain hardening phenomenon, which transforms materials' viscoelastic properties into more rigid and brittle behaviour. In contrast, the LDPE and rLDPE-modified mixtures have better permanent deformation resistance than the unmodified mixtures. This condition means the modified mixtures are less vulnerable to cracking, leading to a potentially higher resistance to fatigue failure. However, the micro strain at one million cycles ($\mu\epsilon$ at 10^6 Nf) has demonstrated otherwise. The higher modification and thus, stiffness, has resulted in slightly higher $\mu\epsilon$ compared to unmodified mixture.

From these results, it can be concluded that the presence of LDPE and rLDPE have insignificantly affecting or improving the mixtures' fatigue resistance. Although the stiffness test has demonstrated the consistency of improvement in line with the modification, this relatively unaffected the fatigue resistance performance.

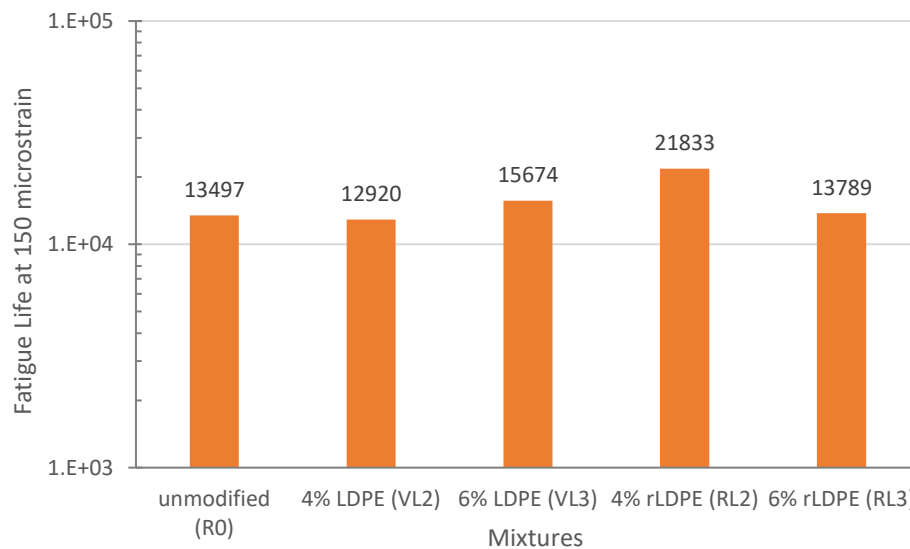


Figure 6. 12: Fatigue lives of the mixtures at 150 $\mu\epsilon$

6.6. Summary

This chapter has presented bitumen-aggregate bonding strength and asphalt mixture tests on stiffness, permanent deformation and fatigue failure. Several conclusions can be drawn as follows:

1. The lower coating loss of modified bitumen than unmodified bitumen from the rolling bottle test clearly demonstrated a better adhesion to aggregate than unmodified bitumen, regardless of the aggregate type. The rLDPE-modified bitumen performs the

best, followed by LDPE-modified and unmodified bitumen. This result is because the modified bitumen has better physical integrity and higher moisture resistance than unmodified bitumen due to the polymer network that strengthens the bitumen. This better adhesion promotes better rutting and fatigue resistance of the mixtures.

2. The modified mixtures demonstrate a higher stiffness modulus than the unmodified mixture. The higher %modification resulted in a higher stiffness of the mixtures. Overall, the rLDPE shows higher stiffness than LDPE-modified mixtures. This result is similar to the bitumen's behaviour. The average stiffness rank from lower to highest is: $R0 < VL2 < RL2 < VL3 < RL3$. The stiffness modulus between LDPE and rLDPE at the same modification rate is slightly different.
3. Similar to bitumen performance, the rLDPE and LDPE modified mixtures perform better in rutting resistance (permanent deformation test of RLAT) and better fatigue resistance (ITFT).
4. From the RLAT permanent deformation test, both LDPE and rLDPE modified mixtures clearly demonstrate the better ability to withstand rutting per load cycle than unmodified mixtures. The RL3 (6% rLDPE) shows the highest resistance to rutting, followed by RL2, VL3, VL2 and R0.
5. From the ITFT fatigue test, the mixtures' fatigue lives show relatively the same result between the unmodified and modified mixtures. This indicates that the LDPE and rLDPE modification have insignificant affect to fatigue resistance performance.

