

**COMPARISON OF ETHYLENE TERPOLYMER, STYRENE
BUTADIENE, AND POLYPHOSPHORIC ACID TYPE MODIFIERS
FOR ASPHALT CEMENT**

by

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Abstract

The objective of this study was to compare different modifiers in two asphalt cements, namely Cold Lake 80/100 obtained from the Edmonton, Alberta refinery of Imperial Oil Limited and a PG 58-28 obtained from a now closed refinery in the Montreal, Quebec area. The modifiers investigated were polyphosphoric acid (PPA), styrene-butadiene-styrene (SBS), and reactive ethylene terpolymer (Elvaloy® RET). The comparisons were done based on both unaged and laboratory-aged materials.

The investigation covers high temperature grading using a dynamic shear rheometer (DSR), low temperature grading using a bending beam rheometer (BBR), ductile strain tolerance as measured in the double-edge-notched tension (DENT) test and percentage recovered strain using multiple shear creep recovery (MSCR) test.

The Superpave® performance grade span was increased for all modifiers with substantial increases in the high temperature rutting parameter $G^*/\sin\delta$, while the BBR parameters, $T(S = 300 \text{ MPa})$ and $T(m = 0.3)$, remained largely unchanged. In the PG 58-28 base asphalt, Elvaloy® modifiers were able to reduce the intermediate Superpave® grade temperature by significant amounts.

All polymer modifiers were good at improving the ductile strain tolerance as measured in the DENT test. In contrast, PPA alone reduces the strain tolerance due to the formation of extra asphaltenes and the likely gelation of the asphaltene-rich phase.

Nearly all the modified samples passed the MSCR test except those with poor compatibility (i.e. SBS blended with Cold Lake without sulfur, Elvaloy® systems

without acid catalyst, and pure PPA modified systems) or no modifier, which did not reach the required elastic recovery at high levels of non-recoverable compliance.

In the BBR test done at low temperatures, all modified systems showed similar elastic recovery and viscous (non-recoverable) compliance. However, in the ductile-to-brittle range the Elvaloy® RET-modified binders showed a definite advantage of a few degrees over the unmodified base asphalts.

Finally, chemical aging tendencies, as measured by weight gain and carbonyl formation, turned out to be very similar for all the investigated compositions.

This study has shown that Elvaloy® RET and SBS have similar performance advantages over unmodified and PPA-modified asphalt cements when tested in the laboratory according to currently prevalent performance grading test protocols. Currently ongoing pavement trials at various locations in Ontario will shed further light on the relative benefits of the modifiers investigated.

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Abbreviations, Acronyms and Symbols

| | |
|------------|--|
| 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 |
| ER | Elastic Recovery |
| 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 |
| MTO | Ministry of Transportation of Ontario |
| NSERC | Natural Sciences and Engineering Research Council of Canada |
| PG (PGAC) | Performance Grade (Performance Graded Asphalt Cement) |
| SBS | Styrene-Butadiene-Styrene Block Copolymer |
| SHRP | Strategic Highway Research Program |
| EWf | Essential Work of Fracture |
| PAV | Pressure Aging Vessel |
| RTFO | Rolling Thin Film Oven |
| SUPERPAVE® | Superior PERforming Asphalt PAVEment |

Symbols

| | |
|----------|---|
| a | length of a sharp crack, m |
| b | Beam width, 12.5mm |
| B | Specimen thickness, m |
| G_{Ic} | Plane-strain fracture Energy, $J.m^{-2}$ |
| h | Beam thickness, 6.25mm |
| J(v) | Viscous compliance |
| J_{nr} | Non-recoverable creep compliance |
| K_{Ic} | Fracture toughness, $N.m^{-3/2}$ |
| P | Load applied, N |
| t | Loading time, s |
| 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, Jm^{-2} |

Chapter 1

Introduction

1.1 Asphalt Material Issues

The use of asphalt cement as a paving material increased dramatically in the early 20th century when petroleum refining became the method of choice for the production of a range of products such as gasoline, jet fuel and lubricants. Initially this black, sticky material was acquired as a waste stream in the refinery process but it was quickly discovered that it turned out to be a good paving material providing a new end use with added value. In today's world an important role is played by highway and road infrastructure in almost all modern economies. In geographic areas that have cold climatic conditions, such as Canada and the northern US, extremes in temperature during winter and summer reduce the life span of asphalt roads, thus the construction and maintenance of such roads creates an important industry. Canada spends billions of dollars every year on asphalt. Of this huge sum only a small fraction is used for the expansion of the road network while most is for the rehabilitation and reconstruction of existing routes. Hence, it is important to select the proper type of asphalt material which provides the best possible road with a long lifespan and also bring in some reduction to the maintenance of the roads due to varied climatic conditions.

1.1.1 Origin

Asphalt has many different names like binder, asphalt cement (AC), performance graded asphalt cement (PGAC), tar and bitumen. It is usually termed to describe different things

at various places such as in Europe bitumen is the preferred term to describe the semi-solid glue that is used for paving of roads whereas in North America the same thing is denoted as asphalt cement or binder. According to the American Association of State Highway and Transportation Officials (AASHTO) asphalt binder is defined as an “asphalt based cement that is produced from petroleum residue either with or without the addition of non-particulate organic modifiers”.

In the Indus Valley dated 3000 BC at Mohenjo Daro, asphalt was used in the construction of water tanks wherein it was used as a sealant and glue for stone blocks [1]. Around 3500 BC, it was suggested that the Sumerians used it as water proofing agent in shipbuilding [1]. In 1595, Sir Walter Raleigh mentioned that the asphalt lake of Trinidad acted as an excellent waterproofing material for the seams of ships [2]. The basic principle of road construction was developed due to the centralized road administrations in European countries that sustained the industrial development. In the United States and France, asphalt was used for road pavement and sidewalk pavement during the 19th century [1]. The asphalt obtained from the asphalt lake of Trinidad is known to be the best natural source of asphalt. Generally the asphalt so obtained is hard and has limited applications in its original form but could be widely used in pavement construction when refined and mixed with petroleum asphalt [2]. Also, a mixture of rocks and natural asphalt known as Gilsonite turned out to be another natural source of asphalt. In 1902, the industrial production of petroleum asphalt started in the US which subsequently turned into a large scale asphalt paving industry. Asphalt obtained today is mainly from the bottom of the barrel: the final product of the petroleum refinery process once all the other

fractions are extracted from crude oil. As asphalt works very well for binding and water proofing it is widely used in road construction. Asphalt is believed to have been present in crude oil for millions of years yet it does not last for very long when applied on roads. There are many factors behind these performances of asphalt out of which one of them is the source of crude oil from which it is obtained and its composition. Also, the performance would depend on the amount and type of aggregates being used, the method of road construction, temperature, moisture content and obviously the volume of traffic [3].

1.1.2 Applications

Asphalt at high temperature is found to be a viscous liquid while at intermediate temperature it is semi-solid and at low temperature it is elastic solid. Also it forms a solid mixture when combined with aggregates, filler and sand. The material used for the construction of flexible pavements is usually stated as asphalt concrete or hot mix asphalt (HMA). There are two main types of asphalt products, namely paving asphalt and roofing asphalt. It is also used at various other places such as in lining irrigation canals, dams, sea defense work and water reservoirs, in adhesives, as a base for synthetic turf, in asphalt-based paint as protective coatings to prevent corrosion of metals and in electric laminates [4]. Owing to its adhesive properties, asphalt was used in ancient times widely to glue stone axe heads to wooden handles [5], to make decorative utensils, for preparing statues, and in making ornaments [6,7]. Its use for mummification in ancient times [8] and photography [9] has also been recorded. In today's day and age there are around 250

applications [2] of asphalt but about 85 % of the total asphalt usage is for road construction.

1.1.3 Constituents

At room temperatures and atmospheric pressure asphalt cement is found to be a semi-solid or solid which can be liquefied by dissolution in petroleum solvents or by heating. By the addition of the proper type of surfactants, it can be emulsified in water. Asphalt consists of two chemical component classes: asphaltenes or maltenes depending upon their solubility in n-heptane or hexane [2]. As maltenes have lower molecular weights, they are soluble in n-heptane or hexane while asphaltenes are not soluble due to their higher molecular weights. Asphalt normally contains between 5 and 25 percent by weight of asphaltenes and may be regarded as a colloidal system of asphaltene micelles dispersed in the maltene (oily) continuous phase [2]. The chemical constituents in asphalt are the following: saturates, aromatics, naphthenics, resins and asphaltenes, the latter of which are polar in nature due to functional groups such as carboxylic acids, phenolics, amines, and thiols. These functional groups cause asphaltenes and resins to cluster with aggregate molecular weights ranging up to 100,000 and more. The polar attraction between the molecules within asphalt and the polar surfaces of aggregates results into the adhesion of the asphalt to the aggregates [2].

In addition to the two main chemical groups, asphaltenes and maltenes, and the small amounts of sulphur, oxygen and nitrogen, trace quantities of metals such as iron, vanadium, nickel, calcium and magnesium are found in most asphalt cements [2].

Asphaltenes are considered to be highly polar and complex materials with molecular weights that range from 1,000 to 100,000 [2]. The amount of asphaltenes present has a considerable effect on the rheological properties of the asphalt cement. An increased amount of asphaltenes increases the viscosity and hardens the materials. Maltenes are further divided into three groups: resins, aromatics and saturates. Resins are polar in nature and mainly function to keep the asphaltenes dispersed and as the adhesive in the asphalt mixture. Aromatics are the low molecular weight naphthenic aromatic compounds. They consist of unsaturated ring systems in non-polar carbon chains. Saturates are the straight and branched chain of aliphatic hydrocarbons. Saturates are non-polar viscous oils.

1.1.4 Distress Types

Usually in all weather conditions the asphalt used for paving roads must remain viscoelastic but this does not happen practically. All asphalts are known to soften up during summer and form rutting or permanent deformation. During winters, neutral molecules in the asphalt arrange themselves into more organized structural forms, which in turn harden the material leading to brittleness and the formation of cracks under high traffic loads. These processes are termed as fatigue and thermal cracking.

Fatigue Cracking: This distress occurs due to repeated traffic loads. As a result of this there are large numbers of relatively short cracks generated (Figure 1) creating roughness and allowing moisture to penetrate the structure. Repairing of this type of distress is ineffective since the distress usually reappears within short periods after the repair.

Rutting: This can be observed as surface depression in the wheel path. This could be due to insufficient compaction during the construction and then heavy traffic load damages it more (Figure 2). It can be hazardous as it pulls vehicles towards the rut path only. Repair is possible by leveling up the deeper ruts or by overlaying a new lift of asphalt concrete. However, ruts that form in lower layers of the pavement will quickly return after a single lift overlay.



Figure 1. A typical area of fatigue distress [10]. Figure 2. Typical rutting distress [10].

Stripping: The stripping of the asphalt cement and mastic happens due to the presence of moisture which can reduce the adhesive properties of the asphalt cement with the aggregate. This may occur after fatigue crack and ruts also. This failure damages the base structure (Figure 3) due to this poor chemistry between aggregates and surface. This may also occur due to a poor drainage system.



Figure 3. A small stripping distress [10]. Figure 4. A typical thermal effect on road [10].

Thermal Cracking: This issue is usually observed due to the occurrence of extremely low temperatures especially in countries like Canada where winters are harsh. Shrinkage of the asphalt surface becomes significant at low temperatures. This type of crack is observed perpendicular to the pavement's centerline or lay down direction (Figure 4). This could be repaired by sealing of the cracks or by overlaying the surface with one or more lifts of asphalt concrete. However, experience has shown that cracks rapidly reappear in the surface through so called reflection cracking.

1.1.5 Modifiers

The aim of asphalt cement modification is to develop pavements with improved resistance to distresses (especially thermal cracking). Modification of asphalt binders with different polymers, fillers, and fibers so as to reduce the susceptibility of asphalt pavement to low temperature cracking has received significant attention in recent years [11, 14].

There are different types of modifiers used to obtain improved performance from asphalt cement. The groups which are mainly used are plastomers, elastomers, anti-stripping additives, and acid modifiers. Plastomers are used to reduce the viscous part of the asphalt resistance to deformation helping to decrease permanent deformation or rutting in asphalt. Polyethylene (LDPE), ethylene-vinyl-acetate, ethylene-acrylate are all polymers commonly used in asphalt cement modification. Elastomers increase the elastic property of the asphalt cement. These additives are thought to help reduce fatigue and thermal cracking distress of asphalt material e.g. styrene-butadiene rubber latexes (SBR), diblock styrene butadiene (SB), and triblock styrene-butadiene-styrene (SBS). An anti-stripping group is used to reduce moisture damage and increase adhesion in asphalt binder and aggregate, e.g. polyamines and fatty amino-amines. Acid modification is the new version of modification through acids in asphalt started back in 1930 [13]. The main function of this modification is to increase the softening point of a binder. Polyphosphoric acid (PPA) is typically used as an acid modifier. It was observed that the use of such modifier helps to increase the grading range at high temperature but there are some negative effects observed according to the source of asphalt [14]. In modified asphalt it is thought that the final product has to become a micro heterogeneous mixture to obtain the most beneficial performance. In this, asphalt forms the continuous phase and the polymers are dispersed throughout [11]. Hence, to obtain good properties of an asphalt binder at an affordable cost, the polymer content needs to be kept around or below 4 % by weight.

To improve the rheological properties of the binder in which the fatigue life and permanent deformation resistance are aimed to be improved, various models are developed. The focus on long-lasting pavements with improved performance particularly at low temperature is the ultimate goal of various forms of modification processes of asphalt.

1.2 Scope

Different modifiers are often used in asphalt to improve physical properties to resist various distress types (rutting, fatigue, thermal cracking, moisture damage, etc.). Three major modifiers were investigated in this thesis: polyphosphoric acid (PPA), styrene-butadiene-styrene (SBS), and reactive ethylene terpolymer (RET or Elvaloy®). This study compared the benefits of each type of modifier in two different base asphalts, namely Cold Lake 80/100 pen grade produced in Edmonton, Alberta, and used widely throughout the U.S. and Canada, and a commercial blend with a Superpave® PG 58-28 grade produced in the Montreal, Quebec area. The findings of this research will allow user agencies to make better choices in terms of what modification to allow for specific paving contracts. This research has the potential to save millions of dollars in tax payer money by extending the life cycle of pavements.

Chapter 2

Background

2.1 General Issues: Asphalt Sources, Uses, Chemical and Physical Properties

2.1.1 Asphalt and Resources

Though the properties of asphalt are long known, it was not used as a paving material until the early 20th century. This is the period when petroleum refining started and asphalt was obtained as the residue of the refining process. This sticky material was initially obtained as a waste stream. Hence, this gave rise to a new industry and an extensively used paving material all over the world. There are mainly two sources of asphalt material.

Natural Sources of Asphalt

Naturally occurring asphalts are found as deposits on the surface in Trinidad and Venezuela. There is a huge deposit of Athabasca tar sands in northern Alberta and about 95 % of natural asphalt cement (as tar sand) is from this place. The major sources of natural asphalt are in Pit Lake, Trinidad; Gard, Auvergne, Ain and Haute Savoie in France; Central Iraq; Latakia, Syria; Maestu, Spain; Butin Island, Indonesia; and the Dead Sea area in Israel and Jordan [15]. These natural substances are found within a limestone or sandstone mixture.

Petroleum Sources of Asphalt

Petroleum asphalt is obtained through the refining of petroleum. Most asphalt in the United States and Canada is produced through the refining of crude oil. Atmospheric and vacuum distillations are the basic units of operation. However, blending, air blowing, solvent deasphalting, solvent extraction, emulsification and modification are available to produce various grades of asphalt depending on the crude sources.

2.1.2 Applications of Asphalt

Asphalt's viscosity decreases at warm temperatures while on cooling it quickly turns hard. In the ancient times, asphalt was used as an adhesive. So, asphalt was used for making small decorated utensils such as bowls, for coating statues for making ornaments, and so on [6, 7]. In the Gilgal Site, a stone axe head was found (8500 B.C.), which was covered with asphalt to glue it to a wooden handle [5]. Recently, due to new natural and synthetic glues this use of asphalt has dramatically decreased. The Persian traveler, Nasir-i-Khusran, when visiting the area near Egypt in 1047 A.D., describes how asphalt was used to coat the roots of fruit trees and thus protect them against "worms and things that creep below the surface". It is possible that the aromatic compounds and sulfur content in the asphalt explain this beneficial effect [16]. Back to 3500 B.C. the shipping industry used asphalt as a waterproofing engineering material. Ancient Phoenicians, Egyptians, and Romans used asphalt to waterproof temples and baths and water tanks. They also used asphalt as a binding material for bricks [6, 7].

It is interesting to know that asphalt was used as a medicine in the ancient times. In the 2nd century A.D., famous doctors of medicine in the Roman and Medieval world used the Dead Sea asphalt for medical purposes. Recently, Professor A. Docstrovsky from Hasassah Medical School in Jerusalem found a valuable material called “bitupal” which was very effective for curing certain skin diseases [17]. This material is still in use and has been produced by the Teva Pharmaceutical Company in Israel [8]. Besides all applications in the ancient world, asphalt has also been used for mummification [8], photography [9], waterproofing and in oil exploration [8]. In the late 18th century, the first use of asphalt as a material for road building was reported in Newark, N. J. [18]. During the 19th and 20th centuries, the use of asphalt as a road-building material increased together with the development of the automobile industry.

2.1.3 Chemical and Physical Properties

2.1.3.1 Chemical Properties

An asphalt binder’s physical properties are determined by its chemical constituents (saturates, aromatics, resins, asphaltenes, etc). Hence, the behavior of the asphalt could be predicted from a basic knowledge of its chemistry, although asphalt cements for hot-mix asphalt pavements are rarely characterized by their chemical composition [11]. An extreme complex mixture of largely organic and organo-metallic compounds is termed as asphalt. The composition of a standard sample of asphalt contains about 82-88 % carbon, 8-11 % hydrogen, 0-6 % sulphur, 0-1.5 % oxygen and 0-1 % nitrogen [2]. Certain metal atoms like Fe, Ni, and V, which act as a fingerprint for the point of origin of the asphalt, are found in trace quantities in asphalt [11].

By precipitation in n-heptane, asphalt can be separated into two chemical groups, namely asphaltenes and maltenes [2]. Asphaltenes do not dissolve in a linear hydrocarbon such as n-heptane as they are polar compounds with a high molecular weight. Their molecular weight ranges from 1,000 to as high as 100,000 g/mol on the basis of the method used to determine them [2]. The ratio of hydrogen to carbon is close to 1:1 and the size of a typical asphaltene molecule is typically between 5 and 30 nm. A strong effect on asphalt's rheological properties depending on the amount of asphaltene present in asphalt cement is observed, which is responsible for the high viscosity in asphalt. It is generally observed that asphalts with a high amount of asphaltenes are harder and have a higher viscosity, while asphalts with less asphaltenes are softer and have a lower viscosity. The maltenes undergo division into three further groups namely saturates, aromatics and resins. The compositions of saturated compounds are straight and branched-chain aliphatic hydrocarbons along with some alkyl-aromatics and alkyl-naphthenes. Around 5 to 20 % of the asphalt cement constitutes of saturates. Approximately 30 to 50 % of the total amount of asphalt consists of aromatics, which are dark brown viscous liquids. Aromatics act as a solvent for other higher molecular weight hydrocarbons (resins and asphaltenes) and are composed of unsaturated ring systems. The resins are composed of hydrogen and carbon along with small amounts of oxygen, sulphur and nitrogen. They are found to be dark brown in color and are strongly adhesive to the aggregate in a pavement mixture. The dispersion of the asphaltenes in the oils (saturates and aromatics) is the main function of resins [2].

Presently as there is not enough asphalt chemical knowledge to adequately predict its performance, in which mainly the basic asphalt binder failure mechanisms that can be described chemically, and hence the physical properties and tests are used.

2.1.3.2 Physical Properties

Characterization of asphalt cements is mainly carried out based on their physical properties. The changes in asphalt cement's rheological properties are manifested in changes in its viscoelastic nature based on the road performance. The paramount in achieving good road performance that relies on an understanding of the molecular dynamics (motion) in asphalts is in relation to the rheological properties. At a given temperature, by changing the extent of molecular mobility, it may be possible to enhance the performance of asphalt. The alteration in the molecular mobility of the asphalt could be done by physical blending of two or more asphalts, the introduction of polymeric materials into asphalts, or through chemical modification of the asphalt [19].

The earliest physical tests were empirically derived tests. In the better part of the 20th century some of these tests (such as the penetration test) have been used that provided good results. To describe asphalt binder physical properties, the later tests (such as the viscosity tests) were the first attempts at using fundamental engineering parameters. It is still quite doubtful for the ties between tested parameters and field performance. In the 1980s and 1990s the Superpave® binder tests were developed with the goal of measuring specific asphalt binder physical properties that are directly related to field performance by

engineering principles. A more thorough characterization of the tested asphalt binder seems to be accomplishing from these tests, which were mainly a bit more complex.

Asphalt is mainly found to be a viscoelastic material [19]. At relatively low temperatures it behaves like an elastic solid while it is a viscous liquid at high temperatures. Hence, under the removal of certain amount of loads (elastic behavior) it is observed that the asphalt is able to return to its original shape. Also, at times permanent deformation (viscous behavior) is observed as some of the input energy that may dissipate in the asphalt. The division of the molecular compounds in asphalt into two general categories such as polar and non-polar compounds is done. The elastic property in the asphalt is derived due to polar compounds, with an example of an asphaltene as a polar compound. The viscous behavior of the asphalt is through non-polar compounds, such as the maltenes fractions. The long chains tend to align and flow and that makes the asphalt behave like a viscous liquid, and not like an elastic solid, as temperature or load increases. Moreover, these molecules shall move back to their original shape (elastic response), but not in the exact conformation as before the disturbance (viscous response) upon cooling or removal of the stress.

2.2 TEST METHODS

2.2.1. Conventional Tests

According to civil engineers, asphalt was not regarded as a macromolecule with viscoelastic properties but was considered as a construction material. It was mainly graded on the basis of needle penetration, softening point and viscosity, that are purely empirical in

nature, during late 19th century [20]. The grading of asphalt cement was based on its field performance from these test methods. These test methods measured an empirical property of the asphalt cement at an arbitrary single temperature and never focused on two distinct properties of asphalt at the same time. The conventional test methods that were commonly used are as follows:

- 1) Needle Penetration Test
- 2) Ring and Ball Softening Point Test
- 3) Ductility and Force Ductility Test

The asphalt consists of four general conventional grades, such as the penetration grade, the cutback grade, the oxidized grade and the hard grade. Usually, out of these four grades, only the penetration grade is used for paving roads. The combination of two test methods or just one method helps to decide all of these grades. The penetration test and the ring and ball softening point test methods help to predict the penetration grade. The combination of the viscosity and softening point methods help to decide the oxidized and hard grades whereas the viscosity method decides the cutback grade. For the roofing and painting purposes, the hard and oxidized asphalt is used, whereas for the blending and surface coating applications the cutback asphalt is used [2].

2.2.1.1 Needle Penetration Test

In 1888 the Baber Asphalt Paving Company [21] invented the penetration test which is the oldest asphalt cement grading test. According to an ASTM standard, the penetration test has been measured since 1959 [10].



Figure 5. Penetration test equipment [10]

This test method involves the penetration of a needle into the asphalt under a standard load of 100 gm, at a standard temperature of 25°C, for a standard time of 5 sec (Figure 5). This is measured in units of decimillimeters, i.e. 0.1 mm. For example, 80 Pen asphalt cement shall have a penetration of the needle at 25°C of 8 mm, means 80 times 0.1 mm. The specification of the reproducibility and repeatability standards is mentioned in the ASTM standard [22]. The value so obtained from the penetration tests helps to decide the grade on the basis of historical field performance and does not relate to any physical material property of asphalt. This test gives a better result than the high temperature viscosity method in terms of low temperature performance and is also an inexpensive test. A linear dependence between the logarithm of penetration and temperature was

described by Pfeiffer and van Doormaal (1936) [23] when they described the temperature susceptibility of asphalt properties as:

$$\text{Log Pen} = aT + c \quad (1)$$

where a and c are constants.

The parameter so obtained is termed as penetration index (PI) that expresses the temperature susceptibility on the basis of penetration values at two different temperatures. At the softening point temperature (Pen = 800), all asphalts have same penetration values. The asphalt properties over a wide range of temperatures in linear equations were expressed by Pfeiffer and van Doormaal with great success.

2.2.1.2 Ring and Ball Softening Test

It consists of a steel ball where the asphalt sample is heated and softened in the medium of glycerol or water. This test is a type of reinforcement for the results obtained by the penetration test. The test is a measurement of the melting interval, which is a consistency test.

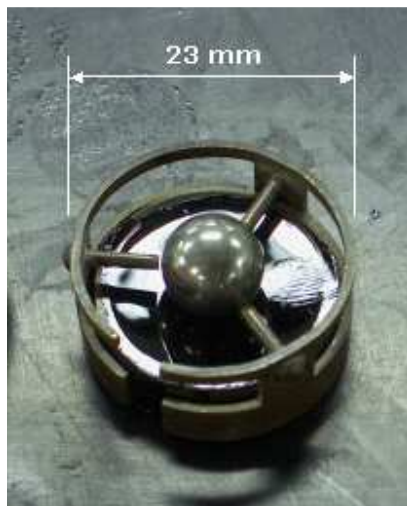


Figure 6. Softening Point Sample [21]

It states the temperature at which an asphalt sample, in a brass ring under the pressure of a steel ball (Figure 6) that touches a base plate of 25 mm placed below the ring, with the temperature of the bath of 5 °C/min [ASTM D36-95]. The softening point is obtained by the temperature at which the steel ball in the ring pushes the soft asphalt samples to a standard distance and is so measured.

2.2.1.3 Ductility and Force Ductility Test

The ductility test is an empirical performance test for mechanical strength and toughness. It measures the elongation in centimeters at which asphalt sample breaks after being pulled at 5 cm/min, and provides a ranking of asphalts in terms of mechanical strength [ASTM D113]. The observation obtained from this test states that asphalts have various capacities of sustaining similar stresses before fracture occurs. It was more likely to take place in the polymer modified asphalts as compared to the unmodified ones. Generally it is observed that before fracture the polymer modified asphalts elongate too much. A

better expression of fracture resistance was obtained by toughness which is defined as the total work necessary to break an asphalt sample.

The force ductility test that provides the force versus strain during extension helps to express the asphalt toughness. The toughness of the asphalt material is expressed by the work to break that is represented by area under the curve. These tests were not used later on as a standard test due to lack of real life toughness correlation and poor reproducibility. The ductility and force ductility tests were measured in a way so as to produce the results that were highly dependent on basis of the specimen's geometry and size.

However, all of these tests do not give an accurate indication of how the materials would perform at a wide spectrum of temperatures which is mainly experienced by the asphalt pavement in service. Instead, they only measure the asphalt sample at a specific temperature. Also, the results of both of these tests are correlated with pavement performance over the years as they are empirical tests [20].

