

**EFFECTS OF TWO WARM-MIX ADDITIVES ON AGING,
RHEOLOGICAL AND FAILURE PROPERTIES OF ASPHALT CEMENTS**

by

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Abstract

Sustainable road construction and maintenance could be supported when excellent warm-mix additives are employed in the modification of asphalt. These warm-mix additives provide remedies for today's requirements such as fatigue cracking resistance, durability, thermal cracking resistance, rutting resistance and resistance to moisture damage. Warm-mix additives are based on waxes and surfactants which reduce energy consumption and carbon dioxide emissions significantly during the construction phase of the pavement. In this study, the effects of two warm mix additives, siloxane and oxidised polyethylene wax, on roofing asphalt flux (RAF) and asphalt modified with waste engine oil (655-7) were investigated to evaluate the rheological, aging and failure properties of the asphalt binders. In terms of the properties of these two different asphalts, RAF has proved to be superior quality asphalt whereas 655-7 is poor quality asphalt. The properties of the modified asphalt samples were measured by Superpave™ tests such as Dynamic Shear Rheometer (DSR) test and Bending Beam Rheometer (BBR) test as well as modified protocols such as the extended BBR (eBBR) test (LS-308) and the Double-Edge-Notched Tension (DENT) test (LS-299) after laboratory aging. In addition, the Avrami theory was used to gain an insight on the crystallization of asphalt or the waxes within the asphalt binder. This study has however shown that the eBBR and DENT tests are better tools for providing accurate specification tests to curb thermal and fatigue cracking in contemporary asphalt pavements.

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Abbreviations and Acronyms

AASHTO	American Association of State and Highway Transportation Officials
AC	Asphalt Cement
ASTM	American Society for Testing and Materials
BBR	Bending Beam Rheometer
CTOD	Crack Tip Opening Displacement, m
DENT	Double-Edge-Notched Tension
DSR	Dynamic Shear Rheometer
eBBR	Extended Bending Beam Rheometer
EWF	Essential Work of Fracture
HMA	Hot Mix Asphalt
LS	Laboratory Standard Test Method
$m(t)$	Slope of the Creep Stiffness Master Curve (m-value)
$S(t)$	Time-dependent Flexural Creep Stiffness, MPa
MPa	Mega Pascal (Pa)
MTO	Ministry of Transportation of Ontario

NSERC	Natural Sciences and Engineering Research Council of Canada
PG (PGAC)	Performance Grade (Performance Graded Asphalt Cement)
PMA	Polymer Modified Asphalt
PPA	Polyphosphoric acid
PAV	Pressure Aging Vessel
PI	Penetration Index
RTFO	Rolling Thin Film Oven
SBR	Styrene-Butadiene-Rubber
SBS	Styrene-Butadiene-Styrene
SHRP	Strategic Highway Research Program
SUPERPAVE™	SUperior PERforming Asphalt PAVement
TFOT	Thin Film Oven Test
VOC	Volatile Organic Compound

Symbols

A	Temperature susceptibility parameter (Penetration test)
a	Length of a sharp crack, m
b	Beam width, 12.5 mm

B	Specimen Thickness, m
G^*	Complex shear modulus, Pa
G'	Storage modulus, Pa
G''	Loss modulus, Pa
h	Beam thickness, 6.25 mm
K	Stress intensity factor, N
L	Ligament length, m
L	Distance between beam supports, 102 mm (BBR)
N	Number of load repetitions
P	Load applied, N (BBR)
t	Loading time, s
T	Temperature, K
W_e	Essential fracture energy, J
w_e	Specific essential work of fracture, J/m^2
W_p	Plastic or non-essential work of fracture, J
w_p	Specific plastic work of fracture, J/m^2
W_t	Total energy, J

w_t	Specific total work of fracture, J/m^2
β	Plastic zone shape factor
δ	Phase angle, $^\circ C$
n	Avrami exponent
z	Avrami exponent
δ_t	CTOD, mm
σ_n	Net section stress or yield stress, N/m^2

CHAPTER 1

INTRODUCTION

1.1 Asphalt Definition

Asphalt can be defined as a dark solid or semi-solid material, depending on temperature, which is normally used in road construction as a binder and in the roofing industry as a waterproof membrane when mixed with fine aggregates and fibres [1]. According to the American Society for Testing and Materials (ASTM), asphalt cement is defined as a “dark brown or black cementitious material occurring in nature or obtained by crude oil refining where the predominant material is mainly bitumen [2].”

1.2 Asphalt Sources

Asphalt is naturally available as rock asphalt, lake asphalt, gilsonite or tar. It is also available artificially through the fractional distillation process of crude oil and as a result of that, referred to as refined bitumen.

1.2.1 Lake Asphalt

Lake asphalt, also known as pitch asphalt, is a type of natural asphalt which is widely used and it is found in distinct surface deposits in countries such as Trinidad, Venezuela and Iraq. A lake in the southern part of Trinidad is recognised as constituting one of the largest deposits in the world and it is estimated to contain about 10 million tonnes of asphalt. This material can be refined by subjecting it to heat at a temperature of 160°C where water is vapourised. The molten residue is also passed through fine screens to eliminate foreign coarse and vegetable matter [3].

1.2.2 Rock Asphalt

Rock asphalt is also a natural asphalt that can be found within porous rocks such as sandstone and limestone at a concentration of up to 12 percent. It has been used since the early seventeenth century in Europe and large deposits were found at Val de Travers in Switzerland, Seyssel in France and Ragusa in Italy. It is extracted through mining or quarrying. Though rock asphalt is somewhat outdated, it is still acknowledged in that it was used in the construction of the very first waterproof asphaltic surfaced roads and streets in New York and Paris [3].

1.2.3 Gilsonite

Gilsonite is a very hard, waterproof natural asphalt which was discovered in the State of Utah in the United States by Samuel H. Gibson in 1880. It can be extracted through the mining process but it is relatively costly due to the rigorous nature of labour involved. In effect, the material is not prevalently used as a paving material [3]. It can however be used in roof and bridge waterproofing materials by modifying the softening point and stiffness of the asphalt [3].

1.2.4 Tar

Tar is the liquid obtained as a result of the destructive distillation of natural organic materials such as coal or wood without the presence of air [4]. The destructive distillation process is referred to as carbonisation. Tar is normally named after the kind of material from which it was obtained. Hence the products of the initial carbonisation process are crude coal tar and crude wood tar [3].

1.2.5 Refined Bitumen

Bitumen is one of the products formed as a result of fractional distillation of crude oil. The heat generated from the earth's crust and applied pressure by the topmost layers of sediments as well as the effects of bacterial action and radioactive bombardments, facilitates the conversion of organisms and vegetable matter into the hydrocarbons of crude oil [3]. The well-known main crude oil producing areas in the world are the Middle East, the United States, Russia and some countries of the Caribbean. However, there are about 1,500 crude oil producing locations in the world [3].

1.3 Constitution of Asphalt

Asphalt is mainly composed of hydrocarbons and the remaining portions are heterocyclic species which contain heteroatoms such as nitrogen, sulphur and oxygen. Asphalt also contains trace amounts of metals such as vanadium, nickel, iron, magnesium and calcium, which are present in the form of inorganic salts and oxides or porphyrine structures [5]. Thus, the asphalt molecular structure can be subdivided into four groups:

- Saturates;
- Aromatics;
- Resins; and
- Asphaltenes.

1.3.1 Saturates

Saturates are composed of straight and branched chain aliphatic hydrocarbons with alkyl naphthenes and alkyl aromatics, which form 5 to 20 percent of the bitumen. They are non-polar viscous oils with an average molar weight ranging from 300 to 2,000 g/mol [3].

1.3.2 Aromatics

Aromatics are dark brown viscous liquids which constitute a fraction of 40 to 65 percent of the asphalt binder. They are also made up of non-polar carbon chains with some unsaturated and predominantly aromatic ring systems and their average molecular weight is similar to that of the saturates in the 300 to 2,000 g/mol range [3].

1.3.3 Resins

Resins serve as a dispersing agent for asphaltenes and are soluble in n-heptane. They are made up of hydrogen and carbon with small quantities of oxygen, sulphur and nitrogen. They form polar dark brown solids or semi-solids with their molecular weight ranging from 500 g/mol to 5,000 g/mol [3].

1.3.4 Asphaltenes

Asphaltenes are complex aromatic materials which contain some nitrogen, sulphur and oxygen in addition to carbon and hydrogen. They constitute 5 % to 25 % of the asphalt and are highly polar and insoluble in n-heptane. Their molecular weight ranges from 1,000 g/mol to 10,000 g/mol [3].

1.4 Structural Aspects of an Asphalt Pavement

1.4.1 Foundation

The foundation as shown in Figure 1.1 is composed of the subgrade and the sub-base. The foundation's function is to carry stress produced by the traffic loading to the sub-grade without subjecting the sub-grade to any kind of distress [3].

1.4.2 Base

The base as shown in Figure 1.1 serves as the main structural element of the pavement design. It is a dense asphalt material which prevents the foundation from getting overstressed by spreading the imposed load. Thus the function of the base is characterised by its rutting and fatigue cracking resistance [3].

1.4.3 Surfacing

The surfacing as shown in Figure 1.1 is composed of the binder course and the surface course. The function of the binder course is to distribute any form of stress from the surface course to the base. The surface course is the upper layer which is usually in contact with traffic and visible to the road user. Hence, a good surface course can be characterised by its fatigue cracking resistance, skid resistance, rutting resistance and resistance to effects of bad weather conditions [3].

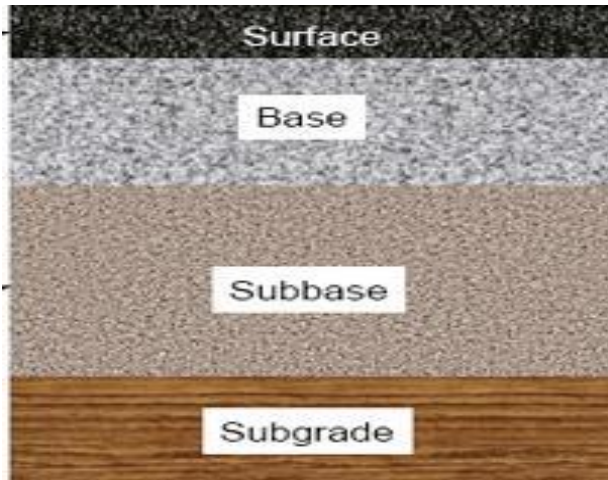


Figure 1.1: Structural layers in an asphalt concrete pavement [3].

1.5 Asphalt Distress

Asphalt distresses are caused by extreme weather conditions, chemicals, thermal stresses and disintegrations over a period of time with the application of repeated traffic loads. In effect, there is failure in the asphalt pavement through fatigue cracking, low temperature cracking, rutting and moisture damage [1].

1.5.1 Rutting

Rutting as shown in Figure 2.1 occurs at high temperatures when the viscosity of the asphalt binder decreases and flow can occur under traffic loading [6]. As a result of that, permanent deformation occurs in the asphalt pavement due to accumulated unrecoverable strain from the repeated loads [9]. Rutting can be predicted using the rutting resistance factor, $G^*/\sin \delta$ (where G^* is the complex modulus and δ is the phase angle for the asphalt cement), which is measured with the Dynamic Shear Rheometer (DSR).



Figure 1.2: Rutting [6].

1.5.2 Fatigue Cracking

Fatigue cracking, as shown in Figure 2.2, occurs at low to moderate pavement temperatures. It is caused by tensile strains generated in the pavement by traffic loading [7]. Fatigue cracking can be predicted using the fatigue resistance factor, $G^* \sin \delta$ (where G^* is the complex modulus and δ is the phase angle for the asphalt cement), which is also measured with the DSR.



Figure 1.3: Fatigue cracking [8].

1.5.3 Low Temperature Cracking

In low temperature cracking, as shown in Figure 2.3, thermal stresses develop in the pavement when the asphalt concrete shrinks and the asphalt binder contracts more than the aggregate at low temperatures. As a result, cracks develop when the thermal stress overcomes the tensile strength of the asphalt mixture [9].



Figure 1.4: Thermal cracking [10].

1.5.4 Moisture Damage (Stripping)

Moisture damage, as shown in Figure 2.4, occurs when the adhesion between the aggregates and the asphalt cement decreases; so the base structure gets damaged. This is accelerated by the presence of moisture, temperature, poor construction materials and traffic loads. Thus, proper drainage, anti-stripping agents and proper compaction can prevent moisture damage [1].



Figure 1.5: Moisture damage [11].

1.6 Performance Grading

Owing to the complex chemical structure of asphalt, it is very difficult to chemically investigate and characterise the performance of asphalt [9]. In order to categorize the performance of asphalt cement, it is imperative to use physical property measurements. Several methods have been developed to classify and predict the performance of asphalt. These methods include:

- Conventional testing;
- SuperpaveTM testing; and
- Ontario Ministry of Transportation (MTO) Test Standards.

1.6.1 Conventional Testing

This method of testing is generally employed to categorize grades of asphalt. The different grades used under conventional specification are:

- Oxidized;
- Cutback;
- Hard; and
- Penetration Grade.

The conventional testing involves tests such as softening point, penetration at 25°C, dynamic viscosity at 60°C, kinematic viscosity at 135°C, specific gravity, storage stability, ductility, elastic recovery and force-ductility tests [1].

1.6.2 Superpave™ Testing

The Strategic Highway Research Program (SHRP) developed the Superpave™ testing methods in 1987 in the USA; owing to conventional test methods which are not always reliable in predicting asphalt performance. The major goal of these developed methods was to construct pavements which performed outstandingly in service. These pavements were then referred to as Superior PERforming PAVements [3]. This method facilitated the classification of the binder with respect to its grade, based on the performance after simulated aging and physical property determination [3]. RTFO and PAV are the aging methods involved while DSR and BBR are later used to measure the properties of the asphalt samples.

1.6.3 Ontario Ministry of Transportation (MTO) Test Standards

Although the Superpave specifications tests help in categorizing grades of asphalts, there was a need to improve the test methods so that poor quality asphalt could be well distinguished from better quality asphalts used historically prior to Superpave and which typically come from Alberta crudes. Thus, the Ontario Ministry of Transportation in collaboration with Queen's University has developed improved test methods which include the following:

- Extended Bending Beam Rheometer (eBBR) Method (LS-308) [12];
- Double-Edge-Notched Tension (DENT) Method (LS-299) [13]; and
- Modified Pressure Aging Vessel Protocols (LS 228) [14].

1.7 Scope and Objectives

In order to support sustainable road construction and maintenance, it is imperative to employ excellent warm mix additives for modification of the asphalt. These warm mix additives provide remedies for today's requirements such as fatigue cracking resistance, durability, thermal cracking resistance, rutting resistance and resistance to moisture damage.

In addressing the issues related to the requirements outlined above, excellent warm mix additives provide outstanding adhesion and wetting properties as well as high temperature stability. Usually these warm-mix additives are based on waxes and surfactants which reduce energy consumption and carbon dioxide emissions significantly during the construction phase of the pavement [15].

In this study, the effects of two warm mix additives, siloxane and oxidised polyethylene wax, on roofing asphalt flux (RAF) and asphalt modified with waste engine oil (655-7) are investigated. In terms of the properties of these two different asphalts, RAF has proved to be good quality asphalt whereas 655-7 is poor quality asphalt.

The objective of this study is to investigate the effects of the commercial surfactant-based and wax-based warm mix additives, on aging, rheological and failure properties of well-defined superior and less quality asphalts, as stated above.

The properties of the modified asphalt samples are measured by Superpave™ tests such as DSR and BBR, as well as modified protocols such as the extended BBR test (LS-308) and the DENT test (LS-299) after RTFO and PAV aging.

In addition, it is an aim of this study to determine the rate of physical hardening of the modified asphalt samples analogous to that of the extended BBR by employing the dilatometric test.

The dilatometric test is used to determine the change in volume of the asphalt binder isothermally due to physical hardening; it is also used to gain an insight on the crystallization of asphalt or the waxes within the binder with the help of the Avrami theory.

CHAPTER 2

BACKGROUND

2.1 Asphalt History

The term “asphalt” originated from the Greek word “asphaltos” which means, “secure”, while the term “bitumen” originated from the Sanskrit word “jatu-krit”, which means “pitch creating” [3]. Back in 2000 BC, asphalt was mainly used as mortar to bind bricks and stones; also as a waterproofing material [3]. The development of modern techniques for petroleum refinery in the early 1900’s, initiated the prevalent use of asphalt as a paving material [2].

2.2 Asphalt Modifications

The performance of asphalt cement can be enhanced when the refinery process from which the asphalt is produced is altered or by selecting the best starting crude. Due to the scarcity of crude that produces good asphalt, and “only a limited number of actions can be taken to control the refining process to make improved asphalt” [16], asphalt binder producers have widely resorted to the use of additives to modify the properties of asphalt to curb these difficulties.

The modification of asphalt was patented as far back as 1843, when polymer modified asphalt (PMA) was first employed. PMA was then used during the 1930’s in Europe to construct test trials so their performance could be assessed. In 1950, neoprene latex was first used in North America as a modifier in asphalt binder [2, 17].

Asphalt is a colloidal dispersion in which asphaltenes are peptized by resins [19, 20]. The colloidal nature of asphalt can be categorized as sol-type or gel-type. A sol-type asphalt has well-

dispersed asphaltenes and an aromatic maltene fraction while a gel-type asphalt has the asphaltenes not well-dispersed as well as a more paraffinic maltene fraction. The gel-type is more susceptible to cracking than the sol-type, which has better physical properties [21, 22]. Below is a schematic representation of the sol-type and gel-type asphalts.

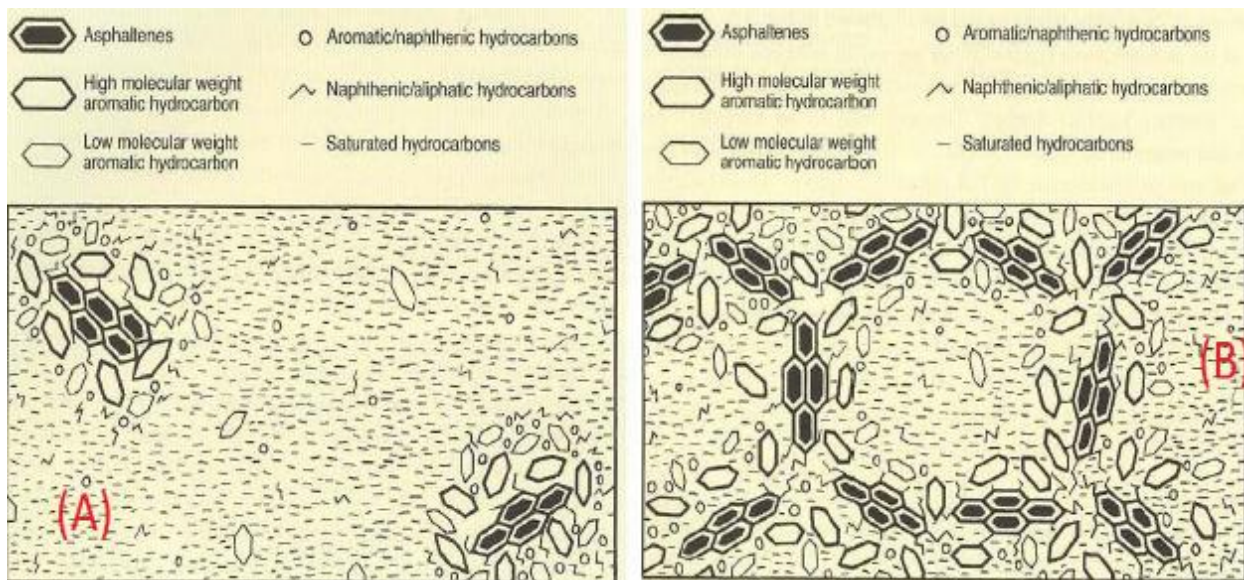


Figure 2.1: (A) Sol-type and (B) gel-type asphalts [3].