CHAPTER VII: CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

The use of polyethylene as a bitumen modifier has been widely studied with commonly known improvements in rutting resistance. The polyethylene family has main members of low-density polyethylene (LDPE) and high-density polyethylene (HDPE), with some other classifications mentioning linear-low-density polyethylene (LLDPE) and medium-density polyethylene (MDPE) that have physical attribute between the main two. This study aims to understand the behaviour of low-density polyethylene (LDPE)-modified bitumen and its use in asphalt mixtures, emphasising two main asphalt deteriorations: rutting and fatigue. Furthermore, since there are two main groups of LDPEs: the purely made (virgin) LDPE and the recycled LDPE from various packaging products, this study also differentiates the two materials as bitumen modifiers.

Laboratory-based experimental works were done, starting by preparing the modified bitumen and conducting standardised tests on bitumen and asphalt mixtures. Some main tests include standard bitumen tests, dynamic shear rheometer tests, optical microscopy analysis, ductile-meter tests, rolling bottles and asphalt mixtures tests on Nottingham Asphalt Tester.

The bitumen test results indicate the rutting resistance improvement as expected on both virgin LDPE and recycled LDPE-modified bitumen. The improvements were indicated by low-strain DMA tests and high-strain and high-temperature MSCR tests. The bitumen LAS test also revealed the fatigue resistance improvement with the modification. In general, the recycled LDPE is noticeably superior in improving the bitumen mechanical properties compared to the virgin LDPE at the same modification rate. The application of asphalt mixtures resulted in similar improvements in rutting resistance but slight or relatively unchanged fatigue resistance. The better adhesion of modified bitumen with aggregates is believed to play a critical role in the improvement, as revealed by the RBT test. The microscopy observation further explained the interaction differences between the virgin and recycled LDPE with bitumen and how this might affect the modified bitumen's mechanical properties. The further detailed and in-depth conclusions from each experimental work and analysis are explained in the following sections.

7.1.1. The LDPE modified bitumen production

Before the modified bitumen production, the two LDPEs, virgin LDPE and recycled LDPE, were tested to ensure their melting point was below the planned production (high shear mixing) temperature at 160-170°C. The melting test resulted in 111°C for LDPE and 123°C for recycled LDPE, which means both materials melt below the modification temperature as expected. Further analysis to differentiate the two LDPEs was done by FTIR for the chemical functional group and DSC for thermal changes characterisation. The bitumen modification was done by high shear mixing at 5000 rpm, temperature of 160-170°C, and effective duration of 30 minutes. From this stage of the experiment, the following conclusion can be drawn:

- (1) Based on the differentiation tests of the LDPE modifier, it is found that the FTIR test has resulted in identical typical peak wavenumber on the virgin LDPE and recycled LDPE, according to (Gulmine et al. 2002). Therefore, it can be stated that based on the general procedure of ATR FTIR spectroscopy, it is not an easy task to distinguish the two materials. However, the DSC tests have successfully differentiated the two materials based on their thermal characteristic.
- (2) The DSC thermal analysis has concluded that the two LDPEs have slightly different characteristics. The virgin LDPE has a melting point of 111°C, a typical T_m of LDPE. Meanwhile, the recycled LDPE has slightly higher T_m with 123°C, which is higher than common LDPE ($\pm 110^\circ\text{C}$) but lower than HDPE ($\pm 130^\circ\text{C}$). This T_m number is a typical result for linear-low-density polyethylene (LLDPE).
- (3) The fact that the recycled LDPE has a different property, thus resulting in different modification enhancement than virgin LDPE, explains the importance of testing different sources of materials to ensure its property. DSC is a powerful method to characterise polymer for bitumen modification, thus ensuring the final products meet the expected or designed criteria.
- (4) The 30 minutes, 5000 rpm, 160-170°C high shear mixing has successfully produced the modified bitumen. The lower T_m of LDPE and rLDPE compared to the modification temperature is believed to contribute to the easy modification. However, higher modifications (8% and 10%) require higher shearing energy due to the high stiffness and viscosity of the bitumen.

- (5) After the modification was completed, without stirring, there were clear signs of phase separation with the polymer-rich bitumen floating to the surface. This phase separation is an expected phenomenon, as much literature has stated.