2.2.2 Superpave® Specification Tests

Because of the failure of conventional grading tests that provided binder properties with little or no correlation to pavement performance, in United States, the Strategic Highway Research Program (SHRP) ran for a period of five years and spent close to \$150 million, in the late 1980's and early 1990's. As a result of this, new test methods have led to a new specification known as Superpave® (Superior Performing Asphalt Pavements) [20,

24]. During the asphalt life in service, the binders are being tested under conditions which better simulate the critical conditions obtained from these new specification test methods. A measurement of the asphalt's fundamental physical properties, that are supposed to be directly related to field performance through sound engineering principles as a result of these tests under Superpave®, was observed. To eliminate the empirical nature of the conventional grading methods, such as penetration and the ring and ball softening point, the research team developed these test methods. The asphalt is given a grade such as PG (or PGAC) XX-YY, where XX represents the high temperature working limit of the asphalt cement and -YY the low temperature limit based on the Superpave® test methods. For an example, PGAC 58-28 asphalt cement is expected to perform without any significant amount of either rutting or thermal cracking at a high temperature limit of 58°C and low temperature limit of -28°C. Moreover, the high temperature grading test is reasonably able to predict rutting performance without any problems. An inadequate amount of time is given for the samples to condition in the low temperature test. As a result, in northern climates many pavements are under-designed for thermal cracking. As an improvement over historical penetration, ring and ball softening point and viscosity methods, these experiences have shown that the Superpave® specification still leaves a reasonable amount of space for improvement [25]. The performance grade (PG grade) does not protect a pavement against typical distress and as a result the asphalt cements graded the same can show significant performance variations [24]. The recent evidence has shown up that Superpave® is more like a purchase-based specification (where the supplier and user of the asphalt cement agree that the product meets the specification

criteria but there is no guarantee for performance in service), but which was supposed to be an entirely performance-based specification method as earlier proposed [26-29].

In Superpave® testing to determine XX and -YY, two important test methods applied are [1]: The Dynamic Shear Rheometer (DSR) Test for XX, and the Bending Beam Rheometer (BBR) Test for -YY. The failure properties of asphalt like rutting and fatigue at high temperatures and medium temperatures is given out with reasonably accurate results by DSR. Moreover, a reasonable result for low temperature cracking is given out by the BBR test method, but still widespread problems with premature and excessive cracking are observed from that test method, which indeed needs some improvement.

Laboratory Aging of Asphalt Cement

Service aging for a period of 8-10 years is supposed to be simulated by the pressure aging vessel (PAV) procedure while the simulation of aging during mixing and construction is carried out by the RTFO procedure in the laboratory. Therefore, the asphalt binder tests involved with in-service performance such as the DSR, BBR and DTT are carried out on samples first aged in the RTFO and then in the PAV while the asphalt binder tests involved with mix and placement properties namely the DSR are done on RTFO aged samples.

2.2.2.1 Rolling Thin Film Oven Test

The simulation of the short-term aging by heating a moving film of asphalt binder in an oven for 85 minutes at 163°C (325°F) is termed the rolling thin-film oven (RTFO) test

(Figure 7). The changes incurred in the physical properties are measured before and after the oven treatment by other test procedures, which determine the effects of heat and air on the asphalt sample. The moving film is created by placing the asphalt binder sample in a small jar and then placing the jar in a circular metal carriage that rotates within the oven.



Figure 7. Rolling Thin Film Oven test equipment [10]

The RTFO test is generally considered superior to the TFO because in less time (85 minutes vs. 5 hours) it achieves the same degree of hardening (aging).

The rolling action is used in RTFO which:

- Allows asphalt binder modifiers, if used, to remain dispersed in the sample.
- Prevents the formation of a surface skin on the sample, which may inhibit aging.
- Allows continuous exposure of fresh asphalt binder to heat and air flow.

2.2.2.2 Pressure Aging Vessel

To simulate the effects of long-term asphalt binder aging that occurs as a result of 5 to 10 years HMA pavement service the pressure aging vessel (PAV) (Figure 8) was applied by

Superpave® [30]. The basic concept of the pressure aging vessel had been used for several years in rubber product aging earlier to Superpave®. In the PAV procedure the RTFO aged samples are taken, which are exposed to a high air pressure and temperature (depending upon expected climatic conditions) for 20 hours as it is an oven-pressure vessel combination.



Figure 8. Pressure aging vessel equipment [10]

It is found to be advantageous if the aging of the asphalt binder samples under pressure is carried out without affecting extremely high temperatures, the oxidation process could be expedited.

2.2.2.3 Dynamic Shear Rheometer (DSR) Testing

To evaluate rheological (flow) properties of asphalt binders from low to high temperatures the Dynamic Shear Rheometer (DSR) is used. For predicting the end-use

performance of materials, an understanding of the rheological properties of asphalt binders is essential. The procedure of the test method consists of a thin film of asphalt cement placed between two parallel plates and the measurement of visco-elastic properties in dynamic oscillation is observed. The dynamic properties of asphalt are measured when the binder sample is sheared and the shear angle and torque are measured. Over a wide range of temperatures and frequencies the DSR measures the complex shear modulus (stiffness) G^* and phase angle δ . In the Superpave® specification, for the grading of asphalt cements for fatigue and rutting, the complex modulus and phase angle are both used [1]. The circular plates used are of a diameter of 8 mm (for higher stiffness conditions) or 25 mm (for lower stiffness conditions) with the 2 mm and 1 mm gap between them, respectively. The shear modulus is measured at 25°C with a frequency of 10 rad/s when the sample is placed between the parallel plates and is subjected to a shear force in the form of torsion. To correlate with theoretical models three different temperatures are employed for the testing and a master creep curve is typically generated. The ratio of the viscous (G'') over the storage or elastic modulus (G') that relates to the phase angle (δ) or loss tangent ($\tan \delta$) is also measured. The phase angle relates to rutting at high temperatures and to thermal cracking at low temperatures.

2.2.2.4 Bending Beam Rheometer Testing

The BBR specification test identifies the low temperature cracking of asphalt as a major distress form for asphalt pavements. Under the Strategic Highway Research Program, the bending beam rheometer (BBR) was developed. The AASHTO standard M320 [31] provides the specification criteria for passing/failing the BBR test. The two important

parameters of asphalt cement are measured by this test. First, it measures the creep stiffness $S(t)$ and second it measures the m -value of the asphalt cement as defined by the slope of the creep stiffness master curve. The low temperature thermal cracking performances of the asphalt pavement are related to the $S(t)$ and $m(t)$ value. An hour of conditioning of the binder samples at room temperature is carried out followed by an hour of conditioning at -10°C and -20°C in refrigerators before testing. The testing temperature and conditioning temperature are the same in this method. After the one-hour test the low temperature grades of asphalt are decided. In this test at a temperature of 10 degrees above the design temperature of the pavement the loading of the specimen in three-point bending is carried out. The testing duration of the binder sample is reduced from 2 hours to 60 seconds on the basis of the 10°C difference which is assumed if the time-temperature superposition is valid [20, 32]. An indication of how the asphalt binders should be able to resist low-temperature cracking is determined from the BBR along with the limiting temperature of the binders.

The stiffness of the specimen is measured at loading times of 8, 15, 30, 60, 120 and 240 seconds in order to determine the master creep stiffness curve. A measure of the binder's ability to relax stress due to viscous flow which is known as the m -value is the slope of this master curve. Hence, the ability to relax stress reduces as m -value reduces [31]. When the stiffness value is below 300 MPa and the creep rate or slope of the creep stiffness master curve (m -value) is greater than or equal to 0.3 then the asphalt material passes. The material fails the specification and could only be used in a warmer climatic condition if either the stiffness is above 300 MPa or the m -value is below 0.3. The current

AASHTO M320 specification is found to be improper through recent investigations on a large number of pavement trials and regular contracts [28, 36-38]. There is a vast difference observed in low temperature fracture performance on the pavements with the exact same low temperature grade [33, 34]. This indicates that the performance grading methods need some improvement.

2.2.3 Multiple Stress Creep Recovery (MSCR) Test

The use of performance-related criteria specific for a distress and related to climate and traffic loading was one of the objectives in the development of the PG asphalt binder specification. In pavement, the test measurements made at temperatures and loading rates consistent with conditions existing is the objective of this method. Although the test temperature where this criteria must be met is derived from the actual pavement temperature, the high temperature criteria stays the same for $G^*/\sin\delta$ (1.00 kPa for unaged and 2.20 kPa for RTFO-aged binder) regardless of the location of the pavement with this approach. The $G^*/\sin\delta$ parameter was unable to adequately capture the benefits of elastomeric modification because of the relatively small impact of phase angle (δ) on the overall value of $G^*/\sin\delta$, while it did capture viscous and elastic effects. The $G^*/\sin\delta$ used in AASHTO M320 did need a look for an improvement to the high temperature parameter due to these issues that were caused. A new procedure, the Multiple Stress Creep Recovery (MSCR) test was developed.

2.2.3.1 MSCR Test and Specification

To evaluate the asphalt binder's potential for permanent deformation; the MSCR test (AASHTO TP70) [35] uses the well-established creep and recovery test concept. The RTFO-aged asphalt binder sample is given a one-second creep load using the DSR. The sample is allowed to recover for 9 seconds after the 1-second load is removed. The test is repeated for 10 cycles with a starting application of a low stress 0.1 kPa for 10 creep/recovery cycles and then the stress is increased to 3.2 kPa.

In the existing PG tests, the material response is significantly different than in the MSCR test. The high temperature parameter, $G^*/\sin\delta$, is measured by applying an oscillating load to the asphalt binder at relatively low shear strain in the PG system. This is one of the reasons why the existing PG high temperature parameter does not accurately represent the ability of some polymer modified binders to resist rutting. The polymer network is never really activated under the very low levels of stress and strain present in dynamic modulus testing. The higher levels of stress and strain that are applied to the binder that occurs as in an actual pavement is used in the MSCR test. The response of the asphalt binder captures not only the stiffening effects of the polymer, but also the elastic effects by using the higher levels of stress and strain in the MSCR test.

Two separate parameters, namely the non-recoverable creep compliance (J_{nr}) and the percentage of recovery (MSCR recovery) during each loading cycle, can be determined in the MSCR test. The average of ten loading cycles at each shear stress level is recorded. A better correlation with rutting potential than $G^*/\sin\delta$, specially for modified asphalt

binders, has been shown by this through numerous field and laboratory studies [36]. The test temperature used for the MSCR test is selected based on actual high pavement temperatures with no grade bumping, unlike in the AASHTO M320 system.

The J_{nr} (determined at 3.2 kPa shear stress) is required to have a maximum value of 4.0 kPa^{-1} for the standard traffic load. The J_{nr} of the asphalt binder needs to be lowered with the required maximum values of 2.0 and 1.0 kPa, respectively, as the traffic increases to heavy and very heavy loading. The data determined at 0.1 kPa shear stress is also important for lower traffic zone whereas the main requirement for J_{nr} is determined at 3.2 kPa shear stress. AASHTO MP19 maintains a requirement that the difference in J_{nr} values between 0.1 kPa and 3.2 kPa shear stress should not exceed a ratio of 0.75 so as to minimize concerns that some asphalt binders may be sensitive to changes in shear stress.

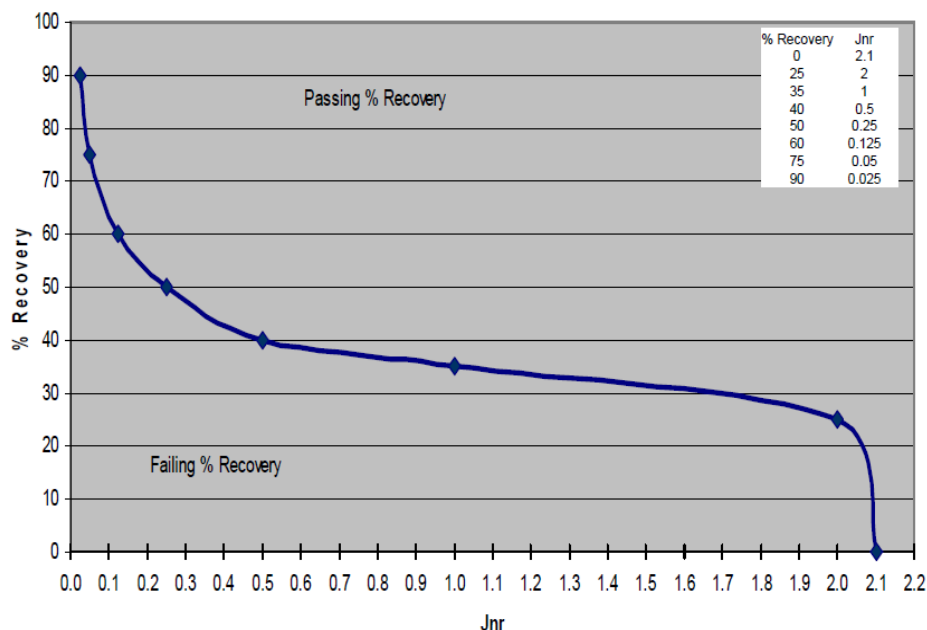


Figure 9. Non-recoverable creep compliance (J_{nr}) versus percentage recovery [37].

To indicate whether an asphalt binder has a sufficient elastic component the MSCR recovery may be used in combination with J_{nr} . The asphalt binders that fall above the curve (Figure 9) are considered to have high elasticity and those that are below the curve are considered to have low elasticity.

The latest improvement to the Superpave® Performance Graded (PG) asphalt binder specification is the MSCR test. A high temperature specification parameter is provided that more accurately indicates the rutting performance of the asphalt binder and is blind to modification by this new test. This provides an improvement in several ways which are as follows [36]:

- J_{nr} is better correlated with rutting potential than $G^*/\sin\delta$.
- To properly characterize the high temperature performance of modified asphalt binders is done by the MSCR test results that could be used with modified and unmodified asphalt binders. It eliminates the need for additional tests.
- There is now criteria to eliminate binders that are overly stress sensitive, which would previously have passed the PG criteria and potentially have been susceptible to rutting in the field.
- The MSCR Recovery does a better job of characterizing polymer-modified asphalt binders and is faster/easier to determine than other “PG Plus” tests like the Elastic Recovery test.
- Regardless of traffic loading, the MSCR test is performed at the actual pavement temperature.

2.2.4 Ontario's Improved Low Temperature Specification Tests

A significant number of researchers in the earlier part of last century have studied the effects of isothermal conditioning on the low temperature rheological properties of asphalt cement. While measuring the rheological properties at low temperatures in asphalt cement, Traxler (1936, 1937, 1961) [38-40] advised that physical (reversible) hardening mechanisms need to be taken into consideration. It was found to be useless to study properties like creep and stress relaxation without studying the physical (reversible) ageing phenomenon as per Struik (1970) [41].

The AASHTO M320 relates to problems are in the absence of a proper chemical ageing method and the absence of true failure tests (BBR and DSR are rheological tests that only measure in the low strain regime whereas thermal cracking is a high strain phenomenon) along with the insufficient physical ageing (conditioning) of the asphalt cement. In Ontario, to address the inadequacies of the AASHTO M320 specification two test methods have recently been developed, which are [25, 30, 31, 42]: DENT test - LS-299 [43]; and Extended BBR test - LS-308 [44].

In recent times, it has been found that a binder's physical hardening (aging) tendency is an important indicator of thermal cracking performance [25, 28, 42, and 45]. The test to study the ductile failure mechanisms in asphalt cement and hot mix asphalt under high strain conditions is termed as the double-edge-notched tension (DENT) test [33, 34, 44]. A good correlation with low temperature and fatigue distress is observed based on the DENT protocol that determines the approximate critical crack tip opening displacement

(CTOD) [33, 44]. In comparison to the regular BBR protocol it is observed that the newly developed test methods, LS-299 and LS-308, give a consistently better ability to predict either good or poor performance. On extended BBR testing, the increase in the conditioning time prior to three-point bending tests is one approach taken in Ontario's recently developed LS-308 method [44].

2.2.4.1 Double Edge Notched Tension Testing (MTO LS 299 Method)

To determine the essential (w_e) and plastic works (w_p) of fracture in the ductile regime at 15°C and at a rate of loading of 50 mm/min is termed as the double-edge-notched tension test (DENT) for asphalt cements, which was developed at Queen's University [36, 38, 47]. The conditioning of the samples at 15°C in the water bath and for 24 hours was carried out before testing them. This set of conditions measuring the resistance to ductile failure under high strain conditions at around freeze-thaw temperatures, where a lot of movement due to water freezing and thawing in the foundation of the pavement is experienced. A benefit of the DENT test is that it is reasonably fast.

Mainly the measurement of the failure energy and the peak force is carried out by this test method. The calculation of the crack tip opening displacement (CTOD) is done from the peak force at a 5 mm ligament length. CTOD is the approximate critical crack opening displacement (m), providing a measure of strain tolerance in the ductile state under near plane strain conditions (high confinement). Then, the fracture behavior of asphalt binders can be determined via crack tip opening displacement (CTOD). A property that correctly ranks performance and provides a high correlation with cracking

distress was revealed that the crack tip opening displacement parameter could be used [43]. The worse condition of the roads could be incurred from the lower value of CTOD. The procedures followed are now outlined in a laboratory standard LS 299 in the Laboratory Testing Manual of the Ministry of Transportation of Ontario [43].

A detailed discussion on the procedure for LS-299 shall be provided in the experimental section. The test procedure consists of the pulling of a notched binder sample until it fails in a water bath. The distances between two opposing notches (ligaments) are 5 mm, 10 mm and 15 mm in length. An approximate accuracy of 85 % is observed for prediction of failure in real world contracts from this test method [25].

2.2.4.2 Extended BBR Testing According to MTO Method LS-308

According to AASHTO M320 criteria ($S = 300$ MPa and $m = 0.3$) the regular tests are carried out to determine a pass and fail temperature after one hour of conditioning. The testing for the m -value and the limiting stiffness temperatures of the specimens is done as per the extended BBR protocol [46], where they are stored for one hour, 24 hours, and 72 hours at $T_{\text{design}} + 10^{\circ}\text{C}$ and $T_{\text{design}} + 20^{\circ}\text{C}$ conditioning and hence the method is called an extended BBR test. Both pass and fail temperatures are selected in order to determine an exact grade according to AASHTO M320 criteria by interpolation. The calculation of the grade temperature and subsequent grade losses are carried out at the end of each conditioning period. The warmest minus the coldest limiting temperature (where S reaches 300 MPa or m reaches 0.3) is the worst grade loss. To provide a high degree of confidence that thermal cracking is completely avoided and not to perfectly correlate with

low temperature cracking distress this method is designed. Although, if the cold spell that occur during the early life of the contract, it is a must to protect the roads that spend most of their time at a relatively warm $T_{\text{design}} + 20$ from a cold spells at $T_{\text{design}} + 10$.

As the method is merely an extension of the BBR test method with slight modifications it provides 95% accuracy and is also easy to repeat and reproduce [25].

2.3 Asphalt Modification

2.3.1 Need of Modification

Over 50 years the asphalt cement modification has been practiced but has received a special attention in the past decade or so. In order to meet specifications some asphalt cements require modification. The following factors are a few that have created additional attention for modifications [46]:

- **Specifications of Superpave® asphalt binder:** The asphalt binders require stiffness at high and flexibility at low temperatures as per the Superpave® asphalt binder specifications developed in the 1990s. This is not possible without asphalt binder modification in regions with extreme climatic conditions.
- **Increased Demand:** In recent years the traffic volume, load and truck tire pressure have increased substantially that could cause increased in rutting and cracking. Many modifiers improve asphalt's stiffness at normal service temperatures to increase rut resistance. It also decreases the asphalt binder's stiffness at low temperatures to improve resistance to thermal cracking.

- **Environmental and Economic Issues.** In order to gain benefit it is both economically and environmentally sound to recycle waste and industrial byproducts (such as tires, roofing shingles, glass and ash). They are often used as additives in HMA when they can benefit the final product without creating an environmental liability.
- **Fund from Public Agency:** Modified asphalt cement is usually higher in initial cost than unmodified asphalt cement, but it should provide a longer service life with less maintenance.

In the market there are numbers of binder additives available, however all modifiers are not appropriate for all applications. There are following improvements in distress can be achieved using different modifiers.

- Higher stiffness at high service temperatures. This will reduce rutting and shoving.
- Lower stiffness and faster relaxation properties at low service temperatures which reduce thermal cracking.
- Increased adhesion between the asphalt binder and the aggregate in the presence of moisture that will reduce stripping.

2.3.2 Polyphosphoric Acid (PPA)

Asphalt is generally modified with sulphur [47, 48], plastomers [49, 50], mineral acids [51], elastomers [52, 53] or thermosets [54, 55] in an attempt to change its characteristics

and to improve performance. The use of polyphosphoric acid (PPA) by itself or in combination with a polymer to modify asphalt is of much interest.

Nowadays, it has been considered that the performance conditions for large loads, or slow traffic could be met by an increase in the higher temperature of the performance grade with the advent of Superpave® and the application of performance grading (PG). Explaining this with an example, the standard grade PG 64-22 which is for normal traffic could be shifted to PG 70-22 for slower heavy traffic and to PG 76-22 for heavy standing or interstate conditions. Generally, asphalt modification is required when the performance grade spans more than 86-90°C (e.g., PG 76-22, PG 64-34). The polyphosphoric acid (PPA) modification can be used as it improves the high temperature rheological properties without affecting the low temperature grade along with the polymer modification which is more commonly used.

The method to treat asphalt is described in the US Patent number 3,751,278 on August 7, 1973. The object of the invention was to provide a method that alters the viscosity penetration relationship of asphalt which could be summarized from that method. Specifying this in more detail it was designed to substantially increase the high temperature characteristics of asphalt particularly in high temperature viscosity and softening point, without notably decreasing asphalt 25°C penetration. To modify asphalt binders the mixtures of condensed derivatives of phosphoric acid (H_3PO_4) with P_2O_5 equivalent or greater than 100 % were used.

As in Figure 10, the phosphorus pentoxide (P_2O_5) and phosphoric acid (H_3PO_4) are the basic compounds for the production of polyphosphoric acid (PPA). Firstly the oxidation of the phosphorus is carried out to form phosphorus pentoxide which then crystallizes as P_4O_{10} , then it is reacted with water and in turn the phosphoric acid is formed. This path to H_3PO_4 is termed as the dry process by which high purity material is obtained. PPA is an oligomer of H_3PO_4 .

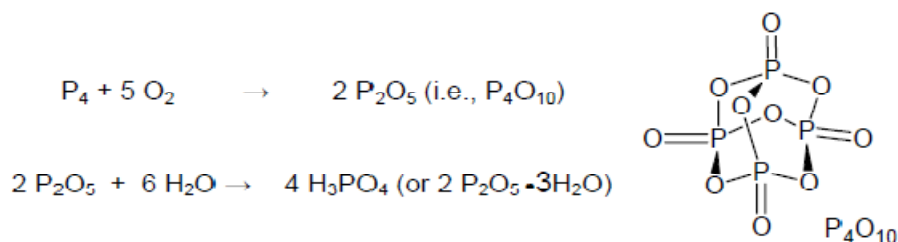


Figure 10. Production and reaction of phosphorus pentoxide [56].

By the dehydration of H_3PO_4 at high temperatures or by heating P_2O_5 dispersed in H_3PO_4 , a high purity material could be produced [57]. These reactions produce different chains lengths and distributions thus forming equilibria as shown in Figure 11. The dispersion method generally produces chains with more than 10 repeat units, while the dehydration method aims to produce short chains. The number of repeat units in the PPA chain, n in Figure 11, differs from one chain to another in the production of PPA and provides a distribution of chain lengths. It was found by Jameson that 100 % phosphoric acid is a mixture of H_3PO_4 (orthophosphoric acid) with about 10 % dimer (pyrophosphoric acid) by weight, when he characterized this distribution [57].

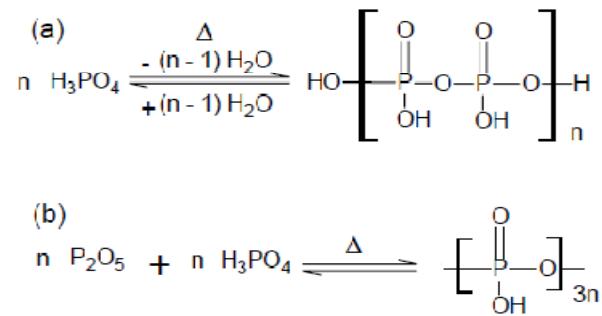


Figure 11. Production of PPA from the dehydration (a) and dispersion (b) methods. n is an integer [56].

The exact reaction between PPA and asphalt can only be inferred with the many functional groups in asphalt. Giavarini et al. [51] pointed to a reaction of PPA with asphaltenes, and Orange et al. [58] showed that it can occur by phosphorylation. Many competing reactions were possible as concluded by Baumgardner et al. [59]. When mixed with asphalt it is noted that PPA may be a very weak acid. The medium must be of sufficiently high dielectric constant (ϵ) for the PPA to dissociate into PPA^- and H^+ .

A disadvantage is that a negative effect on long term fatigue performance may be observed on asphalt modified by polyphosphoric acid (PPA) depending on the source of crude oil [14].

2.3.3 Elvaloy®

Elvaloy® is the trade name for a reactive ethylene terpolymer (RET) that chemically reacts with asphalt, avoiding the problems with separation during storage and transportation as a result of the reaction. The characterization by a low polarity and low

reactivity plastomers of the ethylene polymers are done. Being soluble in hot oils, hot wax and hot hydrocarbons they are like waxes in this respect with a low dielectric constant. They are known to be inert. It is desirable to modify the ethylene polymers for some uses so as to impart more polarity to the polymers, to be able to use them in reactions with other resins and to make them flexible. A high level of esters are required so as to obtain high degree of polarity (to improve the dispersion of these materials in asphalt), that while retaining the hydrocarbon chain as the major feature of the polymer in turn would adversely affects the inherent advantage of the long ethylene chain (low cost, good temperature behavior, etc.) [60].

At the University of Maryland, a study was carried out on the laboratory performance of asphalt modified with Elvaloy® in the year 1995 by Witczak, Hafez and Qi [61]. The modification by 0 %, 1.5 % and 2.0 % Elvaloy® by weight of binder of two different grades of asphalt was carried out. By the addition of Elvaloy® the susceptibility of the mixtures to moisture damage was found to be greatly decreased. Increasing concentrations of Elvaloy® resulted in a marked decrease in the deformation as shown in an analysis of repeated load permanent deformation behavior. RET reacts with the asphaltene fraction of asphalt to increase stiffness and elasticity where SBS forms a network around the asphaltenes (Figure 12).