The production process of asphalt is dependent on the source of crude oil and several other factors. Basic unit operations such as atmospheric and vacuum distillation are employed in the United States and Canada to refine crude oil [1]. Asphalt grades are manufactured by several processes as shown in Table 2.1.

Table 2.1: Various Methods for Production of Asphalt [23]

S.No	Production/process	Base Material	Product
1	Atmospheric and Vacuum Distillation	Asphalt-based crude or crude mix	Asphalt cement
2	Blending	Hard and soft asphalt cements and petroleum distillates	Asphalt cements of intermediate consistency cutback asphalts
3	Air blowing	Asphalt flux	Asphalt cements, roofing asphalt, pipe coating, special membranes
4	Solvent Deasphalting	Vacuum residuum	Hard asphalt
5	Solvent Extraction	Vacuum residuum	Asphalt components (asphaltenes, resin, oils)
6	Emulsification	Asphalt, emulsifying agent and water	Emulsified asphalts
7	Modification	Asphalt and modifiers (polymers, chemicals etc.)	Modified asphalts

Asphalt binders have been modified with various materials but the most widely used modifiers are polymers. Polymeric materials such as plastomers and elastomers are employed in asphalt modification.

When plastomers are stretched, they are able to remain in their stretched position at a large extent if the load is released. In contrast, elastomers will largely return to their initial shape after the load has been released. Plastomers are used in modifying asphalt to decrease permanent deformation while elastomers have a further function of reducing fatigue and low temperature cracking distress in the asphalt pavement. Some examples of plastomers are low density polyethylene (LDPE), ethylene vinyl acetate (EVA) and ethylene acrylate (EA). Examples of elastomers are styrene-butadiene rubber latex (SBR), diblock styrene-butadiene (SB) and triblock styrene-butadiene-styrene (SBS) [24].

Another group of asphalt modifiers are the anti-strip additives which comprise fatty amido amines and polyamines. These anti-strip additives decrease the susceptibility of the asphalt mixture to moisture damage by increasing the adhesion between the asphalt binder and the surface of the aggregates [18].

Polyphosphoric acid (PPA) is also used in the asphalt industry purposely to increase the softening point of the asphalt binder. PPA also helps to increase the grading range of the binder at high temperatures so that better performance of the asphalt binder can be attained [25].

2.3 Warm Mix Asphalt Technology and Additives

Warm mix asphalt (WMA) technology has been employed by asphalt paving industries due to its outstanding performance as compared to the hot mix asphalt (HMA) technology. In 1999, the first application of WMA technology was carried out in Germany on a public road using Aspha-Min[®] zeolite system. However, the first trial of the WMA technology in Canada occurred in 2005, when five different systems were employed. These systems included Aspha-Min[®] zeolite, Sasobit, Evotherm and Colas 3E DB [26].

In order to support sustainable road construction and maintenance, WMA additives are used to provide good adhesion and wetting properties as well as high temperature stability. They also reduce energy consumptions and carbon dioxide emissions significantly during the construction phase of the pavement [15]. Unlike the regular HMA where mixing temperature ranges from 150 to 180°C, warm-mix additives are able to decrease the mixing temperatures to anywhere from 100 to 140°C [27].



Figure 2.2: Emissions from the HMA truck as compared to the WMA truck [28].

The WMA technology involves three different processes:

- Foaming Process

This process was developed and patented in Norway by Kolo Veidekke and Shell Global Solutions. The foaming process facilitates the asphalt mixture production at temperatures ranging from 100 to 120°C. It also facilitates compaction of the asphalt mixture at a temperature range of 80 to 110°C [29]. In the foaming process, small steam bubbles are formed within the asphalt binder to increase the asphalt volume. A type of foaming process is the WAM foam. The WAM foam comprises two steps. The first step involves mixing of a softer binder with aggregates at low temperatures. The second step involves foaming of the harder binder which is then mixed with the aggregates that have already

been mixed with the softer binder. Thus, the foaming process lowers the high shear viscosity of the asphalt binder and also increases the asphalt wettability [29].

- Chemical Modification

In the chemical modification process, water bearing agents are added to the asphalt binder during mixing. In effect, the water that is chemically bound to the asphalt is released. When the aggregate and asphalt mix are heated, the water released forms a well-dispersed steam. This finely dispersed steam reduces the compaction temperature which ranges from 20 to 30°C. Water bearing agents such as Aspha-Min[®] are used in the chemical modification of asphalt binders. Aspha-Min[®] is a hydrothermal crystallized fine powder. The chemical name for Aspha-Min[®] is sodium aluminium silicate [30].

- Organic Additives

Organic additives such as paraffin and low molecular weight ester compounds can be employed to modify the asphalt properties. This modification reduces the viscosity of the asphalt binder at a temperature range of 80 to 120°C. Sasobit is an example of paraffin that melts in the asphalt binder at temperatures ranging from 85 to 115°C. This however decreases the mixing and handling temperatures by 30 to 50°C. The Fischer-Tropsch process is used to produce paraffin by means of coal gasification [31]. Figure 2.3 shows the various products used in warm mix technologies.

WMA processes	Product	Company	Description	Dosage of additive	Country where technology is used	Production temperature °C (or reduction range)
<i>Foaming processes</i>						
Water-containing	Aspha-Min®	Eurovia and MHI	Water-containing technology using zedites	0.3% by total weight of the mix	USA, Germany, France, worldwide	(20–30 °C)
Water-containing	Advera®	PQ Corporation	Water-containing technology using zedites	0.25% by total weight of the mix	USA	(10–30 °C)
Water-based	Double Barrel Green	Astec	Water-based foaming process	2% water by mass of bitumen; anti-stripping agent	USA	116–135 °C
Water based	Ultrafoam GX	Gencor industries	Water-based foaming process	1–2% water by mass of bitumen	USA	Not specified
Water-based	LT Asphalt	Nynas	Foam bitumen with hydrophilic additive	0.5–1 % by mass of bitumen	Netherlands and Italy	90 °C
Water-based	WAM-Foam	Shell and Kolo-Veidekke	Soft binder coating followed by foamed hard binder	2–5 % water by mass of hard binder	Worldwide	100–120 °C
Water based	Low Energy Asphalt	LEACO	Hot coarse aggregate mixed with wet sand	3% water with fine sand	USA, France, Spain, Italy	<100 °C
Water based	Low Emission Asphalt	McConaughay Technologies	Hot coarse aggregate mixed with wet sand, combined with chemicals	3% water with fine sand; 0.4% bitumen weight	USA	90 °C
Water based	LEAB	Royal Bam Group	Direct foam with binder additive. Mixing of aggregates below water boiling point	0.1% of bitumen weight of coating and adhesion additive	Netherlands	90 °C
<i>Organic</i>						
FT Wax	Sasobit	Sasol	Fischer-Tropsch wax	Approx. 2.5% by weight of binder in Germany; , 1.0–1.5% in the U.S.A.	Germany as well as 20 other countries	(20–30 °C)
Montan Wax	Asphaltan B	Romonta GmbH	Refined Montan wax with fatty acid amide for rolled asphalt	2.0–4.0% by mass of bitumen	Germany	(20–30 °C)
Fatty Acid Amide wax	Licomont BS	Clariant	Fatty acid amide	3.0% by mass of bitumen	Germany	(20–30 °C)
	3E IT or Ecoflex	Colas	Proprietary	Yes, but not specified	France	(30–40 °C)
<i>Chemical</i>						
Chemical	Evoterm Technologies	Mead Westvaco	Chemical packages, with or without water	0.5% of mass of bitumen emulsion. Emulsion contains 70% of bitumen	USA, France, Worldwide	85–115 °C
Chemical	Cecabase RT	CECA	Chemical package	0.2–0.4% by mixture weight	USA, France	(30 °C)
Chemical	Rediset	Akzo Nobel	Cationic surfactants and organic additive	1.5–2% of bitumen weight	USA, Norway	(30 °C)
Chemical	Revix	Mathy-Ergon	Surface-active agents, waxes, processing aids, polymers	Not specified	USA	(15–25 °C)
Chemical	Iterlow T	IterChimica		0.3–0.5% by mass of bitumen	Italy	120 °C

Figure 2.3: Various products employed in warm-mix technologies [32].

2.4 Asphalt Cement Aging

Asphalt cement aging or embrittlement is the oxidation that occurs in the asphalt cement during hot mixing, construction and service. The main factors that determine the properties of asphalt cement with respect to aging are time and temperature. This is well elaborated by the time-temperature superposition (TTS) principle [17, 25]. The principle can be related to the aging process so it can be inferred that “the aging process at a lower temperature within a long time interval is equivalent to the aging process at a higher temperature within a short time interval [9].” The hardening effect of the asphalt binder during aging can be classified under chemical aging and physical aging.

Chemical aging occurs when the asphalt binder is affected by oxygen, ultraviolet radiation and temperature changes which results in the change in morphology of the asphalt. Chemical aging however, increases the stiffness of the binder due to oxidation in the binder by air. In effect, the asphalt binder becomes very brittle and more susceptible to cracking upon application of a constant load.

Physical aging also known as reversible aging occurs at low temperatures due to shrinkage of the asphalt binder. Physical aging can also be explained by the asphaltene aggregation and wax crystallization at low temperatures [33]. Several studies have been conducted to investigate the mechanisms of reversible aging process of the asphalt binder. Petersen [34] outlined the reasons for aging as follows:

- Volatility of oily compounds such as saturates and aromatics in the asphalt;
- Crystallization of wax and rearrangement of asphaltene molecules; and
- Heteroatoms oxidation in the asphalt cement.

Struik [35] and Bahia [36], also argued that the physical aging process could be explained using the free volume collapse theory at low temperatures. However, Hesp et al. [33] carried out a study to investigate the physical aging in asphalt at low temperatures; and it was observed that, “the loss in grade temperature peaks at some intermediate condition temperature, suggests that the free-volume collapse – together with the reduction in mobility – is responsible for a large part of the aging.” In short, reversible aging occurs as a result of the shrinkage or free volume collapse of the asphalt binder as well as the decrease in mobility of the asphalt binder constituents.

Asphalt cement aging can also be caused by the presence of interconnected air voids which occur as a result of insufficient compaction. These air voids facilitate oxidative hardening by allowing air to penetrate the asphalt pavement. In effect, premature failure of the asphalt pavement occurs. The aging behaviour of the asphalt binder is also short-term and long-term.

Short-term aging involves the oxidation and volatilization of compounds that are thermally unstable during the HMA preparation. After HMA pavement construction, the asphalt undergoes a long period of environmental exposure which is the long-term aging. The Rolling Thin Film Oven (RTFO) test method is used to simulate short-term aging whereas the Pressure Aging Vessel (PAV) test method is used to simulate long-term aging of the asphalt binder in the laboratory.

2.5 Conventional Testing Methods

Conventional test methods comprises penetration, viscosity and softening point tests which were used as empirical testing methods for asphalt binders during the early 1900’s [37]. In order to

evaluate the properties of asphalt binder, four conventional grades are considered. The conventional grades are cutback, oxidized, hard and penetration grade, which is the most important grade in relation to construction of pavement roads. The combination of the softening point and the viscosity test methods determine the oxidized and hard grades. The penetration grade is determined using both penetration and softening point test methods. However, the viscosity test is used to predict the cutback grade. For blending and surface coating purposes, the cut back grade asphalt is employed whereas the oxidized grade asphalt is used for painting and roofing [24].

2.5.1 Penetration Test

The penetration test is a fast, simple and inexpensive test method used widely to assess asphalt cement by classifying rather than measuring the qualities of the asphalt cement. This empirical test produces a value from which the asphalt grade is selected based on field performance. In this test, the consistency of the asphalt binder is measured at a standard temperature of 25°C, a standard time of 5 seconds and a standard load of 100 grams. This involves measuring the depth of a needle pushed into an asphalt sample under the standard conditions above [38]. The unit of measurement of this test method is decimillimetres, which is 0.1 mm. For example, 80 pen asphalt cement has a needle penetration at 25°C of 8 mm, meaning, 80 times 0.1 mm. A low value of penetration measurement implies harder asphalt and a high value implies soft asphalt. The susceptibility of the bitumen to temperature can be identified if the measurement of penetration is carried out over a range of temperatures. The consistency of the asphalt binder can be related to the changes in temperature by the equation [39]:

$$\log P = AT + K \quad (1)$$

Where:

- P is the penetration at temperature T ;
- A is the temperature susceptibility ; and
- K is a constant.

The A value which is defined as the Penetration Index (PI) can be calculated from penetration measurements at two different temperatures, T_1 and T_2 using the equation [39]:

$$A = PI = \frac{\log (Pen @ T1) - \log (Pen @ T2)}{T1 - T2} \quad (2)$$

Thus the penetration index uses the difference in asphalt binder properties over a temperature range which is relatively small, for the characterisation of asphalt binders.



Figure 2.4: Equipment for testing penetration of asphalt binders [39].

2.5.2 Softening Point Test

The softening point test method is used to indicate the propensity of the asphalt binder to flow at elevated temperatures as encountered in service. The main objective of this test is to determine the softening point of the asphalt binder within the temperature range of 30 to 157°C. The apparatus used is the ring and ball apparatus which is immersed in distilled water or ethylene glycol. The softening point of the asphalt binder is determined at the temperature which the steel ball in the ring pushes the soft asphalt binder to a distance. This method also classifies the asphalt binder by measuring the consistency of the asphalt binder [40].

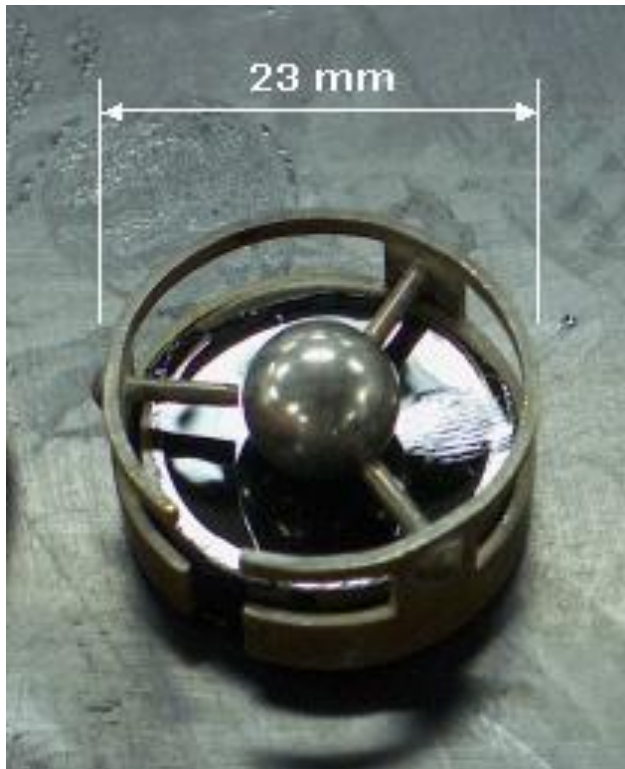


Figure 2.5: Softening point apparatus [39].

2.5.3 Viscosity Test

The ratio of applied shear stress to the induced shear rate of a fluid is referred to as viscosity. The viscosity test of asphalt binders was developed to improve the penetration test in the early 1960's [11]. In this test, the fundamental physical property of the asphalt binder can be measured unlike the penetration test. Although this test measures the physical property of asphalt binders, temperature susceptibility of the binder is a major drawback. This test method is carried out on the unaged (AC grading) asphalt binder as well as the RTFO aged (AR grading) asphalt binder. In order to characterise the properties of the asphalt binder prior to HMA manufacturing process, the AC grading test is employed. The AR grading test is used to simulate the properties of the asphalt binder after the HMA manufacturing process [41]. Brookfield viscometers and capillary viscometers are used to measure asphalt viscosities with respect to their specification requirements [42].



Figure 2.6: Brookfield viscometer and capillary viscometer [43, 44].

2.6 Superpave® Specification Tests

The Strategic Highway Research Program (SHRP) developed the Superpave™ Testing methods in 1987, in the USA; owing to conventional test methods which are not always reliable in predicting asphalt performance. The major goal of these developed methods was to construct pavements which performed outstandingly in service. These pavements were then referred to as Superior PERforming PAVEments [3].

The Superpave binder specification was also aimed at improving the performance of the asphalt binder by reducing the tendency for the binder to cause thermal cracking, permanent deformation and fatigue cracking in asphalt pavements. This specification measures the physical characteristics of the asphalt binder using sound engineering principles. The tests are then run at temperatures analogous to what is encountered by the pavement in service. The measured physical characteristics of the asphalt binder do not change for all the grades. However, the temperatures associated with these physical properties vary depending on the climate in which the asphalt binder would be used [9].

The grade assigned to the asphalt binder according to Superpave specification test is Performance Grade (PG) or Performance Grade Asphalt Cement (PGAC) XX-YY. The XX represents the limiting maximum temperature of the asphalt binder which is determined using the DSR test. The –YY represents the limiting minimum temperature of the asphalt binder which is also determined using the BBR test. An example is a PG 52-34; which implies that the binder is designed to sustain environmental conditions where the average seven-day maximum pavement temperature is 52°C and the minimum pavement design temperature is -34°C. It is anticipated that at this grade, the asphalt binder would resist rutting and low temperature cracking at a

maximum average seven-day temperature of 52°C and a minimum temperature of -34°C respectively [9].

2.6.1 Laboratory Aging of Asphalt Cement

In the laboratory, the PAV is used in simulating aging of the asphalt binder in service, whereas the RTFO is used to simulate aging of the asphalt binder during mixing and construction. The asphalt binder samples aged in the RTFO then undergoes performance tests which are carried out by the DSR. The samples which are further aged in the PAV after RTFO aging undergoes performance tests carried out by the Direct Tension Test (DTT), BBR as well as the DSR.

2.6.1.1 Rolling Thin Film Oven (RTFO) Test

The RTFO test simulates the short-term aging of the asphalt binder. It is used to determine the quantity of volatiles lost from the asphalt. This test method requires an electrically heated convection oven. The test is conducted by heating a thin film of asphalt binder in motion in the oven for 85 minutes at 163°C. The film in motion is prepared by measuring 35 grams of the asphalt binder sample into RTFO bottles and then placing the bottles in a circular metal carriage that rotates at a rate of 15 revolutions per minute within the oven, as shown in figure 2.7. The air flow is maintained at 4000 ml/min. The RTFO test method was designed to improve on the Thin Film Oven Test (TFOT). Some of the advantages the RTFO test method has over the TFOT method are [45]:

- Modifiers are kept well-dispersed in the asphalt during the rolling action;

- Fresh films of the asphalt binder are continually exposed to heat due to the repeatability of the test; and
- The duration of the test is short, that is, 85 minutes instead of 5 hours with TFOT.



Figure 2.7: Rolling Thin Film Oven [8].

After aging, the physical properties of some of the samples are measured with the DSR and the rest of the samples are further aged in the PAV. The mass change can be obtained by using the equation [9]:

$$\text{Mass change (\%)} = \frac{\text{Aged mass} - \text{Original mass}}{\text{Original mass}} \times 100$$

2.6.1.2 Pressure Aging Vessel

The PAV test method is used to simulate long-term aging or in-service aging of the asphalt binder that occurs after 6-10 years by subjecting the binder to high pressure and temperature. This test takes place in the PAV vessel as shown in Figure 2.8, after aging the binder in the RTFO since the asphalt in-service has already undergone mixing and construction process. In this test, the asphalt samples in the pans are kept at a temperature, ranging from 95 to 110°C depending on the climatic condition for the service [46]. The duration and pressure involved in this test are 20 hours and 2070 kPa respectively. The physical properties of the PAV aged samples can be determined by post-experimental tests such as:

- Bending Beam Rheometer (BBR) test;
- Dynamic Shear Rheometer (DSR) test;
- Infra-red (IR) test;
- Direct tension (DT) test; and
- Double-Edge Notched Tension (DENT) test.



Figure 2.8: Pressure aging vessel [41].