7.1.2. Mechanical properties of modified bitumen

This section describes the results and analysis from bitumen tests on standard bitumen tests, Brooklyn viscometer, dynamic shear rheometer, and Ductilometer tests. The findings and the conclusions can be described as follows:

- (1) In general, the LDPE modification increased the bitumen stiffness. Standard bitumen tests concluded a decrease in penetration number and an increase in softening point. Whilst the differences in penetration number of virgin LDPE and recycled LDPE are insignificant, the changes in softening point are noticeably different, especially at a higher than 6%wt modification rate. At the same modification rate, the pen number of virgin and recycled LDPE showed relatively the same number. Meanwhile, the rLDPE increases the softening point higher than LDPE at the same modification rate. This phenomenon explains how the polymer dominance system works better at higher temperatures in the case of rLDPE and relatively lower for LDPE. Meanwhile, the bitumen becomes the dominant factor in the physical property at low temperatures, as presented in the pen number.
- (2) The viscosity test concluded that among the 2%, 4%, 6%, 8% and 10% of bitumen weight LDPE modification, only the lower three are feasible and applicable for asphalt mixture application. The 8% and 10% of LDPE and rLDPE modification resulted in a high viscosity and low workability at general 160°C HMA temperature preparation.
- (3) The complex modulus master curves from DMA indicated the improvement of the rutting resistance of modified bitumen. The disjointed master curves of the rLDPE-modified bitumen showed that this bitumen is thermo-rheologically more complex than those of virgin LDPE with smooth curves. In line with this, the recycled LDPE provides higher rutting resistance improvement at the same modification rate. Additionally, artificial ageing (RTFO) resulted in a more pronounced modification effect.

- (4) Like the DMA conclusion, the MSCR test resulted in better rutting resistance of the modified bitumen. In addition, the higher modification rate resulted in a lower Jnr and higher %R, indicating an enhancement in the material's rutting resistance.
- (5) The bitumen LAS test concluded the better fatigue resistance of modified bitumen through the ability of the bitumen to withstand the initial cracks. Although, the modified bitumen tends to be more prone to further damage when the crack has been initiated.

7.1.3. Ageing, chemical changes, and microscopy work.

Ageing phenomenon observation and chemical changes analysis were done by using FTIR spectroscopy. In addition, microscopy observations were done to understand the polymer-bitumen interaction and dispersion affecting the modified bitumen's physical properties. These observations and analysis resulted in the conclusion as follows:

- (1) Based on the FTIR test, the ageing effect was detected during the production of the modified bitumen. In addition, higher carbonyl and sulfoxide indices were present on the modified bitumen than on the unmodified bitumen, indicating ageing.
- (2) Ageing commonly leads to a stiffer bitumen and is observed to have lower rutting on laboratory tests. However, the Jnr and %R comparison of normal and aged bitumen revealed that the rutting resistance improvement is due to bitumen modification rather than the ageing effect.
- (3) Chemical functional group observation through FTIR concluded similar results between the modified and unmodified bitumen. No functional group changes explain that the interaction between LDPE or rLDPE with the bitumen is merely physical. There is no chemical interaction or reaction between the bitumen and the modifiers.
- (4) The microscopy works revealed a better interaction of bitumen–recycled LDPE than bitumen–virgin LDPE. The main cause is the ability of bitumen to diffuse and interact with the *ethylene* main structure chain in the case of recycled LDPE, forming an intimate bonding of the bitumen-polymer system that is shown as a sizeable polymer-rich phase. On the other hand, in the case of virgin LDPE, the many branches and the molecules' amorphous nature prevents the diffusion and interaction of bitumen into the polymer. This phenomenon results in immiscible virgin LDPE particles in the bitumen phase and a lower modification effect.

7.1.4. Bitumen and aggregate affinity

The bitumen and aggregate affinity are essential in determining the asphalt mixture's performance. Therefore, the rolling bottle affinity test was done by immersing the bitumen-coated aggregates in distilled water and rolling for a specified duration. The test concluded some points as follows:

- (1) The rolling bottle test concluded the increased affinity of bitumen and aggregate in the modified bitumen. The result also indicated the same positive trend between the modification rate and the affinity or bonding strength increase. With the lowest coating lost, the rLDPE-modified bitumen has the best affinity to aggregate, followed by the virgin LDPE and unmodified bitumen.
- (2) The better affinity of bitumen – aggregate is believed to be the main factor improving the asphalt mixture's performance in rutting resistance. The affinity improvement is the result of the ability of the bitumen to withstand water abrasion and aggregates' impacts during the test. This increasing ability is due to a rise in bitumen integrity because of the LDPE polymer network.
- (3) The modification resulted in a tougher bitumen that prevents softening effect of the water diffusion (cohesive failure) that can lead to adhesive failures. In addition, the stronger modified bitumen prevents water intrusion into bitumen-aggregate bonding surfaces that can destroy the adhesion. These two failure mechanisms' prevention is believed to be the deciding factor in the better affinity of bitumen–aggregate, leading to better asphalt mixture performances.