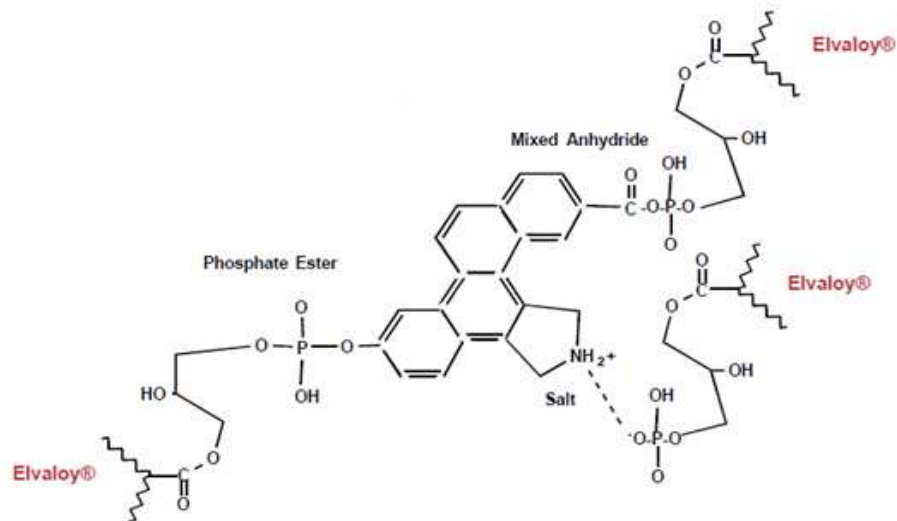


Figure 12. A typical reaction of RET with asphalt [62].

It was found in a study on the low-temperature rheological properties of polymer modified binders that Elvaloy® in combination with granite had a significantly higher (poorer) fracture temperature than with limestone or granite aggregate treated with hydrated lime [63].

A lap shear test was devised for high temperature binder properties that appear to agree with high temperature DSR measurements by Babcock et al. [64] at the DuPont Institute. Due to the loss of integrity within asphalt, the results so obtained indicated that the binder failure at temperatures above 6°C tends to be cohesive failure. On the other hand, from a loss of adhesion between the binder and the substrate at around 6°C and colder, the failure is adhesive. In fact it also showed better performance in this test than SBS or the control neat asphalt, while a chemically reactive polymer is expected to perform better.

2.3.4 Styrene–Butadiene–Styrene (SBS) Polymer

To increase the elasticity of asphalt, styrene–butadiene–styrene (SBS)-type polymers are used which are elastomeric block copolymers. Although the addition of SBS type block copolymers has economic limits and can show serious technical limitations, it is probably the most appropriate polymer for asphalt modification according to a 2001 review in Vision Technology by Becker et al. [65]. A decrease in strength and resistance to penetration is observed at higher temperatures as claimed by some authors in spite of an increase in the low temperature flexibility. However, SBS is the most used polymer to modify asphalts which is followed by reclaimed tire rubber.

An improvement in the performance of the asphalt has been observed on addition of polymers which are the chains of repeated small molecules. A greater resistance to rutting and thermal cracking, and decreased fatigue damage, stripping and temperature susceptibility of the pavements with polymer modification is found. At locations of high stress, such as intersections of busy streets, race tracks, airports, and vehicle weighing stations the polymer modified binders have been used with great success. The styrene–butadiene–styrene (SBS) is the major polymer that has been used to modify asphalt. A comparison of the fatigue and rutting resistance of three PG 70–22 binders, one unmodified, one SBS modified, and one SBR modified was studied in the year 2001 by the Ohio Department of Transportation by Sargand and Kim [66]. Even though all three had the same performance grade it was found that the modified binders were more resistant to both fatigue and rutting than the neat binder.

The transmission electron microscopy was used to better understand the behavior of SBS in asphalt binders [67]. The variation in the morphology was found as a continuous asphalt phase with dispersed SBS particles, a continuous polymer phase with dispersed globules of asphalt, or two interlocked continuous phases depending on the sources of asphalt and polymer. As an indication of resistance to rutting it is the formation of the critical network between the binder and polymer that increases the complex modulus.

The possibility of recycling SBS modified asphalt for resurfacing pavement was also described in the Journal of the Association of Asphalt Paving Technologists (AAPT) by Mohammed et al. [68]. The impact of the extraction and recovery process on the binder was minimal. In Louisiana from Route US61, eight-year-old SBS modified binder was recovered which was found to have experienced intensive oxidative age hardening. The binder was quite brittle at low temperatures. The blends of virgin and recovered polymer modified binder that were anticipated at both low and high temperatures were found to be stiffer. As the percentage of recovered binder increased it was also found that fatigue resistance decreased, whereas the rutting resistance increased. A report was published [69] on the cracking resistance and healing characteristics of Superpave® mixes on the basis of the effect of SBS modification in 2004 by the Florida Department of Transportation and FHWA. Primarily due to a reduced rate of micro-damage accumulation it was found that SBS benefited cracking resistance.

Chapter 3

Experimental

3.1 Materials

3.1.1 Base Asphalts

As mentioned earlier, the composition of asphalt varies with source of the asphalt and its modifiers. For this work we have used two types of base asphalt: one with the performance grade (PG) of 58-28 obtained from a major asphalt producer in the Montreal, Quebec area, and another with a penetration grade of 80/100 produced from Cold Lake crude in the Edmonton, Alberta area. For these two different base asphalts the type and concentration of modifiers were varied to study the effects of both modifier type and base asphalt.

3.1.2 Modifiers

There are multiple types of asphalt modifiers available in the market. Different modifiers have specific properties that help to improve the performance of the asphalt binder. In this experiment three types of modifiers are mainly used with different percentage ratio to compare and identify the minimum concentration for required performance of asphalt binder. One of the modifiers used is styrene–butadiene–styrene (SBS)-type polymer. This type of modifier is widely used for the improvement of the elastic portion in the asphalt binder. The second modifier used in the experiment is Elvaloy® which is a reactive ethylene terpolymer (RET); it is manufactured by the E.I. du Pont Company. This is used so as to impart more polarity to the polymers and to make them flexible. The third major

modifier used for modification is polyphosphoric acid (PPA); it improves the high temperature rheological properties without affecting the low temperature Superpave® grade.

3.2 Preparation of Modified Asphalt Binders

The linear SBS block copolymer has a high molecular mass (between 100,000 to 200,000). When asphalt binder and SBS are blended, the elastomeric phase absorbs the asphalt maltene fraction and swells up to nine times its initial volume. At a suitable SBS concentration, normally between 3 to 5 %, a polymer network is homogeneously formed throughout the asphalt matrix and this changes significantly the asphalt properties [70-72]. On the other hand, as the molecular weights of the polymeric chains are higher than or similar to those of the asphaltenes, they compete for the solvency of the maltene fraction and a phase separation may occur if there is an imbalance between the components. A phase separation indicates incompatibility between the asphalt and polymer and can be avoided by adding aromatic oils or compatibilizer agents to the mixture. The degree of compatibility of SBS varies with source of base asphalt and its composition. However, a high quantity of aromatic oils can dissolve the polystyrene domains and destroy the benefits of the SBS copolymer resulting in a loss of the polymer-modified asphalt binder properties [73, 74]. Since the storage stability and compatibility are very important properties, the aromatic oil plays an important role in the modified asphalt binder with SBS.

Elvaloy® mixing procedures followed the guidelines described in DuPont's "Technical Information" section regarding asphalt modification [60]. The heating of the asphalt could be done at 180°C followed by continuously high shear stirring, keeping it for 10-15 minutes at same temperature. To prepare the mix half-gallon paint cans are needed. The addition of the Elvaloy® to the hot asphalt should be done slowly (about 10 g/min). After the addition of polymer continuous stirring is needed for two hours at 180°C. It is considered that the entire mixing of the polymer completely takes place after two hours. This step is thought to be an important one as during this stage the addition of acid may cause polymer lump formation and would prevent further dissolving of the polymer.

The asphalt modified with polyphosphoric acid usually follows this procedure. The asphalt is heated to 165°C, and stirred with a mechanical stirrer running at 450 rpm while adding the acid. Stirring should continue for a further 20 minutes while maintaining the temperature at 165°C.

3.3 Asphalt Cement Aging

An aging procedure was proposed to simulate short and long term field oxidative aging of asphalt binders in order to understand the failure mechanism of asphalt pavement as per the Strategic Highway Research Project (SHRP) that was concluded in the early 1990s. The development of the Rolling Thin Film Oven (RTFO) and the Pressure Aging Vessel (PAV) was included in this proposal. As a result of the effect of time, temperature, traffic load and environment the PAV asphalt sample were used to simulate "in service" aging

of binders whereas the RTFO samples of asphalt binder is used to simulate short term aging (hot mixing of asphalt and aggregate) [30].

3.3.1 Rolling Thin Film Oven (RTFO) Test

In the RTFO, short-term aging of asphalt binders involves the following steps where the air flow of the RTFO machine is adjusted to 4 L/min and the temperature is set to 163°C (325°F) along with which in a transparent glass tube about 35 g of asphalt sample is measured. As shown in Figure 13 the tubes are arranged on the RTFO machine. Then to induce oxidative hardening (age hardening) the samples are allowed to rotate continuously for 85 minutes. This is typical of the aging that occurs during the hot mixing process or the early stages of the pavement life and it is expected that the aged samples would reflect the rheological changes in the properties of the asphalt binders [75].



Figure 13. Rolling Thin Film Oven (RTFO) with empty glass jars held inside [10].

To determine the effect of heat and air on the moving film of asphalt this test method (RTFO test) is designed. The approximate change in properties during conventional hot mixing is indicated by this test.

3.3.2 Pressure Aging Vessel Test

The pressure aging vessel is mainly used to simulate long-term aging of pavement. The test procedure is as follows where firstly as per the above explanation the asphalt binder samples are aged by the RTFO method followed by which further aging of these samples in a standard steel pan for 20 hours in a vessel (PAV) pressurized with air to 2.1 MPa at a temperature of 100°C (212°F) is carried out. It is expected that PAV-oxidized asphalt binders could be used to estimate the rheological properties of binders after significant aging on the road as the pressure aging vessel system is considered to simulate the aging caused by oxidation during 7-10 years of pavement service. Figure 14 presents a schematic diagram of the PAV system.



Figure 14. Pressure Aging Vessel (PAV) [10]

3.4 Experimental Procedures

3.4.1 Dynamic Shear Rheometry

An oven was preheated to 340°F and the samples were placed in the oven so as to allow them to melt and thus by this means the sample is prepared for the test. Approximately 20-30 minutes is considered to be the average melting time of the sample. A small amount of the melt was poured into the mold of silicon rubber for parallel plate samples. The wells of the mold consist of a diameter of 25 and 8 mm and depth of 3 mm where the test samples were then left to cool at room temperature for 1 hour.



Figure 15. Dynamic Shear Rheometer [76].

A model AR 2000 rheometer from TA Instruments with a liquid nitrogen controlled environmental chamber is used to obtain the data. Figure 15 shows a picture of the dynamic shear rheometer. The determination of the complex modulus (G^*), storage modulus (G'), loss modulus (G''), and phase angle (δ) or loss tangent ($\tan(\delta) = G''/G'$) is done using the TA Instruments data analysis software. There are two parallel plate dimensions (diameters of 8 mm and 25 mm) used for testing. The smaller plate (8 mm) was used for lower temperatures while the larger plate (25 mm) was used for higher temperatures. A diagram of the parallel plate geometries is shown in Figure 16.

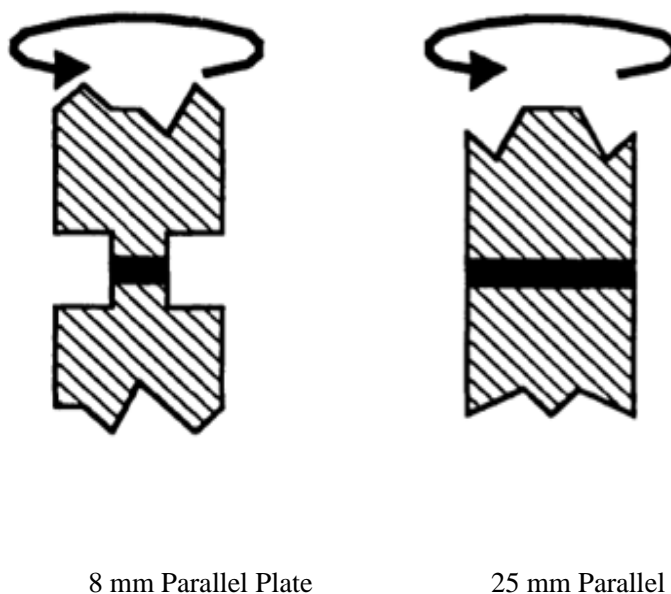


Figure 16. Parallel plate geometries used for dynamic shear rheometer testing [20].

To obtain an idea about the separation of the plate once the sample had been added, the digital gauge was set to zero with the empty plates before conducting a new test. The sample was held between two plates. The lower plate is oscillated while the upper plate is

kept fixed. On the rheometer as the contact and compression of the sample was exerting a tensile force the upper plate was gently lowered. The excess asphalt that had been compressed outside the diameter of the plate was trimmed out using a trimmer when the gap between the two plates was approximately 2.1 mm. Until a final gap of 2 mm was achieved between two plates, the upper plate was lowered up to that level.

3.4.2 Multiple Shear Creep Recovery Test

The Multiple Stress Creep Recovery (MSCR) test consists of the determination of percent recovery and non-recoverable compliance of asphalt binders. This is performed using the Dynamic Shear Rheometer (DSR) at a specified temperature. It is designed for using the residue from the Rolling Thin Film Oven Test (RTFOT).

The sample preparation for the MSCR test is similar to the AASHTO T 315 where a 25 mm plate is used and the temperature control is as the T 315 requirements. The aging of the asphalt binder is carried out with the help of RTFO which is then tested using the DSR instrument. With the 1 mm of gap setting the 25 mm parallel plate geometry is been used. The testing of the sample is done in creep at two stress levels namely 0.1 kPa and 3.2 kPa which are followed by recovery at each stress level. The creep portion of the test lasts for 1 s which is followed by a 9 s recovery. Ten cycles are run at each of the two stress levels for a total of 20 cycles.

The presence of an elastic response in an asphalt binder under shear creep and recovery at two stress levels at a specified temperature is determined using this method.

The stress and strain values are recorded at least every 0.1 s for the creep cycle and at least every 0.45 s for the recovery cycle for the total length of the test on an accumulated basis such that, in addition to other data points, the data points at 1.0 s and 10.0 s for each cycle are recorded. For the completion of the two-step creep and recovery test the total time required is 200 s. Non-recoverable creep compliance has been shown to be an indicator for the resistance of the asphalt binder to permanent deformation under repeated load.

3.4.3 Ductile Failure Testing According to MTO Method LS-299

To control fatigue and thermal cracking in asphalt pavements the double-edge-notched tension test was developed [25, 43]. The melt asphalt is poured in molds with three different notch depths (ligaments between notch tips include 5, 10 and 15 mm). A photograph of how the molds are filled is shown in Figure 17 (a). To ensure a good repeatability, three sets are poured for each binder sample. The method plots the specific total work of fracture (area under the force-displacement curve divided by the cross sectional area of the ligament) versus the ligament length and the regression so obtained is extrapolated to a zero ligament to obtain the essential work of fracture, w_e . The work done to pull a very thin filament of asphalt cement apart just like it would occur in between two large aggregate particles is represented by the essential work of fracture. In order to arrive at an approximate critical crack tip opening displacement (CTOD), the essential work of fracture is subsequently divided by the net section stress in the smallest ligament (5 mm). A measure of strain tolerance in the ductile state in the presence of

significant constraint as it would occur during ductile failure in the hot mix asphalt is provided by the approximate CTOD.

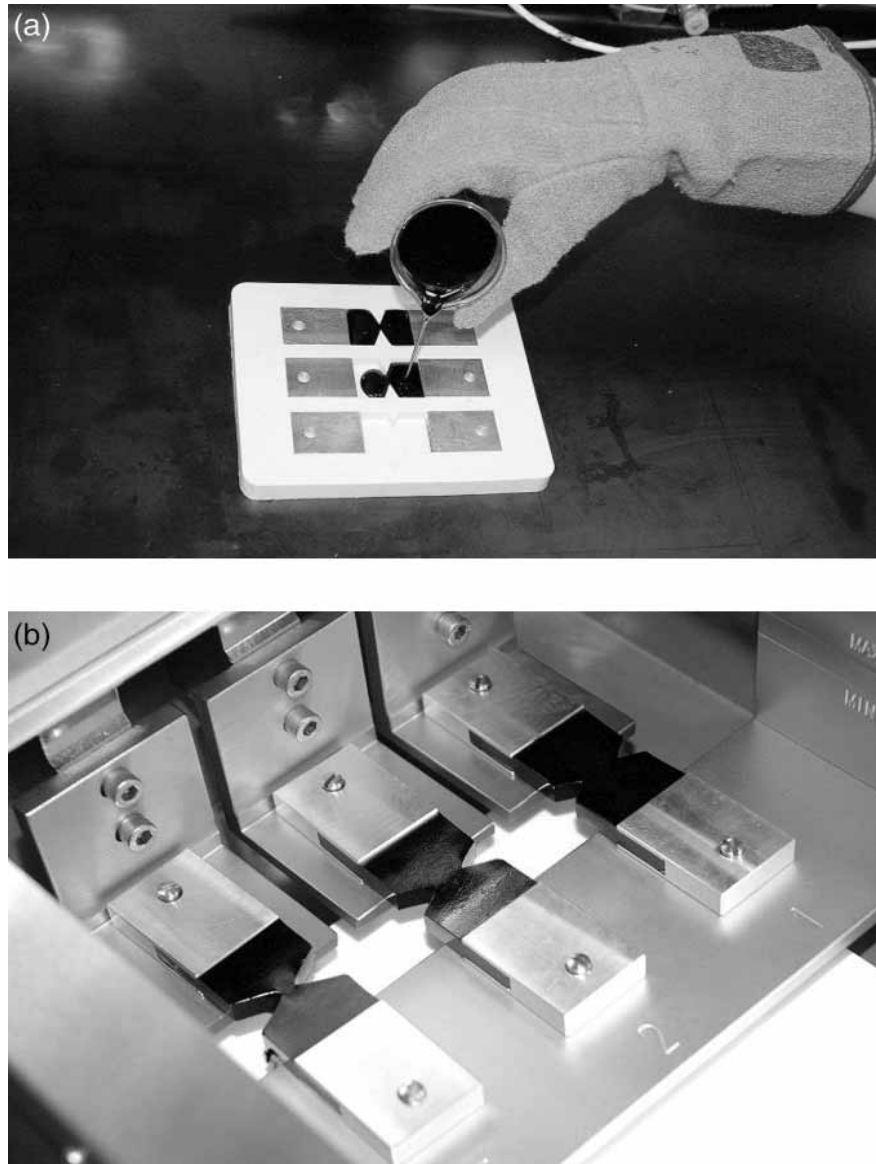


Figure 17. (a) shows the mold preparation (b) shows mold with DENT instrument [77].

For all samples tested in this study the tensile machine was set at a speed of 50 mm/min. Since typical ductile failure occurs over much slower speeds and longer time

periods this test speed consists of a compromise that allowed a test to be finished within a reasonable amount of time [25]. For a detailed description of the exact procedures the reader is referred to the LS-299 method [43].

3.4.4 Regular BBR Testing

The pouring of asphalt cement specimens was carried out into rectangular beams which were then left to cool for approximately one hour at room temperature. Further cooling of these beams at the testing temperature for an additional one hour was done prior to testing in three point bending. A schematic of the aluminum mold and the dimensions of the asphalt beam is given in Figure 18. There are two temperatures, -14°C and -24°C , used for both the conditioning and testing performed. A schematic diagram of three point bending beam rheometer is shown in Figure 19.

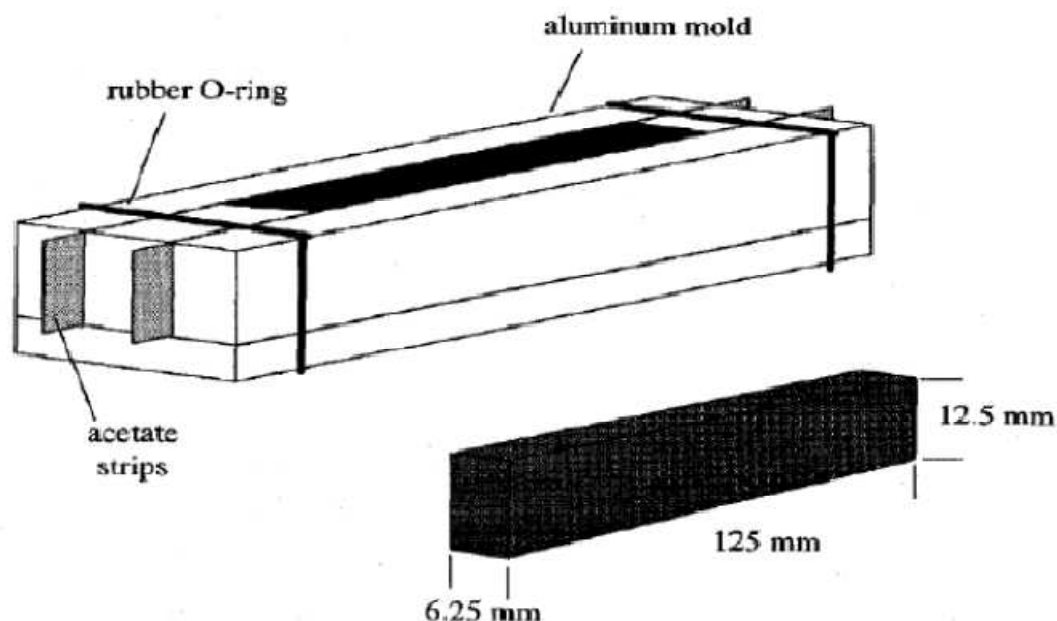


Figure 18. BBR test mold schematic and sample dimensions [77].

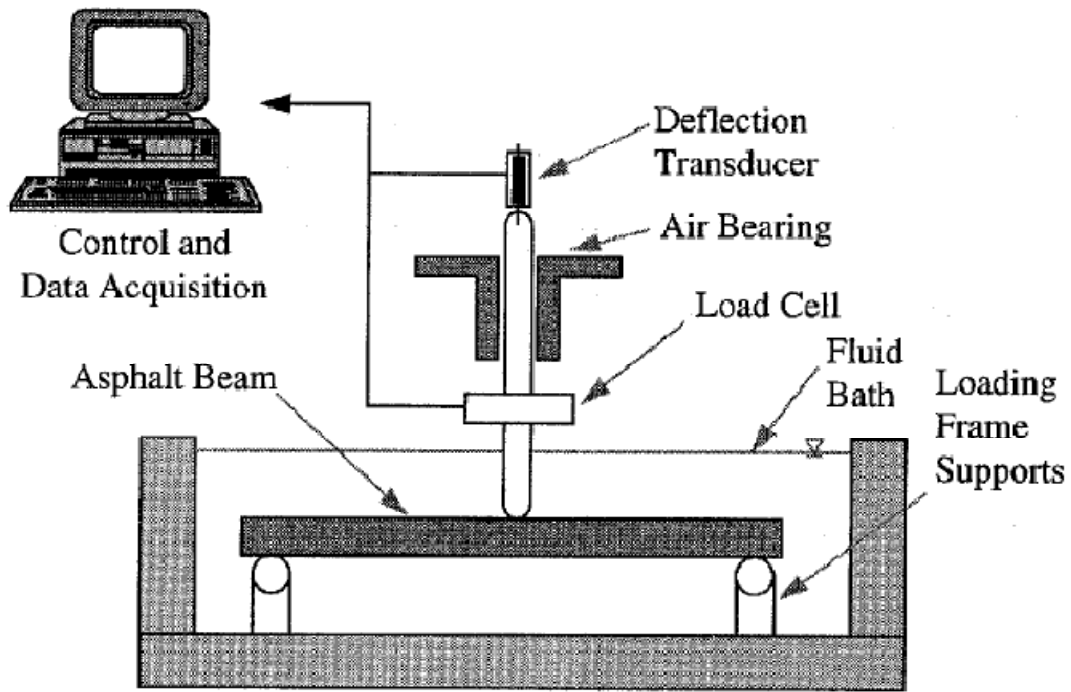


Figure 19. Schematic of three point bending beam rheometer test setup [77].

With a load of approximately 1000 mN for a period of 240 s, the beam specimens were loaded in three-point bending. At a loading time of 60 s the creep stiffness ($S(t)$) and the slope of the creep stiffness master curve ($m(t)$) were calculated while the limiting grade temperature was recorded when the warmest temperature at which $S(60\text{ s})$ reached 300 MPa or the $m(60\text{ s})$ reached 0.3. By interpolation between a pass and a fail temperature which were chosen at 6°C intervals, the limiting S and m temperatures were determined. The testing of all the samples was carried out in duplicate wherein the reproducibility was usually found to be exemplary. The approximate error in all BBR data is $\pm 1^\circ\text{C}$ as determined through round robin tests conducted by the Ontario Ministry of Transportation.

3.4.5 Thin Film Aging

In thin film aging a 700 micron film of asphalt sample is heated at 45°C in an oven. To record the aging process, infrared spectra are taken at regular intervals. These films are considered to be easy to produce. To prepare the 700 micron film, 3.18 g of asphalt is weighed out and placed into a flat bottom container to form a uniform layer. At 45°C the viscosity is found to be too high in order to soften the samples enough and hence they were preheated for around 10 min at 85°C on a hot plate so they would flow readily into thin and homogeneous films.

For each sample 5 replicates were prepared where every lid is to be taken out at various intervals like 1,000 h, 2,000 h, 3,000 h, 4,000 h and the final one at 5,000 h. These lids were placed into the oven in the form of rows and were rotated within the oven at regular intervals. The lids are taken out for the spectral analysis on fixed intervals wherein two spectra are taken and the results obtained were averaged.

The spectral analysis was carried out after 48 hours, 1 week, 2 weeks, 3 weeks, 4 weeks, 6 weeks, 8 weeks, 12 weeks, 16 weeks and 18 weeks. Also, samples were weighed before placing them in the oven as well as after removal at various intervals so as to have a record of the loss of volatile components during the heating process.

3.4.6 Infrared Spectroscopy

Infrared spectroscopy was done for the analysis. Samples were prepared on a KBr disc by placing a small amount of asphalt onto the disc with the help of a clean spatula. As

asphalt is a semi-solid material it easily formed a thin film when placed on a hot plate at 80°C for melting. This is then spread out into a thin, transparent film with the help of the spatula. While heating the sample a precaution is taken by not heating it longer than 30 seconds.

The data analysis was carried out using GRAMS32 software. The area under the CH₃ peak, which is taken as the standard, could be obtained ranging from 1400 to 1330 cm⁻¹. In the same manner the integration of the peaks for carbonyl, sulfoxide, aromatic, butadiene and styrene were calculated. The integral bounds are found approximately at 1760 to 1655 cm⁻¹, 1070 to 985 cm⁻¹, 1650 to 1535 cm⁻¹, 983 to 955 cm⁻¹ and 710 to 690 cm⁻¹, respectively, while the peaks are located at 1700 cm⁻¹, 1030 cm⁻¹, 1600 cm⁻¹, 968 cm⁻¹ and 700 cm⁻¹ [78]. The integral areas are recorded for each with a slight adjustment done at the edges of these bands by sliding them from left or right to cover the valley to valley region.