2.6.2 Dynamic Shear Rheometer (DSR) Method

This test is basically used to determine the rheological properties of an asphalt binder at intermediate to high temperatures using the DSR. This is because the asphalt behaviour is dependent on both loading time and temperature and the DSR is able to include both parameters. The DSR is also termed as oscillatory rheometer or parallel plate rheometer as shown in figure 2.9. In order to determine the rheological properties of the asphalt binder, the complex shear modulus G^* (which is a measure of the total resistance of a material to deformation) and the phase angle δ , (which is an indication of the relative amount of recoverable and non-recoverable deformation) are measured by the DSR [45]. The DSR also measures other rheological properties such as G' (elastic component) and G'' (viscous component) of unaged, RTFO- aged, and PAV- aged asphalt samples for intermediate and high temperature performance grading [9]. The G'' and G' relates to rutting and thermal cracking at high and low temperatures respectively.



Figure 2.9: Dynamic Shear Rheometer (DSR) [47].

To calculate the shear stress and shear strain of an asphalt sample, the DSR measures the torque and angle of rotation as follows [48]:

The oscillatory strain, γ ,

$$\gamma = \gamma_o \sin \omega t \quad (1)$$

Where,

γ_o is the peak shear strain; and

ω is the angular velocity in radians/second.

The shear stress, τ ,

$$\tau = \tau_o \sin (\omega t + \delta) \quad (2)$$

Where,

τ_o is the peak shear stress; and

δ is the phase shift angle.

Then, the complex shear modulus can be calculated as $G^* = \tau_o / \gamma_o$ (3)

According to AASHTO specification, the high temperature PG grade can be determined by relating the complex shear modulus to the phase angle such that for unaged asphalt samples, $G^*/\sin \delta$ should be greater than 1.00 kPa and greater than 2.20 kPa for RTFO-aged samples [9]. These high temperature measurements are related to rutting. To determine the intermediate temperature PG grade, the PAV aged samples are used. According to AASHTO specification,

the intermediate temperature PG grade can also be determined by relating the G^* to the δ such that $G^*\sin \delta$ should not exceed 5000 kPa [9]. This however addresses fatigue cracking.

2.6.3 Bending Beam Rheometer (BBR) Method

The Bending Beam Rheometer (BBR) method was developed under the Strategic Highway Research Program, to measure the creep stiffness $S(t)$ and m -value of the asphalt cement. The creep stiffness and m -value are two important parameters of the asphalt binder determined by the creep stiffness master curve slope. These parameters are related to thermal cracking distress of the asphalt pavement. The specification criteria for passing or failing the BBR test is outlined by the AASHTO standard M320 [46]. The AASHTO M320 specification criteria are centred on the inference of the research conducted by the Shell laboratories in Amsterdam during the 1950's and 1960's. The Shell laboratories concluded that there is a correlation existing between the asphalt binder stiffness at a constant loading time and the failure properties in the binders and mixtures [8, 49, 50]. The limiting temperature is also determined by the BBR which indicates how the asphalt binder is able to resist thermal cracking distress. The Figure below shows the BBR.



Figure 2.10: Bending Beam Rheometer (BBR) [51].

In this test, the asphalt samples used are PAV aged samples which are moulded into beams. Conditioning temperature and testing temperature are the same. Before testing, the beams are conditioned for one hour in an ethanol bath at a desired temperature. The test is conducted by loading the beam in three-point bending at a temperature above the designed pavement temperature. The stiffness of the beam is then measured at loading times of 8, 15, 30, 60, 120 and 240 seconds in order to determine the creep master curve. The m-value is the slope of the master curve and it indicates the ability of the asphalt binder to relax stress as a result of viscous flow [46]. The sample passes the specification when the m-value is equal to or greater than 0.3 and the creep stiffness has a maximum value of 300 MPa. A higher m-value implies that asphalt creeps at a faster rate to decrease the thermal stress. Hence decreases thermal cracking [48].

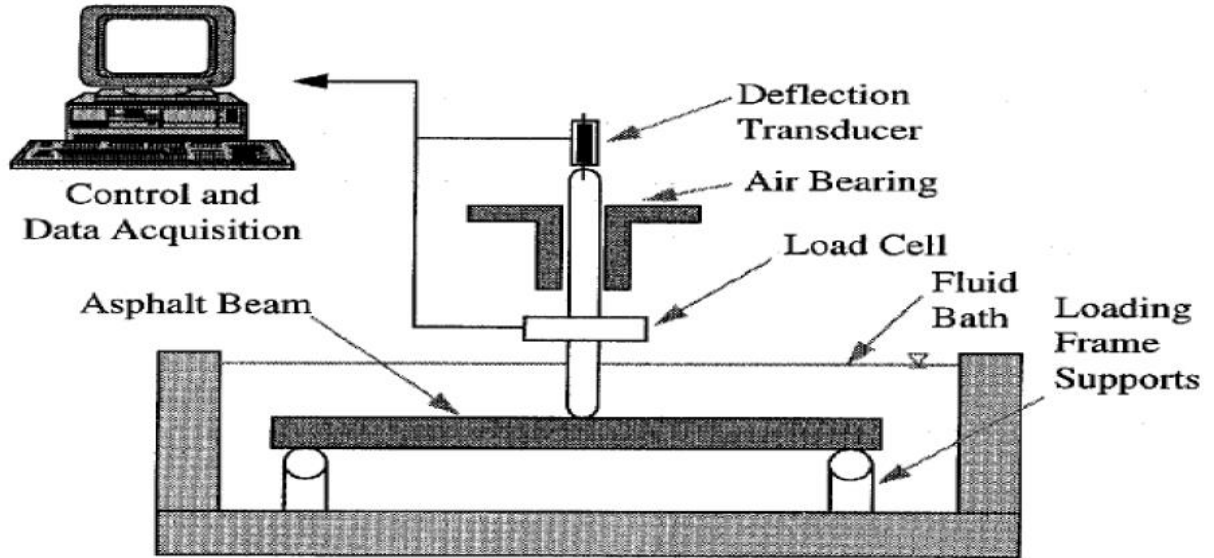


Figure 2.11: Schematic diagram of the bending beam rheometer [45].

The creep stiffness of the asphalt binder can be calculated by the following equation:

$$S(t) = PL^3 / 4bh^3\delta(t) \quad (1)$$

Where:

$S(t)$ = creep stiffness at time, t ;

P = applied load, 100 grams;

L = distance between beam supports, 102 mm b = beam width, 12.5 mm; and

h = beam height, 6.25 mm; and $\delta(t)$ = deflection at time, t .

2.7 Improved Ministry of Transportation of Ontario (MTO) Test Methods

According to Struik [35], it is extraneous to study properties such as creep and stress relaxation without considering physical aging. Thus it is imperative to consider physical hardening when measuring the rheological properties of asphalt binders and not just creep and stress relaxation as suggested by AASHTO M320 specification. To address the problem associated with the AASHTO M320 specification, the Ontario Ministry of Transportation in collaboration with Queen's University has developed improved test methods which comprise:

- Extended Bending Beam Rheometer (eBBR) test (LS-308) [12];
- Double-Edge-Notched Tension (DENT) test (LS-299) [13]; and
- Modified Pressure Aging Vessel protocols (LS 228) [14].

2.7.1 Extended Bending Beam Rheometer (eBBR) Method LS-308

The extended BBR test is conducted to determine the asphalt binder's ability to meet the low temperature performance grade after undergoing a physical aging process over time [12]. Low temperature physical hardening of the asphalt binder varies overtime at different temperatures but the regular BBR is not able to account for this due to the one hour conditioning. In the extended BBR test, the asphalt beams are conditioned for 1 hour, 24 hours and 72 hours at two different temperatures which are:

- $T_1 = T_{\text{design}} + 10^{\circ}\text{C}$; and
- $T_2 = T_{\text{design}} + 20^{\circ}\text{C}$, where T_{design} is the lowest temperature designed for the pavement, prior to testing.

To determine the exact grade as per AASHTO M320 criteria, both pass and fail temperatures are employed by means of interpolation. After each temperature conditioning period, the grade temperature and the subsequent grade losses are calculated. The worst grade loss is then evaluated by finding the difference between the warmest and the coldest limiting temperature (where $S(60\text{ s})$ reaches 300 MPa and $m\text{-value}(60\text{ s})$ reaches 0.3) [52].

The extended BBR test has proved to be an efficient method used in separating well-defined superior asphalt cements from lesser quality asphalt cements because it properly addresses the low temperature performance of the asphalt binder [53].

2.7.2 Double-Edge Notched Tension (DENT) Test LS-299

This test method is used to determine the essential work of failure, the plastic work of failure, and an approximate critical crack tip opening displacement (CTOD) of the asphalt binder, at a specified temperature and rate of loading after thermal conditioning [13]. In this test, asphalt sample are prepared in a double-edge-notched shape and the distances between to opposite notches 5 mm, 10 mm and 15 mm. Conditioning is done in a water bath at a specified temperature. The samples are then pulled in the water bath until they fail, as shown in figure 2.12



Figure 2.12: DENT test setup [6].

Cotterell and Reddel [54] initiated the DENT test as a thermodynamic analysis centred on the Essential Work of Fracture (EWF) method. This was further investigated by Mai et al. [55]. In the DENT method, it is assumed that the total work of fracture (W_t) at a fixed loading rate on a DENT sample comprises two regions:

- The essential work of fracture (W_e) ; and
- The non-essential or plastic work of fracture (W_p) as shown in figure 2.13

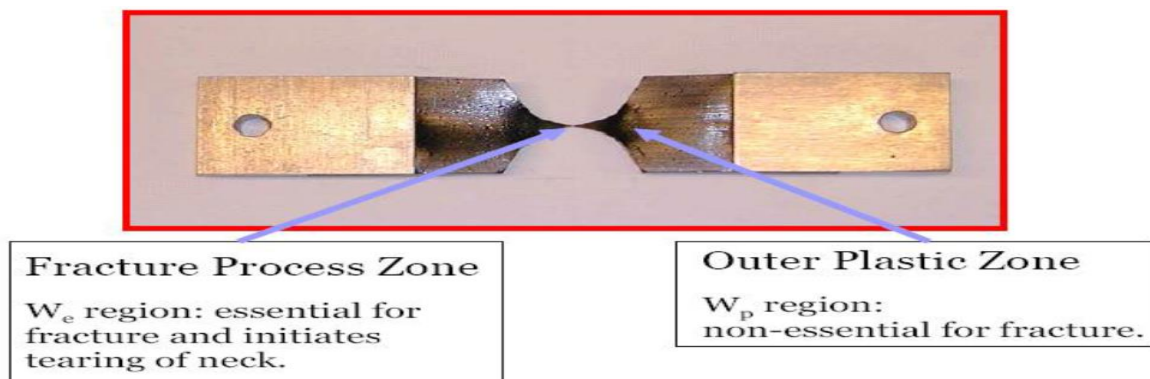


Figure 2.13: Diagram of fracture and plastic zone of asphalt binder [8].

Under the force-displacement curve W_t can be determined as:

$$W_t = W_e + W_p \quad (1)$$

Essential work of failure (W_e) and non-essential work of failure (W_p) can be determined by the following equations:

$$W_e = w_e \times LB \quad (2)$$

$$W_p = w_p \times \beta L^2 B \quad (3)$$

Where,

w_e = specific essential work of fracture (J/ m^2);

w_p = specific plastic work of fracture (J/ m^2);

L = the ligament length in the DENT specimen (m);

B = the thickness of the sample (m); and

β = the shape factor of the plastic zone, which is dependent on the geometry.

Substituting equations 2 and 3 in 1,

$$W_t = (w_e \times LB) + (w_p \times \beta L^2 B) \quad (4)$$

By dividing equation (4) by the cross-sectional area of the plastic zone (LB),

$$\frac{W_t}{LB} = w_t = w_e + w_p \beta LB \quad (5)$$

where,

w_t = specific total work of fracture (J/ m^2).

The specific total work of failure, w_t , versus the ligament length, L in equation (5), gives a straight line with slope and intercept on the w_t axis. The w_e helps to determine the CTOD and as a result fatigue cracking resistance can be predicted [56]:

$$\delta_t = \frac{w_e}{\sigma_n}$$

where,

δ_t = the approximate crack tip opening displacement parameter (m); and

σ_n = the net section stress or yield stress (N/m^2), determined from the 5 mm ligament length DENT specimens.

The CTOD parameter provides a high correlation with fatigue cracking distress. Thus it can be used to predict ductile fracture properties and fatigue cracking of both binders and mixtures [53].

2.7.3 Modified Pressure Aging Vessel Method LS-228

The modified PAV method is employed to accelerate aging of PAV in that the existing PAV method does not efficiently facilitate the prediction of fatigue and thermal cracking distress [57, 58, 59]. This test can be carried out using two methods. In the first method, the weight of the asphalt sample is reduced from 50 +/- 0.5 grams to 12.5 +/- 0.5 grams. In effect, the thickness of the film decreases from 3.2 mm to approximately 0.8 mm. In order to achieve the presence of moisture, one empty TFOT stainless steel pan is loaded with 50 grams of distilled water. In the second method, the duration of aging is increased from 20 hours to 40 hours. One empty TFOT

stainless steel pan is loaded with 50 grams of distilled water to achieve the presence of moisture but the standard film thickness is maintained [14]. The physical properties are then measured when aging is complete.

This improved method is efficient in distinguishing between lesser quality asphalts and superior quality asphalts in that the lesser quality asphalts are penalized during aging in the presence of moisture or in thinner films for longer times [15].

2.8 Dilatometric Test

This test is employed in the laboratory to determine the rate of physical hardening of the asphalt binder analogous to that of the extended BBR. This is achieved by measuring the change in volume of the asphalt binder isothermally. A dilatometer system is used to measure the change in volume of the asphalt binder at a constant temperature. The asphalt sample used is the PAV-aged sample. The dilatometer consists of a capillary tube attached to a ruler or a pressure transducer and an aluminium cell which contains the asphalt sample as well as silicone oil. During the test, the change in height of the silicone oil in the tube is measured with a ruler as the asphalt sample shrinks at a specified temperature and time. The height of the silicone oil can also be calculated from pressure measurements when the ruler is replaced with a pressure transducer [61, 62].

The dilatometric test is also used to gain an insight on crystallization of asphalt binders or the waxes within the binder using the Avrami theory. The Avrami theory is able to explain the isothermal crystallization kinetics of asphalt. In 1991, the Avrami equation was used by Pechenyi and Kuznetsov [60] to model volume contraction of asphalt. Based on the study conducted, Pechenyi and Kuznetsov [60] suggested that the nature of equilibrium formation of

asphalt cement is analogous to the nature of crystallisation of the asphalt. Below is the Avrami equation:

$$C_t = 1 - \exp(-Zt^n)$$

Where,

C_t is the degree of crystallization at time t ;

Z is the crystallization rate constant; and

n is the Avrami exponent which depends on the crystal dimension and time-dependence of nucleation. Z contains all the temperature dependent terms including nucleation density and linear growth rate.

The degree of crystallization can be determined by ratio of volumes in the dilatometer:

$$1 - C_t = \frac{V_t - V_\infty}{V_0 - V_\infty}$$

Where V_0 , V_∞ , and V_t are the volumes of the sample initially, at equilibrium, and after isothermal respectively keeping t constant. By plotting $\log\left(-\log\frac{V_t - V_\infty}{V_0 - V_\infty}\right)$ against $\log(t)$, the Avrami exponent can be determined from the slope of the line, and Z can be determined from the intercept [60].

Below is the dilatometric set-up:

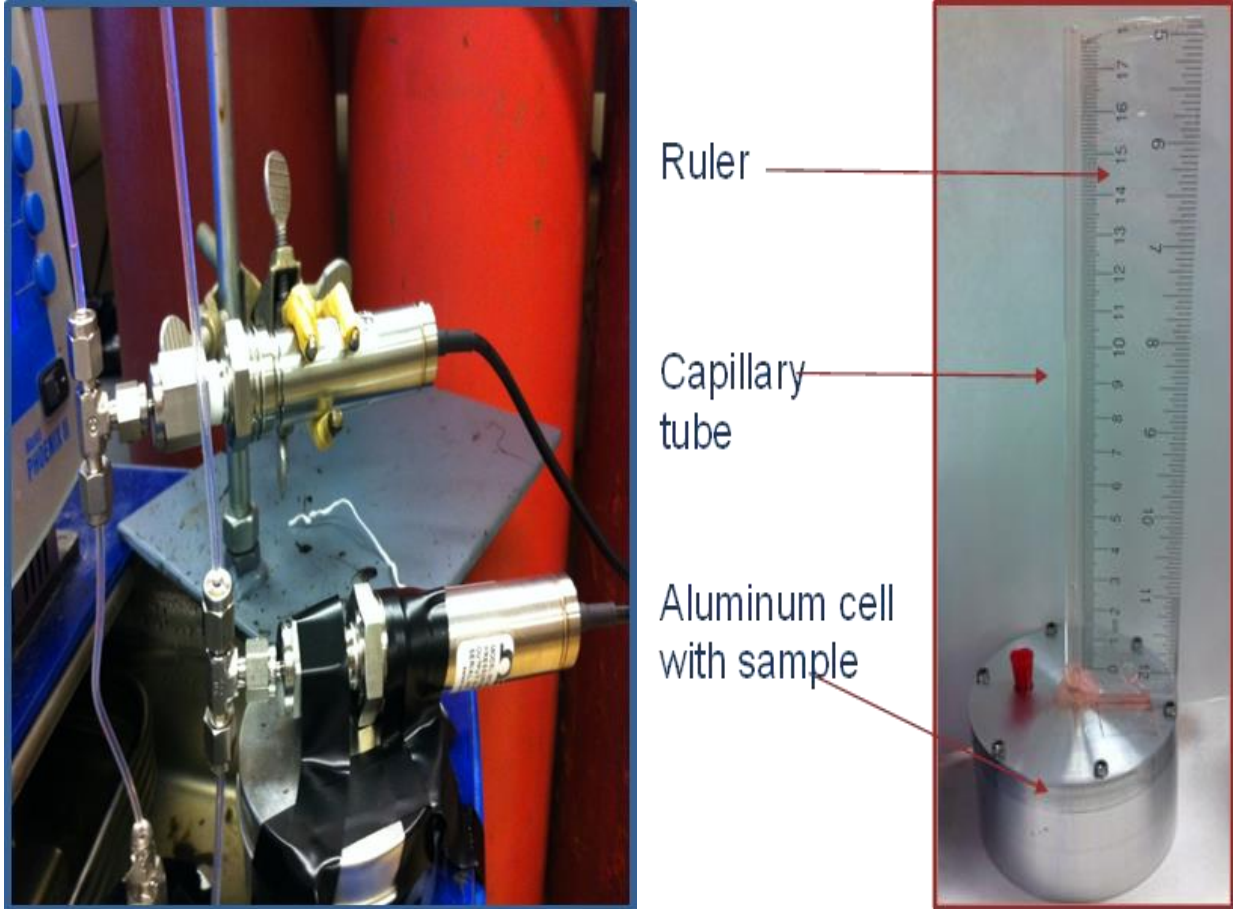


Figure 2.14: Dilatometric set-up

Chapter 3

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 Materials

In this study, the materials used were obtained from various commercial sources. The asphalt cements used included:

- Roofing asphalt flux (RAF) obtained from the Imperial Oil refinery in Nanticoke, Ontario; and
- Asphalt modified with waste engine oil (655-7) obtained during the construction of a pavement trial north of Timmins, Ontario.

The warm-mix additives employed were a siloxane-based surfactant of proprietary composition and an oxidized polyethylene wax.

The siloxane-based surfactant (TEGO[®] ADDIBIT) used is an organo-modified siloxane foam stabilizer obtained from Evonik Industries, New Jersey, in the United States of America [68]. This TEGO[®] ADDIBIT is characterized by its superior adhesion and wetting properties and high temperature stability. In effect, it allows a significant reduction of amine emissions during asphalt production and processing.