7.1.5. Asphalt mixture performance

The following conclusions can be drawn from the asphalt mixture test results in the Nottingham Asphalt Tester:

- (1) The Repeated Load Axial Test resulted in the rutting resistance improvements of the modified asphalt mixtures that are in line with the addition of the LDPE modifier. The higher modification resulted in a lower specimen's axial deformation or higher rutting resistance. At the same modification rate, the recycled LDPE produced a higher rutting resistance than virgin LDPE. This result is similar to the rutting resistance behaviour in the bitumen test.

- (2) Higher stiffness results were shown on the LDPE-modified asphalt mixtures compared to the neat mixtures. Similar to rutting behaviour, the recycled LDPE has shown a slightly higher stiffness number than virgin LDPE at the same modification rate.
- (3) The indirect tensile fatigue test resulted in insignificant fatigue life changes of modified mixtures. In general, the fatigue lines of the unmodified and modified mixtures are overlapping and relatively have similar value. This result also demonstrated in the bitumen's fatigue performance.

7.1.6. Bitumen and asphalt mixture properties

Some general conclusions about the LDPE-modified bitumen performance, the correlation to the asphalt mixtures performance, and the potential application in road pavements can be stated as follows:

- (1) The LDPE modifications show better bitumen and asphalt mixture properties in rutting resistance, and relatively low or insignificant changes in fatigue resistance. At the same modification rate, the recycled LDPE performs better in modifying the bitumen to rutting resistance than the virgin LDPE.
- (2) The rutting and fatigue performance improvements are demonstrated in the modified bitumen and the asphalt mixtures. This consistency indicates good applicability of the bitumen in field pavement applications.
- (3) The ring and ball (RnB) test concluded the increase of modified bitumen's softening point. The rolling bottle test (RBT) demonstrated the better bitumen – aggregates bonding of the modified bitumen, believed to be the critical factor in the mixtures' better performances. The test also indicated a better water susceptibility of the modified bitumen. The modified bitumen's stiffer nature from the RnB test and the water-immersed RBT results indicate the LDPE-modified mixtures are very potential in the application in a warm and wet region, especially when the pavements are exposed to high air temperature and water.
- (4) The DSC test showed the differences between the virgin LDPE and the recycled LDPE used in this study. This result concluded that linear-low-density polyethylene is more suitable for bitumen modification than low-density polyethylene. The 6% recycled LDPE, or LDPE with $T_m=123^{\circ}\text{C}$ categorised as linear-LDPE, has proven to beneficially improve 50/70 pen grade bitumen in rutting and fatigue resistance. In addition, the

6% modification improves bitumen properties while maintaining the workability of the modified bitumen for HMA applications.

7.2. Recommendations for Future Research

The study has concluded the beneficial use of low-density polyethylene-modified bitumen and asphalt mixtures. However, for a better understanding of this material's use from various points of view, further research is recommended as follows:

- (1) The better modification of recycled LDPE compared to virgin LDPE can be associated with better bitumen diffusion and swelling to polymer with lower ethylene branches. This phenomenon can be seen from the large polymer phase captured in the microscopy images. A further in-depth study on the molecular interaction of the two materials can be beneficial to improve bitumen properties or potentially prevent the commonly known phase separation.
- (2) This study concluded that the 6% bitumen weight of recycled LDPE (LDPE with $T_m=123^{\circ}\text{C}$) is the best modification rate. However, a further detailed study of numbers around 6% can be beneficial for a better understanding of the modification threshold. It is also recommended to study other bitumen pen numbers further.
- (3) The higher bitumen softening point, higher asphalt mixture stiffness, and lower coating loss in the water-immersed RBT test demonstrate the potentially better performance of the LDPE-modified mixtures in warm and wet regions. A further study in this regard can lead to a better understanding and conclusion.
- (4) Reusing recycled material, such as LDPE plastics, is considered sustainable. However, a detailed study of the application in bitumen and asphalt mixtures was scarce. Therefore, a study in sustainability, the life cycle analysis (LCA), or other environmental points of view will be beneficial for further need, e.g., regulations of LDPE modifications of asphalt mixtures.

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