The indices are calculated for all individual regions from the ratio of integration of the above mentioned peak divided by the CH₃ peak integration value. This gives the index for a particular region. For example, the carbonyl index was calculated by taking the ratio of the integral of the carbonyl peak to the integral of the CH₃ peak.

Chapter 4

Results and Discussion

4.1 Dynamic Shear Rheometer Testing

4.1.1 High Temperature Superpave® Grading

The high temperature Superpave® grades, which are considered a measure of rutting resistance during summer, were determined for all straight and modified asphalt cements according to standard procedures in a dynamic shear rheometer (DSR). The findings are presented in Figures 20 and 21, below.

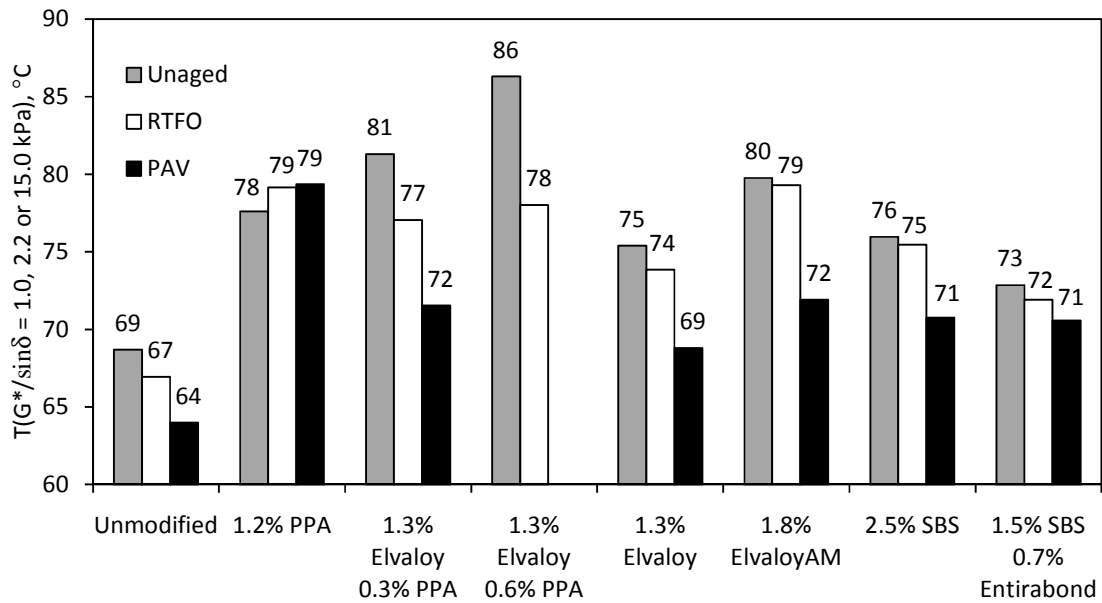


Figure 20. Comparison of high temperature Superpave® performance grades of base asphalt Cold Lake 80/100 with different modifiers. Note: The first three Elvaloy®-modified samples used Elvaloy® Grade 4170 while the last used Elvaloy® AM as indicated.

It should be noted that the regular Superpave® grade is determined by the lowest of the limiting unaged and RTFO values (i.e., the grade is set by whichever material, unaged or RTFO, reaches its specified limit for $G^*/\sin\delta$ at a lower temperature). Both Figures 20 and 21 also show a limiting temperature where the PAV residue reaches a (somewhat arbitrary) value of 15.0 kPa. This was done to investigate how further aging, as is done in for instance the pressure aging vessel (PAV), affected the $G^*/\sin\delta$ rutting parameter for different modifiers.

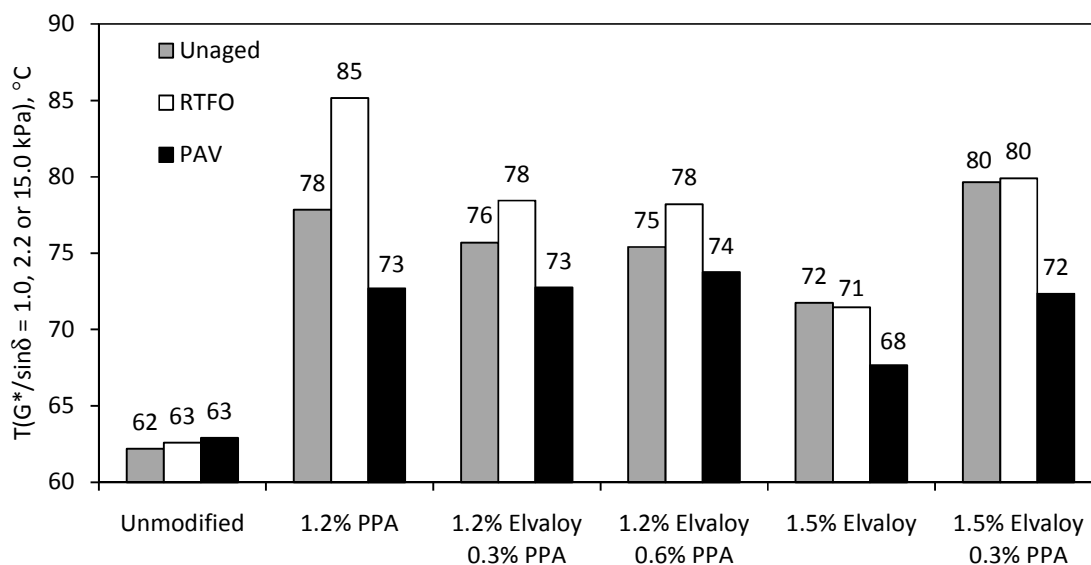


Figure 21. Comparison of high temperature performance grade of PG 58-28 base asphalt with different modifiers. Note: All Elvaloy®-modified samples used the Elvaloy® 4170 grade.

It can be observed from Figure 20 that all the modifiers are able to increase the high temperature Superpave® grade for the Cold Lake 80/100 base asphalt by significant

amounts. One more similar point that comes out is the percentage of polyphosphoric acid (PPA) having an impact on the performance grade. The sample with 1.2 % PPA appears to have a performance grade that is slightly higher than those of the other polymer-modified systems. However, this is likely due to the fact that these materials were formulated to obtain nearly the same ring and ball softening points ($T_{R\&B}$) by the E.I. du Pont Company laboratory in Prague, Czechoslovakia. The other notable finding is that the sample with only 1.3 % Elvaloy® 4170 in Cold Lake 80/100 without any PPA reached a slightly lower high temperature grade compared to the sample containing additional PPA (both 0.3 and 0.6 wt %). Hence, it appears that there is a synergistic effect for having both PPA and polymer present.

High temperature behaviors of the PG 58-28 samples with varying amounts of two different modifiers can be summarized similarly. All of the different modifiers are able to increase the high temperature Superpave® grade by significant amounts from the ~PG 62 level of the base asphalt. The addition of PPA to the Elvaloy® samples appears to have a beneficial effect. The sample with only 1.2 % PPA appears to again outperform the others by a small amount. It is further interesting to note that three of the four Elvaloy®-modified samples increase their limiting temperature after RTFO aging. This contrasts with the Cold Lake systems where three out of four Elvaloy® systems show a decrease after RTFO aging albeit a slight one.

4.1.2 Intermediate Temperature Superpave® Grading

The intermediate Superpave® grades, which are supposed to provide a measure of fatigue cracking resistance, were similarly determined according to standard procedures in a dynamic shear rheometer. The findings are presented in Figures 22 and 23, below.

The results for the Cold Lake 80/100 systems show that the temperature at which the loss modulus ($G'' \equiv G^* \sin \delta$) reaches 5,000 kPa, is decreased for all of the PPA and Elvaloy®/PPA systems while there is a lesser decrease for the two SBS-modified systems. The Superpave® specification considers a low loss modulus (soft and compliant materials) to be beneficial for resisting fatigue cracking. Hence, it may be expected that all these modifiers impart at least some benefit in terms of fatigue resistance over the straight Cold Lake 80/100 asphalt cement. However, it must be noted that the loss modulus has been largely abandoned for specification grading because it has proven difficult to accurately correlate the parameter with fatigue cracking distress in controlled accelerated loading experiments.

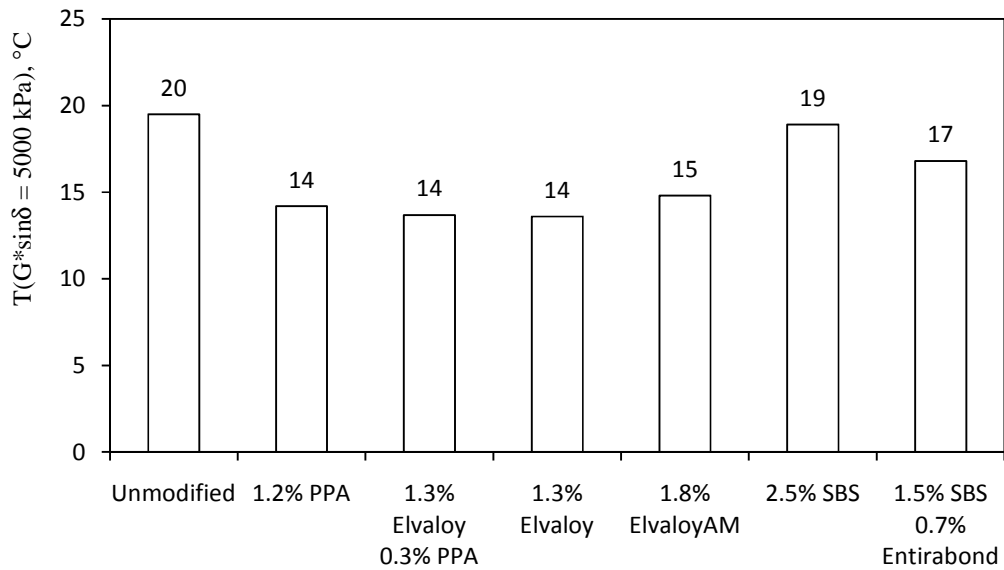


Figure 22. Comparison of intermediate temperature performance grades of Cold Lake 80/100 base asphalt with different modifiers (PAV residues).

The results for the PG 58-28 modified systems show similarly that the temperature at which the loss modulus ($G'' \equiv G^* \sin \delta$) reaches 5,000 kPa is decreased for all of the PPA and Elvaloy®/PPA systems. The reductions in loss modulus are now rather significant, with the limiting temperature decreasing by as much as $\sim 8^\circ\text{C}$ for the two systems containing both polymer and PPA. Hence, for these modifiers the benefit in terms of fatigue resistance over the straight PG 58-28 asphalt cement can be expected to be significant. This fact is likely due to the effect of the polymer and acid on the phase structure of the asphalt cement. A slight degree of phase separation, imparted by the polymer reacting with the asphaltenes, could lessen the continuous phase stiffness (viscosity) and thereby lower the complex modulus.

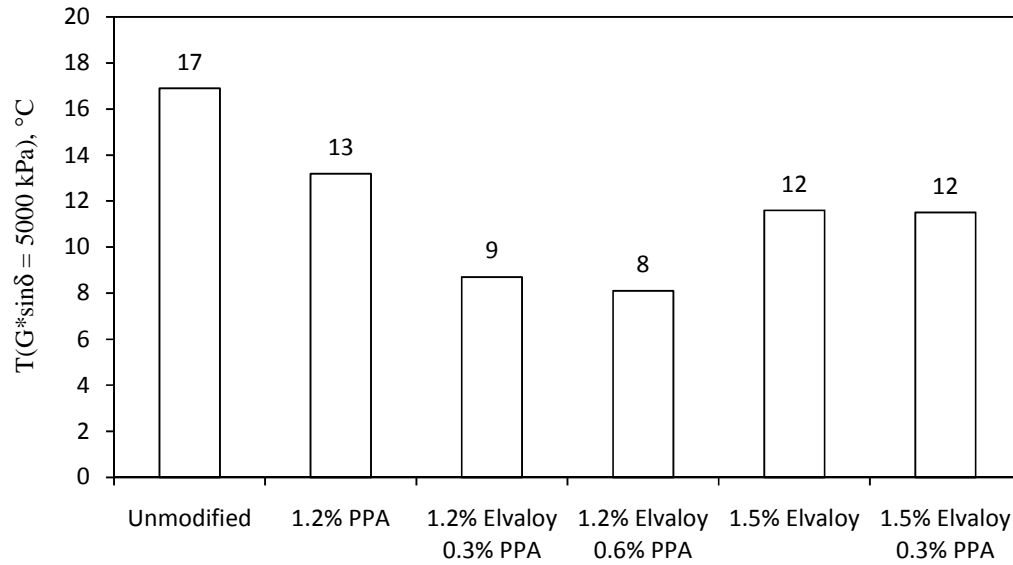


Figure 23. Comparison of intermediate temperature performance grades of PG 58-28 base asphalts with different modifiers (PAV residues).

However, it must be stressed once more that the loss modulus has proven to be a rather poor indicator for fatigue cracking performance in real-world experiments. Hence, this thesis will also investigate true failure properties of the above materials. Tests that take the sample to high strains and failure are more representative and will therefore likely provide a better indicator for fatigue resistance.

4.1.3 Master Curve Generation

The major purpose of the master curves, which employ a shift in the X-axis of a log-log plot to create a smooth line or curve, is to analyze the rheological simplicity of the samples. If there were any deviation in the curves, it would indicate that a separation of distinct phases likely to occur within the asphalt during testing.

With samples of Cold Lake asphalt, aside from the occasional stray point in all of the systems, the only true deviation in the master curves was found in 1.2 % PPA samples. The pattern produced by the master curve for asphalt modified with 1.2 % PPA is the one that almost appears to explain two separate curves; one for unaged points that produced a continuous line, and one for the RTFO and PAV data points shown to change up in a different curve. This occurrence may signify a phase transition that occurred during the aging of the asphalt mixture containing only PPA.

The similar results found for the PG 58-28 base asphalt where sample modified with 1.2 % PPA which produces a slightly different curve with aged material. Also a comparable observation was drawn from the asphalt that was modified with 1.5 % Elvaloy® where PAV aged material shown off curve in contrast to the unaged and RTFO material.

4.1.4 Black Space Diagrams

Black space diagrams were prepared for all straight and modified asphalt cements in order to provide a picture of how the low-strain rheological behavior varies with type of modifier and level of aging. In general, it is a good attribute for an asphalt cement to have a high phase angle at high stiffness (allowing stress relaxation and thus reducing the tendency for thermal cracking) and a low phase angle at low stiffness (preventing rutting). The results for this analysis are provided in Figures 24-34 below.

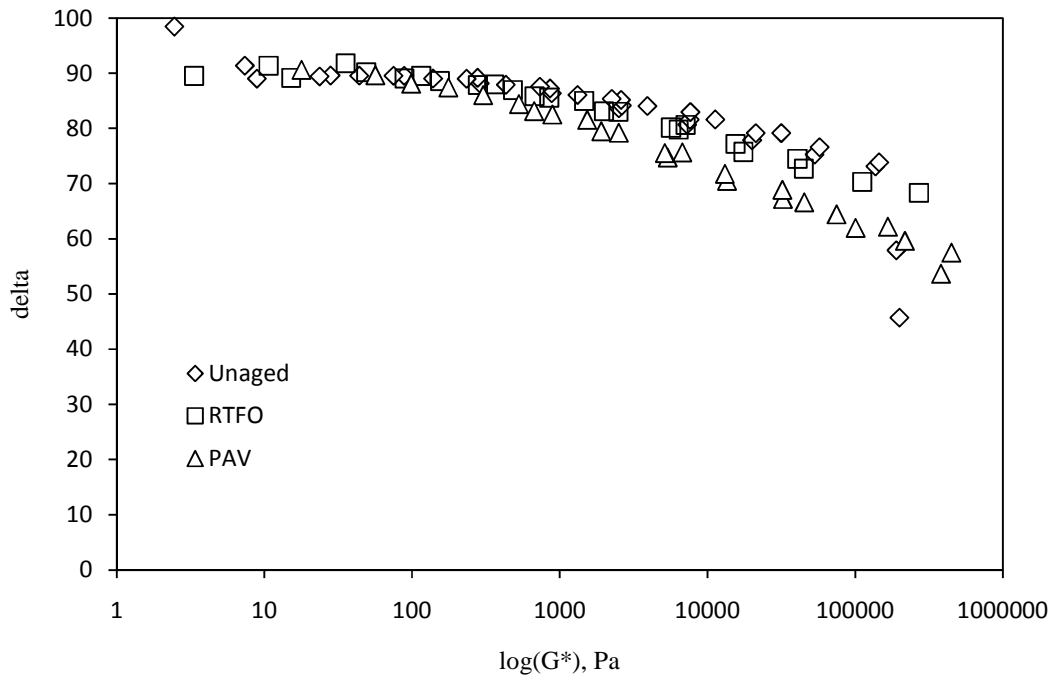


Figure 24. Black space diagram for Cold Lake 80/100 unmodified, unaged and RTFO- and PAV-aged materials.

Figure 24 shows the control sample which is an example of asphalt cement that could be subject to both rutting (rather high phase angle at low stiffness) and fatigue cracking (steep plunge in phase angle at higher stiffness). However, it should be noted that the rutting resistance should largely be determined by the structure of the aggregate skeleton (mixture design) and therefore the Cold Lake 80/100 is still considered to be very good asphalt.

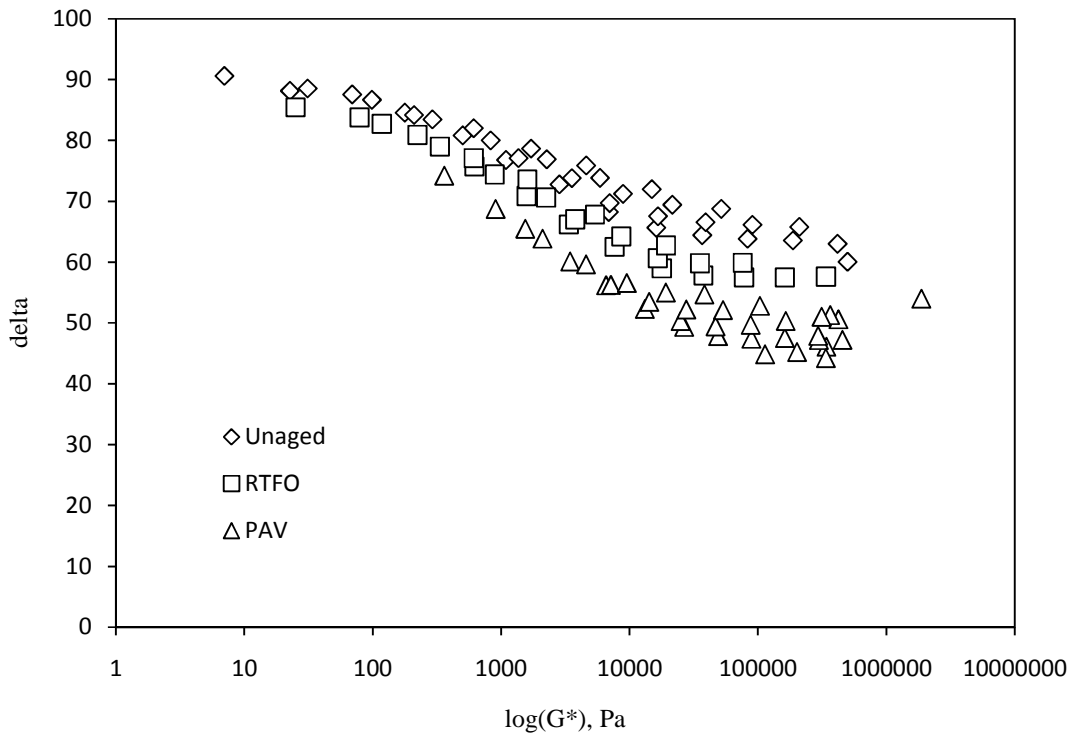


Figure 25. Black space diagram for Cold Lake 80/100 with 1.2 % PPA.

Figure 25 provides the Black space diagram for Cold Lake 80/100 + 1.2 % PPA. This asphalt cement possesses a high temperature grade that is above those of the others due to the largely gelled nature of the material.

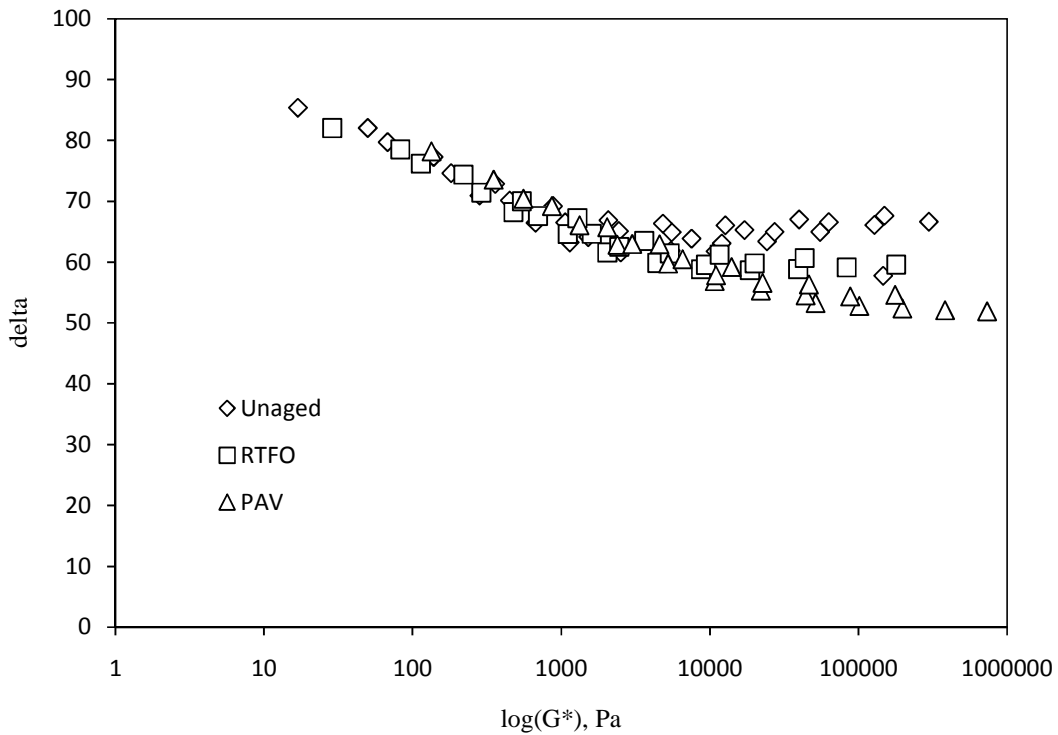


Figure 26. Black space diagram for Cold Lake 80/100 with 1.3 % Elvaloy® and 0.3 % PPA.

The asphalt in Figure 26 includes 1.3 % Elvaloy® and 0.3 % PPA additives, which seemed to significantly enhance the performance of the original asphalt binder. As the stiffness increased, the change in phase angle levels out, indicating that the asphalt would perform better than any sample shown here under low temperature circumstances. Also, the Black space diagram reveals a consistent pattern in the phase angle-complex modulus through unaged, RTFO and PAV samples. However, it should be noted that for all these Black space diagrams the samples were tested only up to a stiffness of around 1 MPa and temperatures above 34°C. This is normally considered to be a safe zone for thermal and

fatigue cracking which is thought to occur at temperatures below 20°C and a stiffness of 300 MPa or higher.

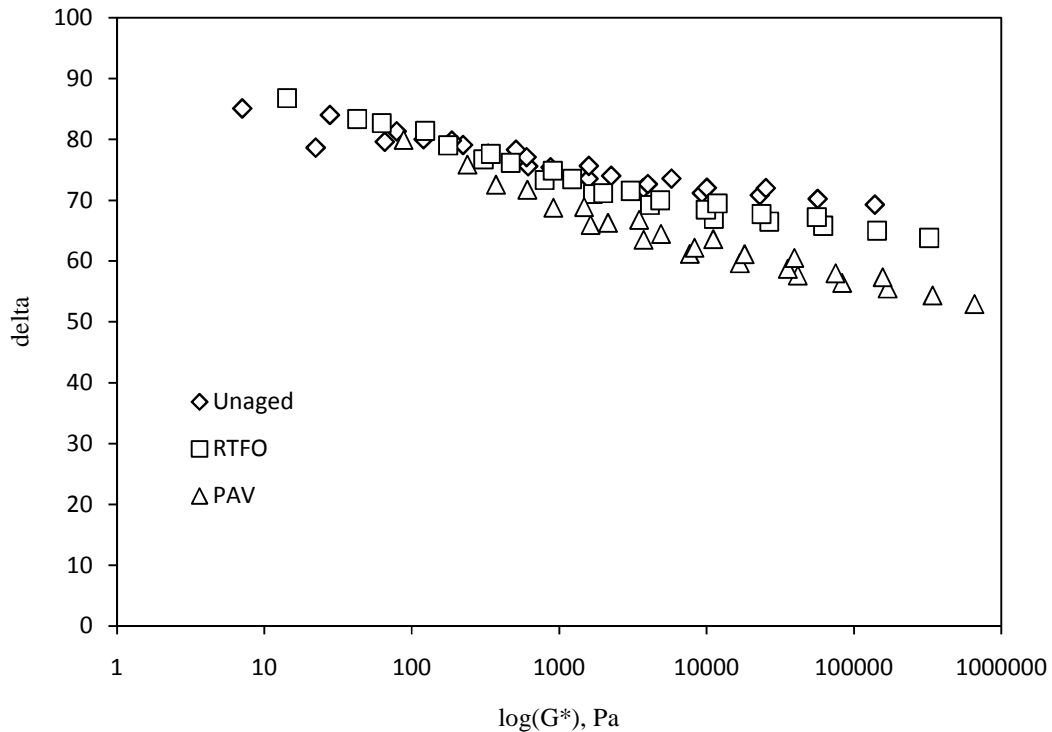


Figure 27. Black space diagram for Cold Lake 80/100 with 1.3 % Elvaloy®.

The samples from Figure 27 shows a slight improvement from the control in that the rate of change of the phase angle with respect to complex modulus gradually decreases with time, although it does not appear to be as ideal a mixture as the one for which the data are presented in Figure 26. The large discrepancy between the RTFO and PAV readings may also bring about issues with asphalt aging, but the variation does not seem to be as great as seen in Figure 25.