The oxidized polyethylene wax used was obtained from Westlake Chemicals of Houston, Texas in the United States of America [67]. Besides having a positive effect on the asphalt compaction, this additive is also reported to improve the high temperature rutting performance in service.

The grade and source information of the different asphalts employed are provided in Table 3.1. According to the AASHTO M320 specification, the high temperature PG grades are determined

based on the lowest temperature at which the following criteria are met: $G^*/\sin \delta = 1.00$ kPa for unaged binder or $G^*/\sin \delta = 2.20$ kPa for RTFO residue.

The intermediate temperature PG grades are reached at the temperature for which $G^*\sin \delta$ is less than 5,000 kPa for a PAV residue.

The low temperature PG grade is reached based on a creep stiffness that reaches 300 MPa and or an m-value that reaches 0.300 for PAV residue [9].

Table 3.1 Base Asphalt Cements Used in the Study

Binder	Source	PG, °C
RAF	Imperial Oil, Nanticoke, Ontario	51-34
655-7	MTO, Northern Ontario	52-34

3.2 Preparation of Modified Asphalt Binders

3.2.1 Mixing

Either 1 percent siloxane or 2 percent oxidized polyethylene wax warm-mix additives were added to the RAF and 655-7 respectively and mixed vigorously to homogeneity. After that, 1 percent siloxane and 2 percent siloxane was added to another set of gallons of 655-7 and RAF respectively and mixed to homogeneity. In addition, 2 and 4 percent oxidized polyethylene wax was then added to another set of gallons of RAF and mixed vigorously to homogeneity. Mixing of the base asphalts and the warm-mix additives was carried out at temperatures of between

150°C and 180°C. A summary of the samples prepared for this investigation is provided in Table 3.2.

Table 3.2 Summary of Samples Used in the Study

Sample	Additives	Additive Content (by weight), %	Additives Type
RAF	TEGO [®] ADDIBIT	1	siloxane
RAF	TEGO [®] ADDIBIT	2	siloxane
RAF	EE-2	2	oxidized polyethylene wax
RAF	EE-2	4	oxidized polyethylene wax
655-7	TEGO [®] ADDIBIT	1	siloxane
655-7	EE-2	2	oxidized polyethylene wax

3.3 Asphalt Cement Aging

Asphalt cement aging as proposed by the Strategic Highway Research Program (SHRP) has been useful in simulating both short-term and long-term aging of asphalt binders in the asphalt paving industry. Short-term aging which occurs during the HMA preparation is simulated by the Rolling Thin Film Oven (RTFO) test whereas long-term aging, which occurs after the HMA preparation and construction, is simulated by the Pressure Aging Vessel (PAV) test.

3.3.1 Rolling Thin Film Oven (RTFO) Test

The RTFO test method requires an electrically heated convection oven. This test was conducted by heating a thin film of asphalt binder in motion in the oven for 85 minutes at 163°C. The film in motion was prepared by measuring 35 grams of the asphalt binder sample into RTFO bottles

which were then placed in a circular metal carriage that rotates at a rate of 15 revolutions per minute within the oven. The air flow was maintained at 4,000 mL/min.

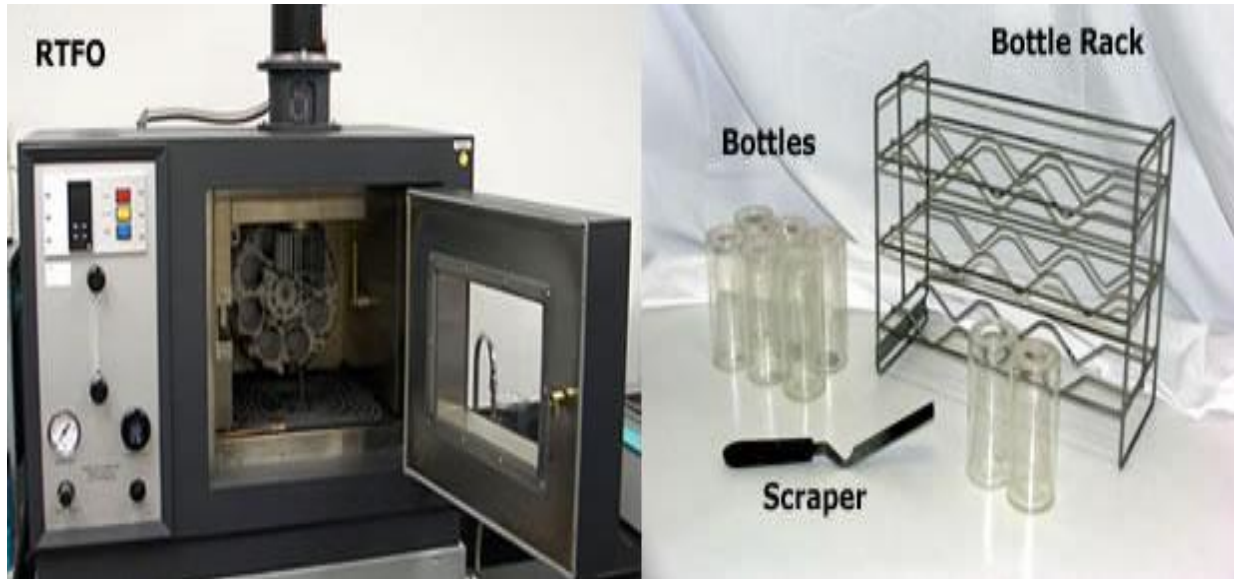


Figure 3.1: RTFO equipment [63].

3.3.2 Pressure Aging Vessel (PAV) Test

In this method, 50 grams of RTFO-aged binder was weighed and kept in several pans (50 grams per pan). The pans were arranged in a rack and placed in the PAV. The test was carried out at a temperature and pressure of 90°C and 2.08 MPa respectively for 20 hours. However, temperatures employed in this test are constant based on the climate as shown in Table 3.3.

Table 3.3 PAV Test Temperatures [64]

Temperature	Simulation
90°C	cold climate
100°C	moderate climate
110°C	hot climate

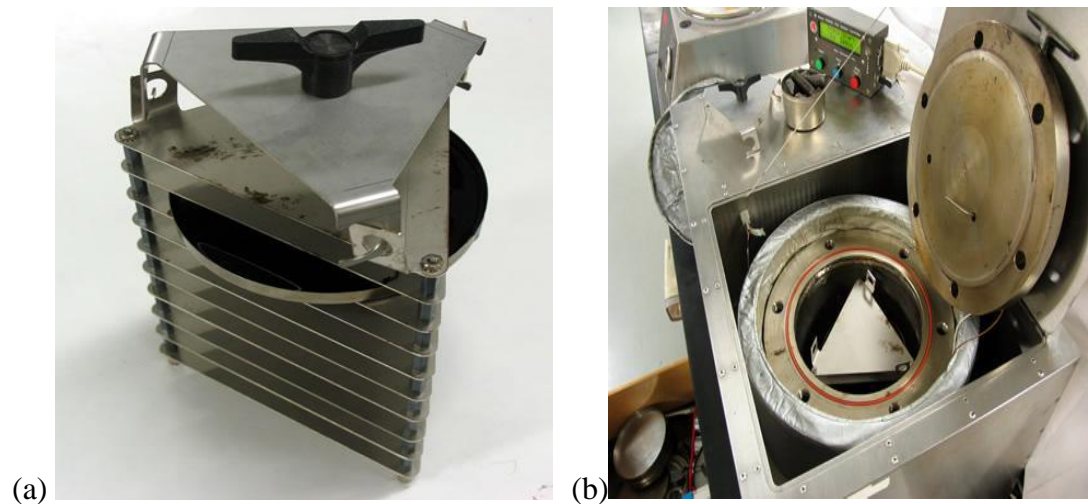


Figure 3.2 a) PAV rack with one pan of sample inserted, b) PAV viewed from the top with the rack inserted [65].

3.4 Dynamic Shear Rheometer (DSR) Method

The DSR is used to evaluate the fatigue cracking resistant of the asphalt pavement in service at intermediate temperatures as well as the rutting resistance of the asphalt binder at high temperatures. This test was conducted on unaged, RTFO-aged and PAV-aged samples. The

PAV-aged samples are used to find the intermediate temperature grade while RTFO-aged samples are used to find the high temperature grade. The sample was first heated at 163°C in an oven for 45-60 minutes. After, the samples were stirred to ensure uniformity and then poured into silicone molds of specified dimensions as shown in Figure 3.3(a). The instrument and the computer were then turned on and the proper geometry was selected as shown in Table 3.5. Table 3.4 shows the DSR test parameters.

Table 3.4: DSR Test Parameters [55]

Test Parameter	Value
Total test time	2 hours
Soak period at each temperature	10 minutes
Measurement period	10 seconds
Temperature range	-10°C to 82°C
Oscillation frequency	10 rad/s
Shear strain	0.10 percent

Table 3.5: DSR Test Geometry [1]

Asphalt Condition	Spindle Geometry	Measuring Gap
Unaged	25 mm	1 mm
RTFO-aged	25 mm	1 mm
PAV-aged	8 mm	2 mm

The gap between the moveable plate and the fixed plate was then zeroed by the instrument. After zeroing the gap, the trimming temperature was set to 46°C and the sample was placed on the fixed plate. The DSR software was then used to move the plates together until the gap between the plates was equal to the test gap plus 0.05 mm. Excess binder oozing out of the plates due to compression was removed using a heated trimming tool as shown in Figure 3.3(b). The test plates were then moved to the desired testing gap. The test was initiated only after the specimen had been at the desired temperature for a minimum of 10 minutes. A specific target torque was used by the DSR software to rotate the upper plate based on the material being tested; such as unaged binder, RTFO residue and PAV residue. The DSR was used to condition the sample at a frequency of 10 rad/sec for 10 cycles. However, the DSR takes measurements over the next 10 cycles and the prominent measurements involved are the complex shear modulus (G^*) and the phase angle (δ).

According to the AASHTO M320 specification, the high temperature PG grades are evaluated based on the following values:

- $G^*/\sin \delta \geq 1.00$ kPa for unaged binders; and
- $G^*/\sin \delta \geq 2.20$ kPa for RTFO-aged binders.

For intermediate temperature PG grades, $G^*\sin \delta$ should be less than 5,000 kPa as per the AASHTO M320 specification [9].



Figure 3.3 (A) DSR sample molds and (B) DSR test equipment [66].

3.5 Bending Beam Rheometer (BBR) Method

The regular BBR test was carried out using PAV-aged samples to simulate the thermal cracking of the pavement in service. In this test, the asphalt binder was heated for about 45-60 minutes in an oven at 163°C. The binder was gently stirred after taking it out of the oven to get rid of any air bubbles present. Next, the binder was poured into silicone molds which shaped the binder into beams. The asphalt binder was then left to cool for 45-60 minutes in the mold. The sample was trimmed down with a hot trimming tool after it had sufficiently cooled, to remove excess asphalt

on top of the beam. A total of 12 asphalt beams were prepared for each analysis. The asphalt beams were conditioned for one hour at -8°C and -18°C in a cooling bath containing pure ethanol. The asphalt beams were tested at -8°C and -18°C . The test was conducted by loading the beam in three-point bending for a period of 240 seconds with a load of approximately 980 mN. The graph of load and deflection versus time was then plotted continuously and automatically by the rheometer software. Figure 3.5 illustrates the deflection of asphalt beam in a typical BBR test. The creep stiffness (S) and the creep rate (m) were then calculated at a loading time of 60 seconds.

According to the AASHTO M320 standard, the creep stiffness can have a maximum value of 300 MPa and the creep rate (m-value) can have a minimum value of 0.3 [9].

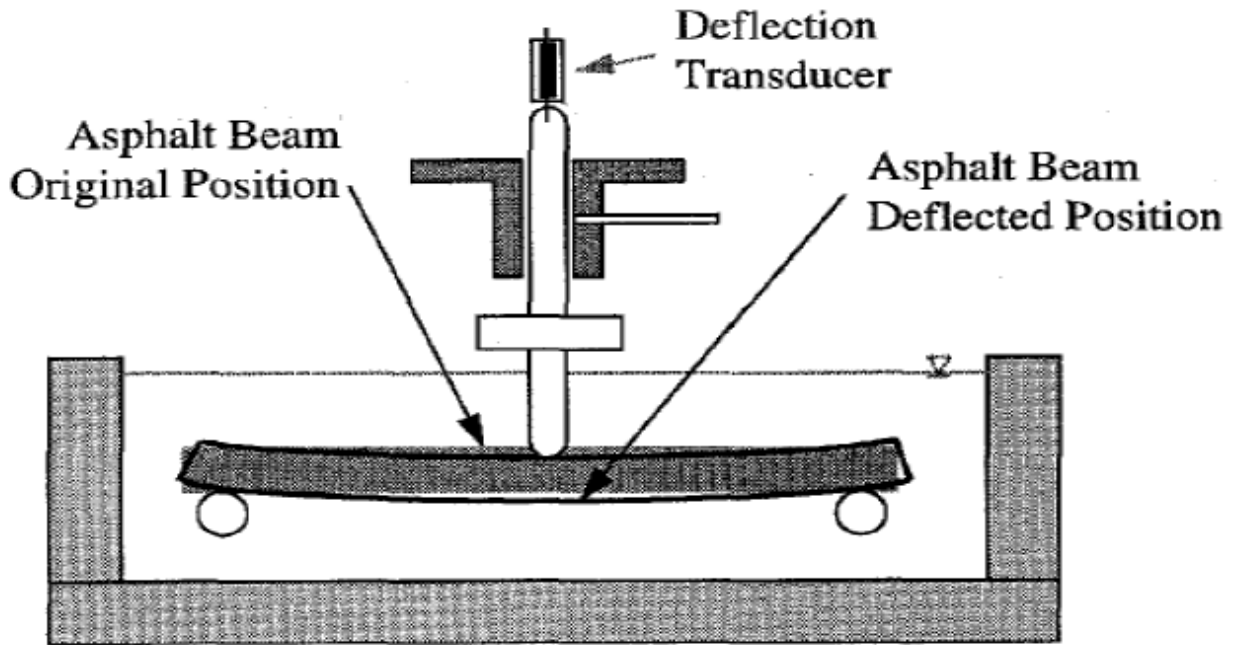


Figure 3.4: Deflected asphalt beam on bending beam test [45].

3.6 Extended Bending Beam Rheometer (eBBR) Method LS-308

The extended Bending Beam Rheometer (eBBR) test is conducted to determine the asphalt binder's ability to meet the low temperature performance grade after undergoing a physical aging process over time [12]. The critical cracking temperature, which is the temperature at which the maximum stress is greater than the material strength, is determined [8]. In this test, 12 beams were prepared. Six of the beams were conditioned at -18°C and the remaining 6 beams were conditioned at -8°C in a cooling bath before testing at -8°C and -18°C . The duration of conditioning at both temperatures was 1 hour, 24 hours, and 72 hours. The temperatures at -8°C and -18°C were chosen so that a pass or fail temperature for the asphalt binder could be determined.

In order to determine the exact grades according to AASHTO M320 criteria both pass and fail temperatures were employed and the continuous (exact) grade was obtained by means of interpolation. The interpolation involves plotting the grade on a semi-logarithmic scale [46]. After each temperature conditioning period, the grade temperature and the subsequent grade losses were calculated. The worst grade loss was then evaluated by finding the difference between the warmest and the coldest limiting temperature (where S reaches 300 MPa and the m -value reaches 0.3) [52]. Thus this method helps in attaining a high degree of confidence to avoid low temperature cracking [53].

3.7 Double-Edge Notched Tension (DENT) Test Method LS-299

This test method is used to determine the essential work of failure, the plastic work of failure, and an approximate critical crack tip opening displacement (CTOD) of the asphalt binder, at a

specified temperature and rate of loading after thermal conditioning [13]. In this test, the sample was heated in an oven at 163°C until it became liquid enough to pour into brass molds of different ligament length assembled on brass plates. In order to prevent the test material from getting stuck on the mould, a thin plastic sheet and a thin layer of talc powder with glycerol was used on the base plates and brass molds. The sample was stirred after taking it out of the oven to ensure homogeneity and then poured in the molds as shown in Figure 3.5.



Figure 3.5 DENT sample preparation [11].

The ligament lengths between the notches are 5 mm, 10 mm and 15 mm. The samples were allowed to cool for an hour. After cooling, the excess material was trimmed with a hot trimming tool to make the molds level full. Prior to the preparation of the molds and the heating of the sample, the water bath was set at 15°C. The samples were conditioned in the water bath at 15°C

for 3 hours before testing. During testing, the binder was pulled until failure occurred in the water bath as shown in Figure 3.6 and the necessary parameters were recorded. This was carried out using the DENT software.

To calculate the essential work of failure, the plastic work of failure, and the CTOD parameters, an excel spreadsheet was used. The test was repeated for each ligament length for reproducibility.

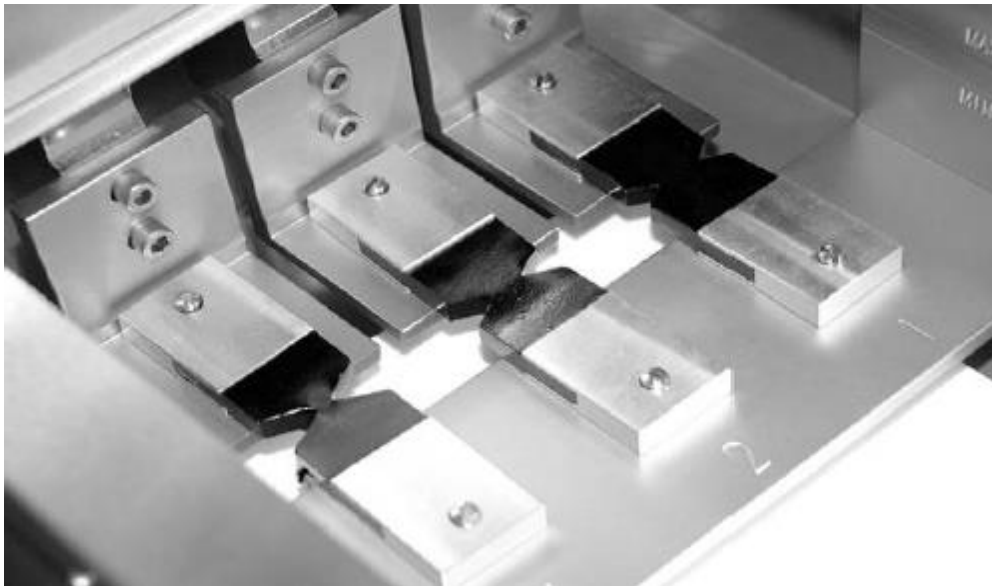


Figure 3.6: Double-Edge-Notched Tension (DENT) test set up [6].

3.8 Dilatometric Test

A dilatometer system was used to measure the changes in volume of the asphalt binders. Samples of approximately 35 g were poured in silicone molds and cooled for 45 minutes at room temperature. The samples were put in a cooling bath at -10°C for about 10 minutes before being placed in the dilatometer. The dilatometer was filled with around 25 ml of silicone oil, and the

system was put in an air circulating cooler at -8°C . Approximately 1-3 ml of silicone oil was added after 30 minutes.

The height of the column of silicone oil was recorded at 1.5, 2, 3, 5, 7, 24, 48, and 72 hours. The height of the column at 1.5 hours was used as a reference point to allow the silicone oil to reach equilibrium, and to account for an induction time. The density of the asphalt was assumed to be 1 g/ml at 1.5 hours.

$\log(-\ln(\text{fractional volume}))$ was plotted against $\log(\text{time})$ to determine the equilibrium volume of the binders. The fractional volume was calculated as the volume at time t divided by the volume at 1.5 hours. The $\log(-\log\frac{V_t-V_{\infty}}{V_o-V_{\infty}})$ was plotted against $\log(t)$. The Avrami exponent n was determined from the slope of the line, and the rate constant Z was found using the intercept. The figure below shows the dilatometric set-up.

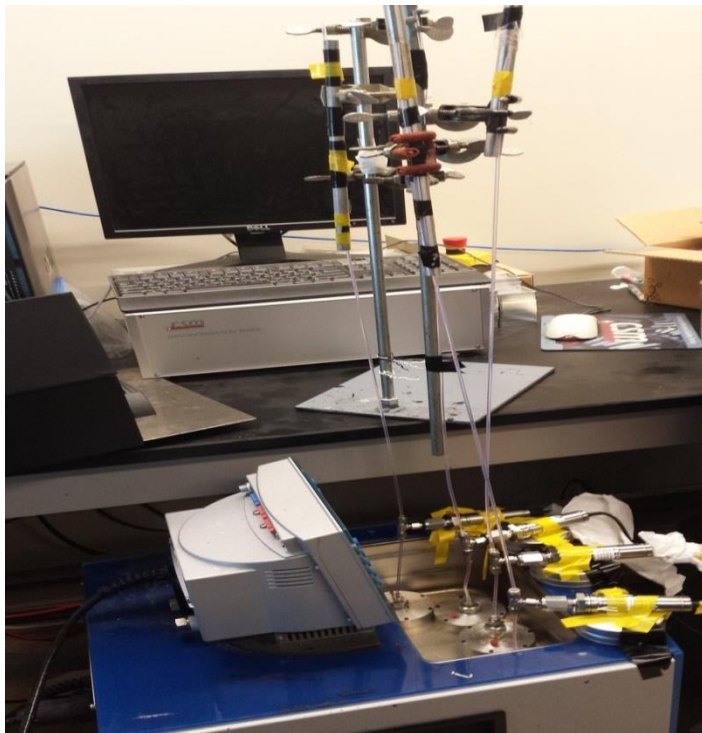


Figure 3.7: Dilatometric set-up.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Dynamic Shear Rheometer Analysis

4.1.1 High Temperature Grading

The modified samples were all aged in the rolling thin film oven (RTFO) and pressure aging vessel (PAV) according to standard protocols, prior to any physical property measurement. In order to determine the high temperature grades, all the unaged and RTFO residues were tested using a TA Instruments AR2000ex DSR. Figure 4.1 shows the high temperature performance grades (PG) for all the modified samples.

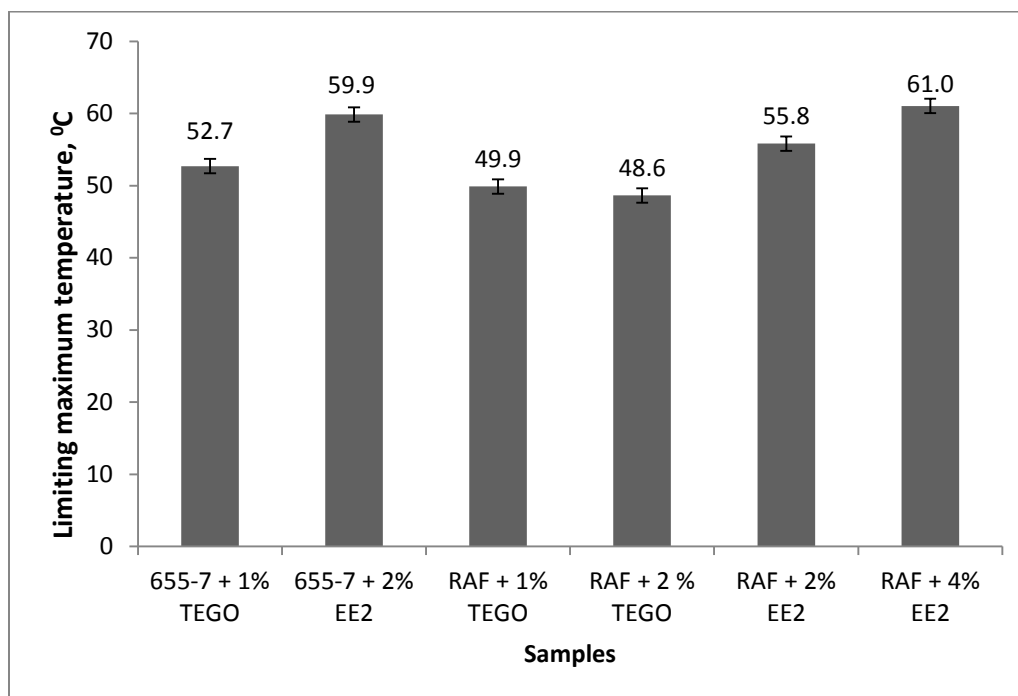


Figure 4.1: High temperature grades for RAF and 655-7 with their various additive compositions.

The limiting maximum temperature PG was assessed based on the rutting resistance factor ($G^*/\sin \delta$). For the unaged samples, $G^*/\sin \delta$ should be a minimum of 1.0 kPa and for the RTFO aged samples, $G^*/\sin \delta$ should be a minimum of 2.20 kPa. The higher value of limiting maximum temperature grades of RAF + 4 % oxidised polyethylene wax and 655-7 + 2 % oxidised polyethylene wax indicate that they have high resistance to rutting at higher temperature and would show good performance at high temperature climatic regions as compared to the other modified binders. This high resistance behaviour is due to the presence of high content of the elastic component and low content of the viscous component in RAF + 4 % oxidised polyethylene wax and 655-7 + 2 % oxidised polyethylene wax. In addition, at high temperatures, these types of binders would be stiff and durable. RAF + 1 % siloxane and RAF + 2 % siloxane showed low values of limiting maximum temperature comparatively. This implies that, the binders have high contents of the viscous component.

The presence of the additives influenced the high temperature grades of the asphalt. The oxidised polythene wax increased the elastic component of both the superior quality asphalt (RAF) and the inferior quality asphalt (655-7) whereas the siloxane increased the viscous component appreciably. Thus, the oxidised polythene wax improved the high temperature grade of 655-7 asphalt by 7°C as well as RAF by 11°C [69].

4.1.2 Intermediate Temperature Grading

The intermediate grades were determined for the PAV residues according to standard protocols using the DSR. According to the AASHTO M320 specification, the intermediate temperature PG grade is determined by the temperature at which $G^* \cdot \sin \delta$ is less than 5000 kPa for a PAV

residue [9]. Figure 4.2 shows the intermediate temperature performance grades for all the modified samples.

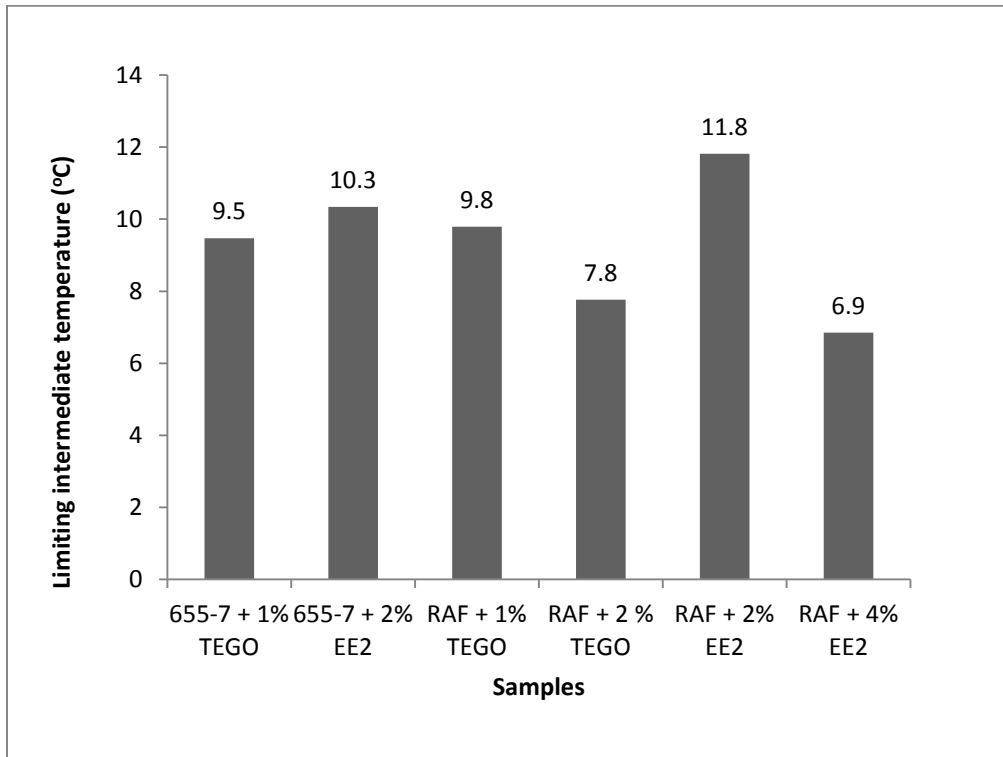


Figure 4.2: Intermediate temperature grades for RAF and 655-7 with their various additive compositions.

The intermediate Superpave grades provide a measure of resistance to fatigue cracking for asphalt binders. From the results it can be observed that RAF + 4 % oxidised polyethylene wax has the lowest intermediate temperature grade which implies that it is less susceptible to fatigue cracking as compared to the other modified binders. However, it must be noted that the intermediate Superpave® grades do not accurately correlate with fatigue cracking distress as compared to the DENT test where the CTOD is able to accurately assess fatigue cracking resistance of the asphalt binders since it has a high correlation with fatigue cracking.

4.1.3 Grade Span

The Superpave grades and grade span for the modified asphalt binders are summarized in the table below.

Table 4.1: Superpave grades and grade span for RAF and 655-7 with their various additive compositions

Samples	High Grades (T_{\max}) (°C)	Intermediate Grades (T_{int}) (°C)	Low Grades (T_{\min}) (°C)	Grade Span (°C)
655-7 + 1 % TEGO	52.7	9.5	-31	83.7
655-7 + 2 % EE2	59.9	10.3	-30	89.9
RAF + 1 % TEGO	49.9	9.8	-35	84.9
RAF + 2 % TEGO	48.6	7.8	-33	81.6
RAF + 2 % EE2	55.8	11.8	-33	88.8
RAF + 4 % EE2	61.0	6.9	-31	92.0

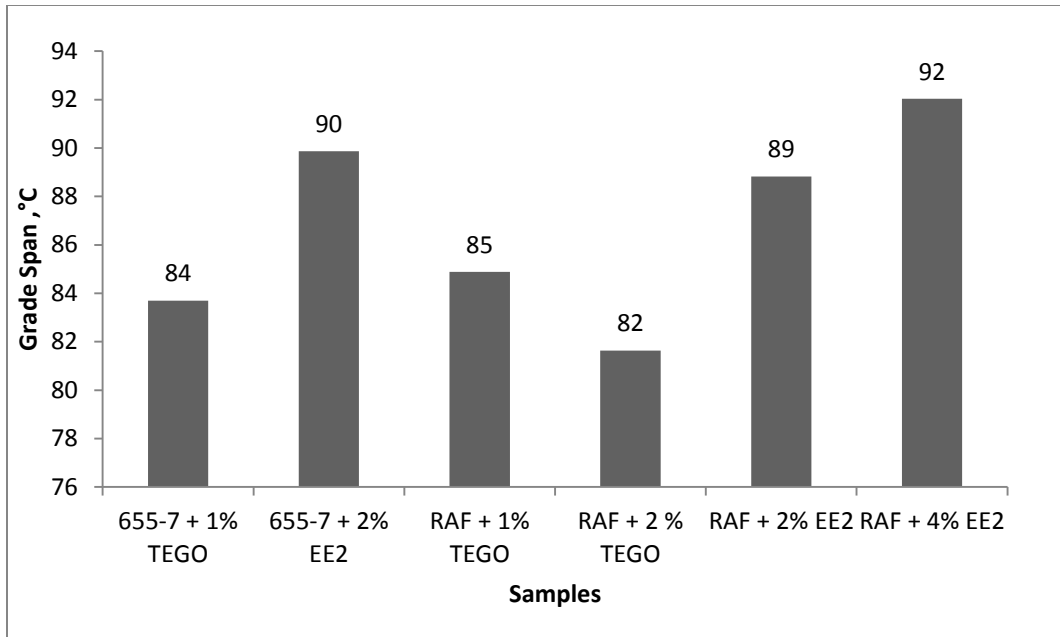


Figure 4.3: Grade span for RAF and 655-7 with their various additive compositions

The grade span can be explained as the difference of high temperature grade and low temperature grade of a particular binder. A high grade span implies that the asphalt binder can be used at a climatic region of wide range of temperatures and a low grade span implies that the asphalt binder would perform poorly at a climatic region of wide range of temperatures.

The results in Figure 4.3 shows that RAF + 4 % oxidised polyethylene wax and 655-7 + 2 % oxidised polyethylene wax have higher grade spans comparatively so should perform better at a climatic region of wide range of temperatures. Nevertheless, the remaining samples have reasonably high grade spans so would not perform badly.

4.1.4 Black Space Diagrams

A black space diagram is a graphical representation which determines the phase angle with the complex modulus at different temperatures after the DSR test. The Black space diagram is able to distinguish between a single phase asphalt binder with a homogenous composition and a

multiple phase asphalt binder with a heterogeneous composition. Thus, the rheological properties of the asphalt binder are characterised using the Black space diagram. Asphalt binders with a single phase system are referred to as rheologically simple binders whereas asphalt binders which have two or more phase systems are referred to as rheologically complex binders. Black space diagrams are employed to determine whether an asphalt binder is rheologically simple or complex. A rheologically simple asphalt binder will not show any anomalous behaviour; and will also have a smooth progression of curves at different temperatures in a Black space diagram. This implies that the binder would have a special pattern in the diagram. However, a rheologically complex binder would rather show a discontinuity in the progression of curves at different temperatures. This implies that the asphalt binder would have phase separated. Rheologically simple binders are easily predicted since their behaviour is typical of a conventional viscoelastic material [11]. On the other hand, rheologically complex binders are difficult to predict in that their behaviour does not follow that of a conventional viscoelastic material [11]. The figures below display the Black space diagrams at both high and low temperatures of the modified asphalt binders.

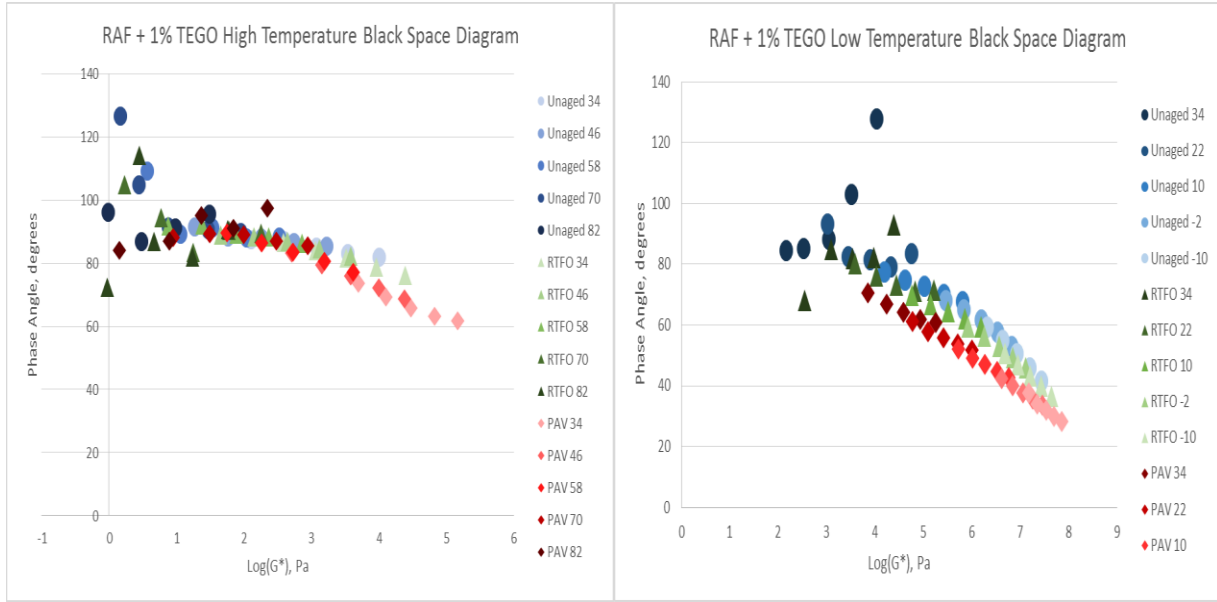


Figure 4.4: Black space diagrams of RAF with 1 % siloxane at both high and low temperatures

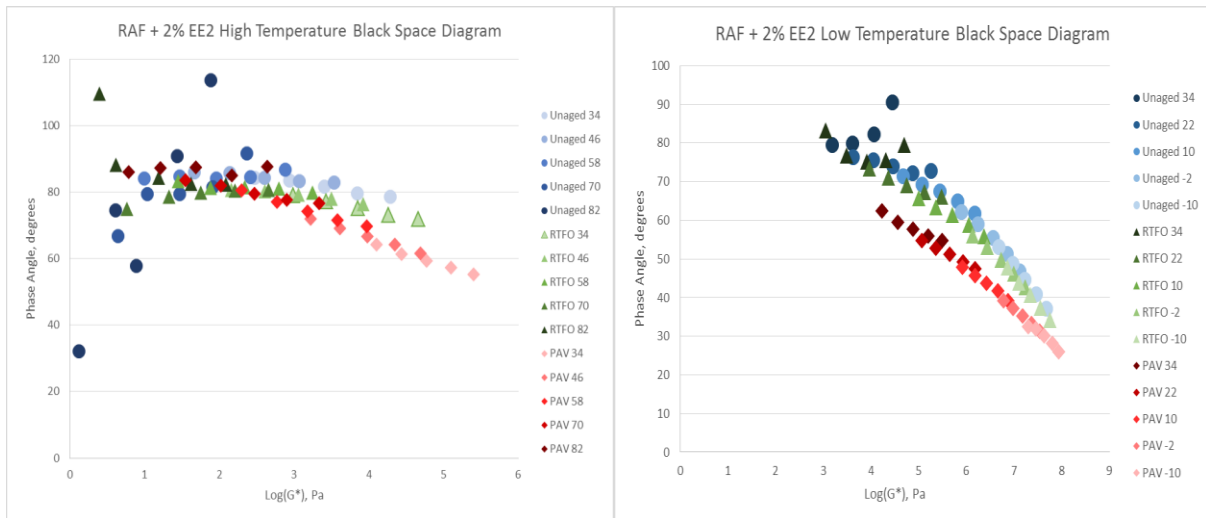


Figure 4.5: Black space diagrams of RAF with 2 % oxidised polyethylene wax at both high and low temperatures

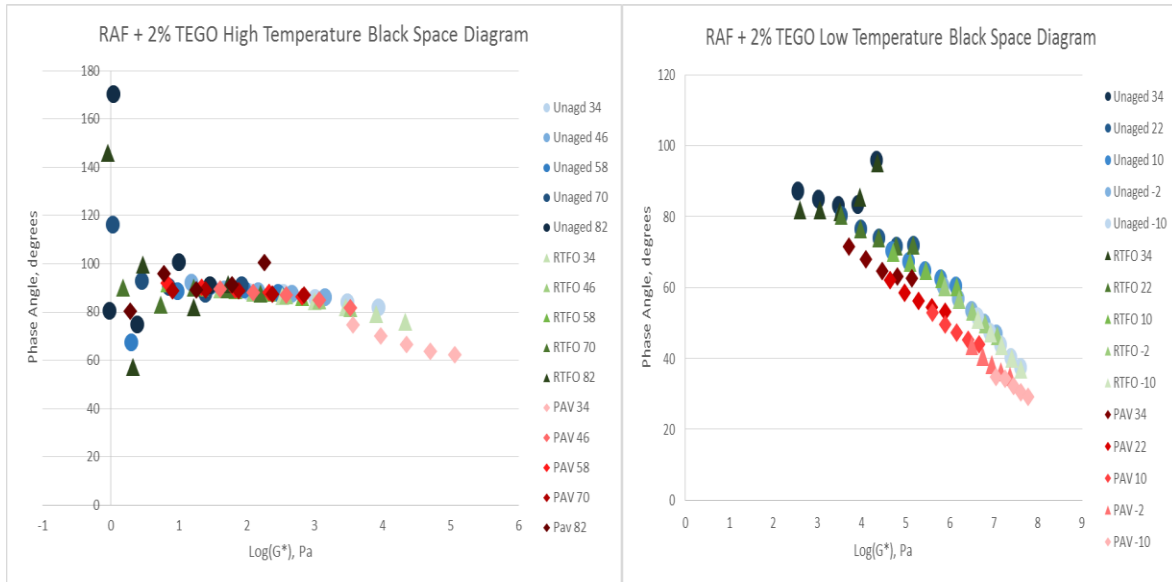


Figure 4.6: Black space diagrams of RAF with 2 % siloxane at both high and low temperatures