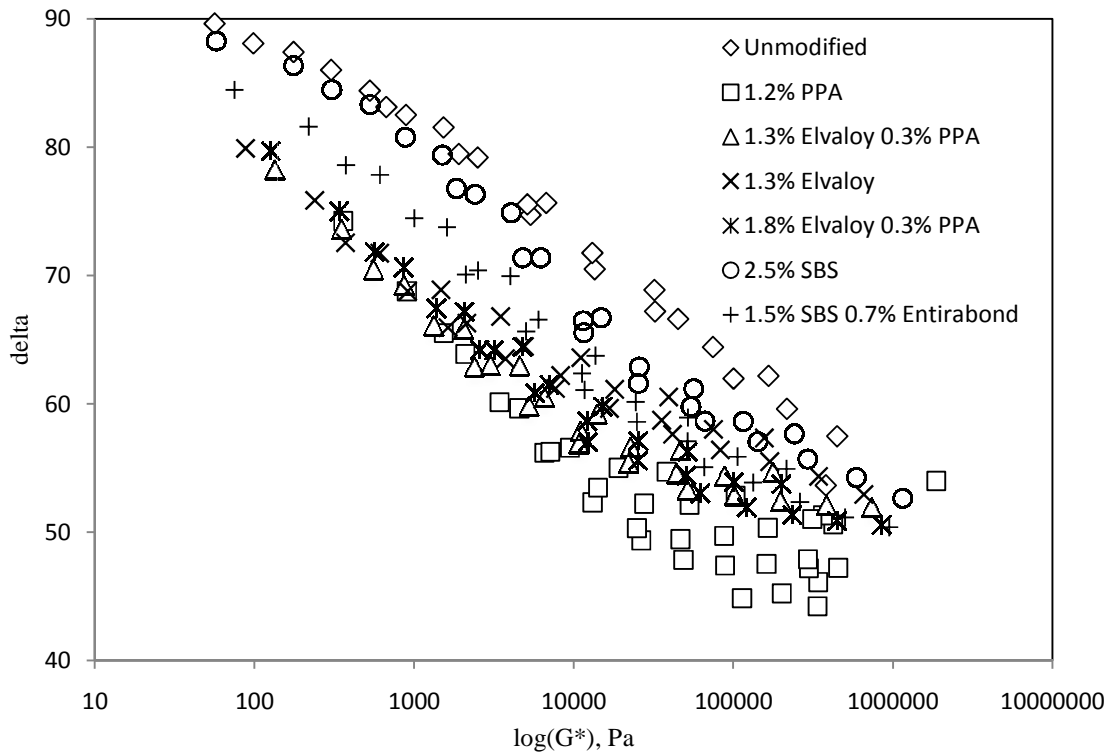


Figure 28. Black space diagram for different RTFO/PAV-aged Cold Lake 80/100 asphalts.

Figure 28 shows a comparison between all the different modifiers in Cold Lake 80/100 systems. The graph shows that the general trend is the same as for the high and intermediate performance grades that is the 1.2 % PPA likely performs worst from a cracking perspective and best from a rutting perspective. The unmodified (PAV) performs worst from a rutting perspective and likely best from a cracking perspective. However, it needs to be stressed once more that the Black space diagrams reflect data at low strains in the linear viscoelastic regime. This contrasts with real-life cracking which occurs under high strain conditions at much higher stiffnesses.

The Black space diagrams for the PG 58-28 and modified PG 58-28 systems are given in Figures 29-34, below.

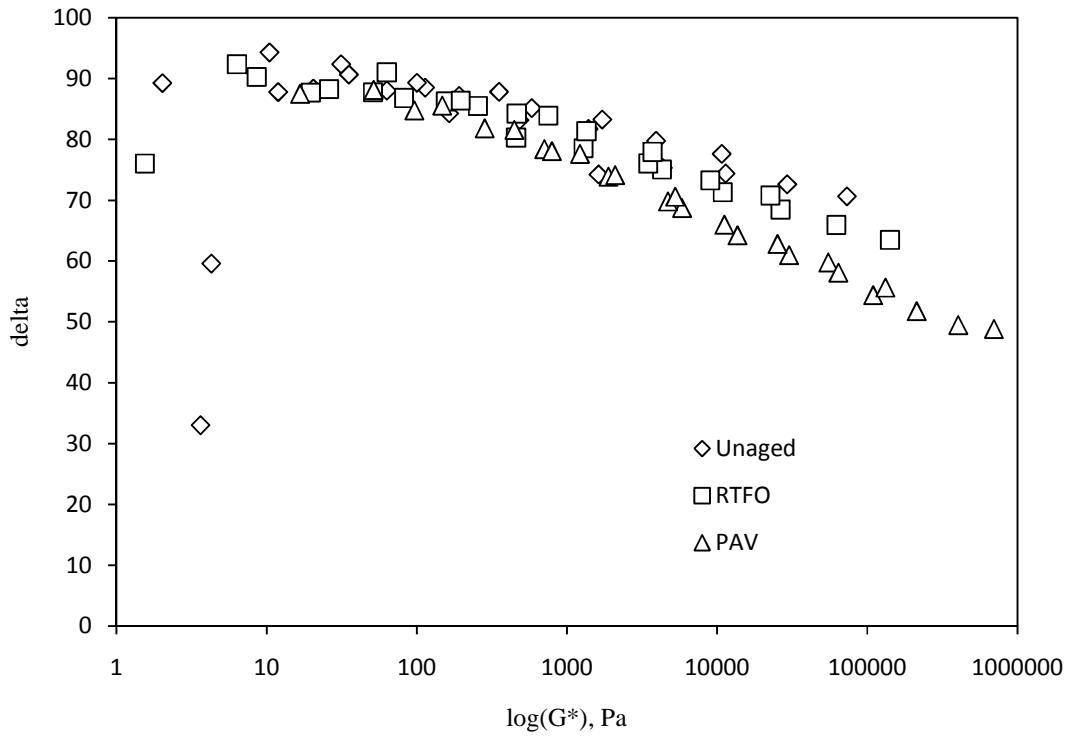


Figure 29. Black space diagram for unmodified PG 58-28.

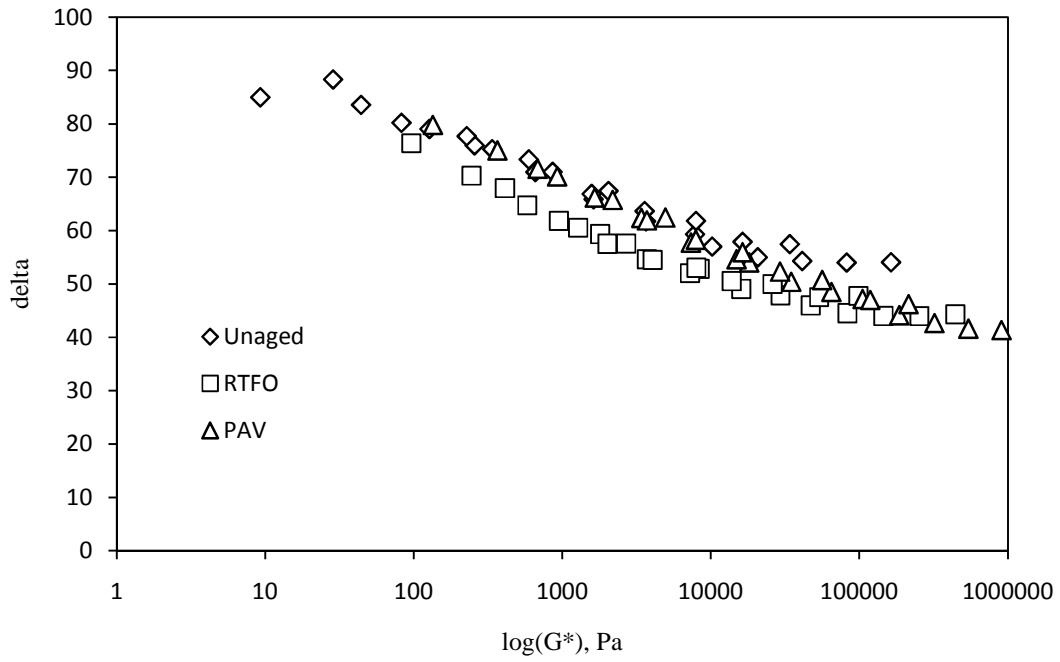


Figure 30. Black space diagram for PG 58-28 modified with 1.2 % PPA.

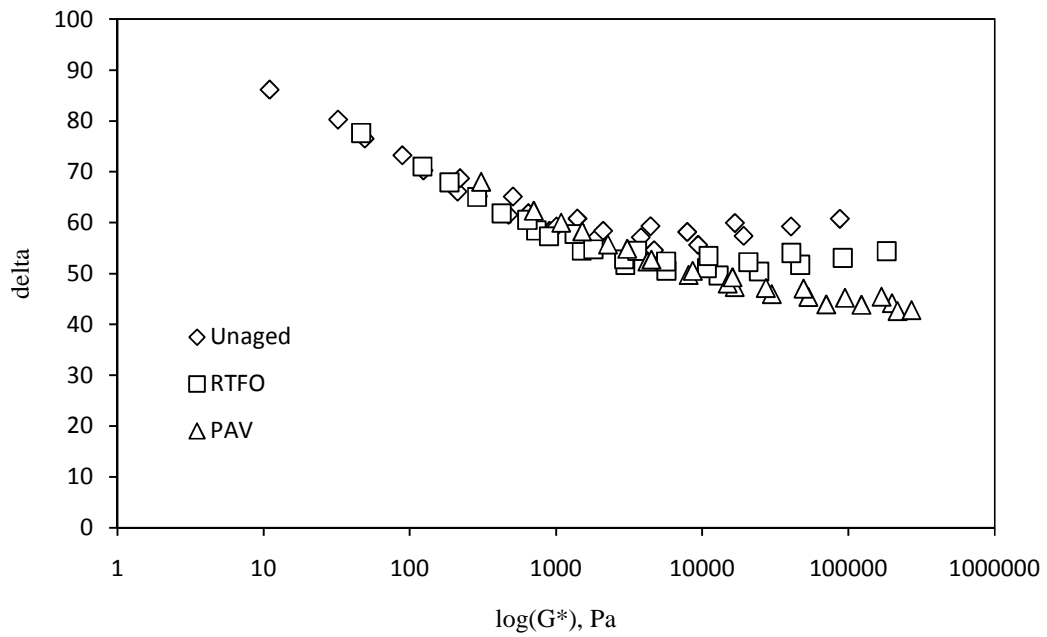


Figure 31. Black space diagram for PG 58-28 modified with 1.2 % Elvaloy® + 0.3 % PPA.

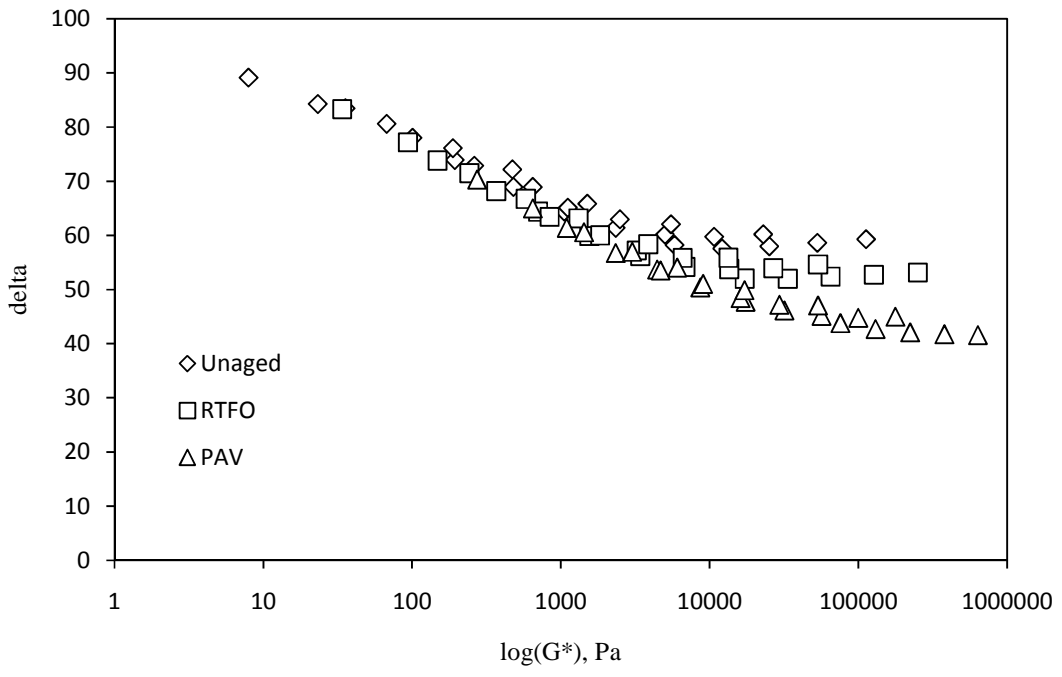


Figure 32. Black space diagram for PG 58-28 with 1.2 % Elvaloy® + 0.6 % PPA.

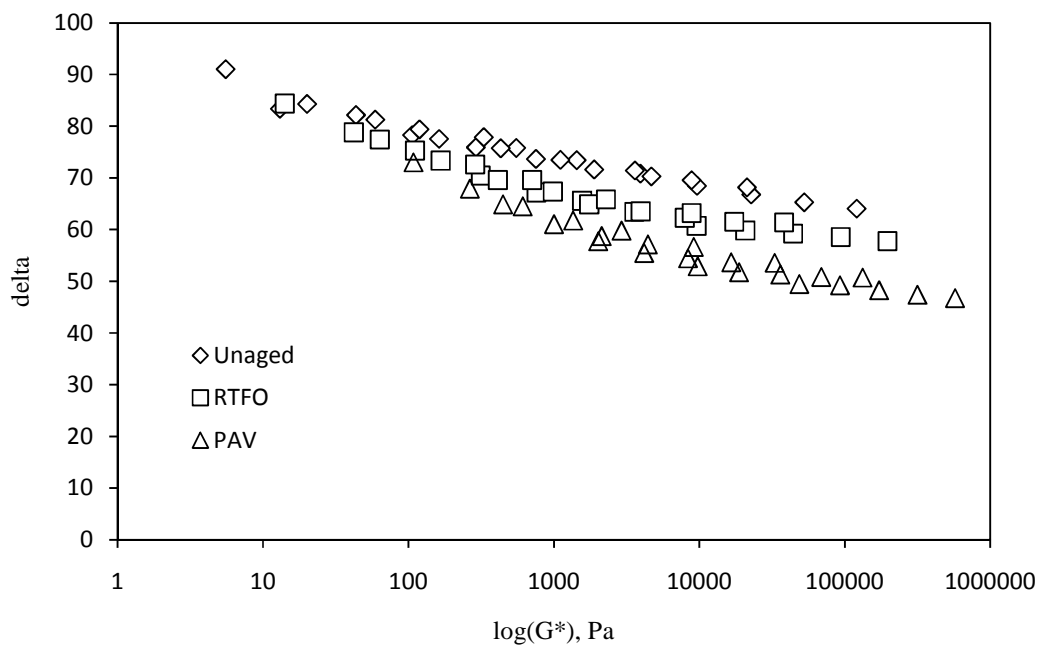


Figure 33. Black space diagram for PG 58-28 with 1.5 % Elvaloy®.

For this section, each of the asphalt samples was grouped together according to the modifier that they contained (for example, 14, 44 and 45 were grouped together because they were all unmodified asphalts). This way, the effect of aging on the rheological properties of the different samples can be readily compared. Black space diagrams intend to reveal how the phase angle (a measure of the asphalt's degree of elasticity or sol-gel character) decreases as the samples harden. Ideal asphalts would retain lower phase angles at low stiffness values and higher phase angles at high stiffness.

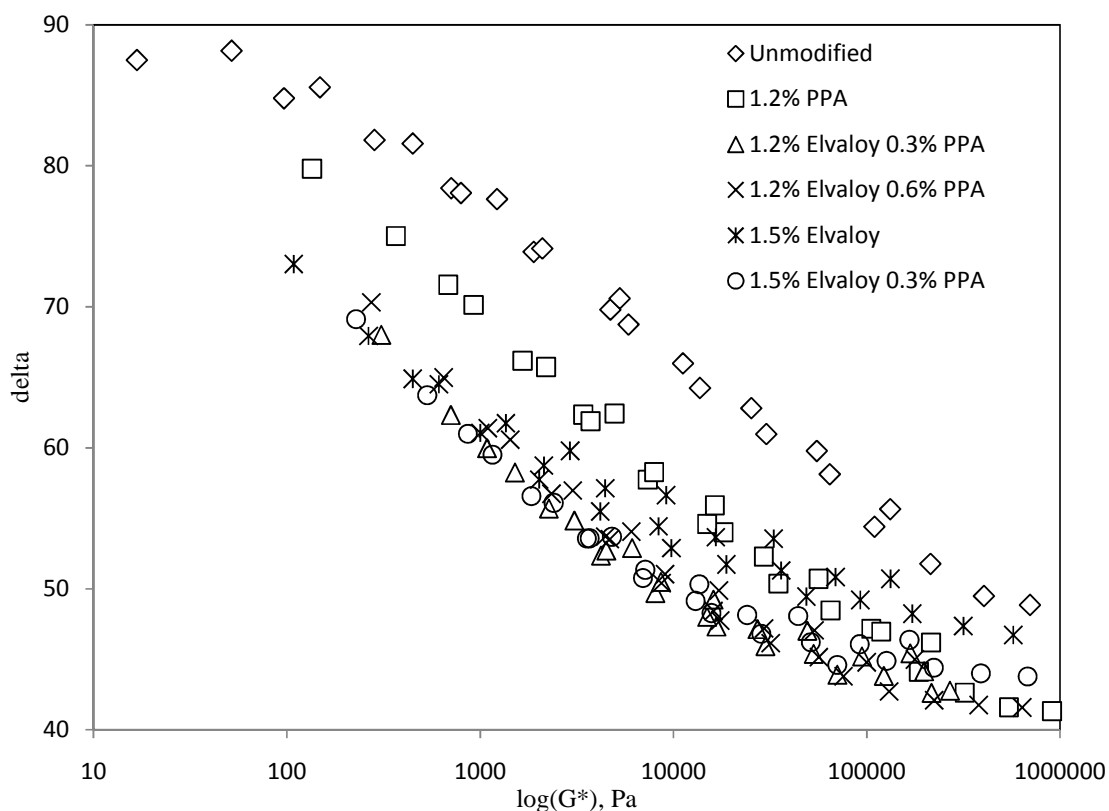


Figure 34. Black space diagram for laboratory aged (PAV) PG 58-28 with different modifiers.

Figure 30 shows that the phase angle values for the 1.2 % PPA modified asphalt seemed to decline at a faster rate with aging than what happens for the other samples containing polymer. Similarly, it could also be observed from the Black space diagram of the Elvaloy® polymer modified asphalt without PPA in Figure 33 that having only polymer in the asphalt would not be ideal. The fluctuations in the phase angle-complex modulus relationships varied greatly between the unaged, RTFO and PAV aged asphalts. Thus, asphalts containing a combination of the two modifiers could be identified as more suitable than adding Elvaloy® or PPA individually. When comparing Figures 30 and 31, one could observe that when 1.2 % Elvaloy® was added to 0.3 % PPA to obtain a material with similar performance grade to the 1.2 % PPA system, the slope of the Black space diagram flattened, thereby decreasing the overall change in phase angle with stiffness and thus creating a more beneficial modifier effect.

4.1.5 Cole-Cole Plots

The basis for a Cole-Cole plot is similar as a Black space diagram in that it compares the relative phase angle for asphalt when the complex modulus increases in magnitude. Since the complex modulus is the hypotenuse of a triangle containing G' and G'' as its sides, G^* is represented by the distance from the origin to any point on the Cole-Cole plot, and the phase angle is simply the angle between that vector and the origin.

It can be seen for Cold Lake 80/100 base asphalt from Figure 35 that the PAV asphalt binders have a high phase angle, meaning that the viscous component of the asphalt is

dominant; hence, there is a high chance of rutting to occur at intermediate to high temperatures in mixtures that are poorly designed or contain lower quality aggregates.

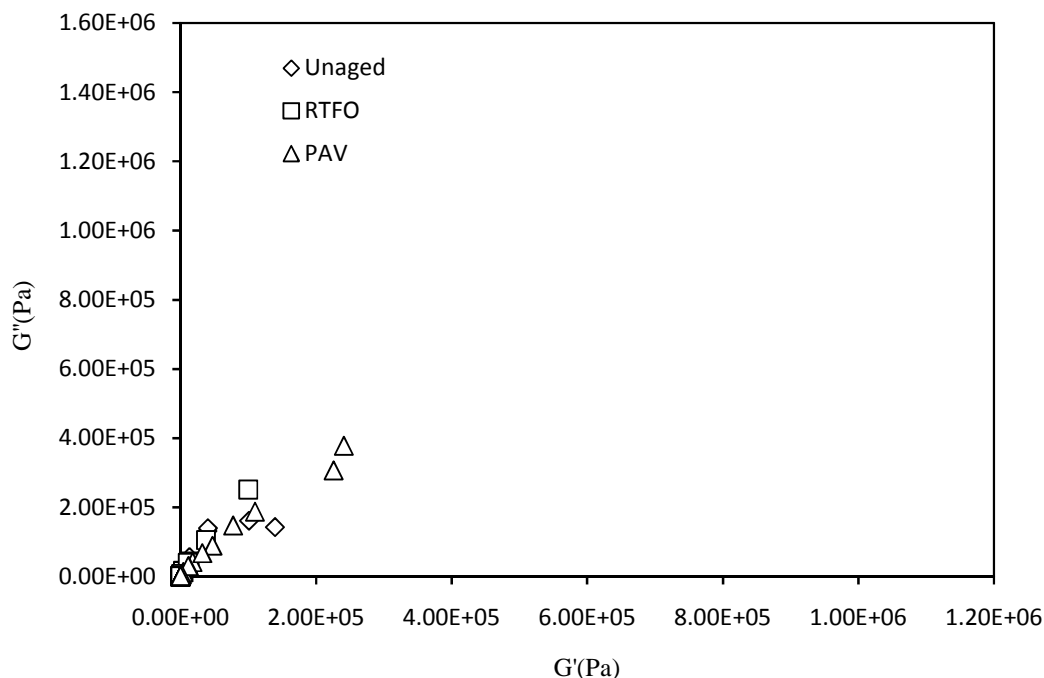


Figure 35. Cole-Cole plot for Cold Lake 80/100 unmodified, unaged and RTFO- and PAV-aged materials.

The polyphosphoric modified asphalt depicted in Figure 36 indicates a material that has a lower phase angle at high temperatures, indicating a higher performance grade and smaller chance of rutting. However, it can be observed that as the stiffness values increased rather dramatically upon PAV aging (triangle in upper right corner of the graph), the phase angle decreased at a higher rate compared to straight Cold Lake 80/100 (Figure 35), which could be an issue if the trend continued at lower temperatures. Additionally, the rapid change in phase angles between the unaged, RTFO and PAV

samples should be noted. This characteristic reveals a potential dramatic decline in performance of the asphalt as it ages.

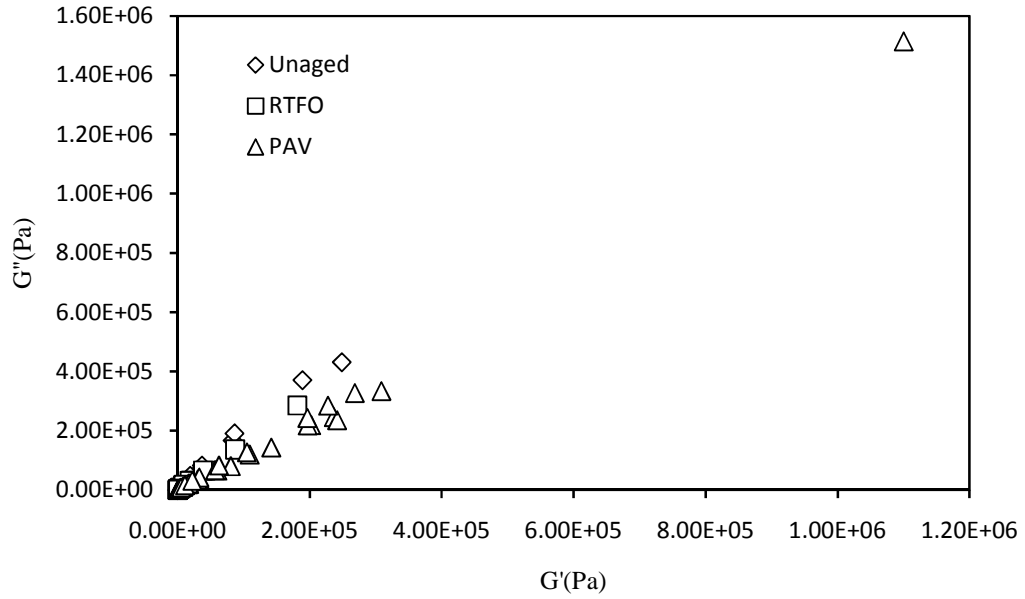


Figure 36. Cole-Cole plot for Cold Lake 80/100 with 1.2 % PPA.

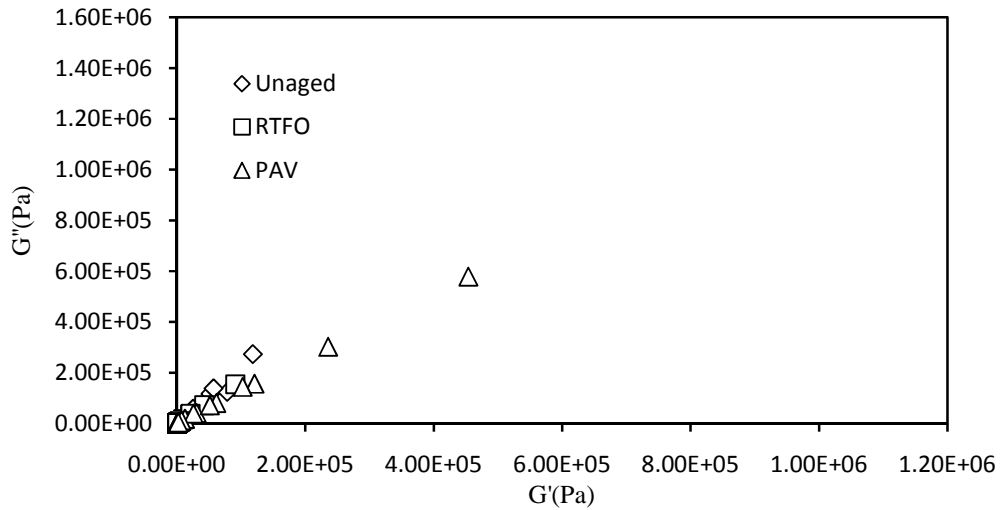


Figure 37. Cole-Cole plot for Cold Lake 80/100 with 1.3 % Elvaloy® and 0.3 % PPA.

Finally, Figures 37 and 38, which show asphalt binders containing 1.3 % Elvaloy® but differ in that the system in Figure 37 contains an additional 0.3 % PPA, reveal relatively similar Cole-Cole plot characteristics. Both mixtures appear to have a relatively low phase angle at low stiffness (compared to Figure 35), and the phase angle does not appear to deviate much in either case with aging, which is beneficial. The asphalt sample with an additional 0.3 % PPA appears to have a lower overall phase angle in the Cole-Cole plot, which is very desirable at high temperatures.