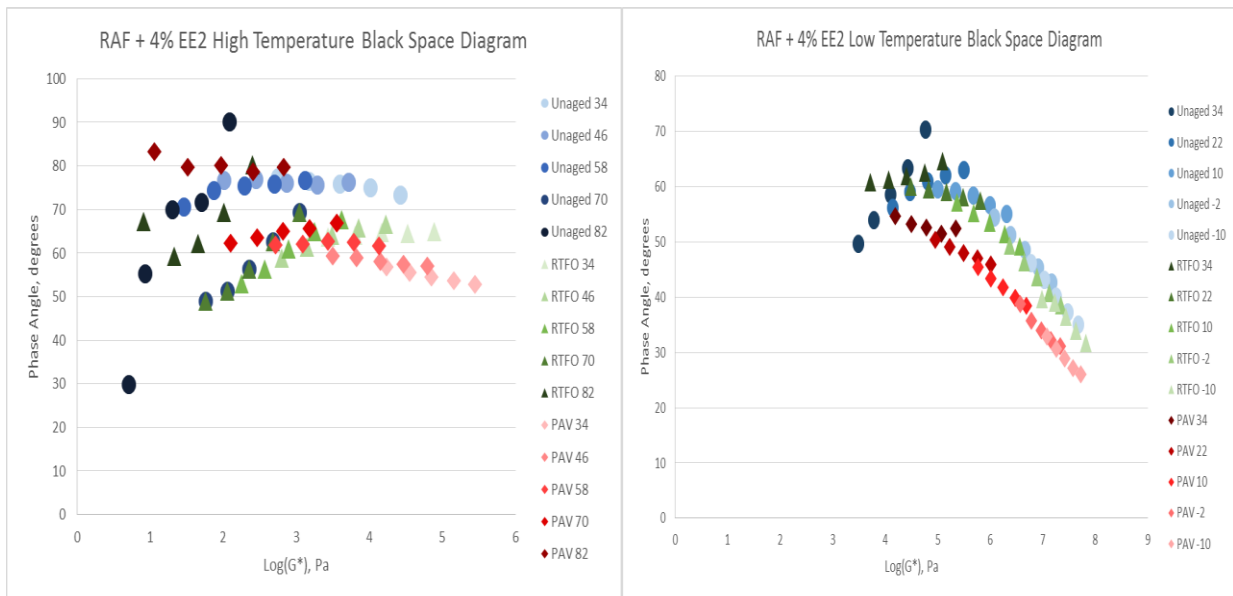


Figure 4.7: Black space diagrams of RAF with 4 % oxidised polyethylene wax at both high and low temperatures

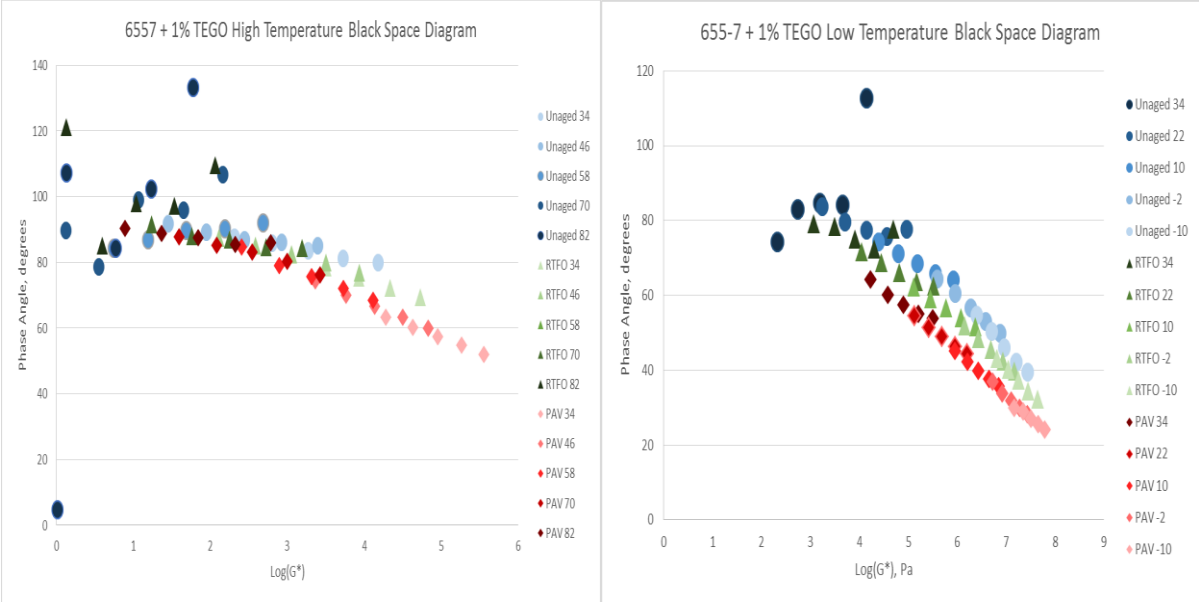


Figure 4.8: Black space diagram of 655-7 with 1 % siloxane at both high and low temperatures

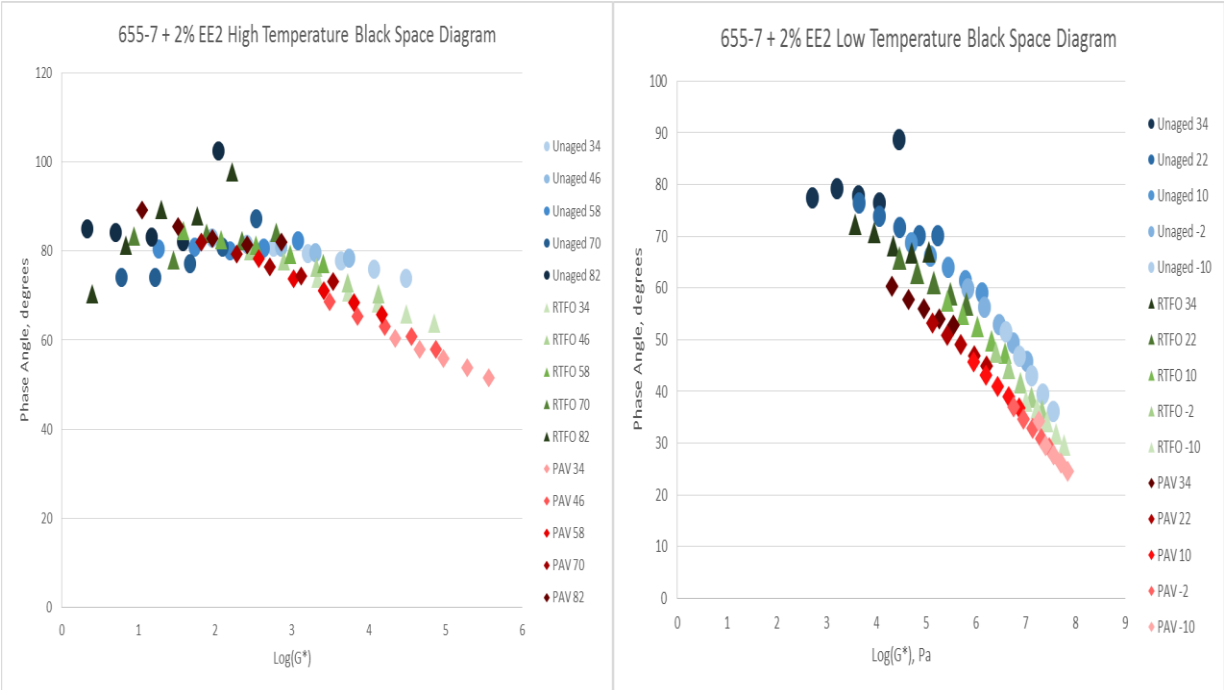


Figure 4.9: Black space diagram of 655-7 with 2 % oxidised polyethylene wax at both high and low temperatures

By observing the Black space diagram for unaged, RTFO-aged and PAV-aged samples, it is seen that RAF with 1 % and 2 % siloxane is rheologically simple at both high and low temperatures. Also, it can be noticed in the Black space diagram that, RAF with 2 % and 4 % oxidised polyethylene wax and 655-7 with 1 % siloxane and 2 % oxidised polyethylene wax showed rheologically simple behaviour at low temperature and deviated from the rheologically simple behaviour at high temperature. This might be due to the phase separation at higher temperature. Also, the presence of the oxidised polyethylene wax changed the asphalt to a gel-type state at high temperature which caused the phase separation. However, the phase separation of 655-7 with 1 % siloxane might be due to the poor stability of the asphaltene.

4.2 Regular BBR Analysis

The regular BBR grades for the modified asphalt samples were determined according to AASHTO M320 standard test method. The test was carried out by conditioning the asphalt beams at -8°C and -18°C prior to testing at both temperatures. The creep stiffness ($S(t)$) and slope of the creep stiffness master curve ($m(t)$ -value) were determined using three point bending.

4.2.1 Low Temperature Grades

According to the AASHTO M320 specification, the low temperature PG grades are decided based on the limiting temperature where stiffness = 300 MPa or m -value = 0.300 for the PAV residue and the warmest of these two temperatures is used as a minimum performance grade temperature of the asphalt binder [52]. A higher m -value indicates that the asphalt binder creeps at a faster rate to reduce the thermal stress and this is ideal to reduce low temperature cracking [9]. The results are summarized in Figure 4.10.

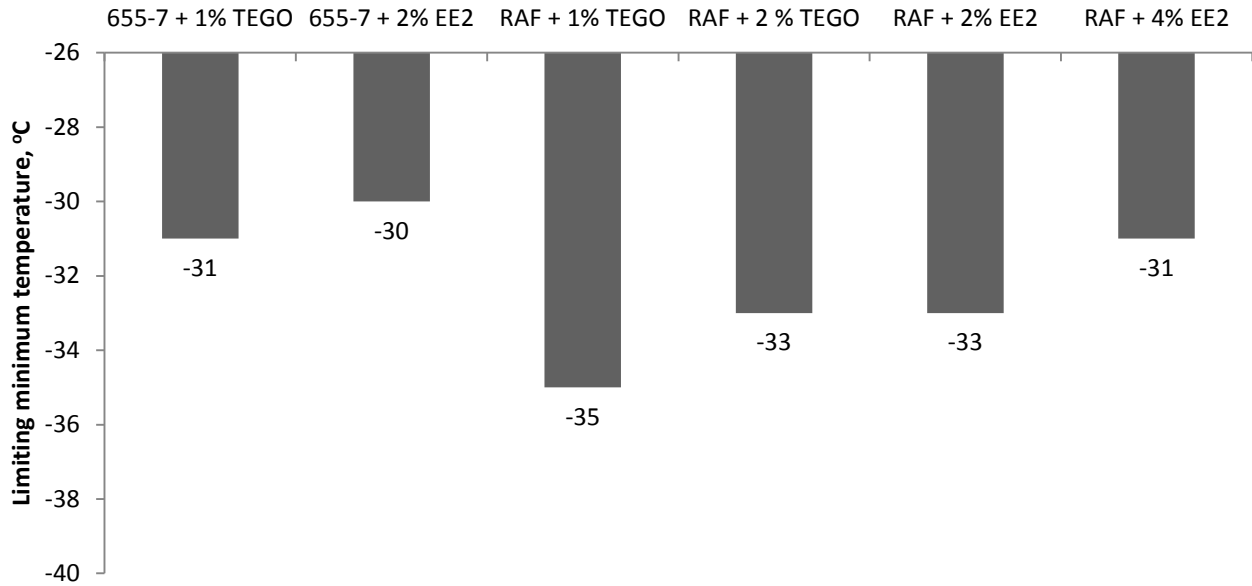


Figure 4.10: Low temperature grades of RAF and 655-7 with their various additive compositions.

According to the Superpave grading method, RAF is PG-34 as well as 655-7[1, 69]. As shown in Figure 4.10, the RAF samples modified with siloxane did not show any significant change in grades because the siloxane maintained the sol-type state of the asphalt; as a result the asphalt was compliant and less elastic. However, RAF modified with 4 % oxidised polyethylene wax shows a decrease in grade of 3°C as compared to the RAF modified with 2 % oxidised polyethylene wax which shows no significant change in grade. This can be attributed to crystallization of the wax due to the increased wax content of the asphalt. In effect, the binder becomes very stiff and susceptible to thermal cracking. Furthermore it is seen in Figure 4.10 that the 655-7 samples with siloxane and oxidised polyethylene wax additives respectively show a decrease in grade. This implies the asphalt binder was not compliant regardless of the additives added. The results shown are however elaborated by the extended BBR analysis which accurately evaluates the physical hardening of asphalt binders.

4.2.2 Bending Beam Rheometer Grading of Modified PAV residue

The findings below were obtained by the staff at Imperial Oil Research Center in Sarnia, Ontario, Canada, in relation to the study of the effect of warm-mix additives on two different asphalt cements as well as the chemical aging process. Table 4.2 shows the summary of modified asphalt binders involved.

Table 4.2: Summary of modified asphalt binders involved.

Sample	Binder type	Additives	Additive content (by weight), %
A	RAF	EE-2	2
B	RAF	EE-2	4
C	RAF	TEGO [®] ADDIBIT	1
D	RAF	TEGO [®] ADDIBIT	2
E	655-7	SASOBIT E-1	1
F	655-7	SASOBIT E-1	3
G	655-7	REDISET LQ 1102	1
H	655-7	REDISET-WMX 8017A	1
I	655-7	SONNEWARM	1
J	655-7	EVOTHERM	1
K	655-7	EE-2	2
L	655-7	TEGO [®] ADDIBIT	1

According to LS-228 protocol, the PAV condition was altered by changing the PAV conditioning time from 20 hours to 40 hours while maintaining the weight of the asphalt cement at 50 g, to allow more time for aging to occur in order to verify its level of efficiency in the accurate prediction of the effect of physical aging on the performance of the asphalt binder. Another way of aging was carried out by decreasing the sample weight from 50 g to 12.5 g while maintaining the test time at 20 hours to observe the effect of reduction of sample size on the aging process. The results of these tests are summarised in Figure 4.11 and Figure 4.12.

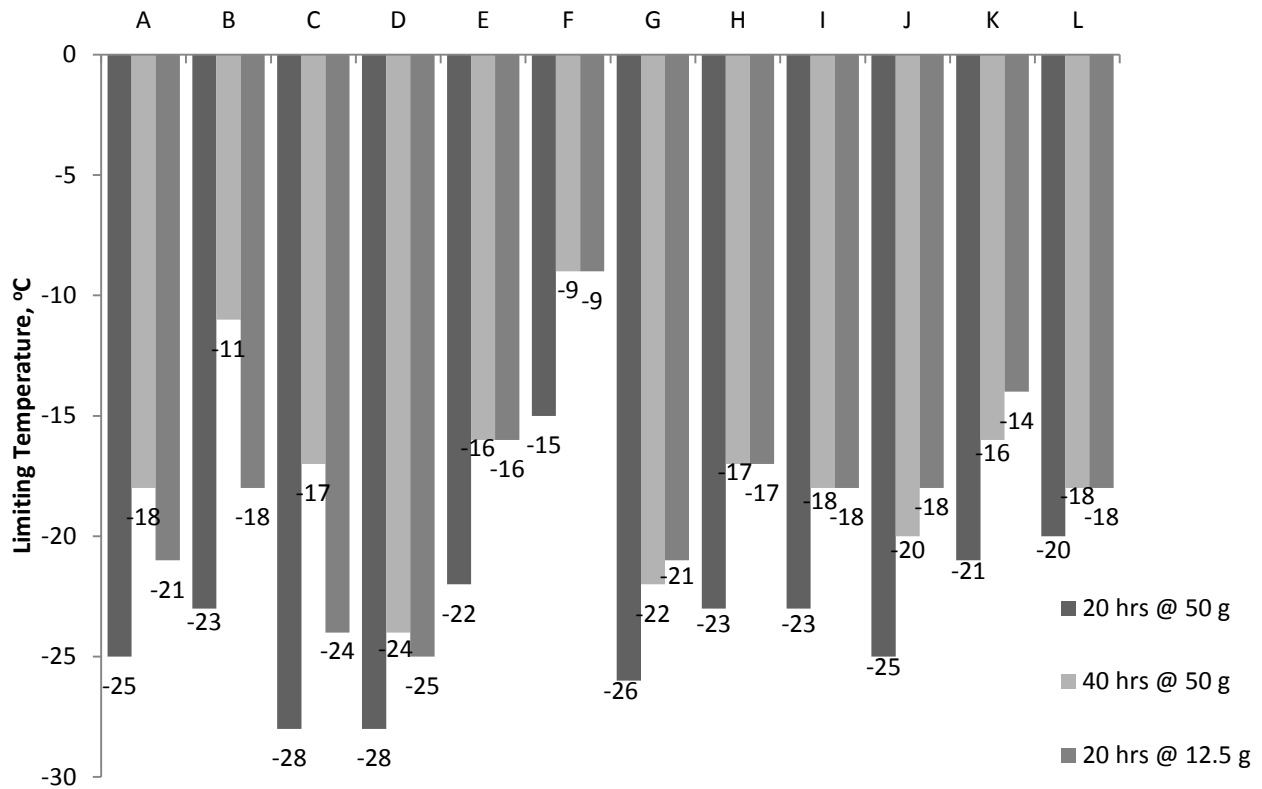


Figure 4.11: Limiting grade temperatures at different PAV aging conditions for RAF and 655-7 with their various additive compositions.

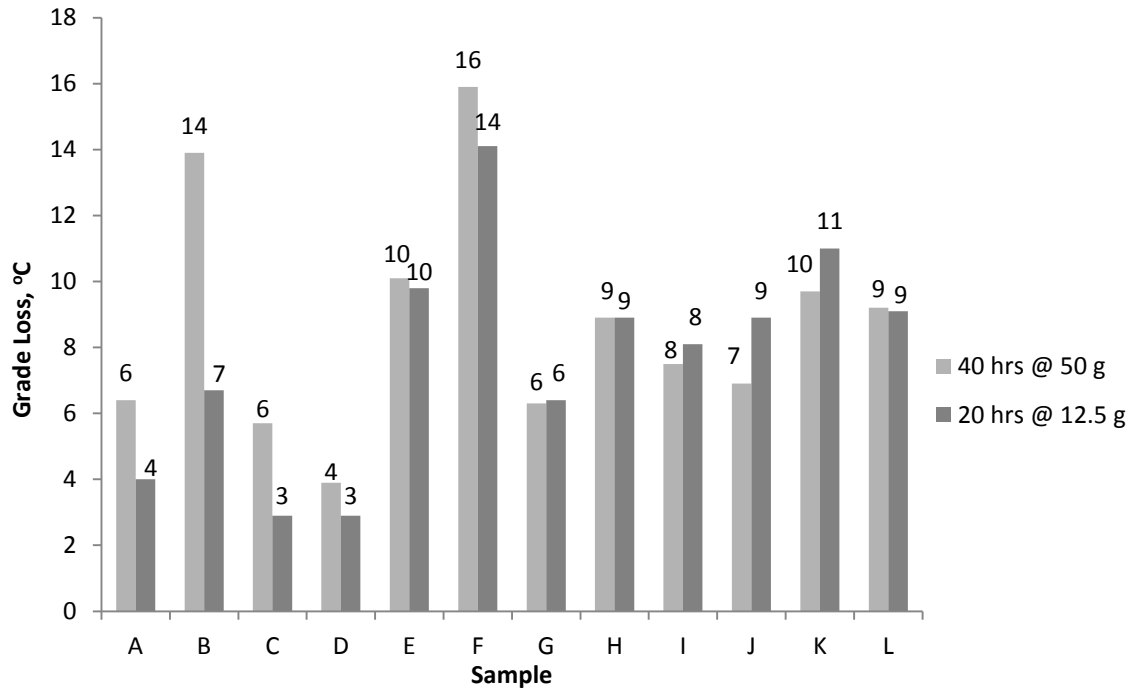


Figure 4.12: Grade loss between PAV (50 g @ 40 hr) and PAV (12.5 g @ 20 hr) for RAF and 655-7 with their various additive compositions.

The results show that by extending the PAV aging period from 20 hours to 40 hours, and by altering the weight of the asphalt cement for the test from 50 g to 12.5 g, a phenomenal aging is observed in the asphalt binders. The limiting temperatures of all the PAV tests at 40 hours as well as at 20 hours (12.5 g) are all warmer than their respective minimum performance grade temperatures. Also, their grade losses were higher as compared to the 20 hours at 50 g. In addition, it can be observed in Figure 4.12 that at 40 hours and 20 hours (12.5 g), all the 655-7 samples with their various additive compositions have higher grade losses as compared to the RAF with siloxane additive; which could be related to the presence of the waste engine oil in the 655-7 binder. This indicates low durability and these samples would show premature and excessive cracking. However, RAF with oxidised polyethylene wax showed high grade loss at 40 hours and 20 hours (12.5 g), due to the crystallized wax in the asphalt binder such that oxidative

hardening was increased. This also indicates that the asphalt binder is susceptible to premature cracking. Thus, by altering the conditions governing the standard PAV aging method, there is a higher probability to predict accurately the effect of physical aging on the performance of the asphalt binder in the pavement at low temperatures.

4.3 Extended BBR Analysis

The asphalt samples were further tested according to MTO standard test methods (LS-308) after regular BBR test. The effect of various additives on the two different asphalt binders was investigated for physical hardening over long periods of time. LS-308 conditions at 10°C and 20°C above pavement design temperature for periods of 1 hr, 24 hrs and 72 hrs simulated the effect of extended exposure to two different cold temperatures [12]. The LS-308 method provides a great improvement over AASHTO M320 specification since it is able to accurately account for the durability of the asphalt binder at extremely low temperatures.

4.3.1 Low Temperature Grades

The asphalt binders were conditioned for 1 hr, 24 hrs and 72 hrs at isothermal conditions, that is, -8°C and -18°C. The limiting temperatures where $m(60) = 0.3$ and $S(60) = 300$ MPa were determined according to AASHTO M320 standard protocol and the warmest temperature among the two limiting temperatures gave the minimum performance grade temperature. The grade losses were then also determined to measure the durability of the binders. The following Figure displays the low temperature grades according to Ontario's extended BBR protocol [12].

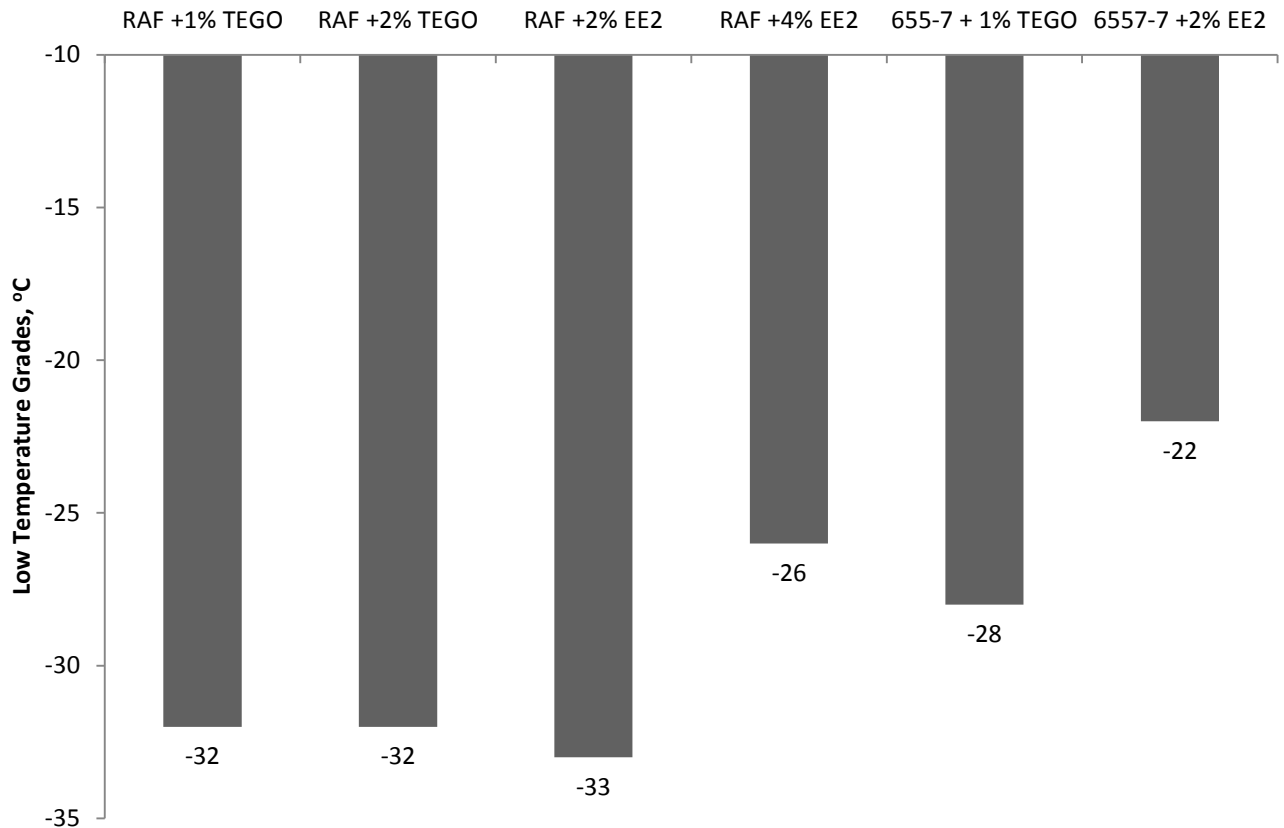


Figure 4.13: Low temperature grades of RAF and 655-7 with their various additive compositions.

As shown in Figure 4.13, the RAF samples modified with siloxane did not show any significant change in grades because the siloxane maintained the asphaltene colloidal stability; as a result, the asphalt was compliant and less elastic. However, the RAF modified with 4% oxidised polyethylene wax shows a significant decrease in grade of 8°C as compared to the RAF modified with 2% oxidised polyethylene wax which shows no significant change in grade. This can be attributed to the increased wax content of the asphalt which immobilizes the amorphous state due to crystallisation of the wax. In effect, the physical hardening rate of the binder increased and the binder turned very stiff. Furthermore, it is seen in Figure 4.13 that the 655-7 samples with siloxane and oxidised polyethylene wax additives display a significant decrease in grade which is

worse than that of the regular BBR grades. The 655-7 sample with siloxane additive had a decrease in grade because the asphaltene colloidal stability of the 655-7 binder is very bad. In effect, the binder had a volume collapse and the relaxation ability of the binder was poor. However, the worst low temperature grade of the 655-7 binder with oxidised polyethylene wax additive could be attributed to the crystallisation of the wax as well as the physical hardening of the binder. As a result the binder was so stiff that it lost its relaxation ability. Thus, both additives could not enhance the performance of this inferior quality asphalt.

4.3.2 Grade Loss

The grade losses for all the modified binders were evaluated according to LS-308 protocol. According to LS-308 specification, the asphalt binders with grade loss lower than 6°C are considered better than those with more than 6°C in terms of durability of the binder in service.

The following figure shows the grade losses for all the modified binders.

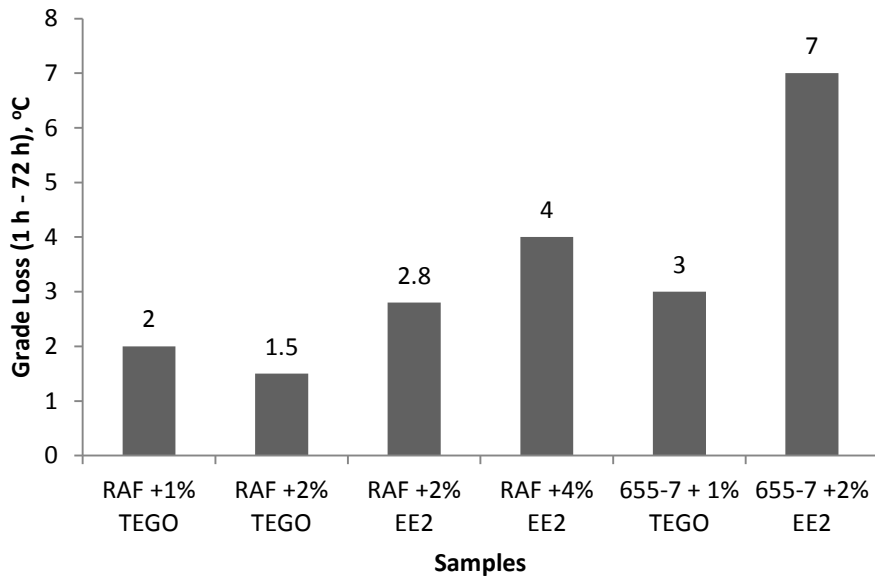


Figure 4.14: Grade losses due to physical hardening at -8 °C and -18 °C for 72 hours.

As shown in Figure 4.14, sample 655-7 + 2 % oxidised polyethylene wax displayed a higher grade loss of 7°C. This indicates that the sample has a severe cracking problem and would show low durability in service. However, RAF + 4 % oxidised polyethylene wax which had a grade loss of 4°C would show a tendency of physical hardening than the other modified samples with grade losses less than 4°C.

4.4 Double Edge Notched Tension (DENT) Testing

In order to have a better comprehension of the ductile properties of asphalt binders, the essential work of fracture, EWF, concept was employed to determine the strain tolerance and the failure characteristics of asphalt cements using the DENT test [70]. The DENT method has been successfully used to classify asphalt binders with respect to their performance and also to distinguish superior quality binders from poor quality binders. In this test, the same ductility testing was carried out for all asphalt binders by stretching them at a constant rate of 50 mm/min in an isothermal water bath at 15°C until fracture occurred, as per the Ministry of Transportation of Ontario LS-299 standard testing procedure [13]. Figure 4.15 shows the raw force-displacement trace for duplicate DENT tests on RAF + 4 % oxidised polyethylene wax at 50 mm/min and 25°C. Figure 4.16 shows the raw force-displacement trace for duplicate DENT tests on RAF + 1 % siloxane at 50 mm/min and 25°C. Figure 4.17 shows the raw force-displacement trace for duplicate DENT tests on RAF + 2 % siloxane at 50 mm/min and 25°C.

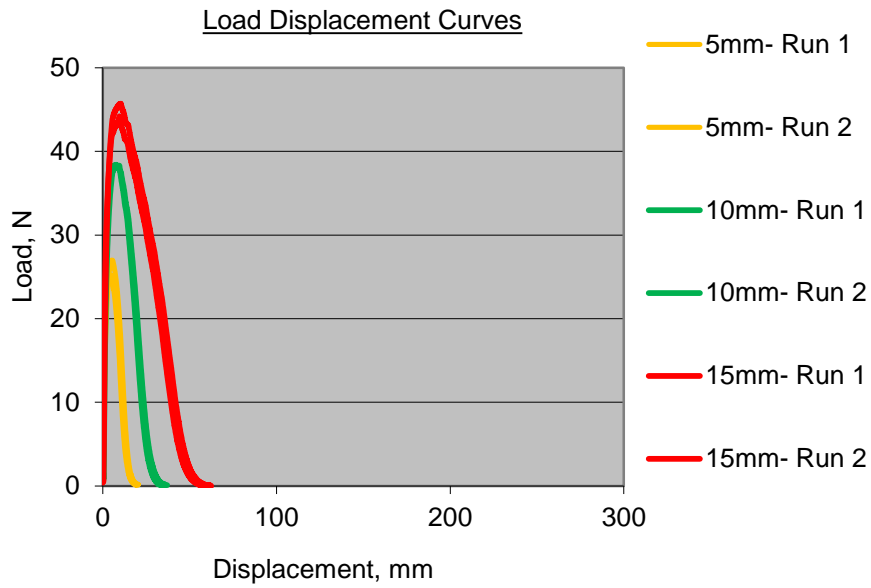


Figure 4.15: Representative force-displacement data for the DENT test (RAF + 4 % EE2).

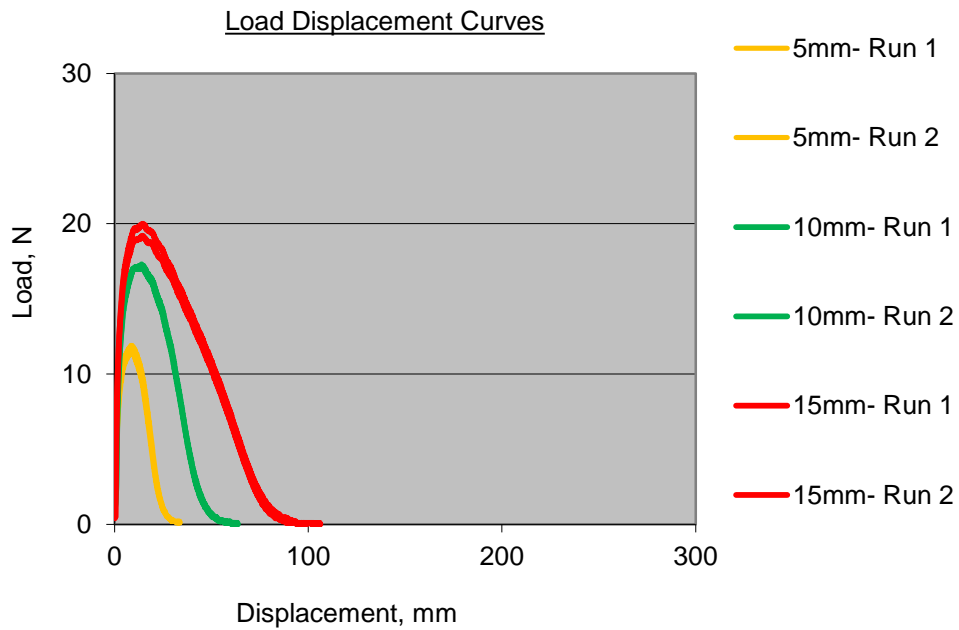


Figure 4.16: Representative force-displacement data for the DENT test (RAF + 1 % Tego)

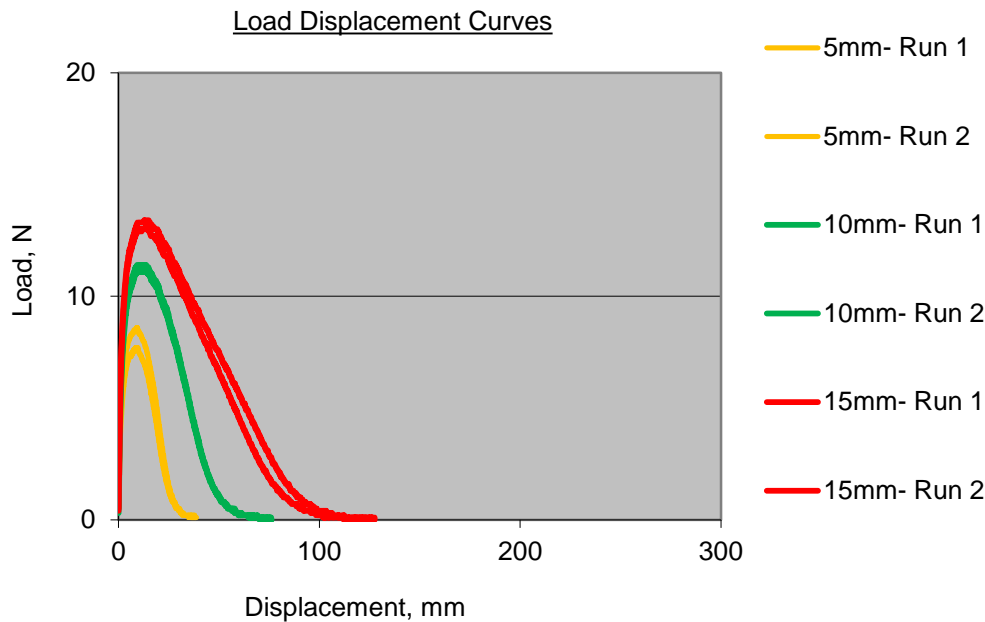


Figure 4.17: Representative force-displacement data for the DENT test (RAF + 2 % Tego).

This test method was observed being reproducible and the tests conducted for various ligament lengths were similar but different for each binder as shown in Figure 4.15, Figure 4.16 and Figure 4.17. Figure 4.15 is a representative of all other modified binders since they exhibited the same pattern of reproducibility. Also, the force-displacement curve of RAF +1 % siloxane and RAF + 2 % siloxane as shown in Figure 4.16 and Figure 4.17 differed significantly as compared to RAF + 4 % oxidised polyethylene wax .This could be explained by the different additives used to modify the asphalt binders and as a result, RAF +1 % siloxane and RAF + 2 % siloxane were softer binders compared to the other binders which were somewhat elastic and stiff.

4.4.1 Essential Works of Failure (W_e)

The essential work of failure is a material property since it is not dependent on the geometry of the asphalt cement sample. The EWF model is basically used to determine the resistance of the fatigue cracking in asphalt cement pavement. The EWF model concept is best applied when the

values of the essential work of failure and the plastic work of failure are relatively high in that cracking in the pavement occurs only when the strain tolerance of the pavement is exceeded [1]. However, it is assumed that high values of essential work of failure and plastic work of failure are good for resistance to fatigue cracking [11]. Figure 4.18 shows the essential work of failure of all the modified asphalt binder tested.

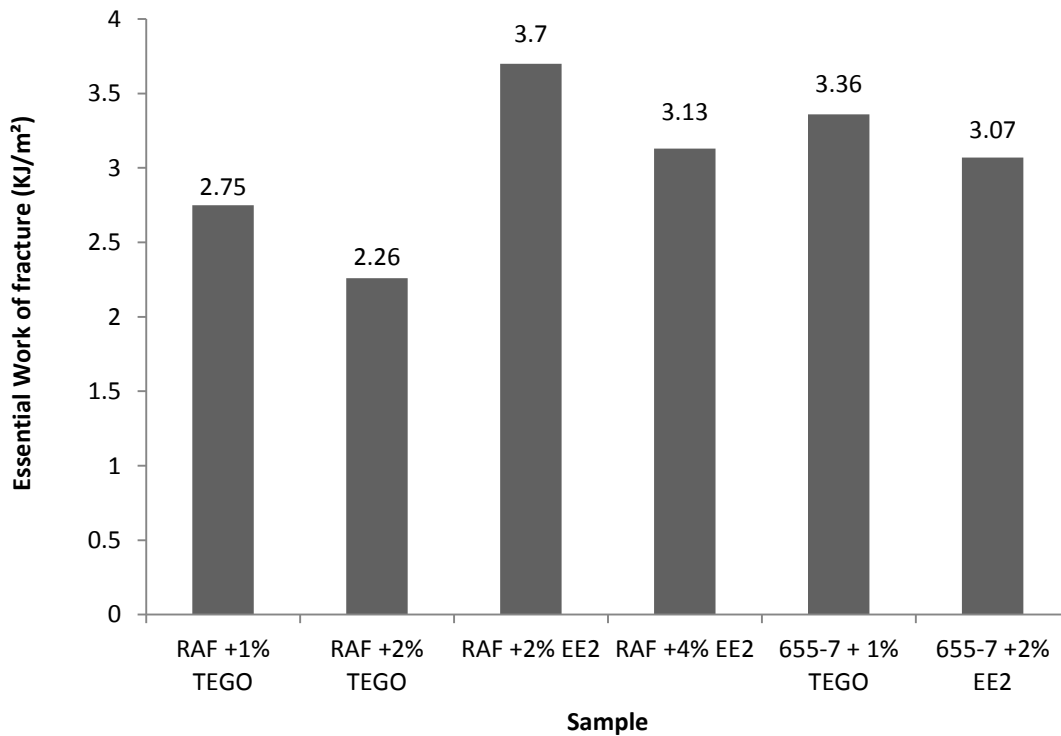


Figure 4.18: Essential work of failure for RAF and 655-7 with their various additive compositions.