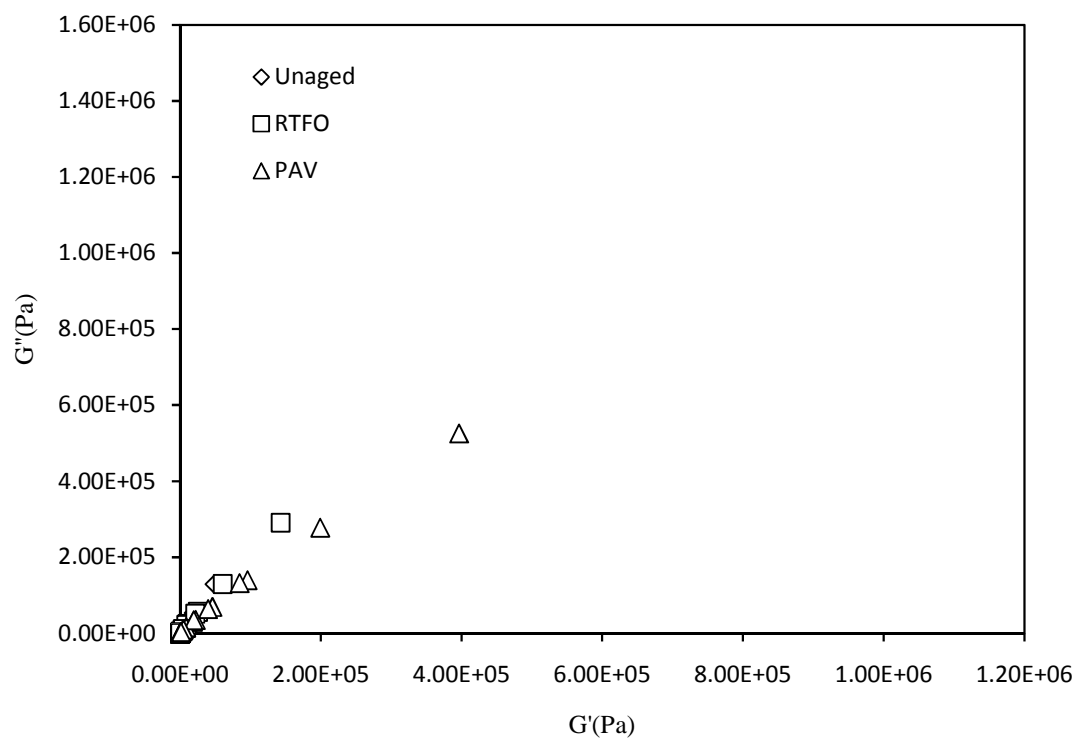


Figure 38. Cole-Cole plot for Cold Lake 80/100 with 1.3 % Elvaloy®.

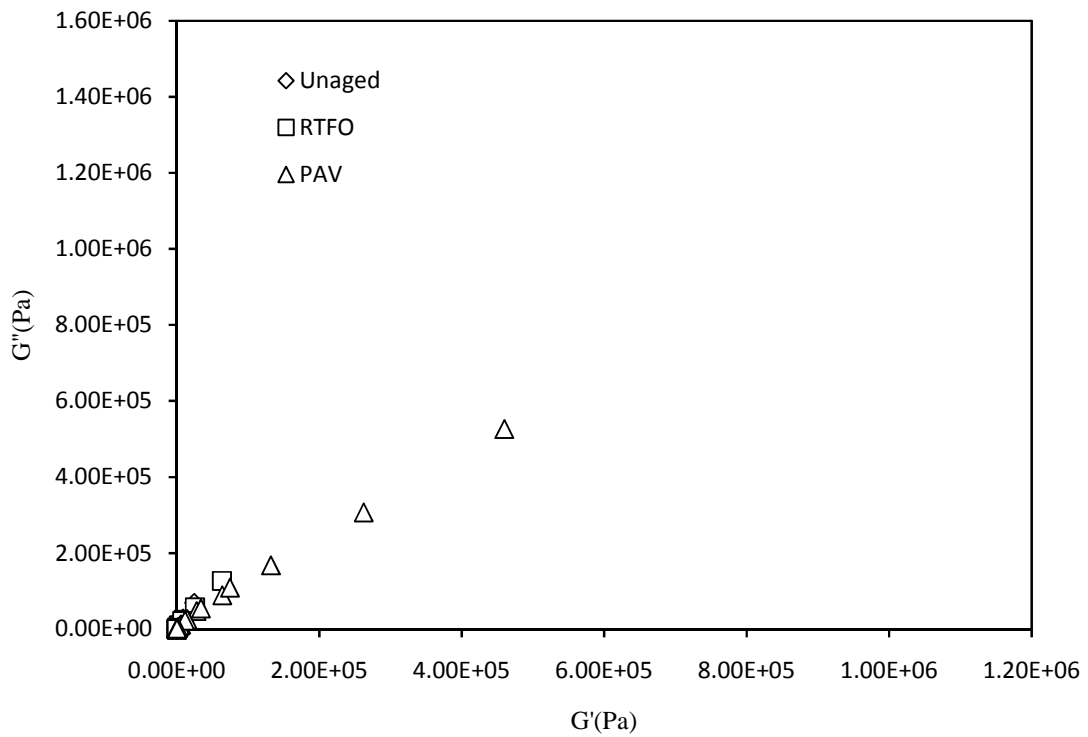


Figure 39. Cole-Cole plot for PG 58-28 unmodified.

From the Cole-Cole plots for 58-28 base asphalt, it could also be seen that having only 1.2 % PPA (Figure 40) or 1.5 % Elvaloy® (Figure 43) created for asphalts that had inconsistent rheological relationships between different levels of aging.

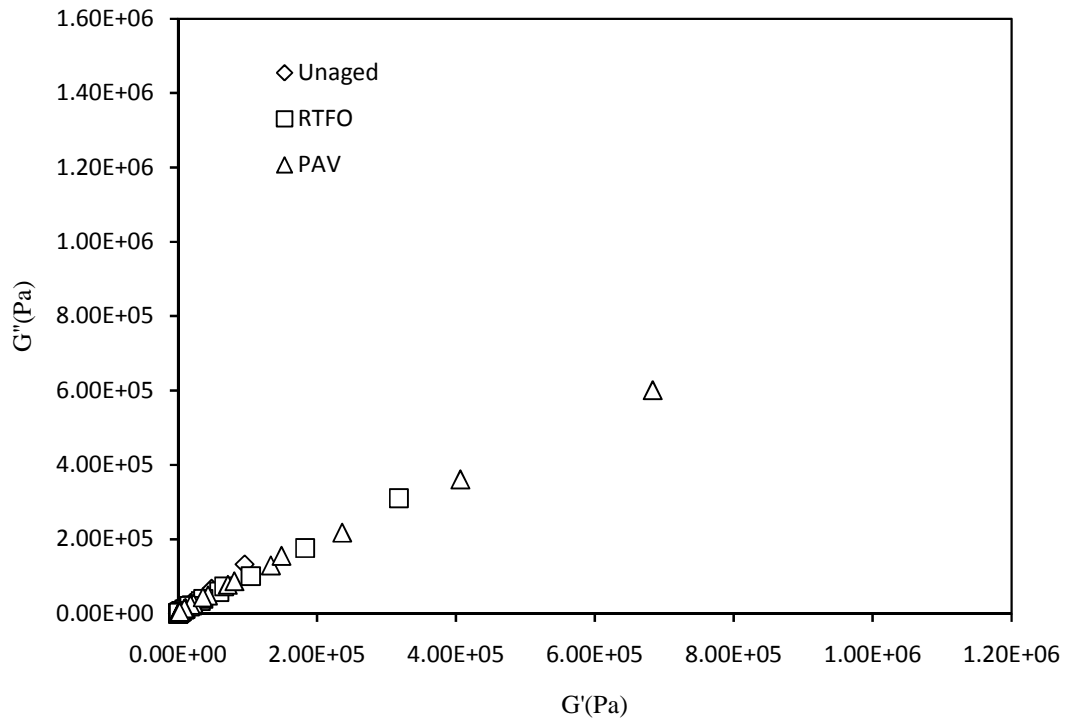


Figure 40. Cole-Cole plot for PG 58-28 with 1.2 % PPA.

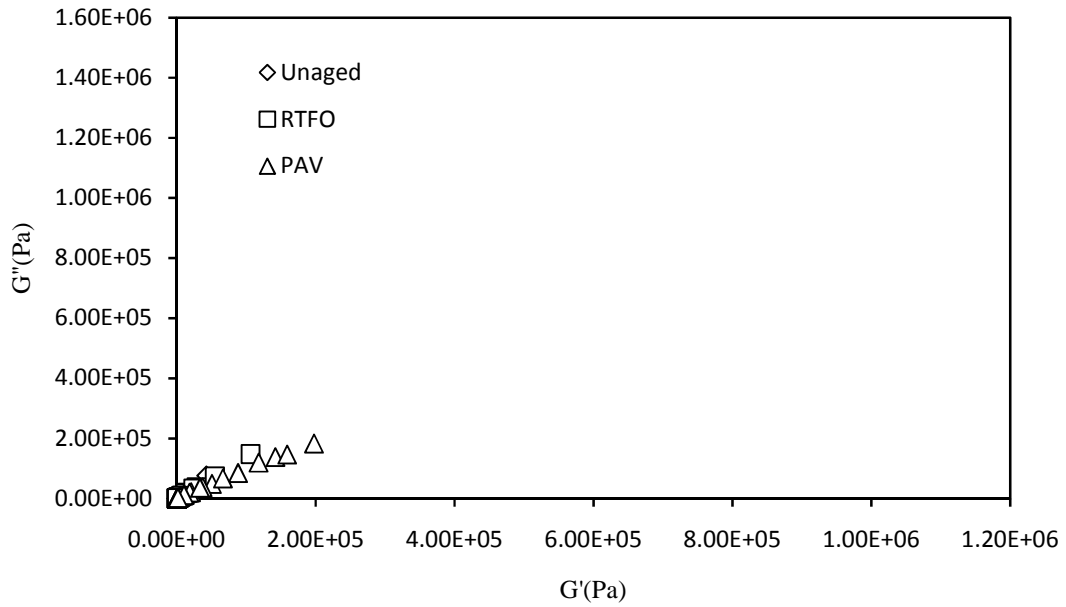


Figure 41. Cole-Cole plot for PG 58-28 with 1.2 % Elvaloy® + 0.3 % PPA.

The samples containing different modifiers (e.g., 1.2 % PPA in Figure 40) which appeared to have the lowest phase angle within a rather high stiffness range will likely show resistance to rutting at higher temperatures.

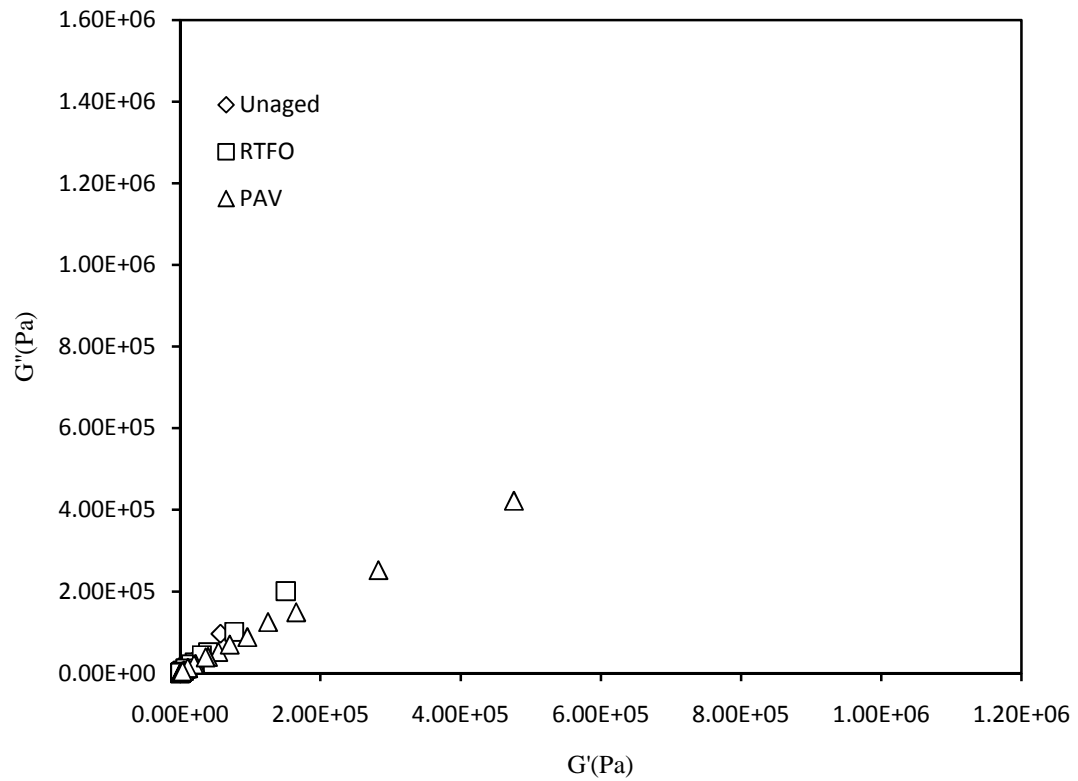


Figure 42. Cole-Cole plot for PG 58-28 with 1.2 % Elvaloy® + 0.6 % PPA.

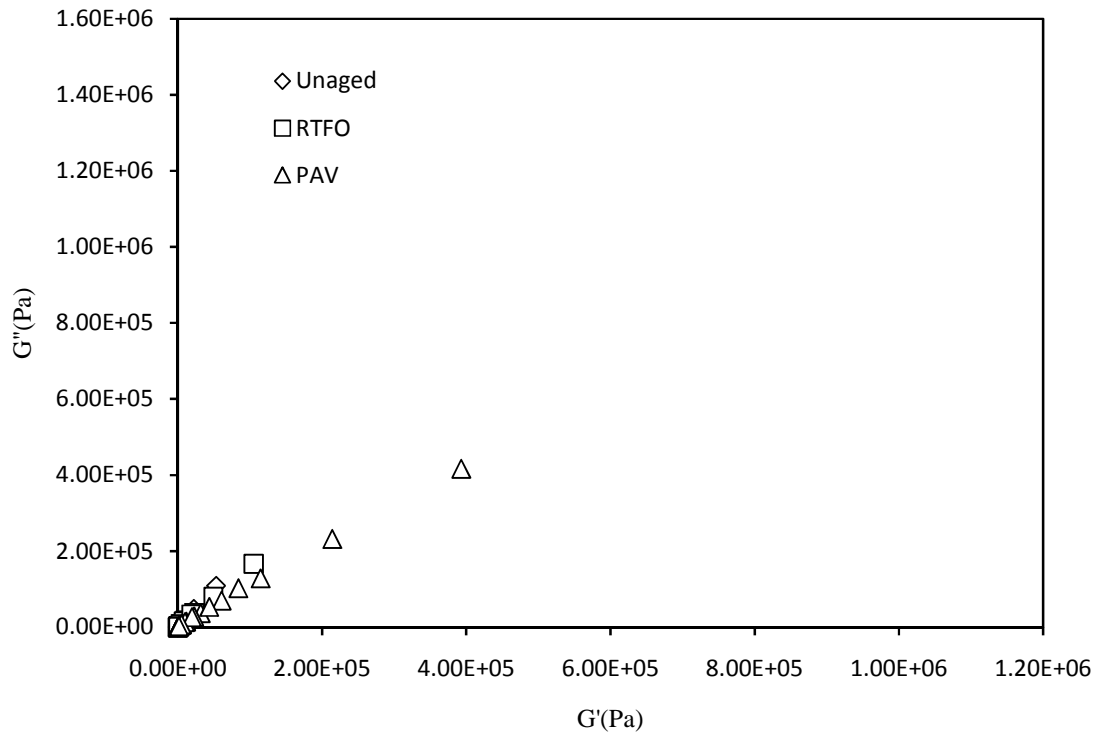


Figure 43. Cole-Cole plot for PG 58-28 with 1.5 % Elvaloy®.

4.2 Multiple Shear Creep Recovery Testing

The Multiple Shear Creep Recovery test (commonly known as the MSCR test) has recently been developed to better control rutting as a pavement distress mechanism. The test applies a creep stress of either 0.1 kPa or 3.2 kPa to a thin asphalt film for 1 second and allows this film to recover for 9 seconds. This is repeated 10 times at each stress level. The raw data of displacement versus time is then used to calculate the non-recoverable compliance, $J(nr)$, and the elastic recovery, % ER. This test has been related in a totally empirical fashion to asphalt cement rutting performance [35].

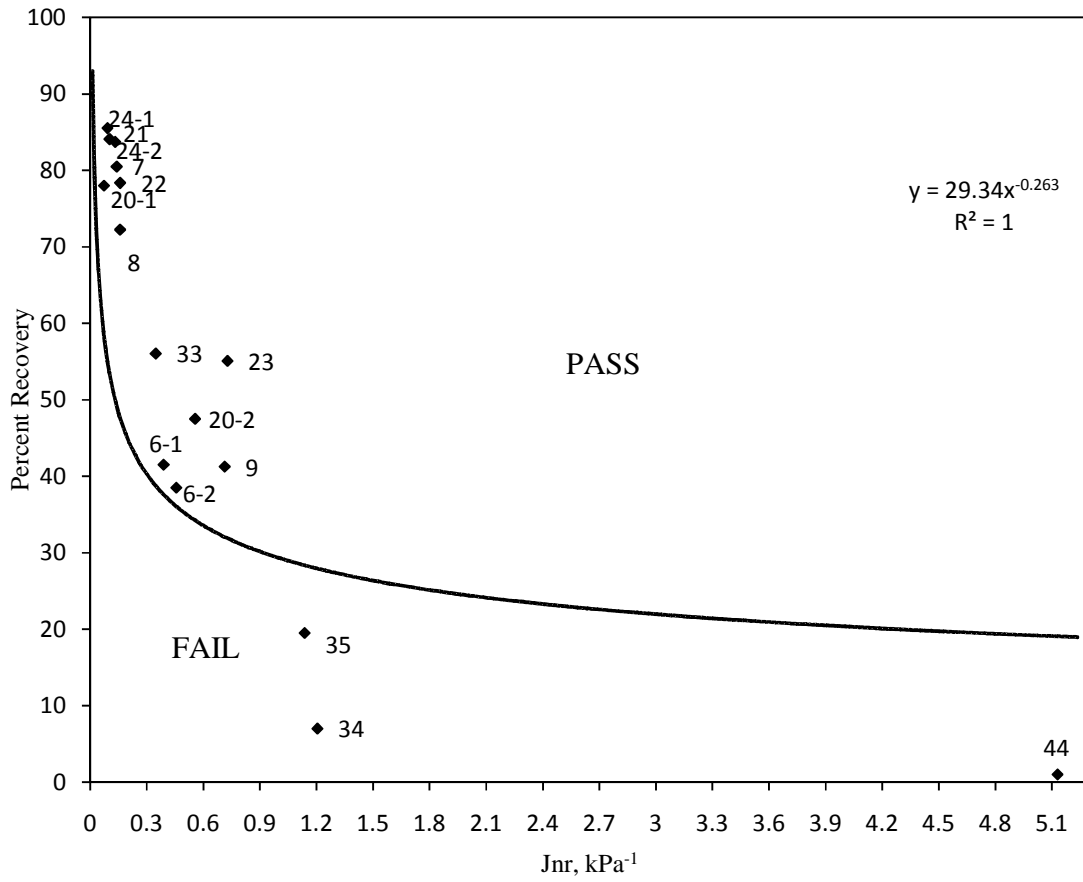


Figure 44. Non-recoverable creep compliance at 0.1 kPa versus percent recovery test at 64°C [37].

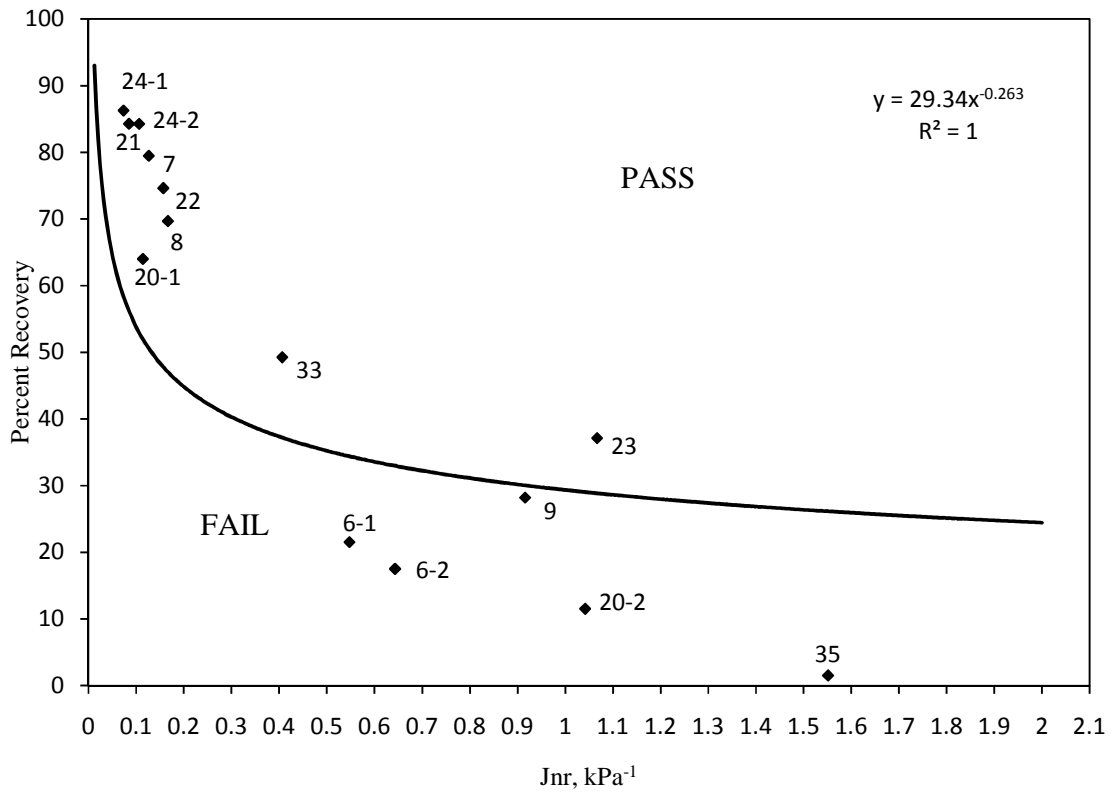


Figure 45. Non-recoverable creep compliance at 3.2 kPa versus percent recovery test at 64°C [37]. Note: It was impossible to test sample 34 (Cold Lake 80/100 + 2.5 % SBS) at the highest stress level due to instrument instability.

Table 1. List of samples with modifier content

| Sample No. | Asphalt | Ageing | Elvaloy® [%] | PPA [%] |
|------------|---------|--------|------------------|------------------|
| 6 | 80/100 | RTFO | - | 1.2 |
| 7 | 80/100 | RTFO | 1.3 | 0.3 |
| 8 | 80/100 | RTFO | 1.3 | 0.6 |
| 9 | 80/100 | RTFO | 1.3 | - |
| 20 | 58-28 | RTFO | - | 1.2 |
| 21 | 58-28 | RTFO | 1.2 | 0.3 |
| 22 | 58-28 | RTFO | 1.2 | 0.6 |
| 23 | 58-28 | RTFO | 1.5 | - |
| 24 | 58-28 | RTFO | 1.5 | 0.3 |
| 33 | 80/100 | RTFO | 1.8% Elvaloy® AM | 0.3% PPA |
| 34 | 80/100 | RTFO | 2.5% SBS k1101 | - |
| 35 | 80/100 | RTFO | 1.5% SBS k1101 | 0.7% Entirabond® |
| 42 | 80/100 | RTFO | - | - |
| 44 | 58-28 | RTFO | - | - |
| 61 | 80/100 | RTFO | 2.5% SBS k1101 | 0.1 % Sulfur |

The results provided in Figures 44 and 45 show that nearly all systems pass the MSCR test criteria by falling above the curve. The only exceptions are provided by Cold Lake 80/100 + 1.2 % PPA (number 6), Cold Lake 80/100 + 1.3 % Elvaloy® (number 9), Cold Lake 80/100 + 2.5 % SBS (number 34) and Cold Lake 80/100 + 1.5 % SBS + 0.7 % Entirabond® (number 35). These systems all lack stability in that their phase structure

can provide high Superpave® grades (see Figure 20) but they do not stand up to repeated shear deformation as is imposed by the MSCR test. The SBS-modified system (number 34) performed poorly due to the fact that no sulfur was used for their compatibilization. Had this been done then they would likely have shown improved elastic recovery (number 61) at 58°C test temperature and this is considered to be beneficial for rutting resistance.

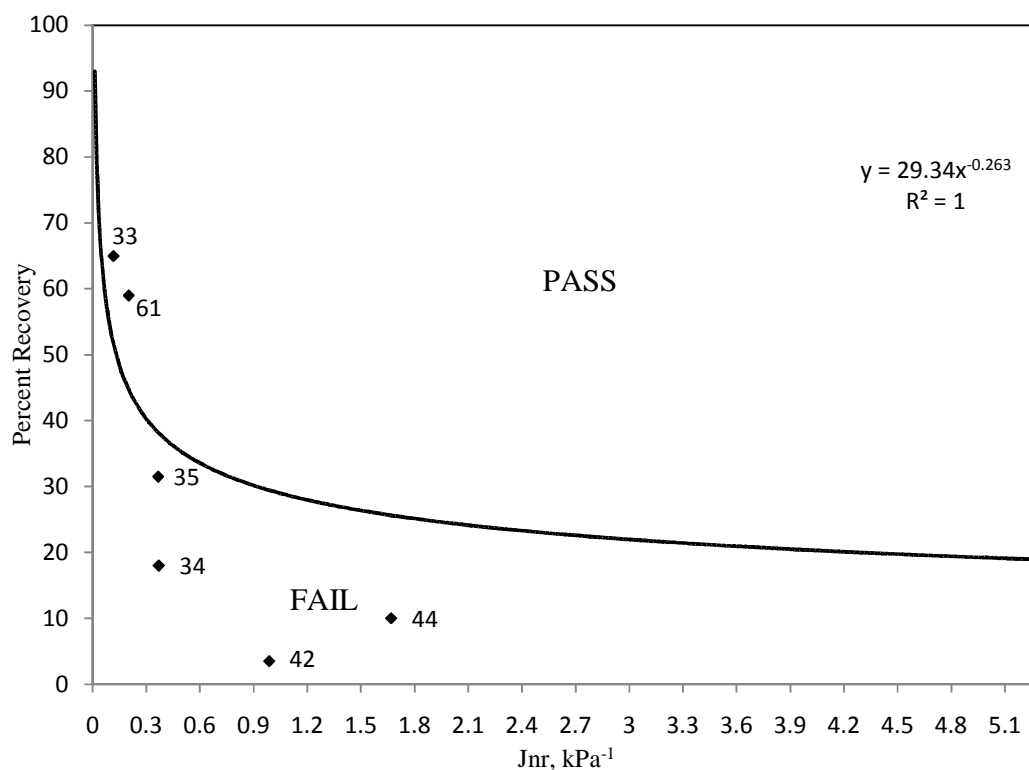


Figure 46. Non-recoverable creep compliance at 0.1 kPa versus percent recovery test at 58°C [37].