It can be observed that the specific essential work of failure is high for RAF + 4 % oxidised polyethylene wax and 655-7 + 2 % oxidised polyethylene wax indicating that they have high strain tolerance to resist fatigue cracking. The remaining samples with low values of essential

work of failure indicate that they have low strain tolerance and they could exhibit poor performance in service.

4.4.2 Plastic Work of Failure (β_{wp})

The energy responsible for the non-essential or plastic deformation outside the fracture zone is the plastic work of failure. The shape of the plastic zone, which is the β factor, describes where the non-essential work is dissipated. The β factor can have different values depending on the geometry of the plastic zone. However, the β factor is not of primary importance since it is non-essential. The essential work of failure and the CTOD are rather of more interest. A high plastic work of fracture usually occurs in an asphalt mixture when the asphalt binder is high, which in turn makes it less susceptible to fatigue cracking. The high binder content provides a higher strain tolerance in the asphalt pavement [8]. RAF + 4 % oxidised polyethylene wax and 655-7 + 2 % oxidised polyethylene wax have higher plastic works of failure (β_{wp}) as compared to the other modified asphalt binders as shown in the Figure 4.19. This is as a result of the presence of the oxidised polyethylene wax which increases the wax content of the asphalt such that the asphalt becomes a bit stiff and elastic at the test temperature (15°C) and exhibits a high strain tolerance. The remaining samples exhibited relatively low values of plastic works of failure (β_{wp}).

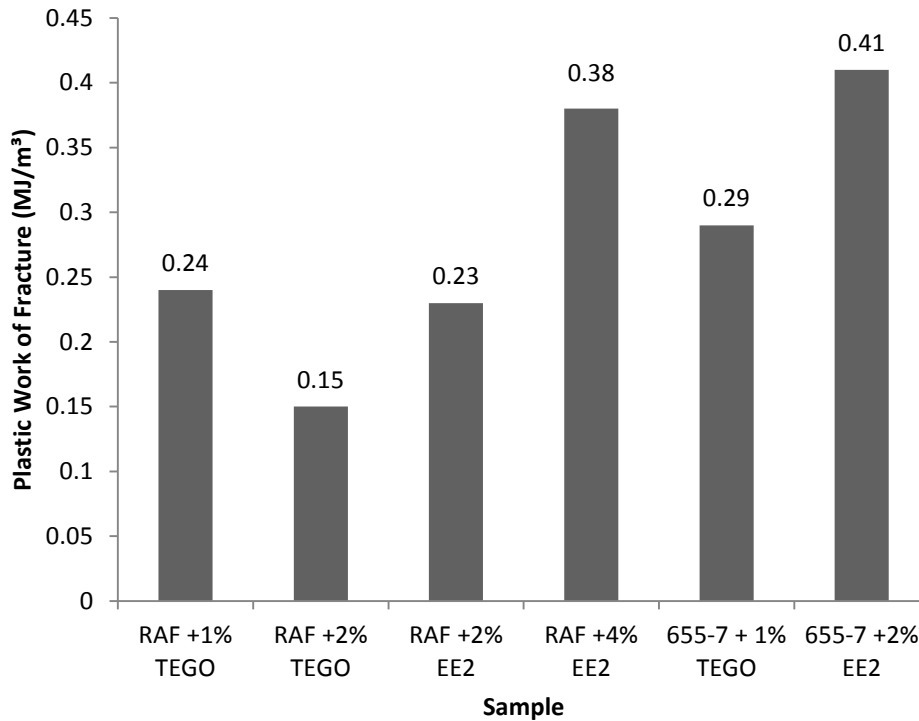


Figure 4.19: Plastic work of failure for RAF and 655-7 with their various additive compositions.

4.4.3 Approximate Critical Crack Tip Opening Displacements

The CTOD parameter provides a measure of strain tolerance in the ductile state under conditions of severe confinement. CTOD explains how the propagation of cracking occurs under ductile conditions during periods of increased loading and strain in the asphalt pavement [56]. Although the essential work of failure and the plastic work of fracture are able to predict fatigue cracking in the asphalt pavement, the correlation existing between the CTOD and the fatigue properties are higher comparatively due to its high accuracy when predicting fatigue cracking and ductile fracture properties of both binders and mixtures [53]. It has been proved that this parameter “shows promise for performance grading of both binders and mixtures for fatigue cracking at temperatures and rates of loading that cover the ductile regime” [71]. Figure 4.20 shows the CTOD values obtained per sample.

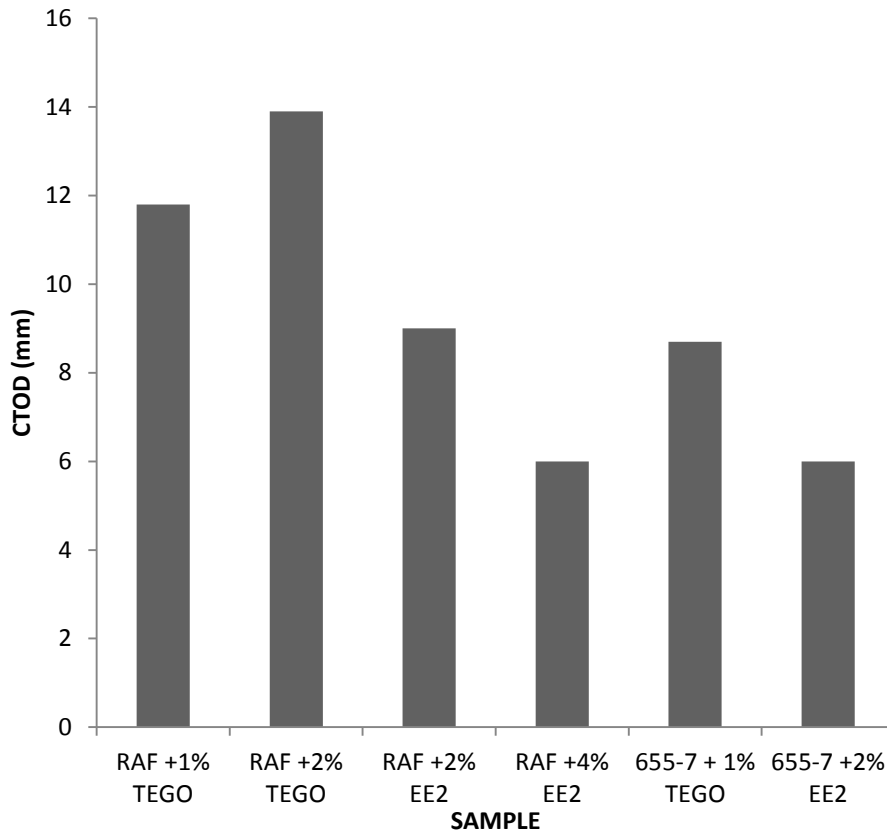


Figure 4.20: CTOD values for RAF and 655-7 with their various additive compositions

It can be observed that RAF + 4 % oxidised polyethylene wax and 655-7 + 2 % oxidised polyethylene wax has shown a negative effect on the strain tolerance in the ductile state, thus they are more susceptible to premature cracking in service comparatively. This was analogous to their physical hardening behavior from low temperature grading and extended BBR testing. RAF + 2 % oxidised polyethylene wax and 655-7 + 1 % siloxane are less susceptible to fatigue cracking as compared to RAF + 4 % oxidised polyethylene wax and 655-7 + 2 % oxidised polyethylene wax which had the lowest CTOD values. However, RAF + 1 % siloxane and RAF + 2 % siloxane which had higher CTOD values should have a better resistance to fatigue cracking.

4.5 Dilatometric Test

The dilatometric results were obtained by summer student Madeline Howell. The test was used to gain an insight on the crystallization of asphalt binders or the waxes within the binder using the Avrami theory which is able to explain the isothermal crystallization kinetics of asphalt cement. The following figures below outline the results obtained.

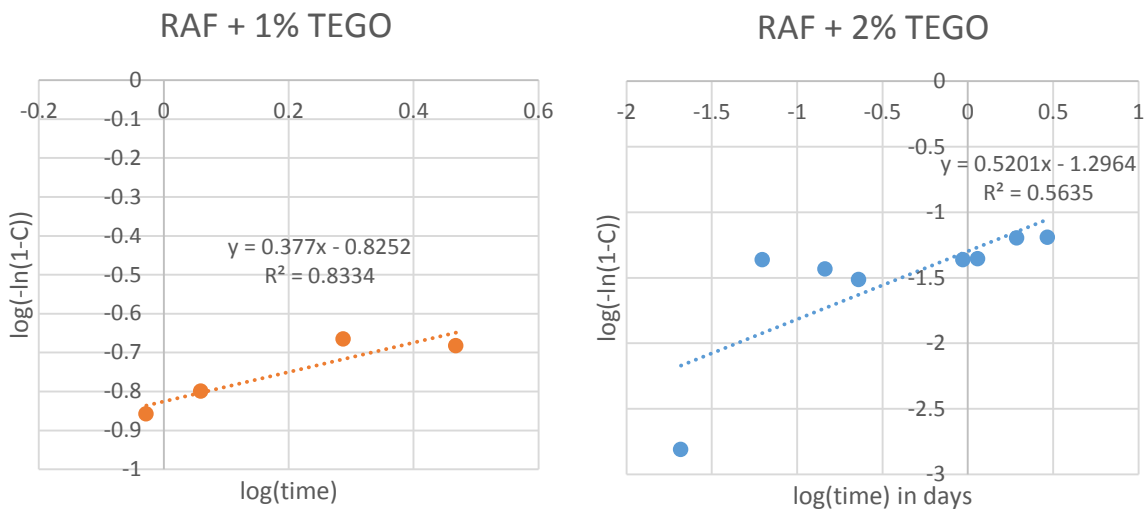


Figure 4.21: Linear plots of Avrami coordinates of RAF with 1 % and 2 % siloxane.

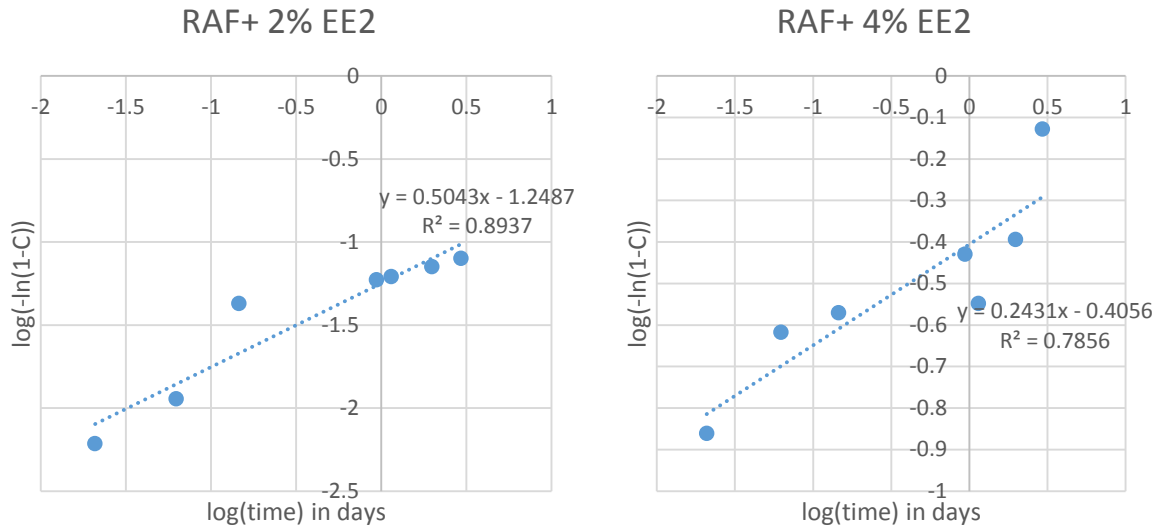


Figure 4.22: Linear plots of Avrami coordinates of RAF with 2 % and 4 % oxidised polyethylene wax.

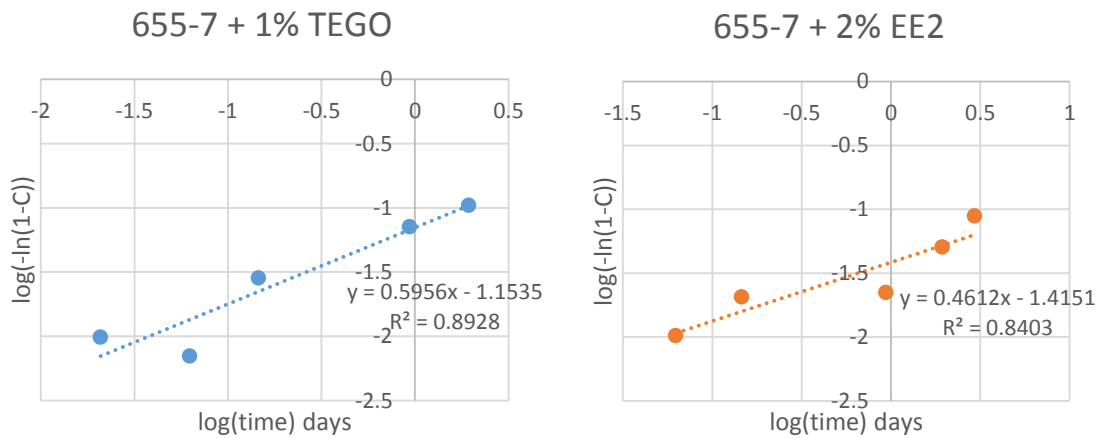


Figure 4.23: Linear plots of Avrami coordinates of 655-7 with 1 % siloxane and 2 % oxidised polyethylene wax.

Table 4.3: Summary of Avrami exponents and R-squared value obtained from the linear plots.

Sample	<i>n</i>	<i>Z</i>	R-squared
655-7 + 1% TEGO	0.556949	0.041147	0.96835
655-7 + 2% EE2	0.481711	0.06543	0.952217
RAF + 4% EE2	0.243138	0.39298	0.785596
RAF + 2% EE2	0.504265	0.056397	0.893749
RAF+ 1% TEGO	0.377038	0.14954	0.833419
RAF + 2% TEGO	0.520119	0.05053	0.563521

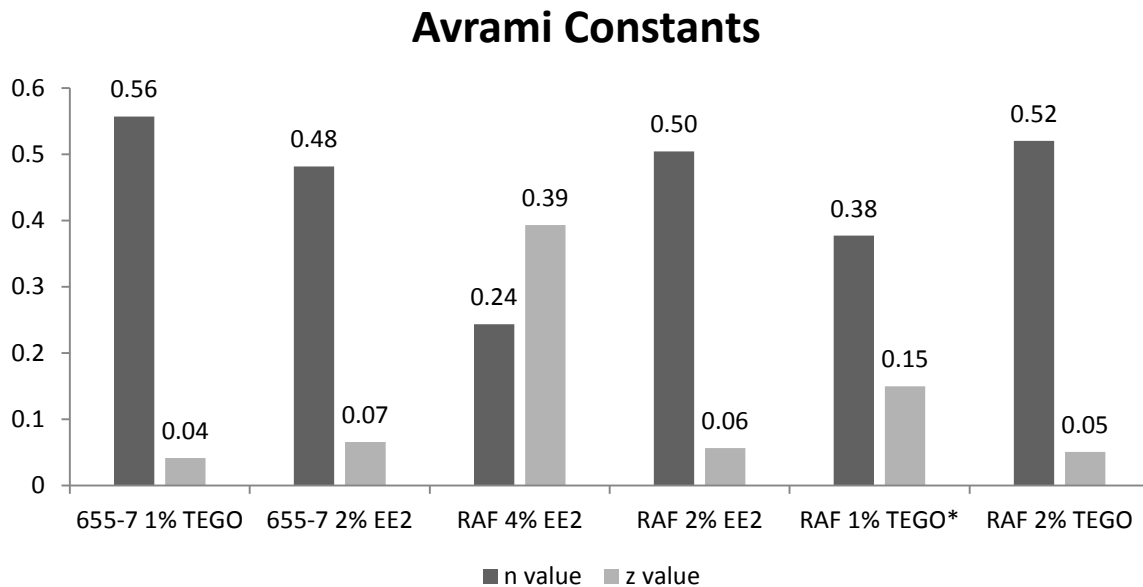


Figure 4.24: Avrami constants of RAF and 655-7 with their various additive compositions.

It can be observed that the results were linear when plotted in Avrami coordinates, suggesting that the formation of equilibrium structures during isothermal holding is similar to that of polymer crystallization. The Avrami exponents were low, ranging from about 0.2 to 0.6. Fractional constants are inconsistent with the Avrami theory, and may be caused by a mixture of instantaneous and sporadic nucleation. Also, secondary crystallization that occurs after the initial process is not considered by the Avrami theory, and this may also have contributed to this deviation [60].

Low Avrami constants are attributed to the existence of one-dimensional fibrillar growth with size limitation. However, it is possible that bitumen does not form perfect crystals, rather partially ordered structures. Also, further growth is limited in the bitumen due to fast crystallization which occurs initially such that only fractions of the asphalt binder, including waxes, may crystallize, leading to low exponents [60].

The Avrami exponents were quite similar, and mostly within experimental error of each other. RAF + 4 % oxidised polyethylene wax had the smallest Avrami exponent, suggesting that equilibrium structures formed are less organized than those formed in the other samples. Smaller R-squared values were obtained for the modified RAF samples as a result of the fluctuation of the height of the silicone oil.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Based on the literature review, experimental procedures, results and the discussions made in the previous chapters, the following summary and conclusions are given:

- The oxidised polyethylene wax improved the high temperature performance grade of both superior (RAF) and inferior (655-7) quality asphalts; so the use of this warm-mix additive in the modification of asphalt would show good performance at high temperature climatic regions.
- The changes in grade span temperature within the two different asphalts due to the various additives employed were found to be significant. The oxidised polyethylene wax improved the grade span of both asphalts. This makes the additive suitable in asphalts which would be used at a climatic region of wide range of temperatures.
- The Black space diagrams shows that both asphalt cements with their various additive compositions are rheologically simple at low temperatures. At high temperatures, only RAF with siloxane additive had no phase separation. The addition of siloxane to 655-7 and also the addition of oxidised polyethylene wax to both binders caused a phase separation of the asphalt cements.
- The effect of physical aging on the performance of the asphalt binder in the pavement at low temperatures is accurately predicted by altering the conditions governing the standard PAV aging method.

- The approximate CTOD provided a remarkable correlation with fatigue cracking distress in service. The changes in ductile strain tolerance within both asphalts due to the various additives employed were found to be very significant.
- The siloxane and the oxidised polyethylene wax could not enhance the low temperature performance of the inferior quality asphalt. The extended BBR test accurately evaluated the physical hardening of the asphalt binders as compared to the regular BBR test.
- The addition of oxidised polyethylene wax increases the risk of thermal cracking susceptibility in the pavement performance. This additive displayed a negative effect on the strain tolerance in the ductile state as well as the low temperature grading in the extended BBR test.
- Low Avrami exponents of bitumen are attributed to the limited growth in bitumen due to the fast crystallization of waxes present in bitumen.
- Increased concentration of oxidised polyethylene wax in asphalt as shown in RAF with 4 % oxidised polyethylene wax, forms less organised bitumen structures which allow for an increased rate of physical hardening and volume shrinkage.

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