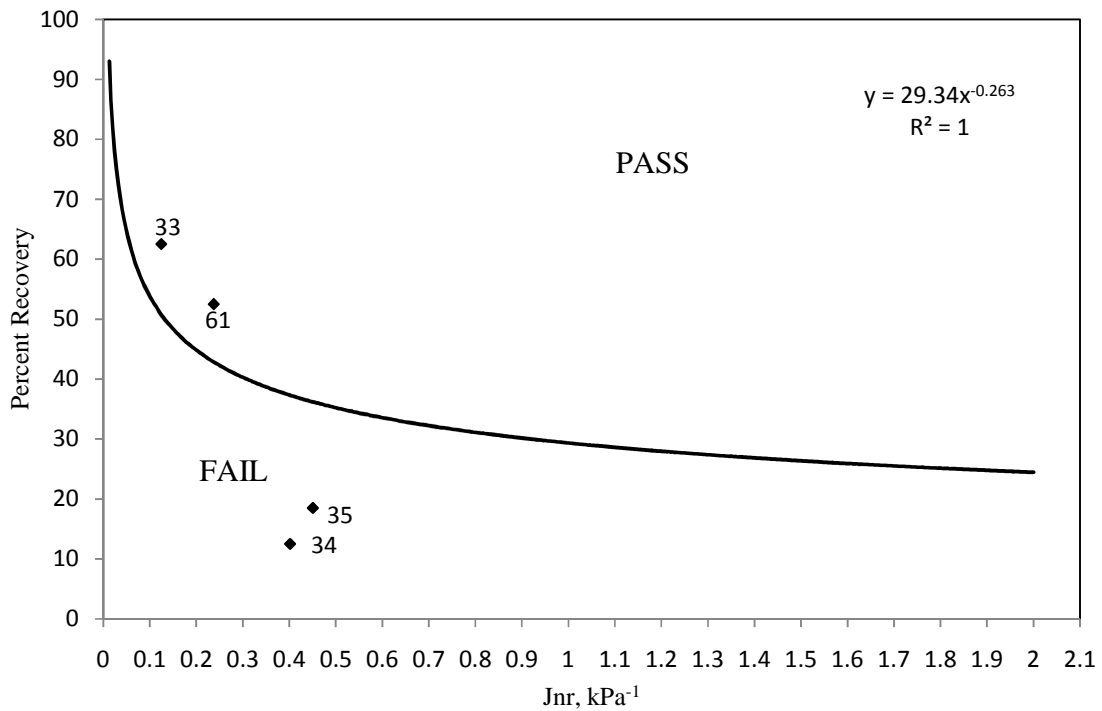


Figure 47. Non-recoverable creep compliance at 3.2 kPa versus percent recovery test at 58°C [37].

The results for the 1.2 % PPA modified system (number 6) is interesting in that this material did particularly well in the Superpave® specification (see Figure 20) but fails in the MSCR test. This is likely due to the way in which PPA modifies the colloidal structure by gelation. The gel structure can stand up under low shear stresses and strains (as is done in the DSR test to determine the Superpave® grade) but fails under higher shear stresses as they are applied in the MSCR test. Similar findings come out in the double-edge-notched tension tests as will be discussed next.

4.3 Double-Edge-Notched Tension Testing

The double-edge-notched tension test was developed to measure the asphalt cement's strain tolerance in the ductile state. Hence, it should provide some measure of resistance to fatigue cracking since the cracks can only open up under flexure when the strain tolerance is exceeded. The materials were tested as both RTFO-aged and PAV-aged residues to investigate how additional aging in the PAV changes the ductile failure properties. The results of this investigation are provided in Figures 46-48, below.

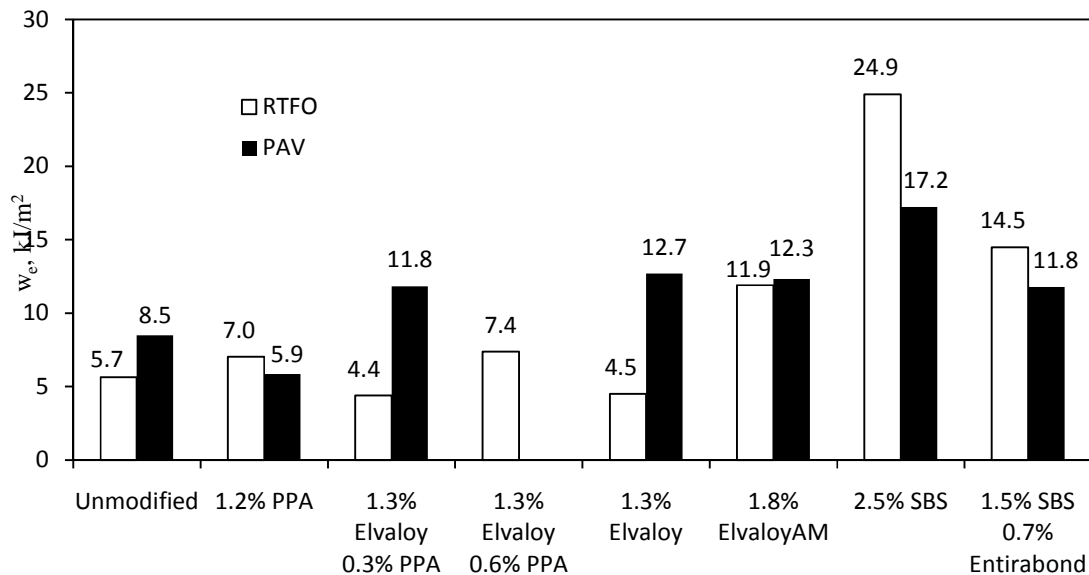


Figure 48. Specific essential works of failure for straight and modified Cold Lake 80/100 asphalt cements.

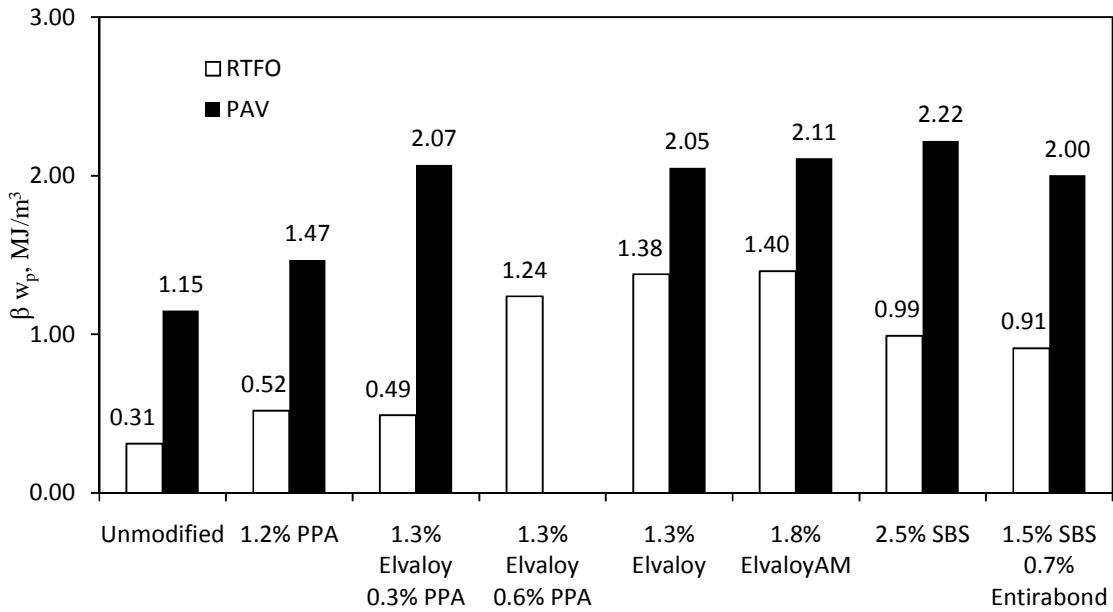


Figure 49. Specific plastic works of failure for straight and modified Cold Lake 80/100 asphalt cements.

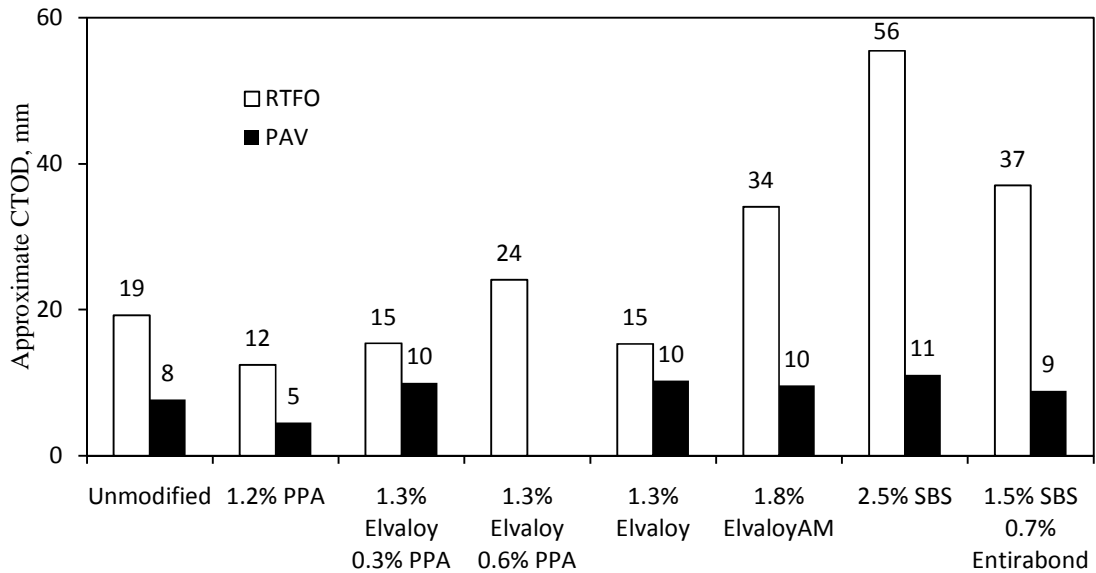


Figure 50. Approximate critical crack tip opening displacements (CTOD) for straight and modified Cold Lake 80/100 asphalt cements.

The DENT test results for the Cold Lake systems are interesting in several respects. First, the 1.2 % PPA system has deteriorated properties and the polymer modifiers have improved performance. Second, the SBS-modified systems have superior performance as RTFO residues but this advantage disappears for the PAV residues. Third, the CTOD for all modified samples appears to be similar and better than the unmodified control.

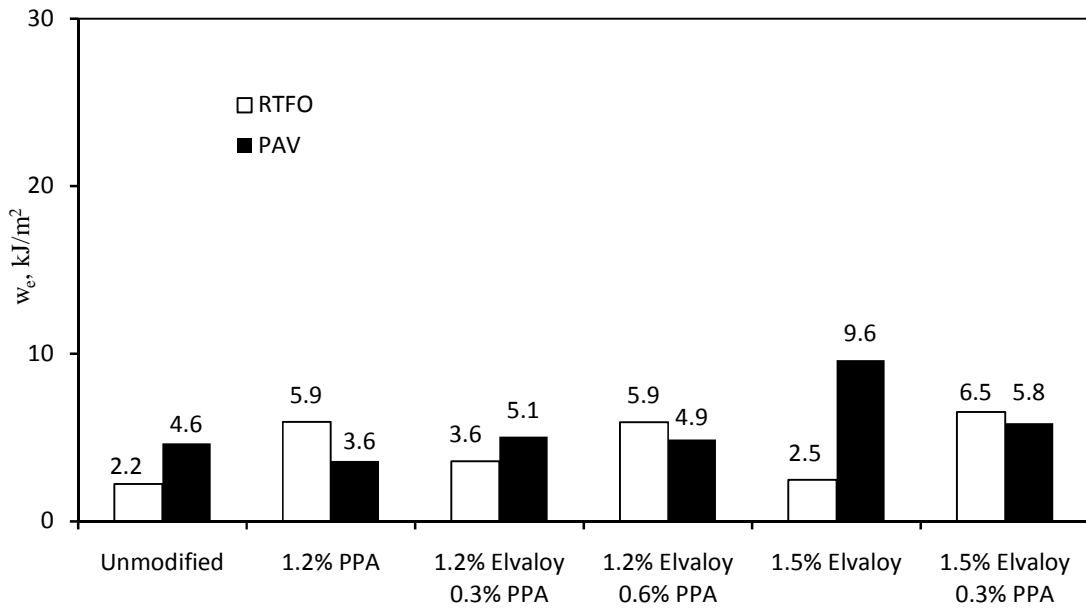


Figure 51. Specific essential works of failure for straight and modified PG 58-28 asphalt cements.

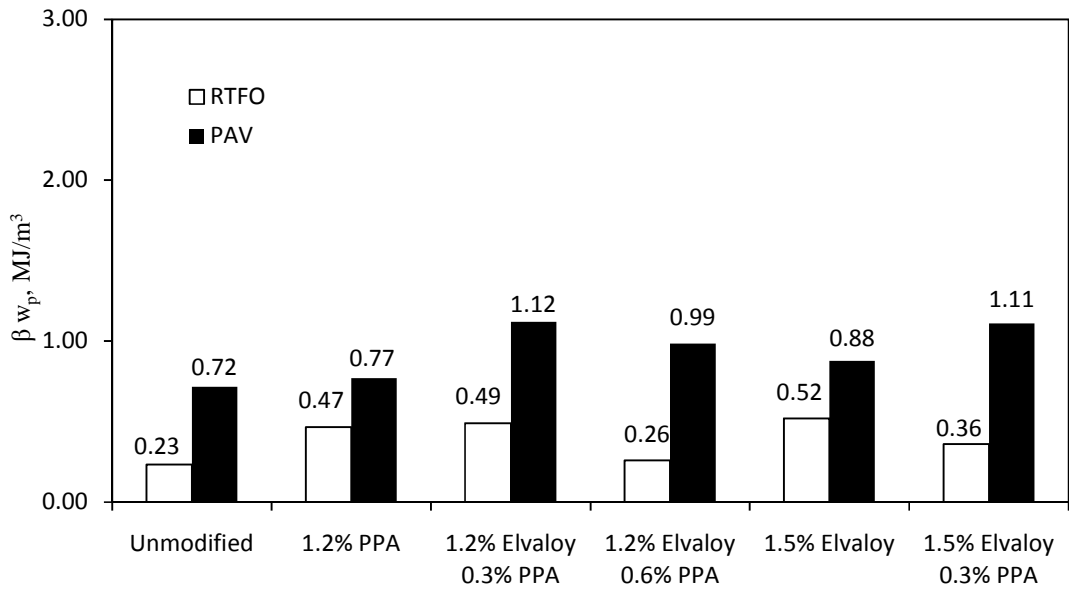


Figure 52. Specific plastic works of failure for straight and modified PG 58-28 asphalt cements.

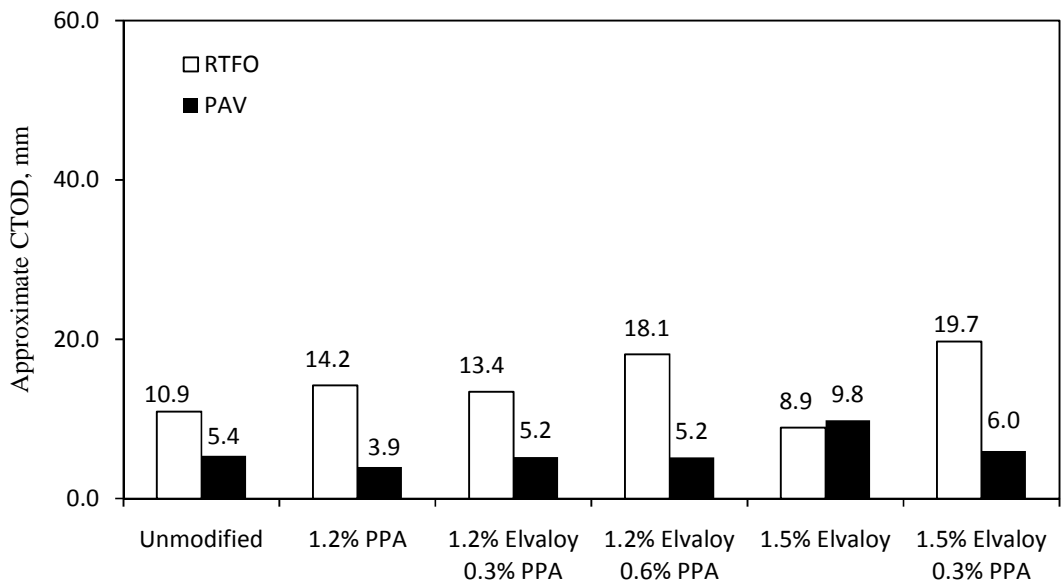


Figure 53. Approximate critical crack tip opening displacements (CTOD) for straight and modified PG 58-28 asphalt cements.

The straight and modified PG 58-28 systems show (Figure 49-51) similar findings as for the Cold Lake 80/100 base asphalt. The CTOD is improved in well-compatibilized systems but the additional PAV aging takes away significant strain tolerance. Hence, we may conclude that there is a benefit from polymer modifiers as opposed to straight acid modification but that these properties change rather dramatically during oxidative aging and that such changes are dependent on the base asphalt.

4.4 Bending Beam Rheometer Testing

4.4.1 Low Temperature Superpave® Grading

The Superpave® low temperature grades as determined with the bending beam rheometer (BBR) are provided in Figures 52-57 below. The approximate error in all BBR data is $\pm 1^{\circ}\text{C}$ as determined through round robin tests conducted by the Ontario Ministry of Transportation.

The limiting stiffness temperatures as provided in Figure 52 show that there are no large differences for the different modifiers in Cold Lake asphalt. The range for the unaged materials is from -22.7°C to -20.9°C while the range for the PAV materials is from -19.9°C to -17.3°C . In the context of the repeatability of this test (which is approximately $\pm 1^{\circ}\text{C}$) these results are all similar.

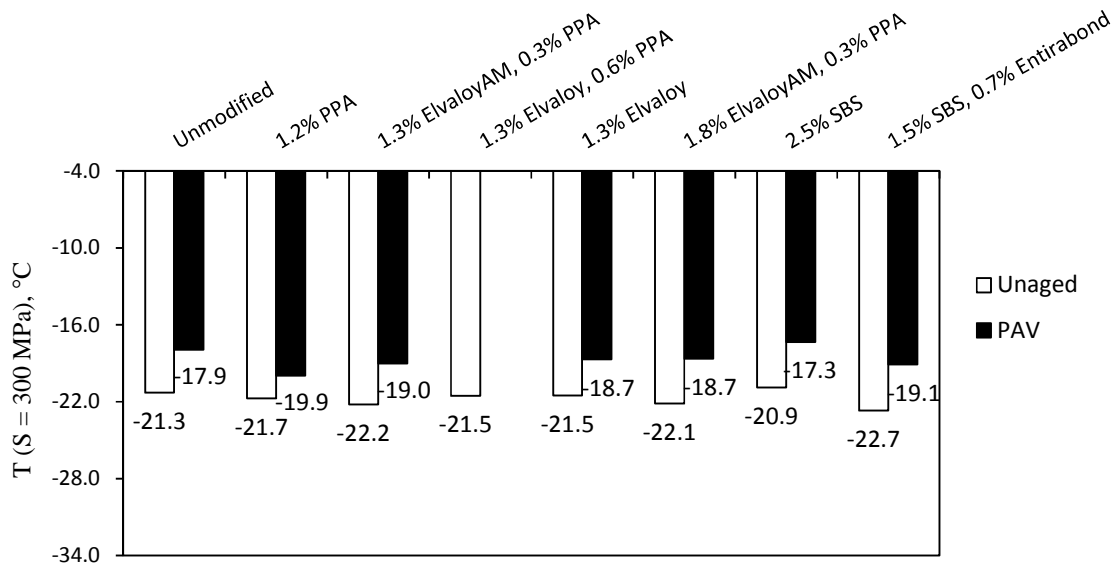


Figure 54. Temperature at which stiffness $S(t) = 300$ MPa for straight and modified Cold Lake 80/100 asphalt cement. (Note: Sample 1.3 % Elvaloy® + 0.6 % PPA could not be tested as a PAV residue since it gelled before it could be poured.)

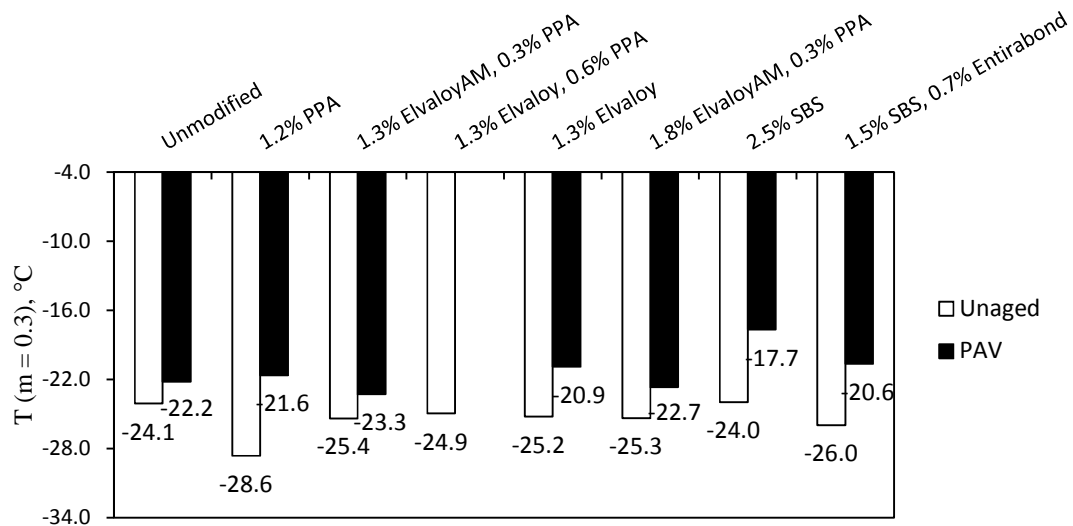


Figure 55. Temperature at which slope $m\text{-value} = 0.3$ for straight and modified Cold Lake 80/100 asphalt cement.

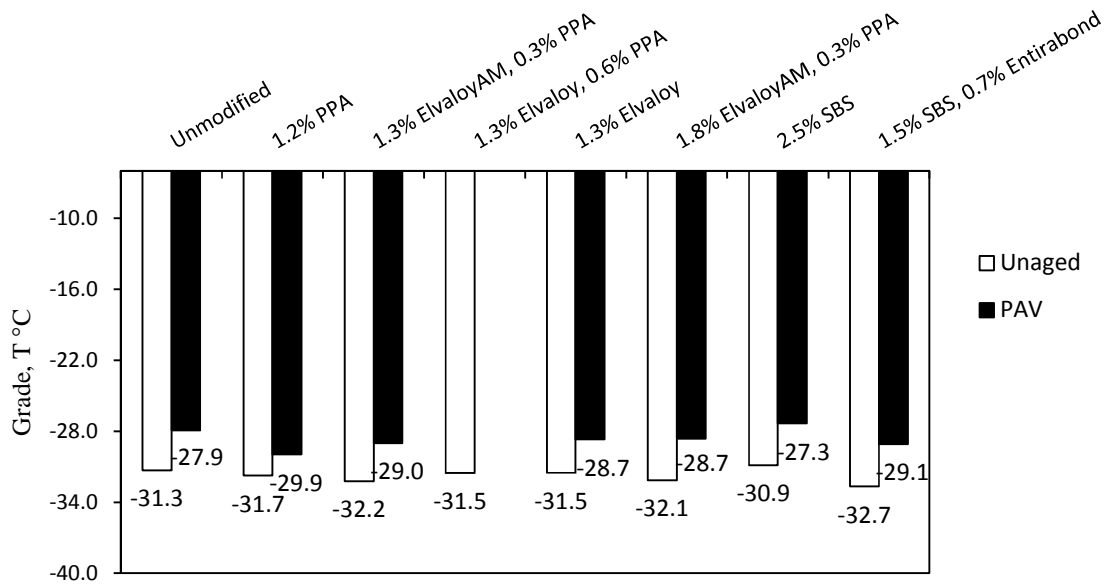


Figure 56. Low temperature Superpave® grade for straight and modified Cold Lake 80/100 asphalt cement.

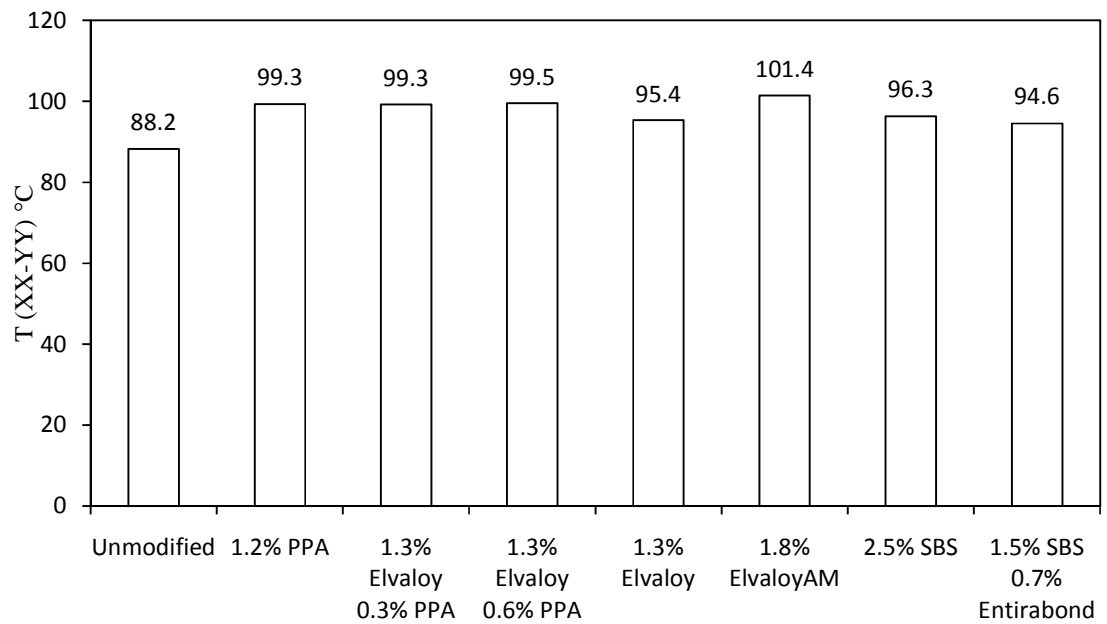


Figure 57. Grade span XX-YY for straight and modified Cold Lake 80/100 asphalt cements.

Similar to the findings in Figure 52 for the limiting stiffness temperatures, the limiting m-value and grade temperatures are similar for all different modifiers. The range in Superpave® grade temperatures for the unaged materials is from -32.7°C to -30.9°C while for the PAV-aged materials this is from -29.9°C to -27.3°C.

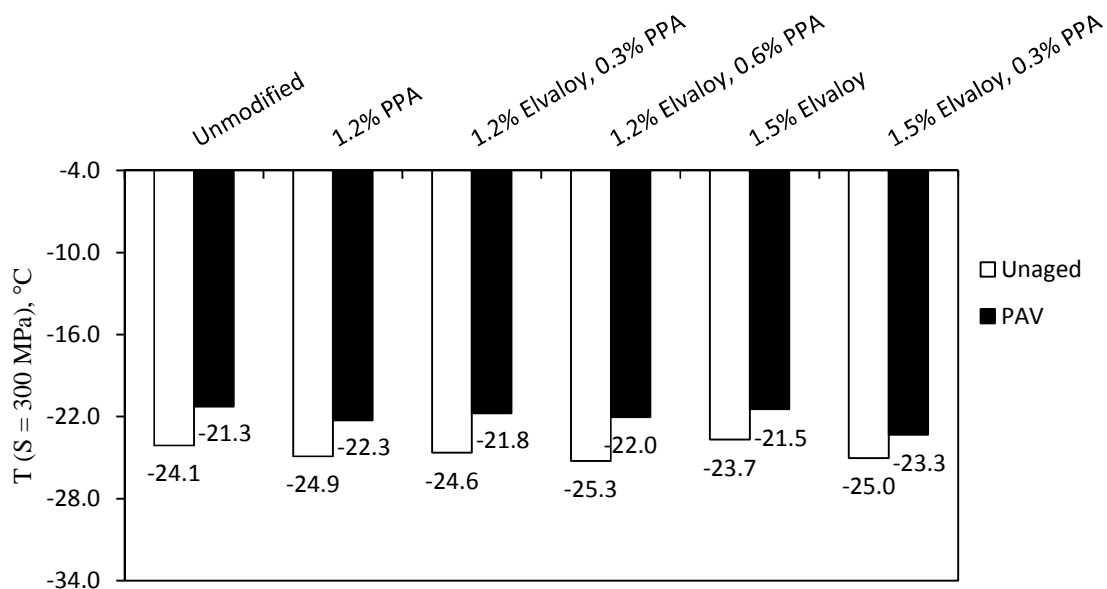


Figure 58. Temperature at which stiffness $S(t) = 300$ MPa for straight and modified PG 58-28 asphalt cement.

More interesting findings are provided in Figure 56 to 59 for the PG 58-28 systems. Again the limiting stiffness temperature is rather unresponsive to the addition of various additives. However, the effect of 1.2 % PPA and 1.5 % Elvaloy® and 0.3 % PPA on the colloidal stability and hence the m-value for the PG 58-28 shows that the performance at low temperatures can decrease quite dramatically. These systems graded at -23.6°C and -25.6°C, respectively, which is significantly lower than the control and other modified

systems. This shows that this base asphalt is less amenable to modification and caution is warranted.

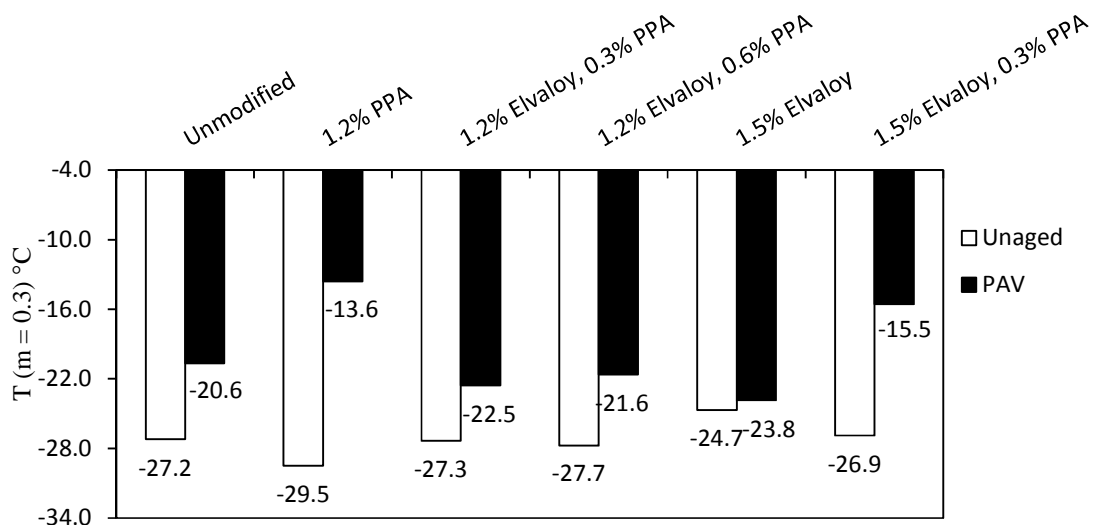


Figure 59. Temperature at which slope m-value = 0.3 for straight and modified for straight and modified PG 58-28 asphalt cement.

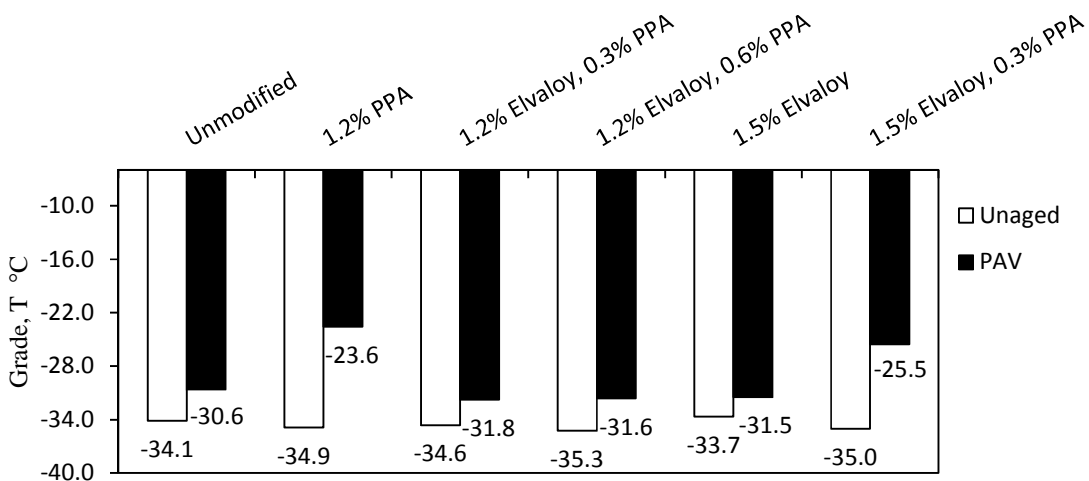


Figure 60. Low temperature Superpave® grade temperatures for straight and modified PG 58-28 asphalt cements.

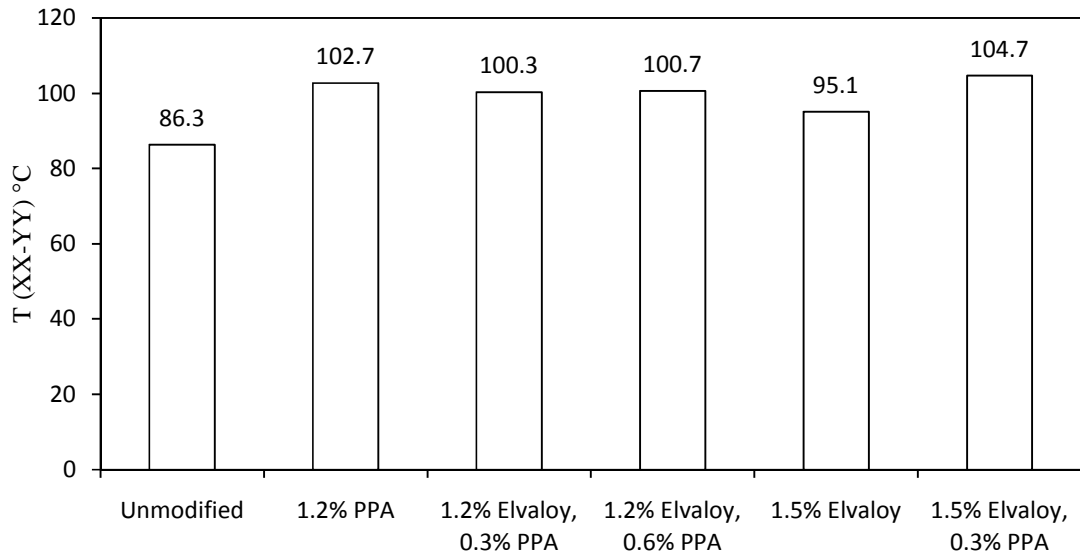


Figure 61. Grade span (XX-YY) for straight and modified PG 58-28 asphalt cements.

4.4.2 Recovery Test

In addition to the regular BBR grading, the elastic versus viscous properties were assessed for all systems by unloading the BBR beam for an additional 720 s after the 240 s of loading. The recovered displacement allows the calculation of the percentage elastic recovery while the permanent displacement allows the calculation of the viscous or non-recoverable creep compliance. The results for this investigation are provided in Figures 60-67 below.

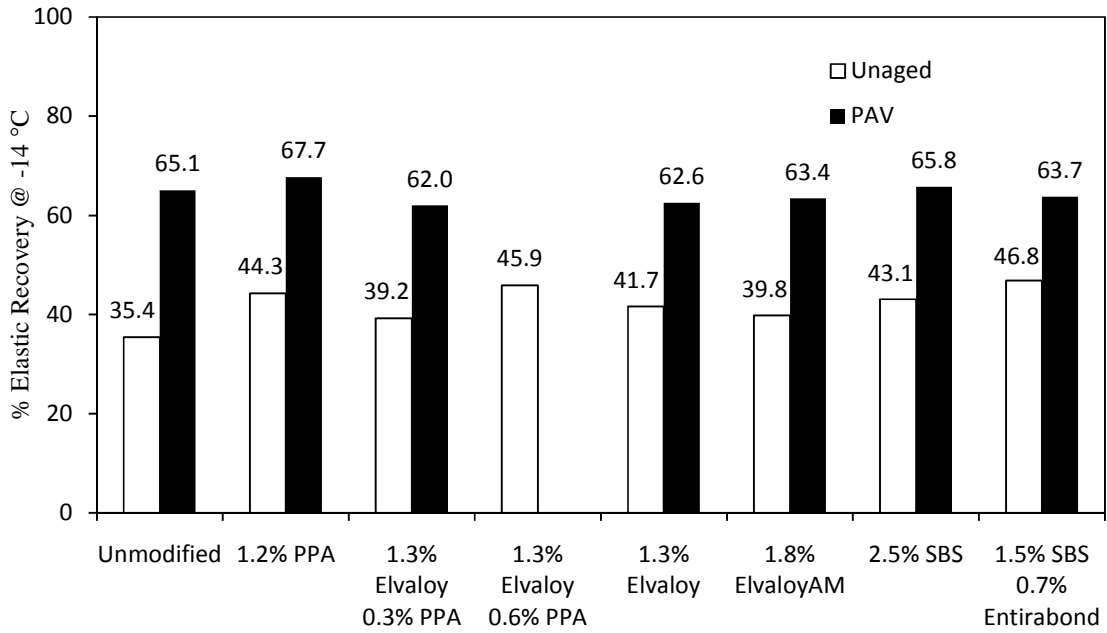


Figure 62. Percentage elastic recovery for Cold Lake 80/100 materials at -14°C.

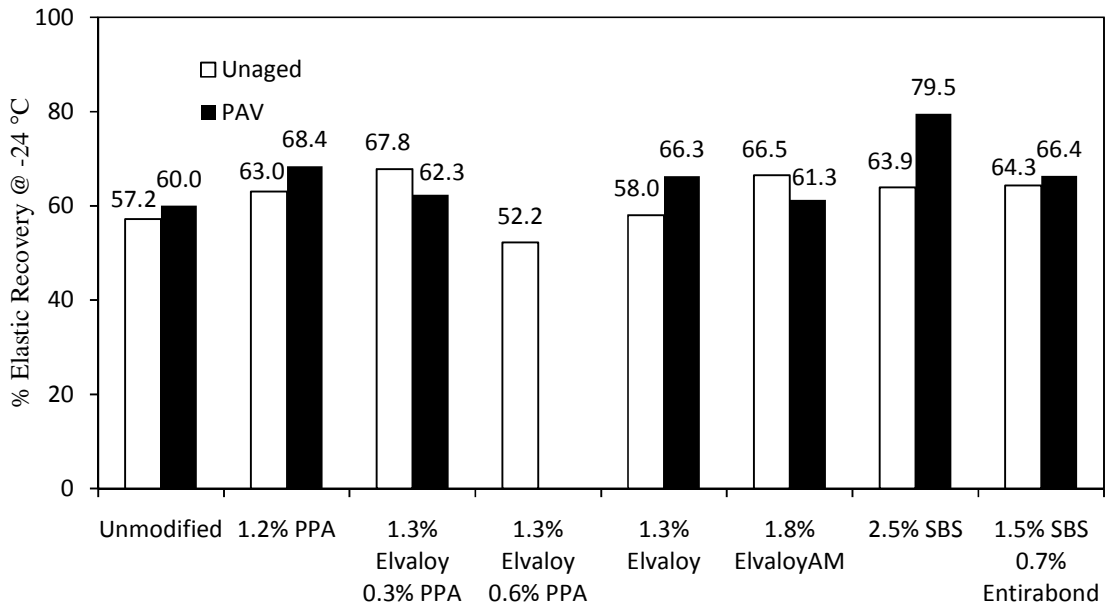


Figure 63. Percentage elastic recovery for Cold Lake 80/100 materials at -24°C.

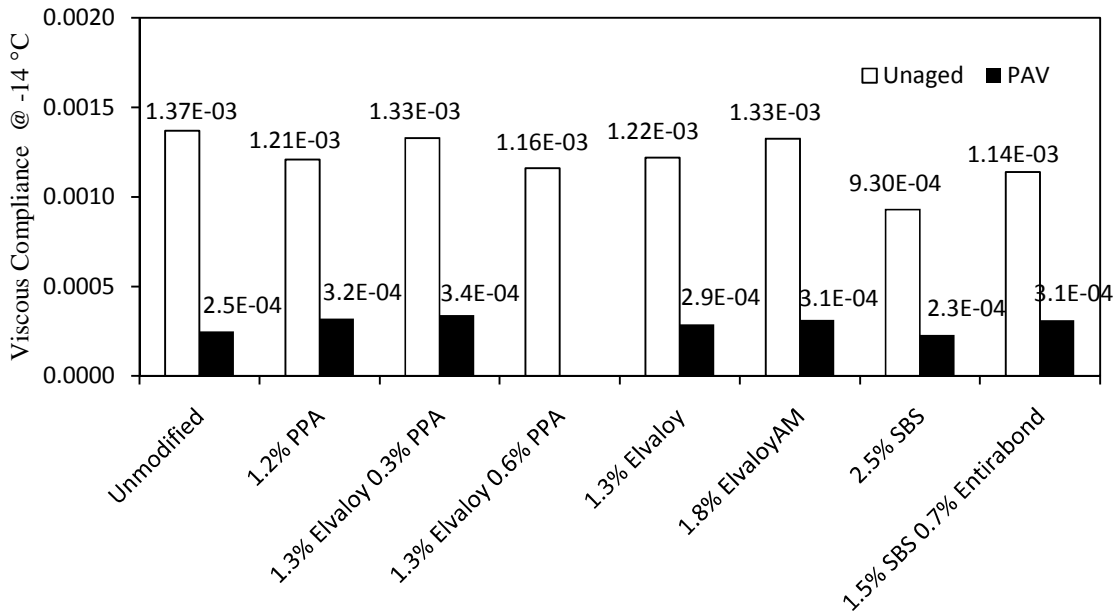


Figure 64. Viscous compliance J(v) for Cold Lake 80/100 materials at -14°C.

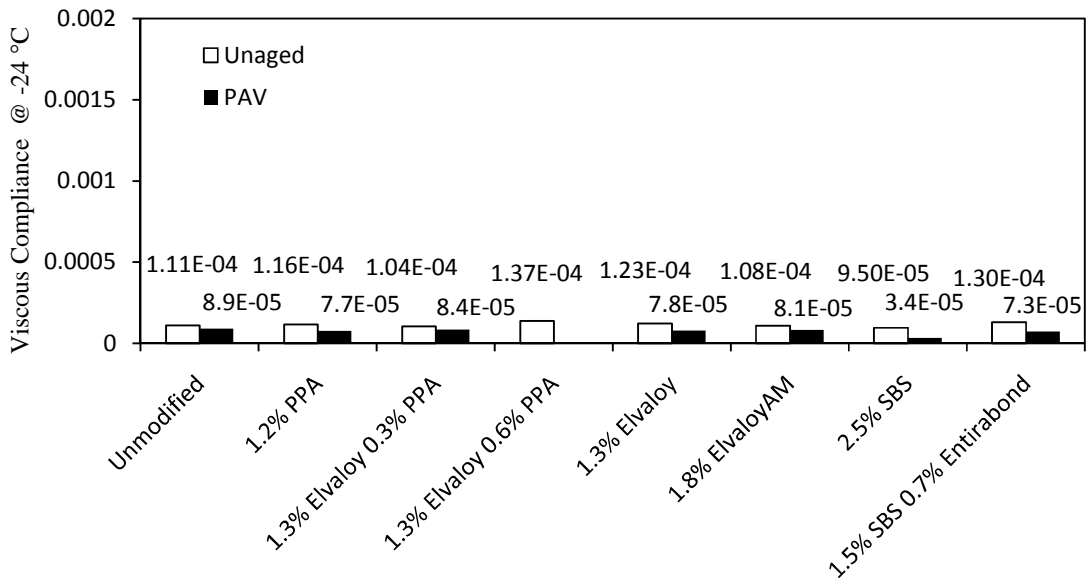


Figure 65. Viscous compliance J(v) for Cold Lake 80/100 materials at -24°C.

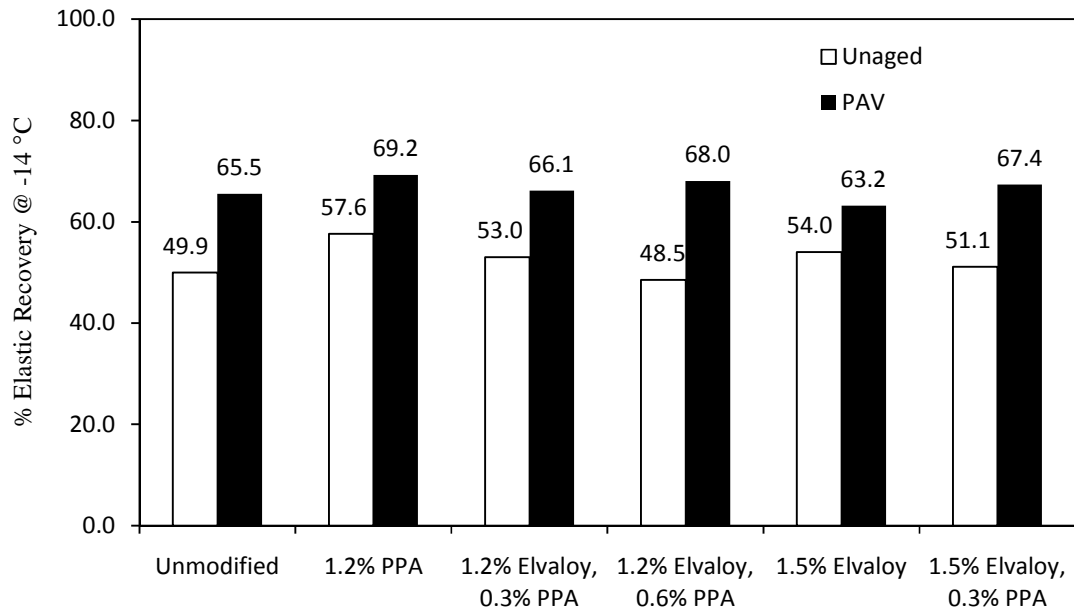


Figure 66. Percentage elastic recovery for PG 58-28 materials at -14°C.

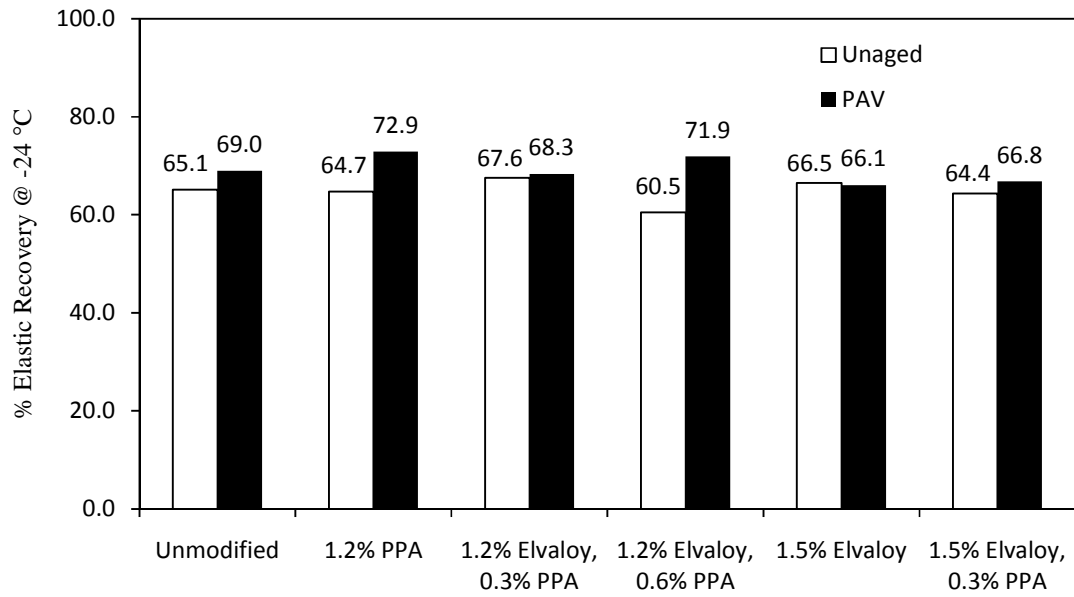


Figure 67. Percentage elastic recovery for PG 58-28 materials at -24°C.

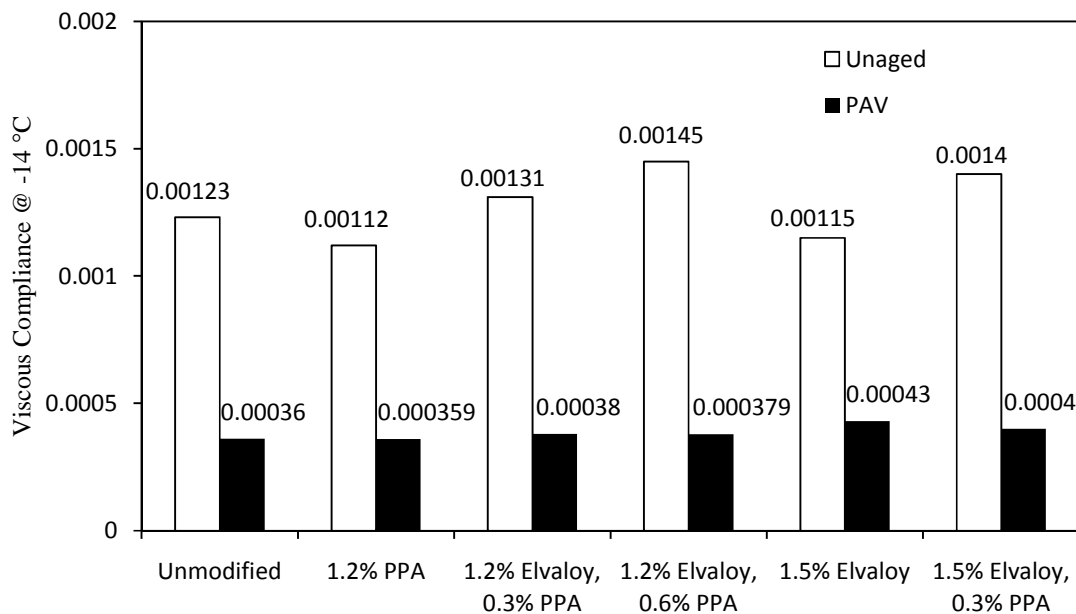


Figure 68. Viscous compliance $J(v)$ for PG 58-28 materials at -14°C .

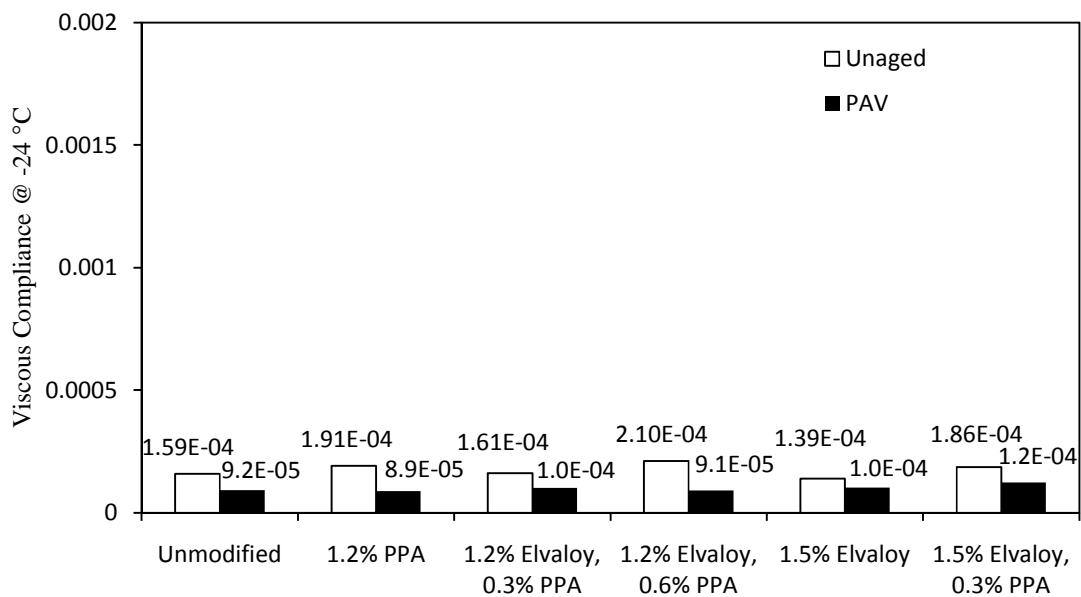


Figure 69. Viscous compliance $J(v)$ for PG 58-28 materials at -24°C .

These figures show that the findings are similar as for the regular BBR tests in that there are no major differences between different modifiers. The only exception may be for the Cold Lake 80/100 + 2.5 % SBS system which appears to show a significantly lower viscous compliance at both -14°C and -24°C for the PAV residue. This could be an indication of a higher thermal cracking tendency or it could be a testing error. The Elvaloy-modified binders on the other hand show a slight yet significantly improved viscous compliance at -14°C (Figures 64 and 68). Further work on these materials would have to provide more insight on this issue.

4.5 Effect of Modification Type on Chemical Aging Tendency

The chemical aging tendency was investigated by weighing the thin film oven-aged samples at regular intervals for up to 4,000 hours. In addition, the carbonyl functional groups were measured for up to 1,400 hour. The results for these investigations are provided in Figures 68-71 below.

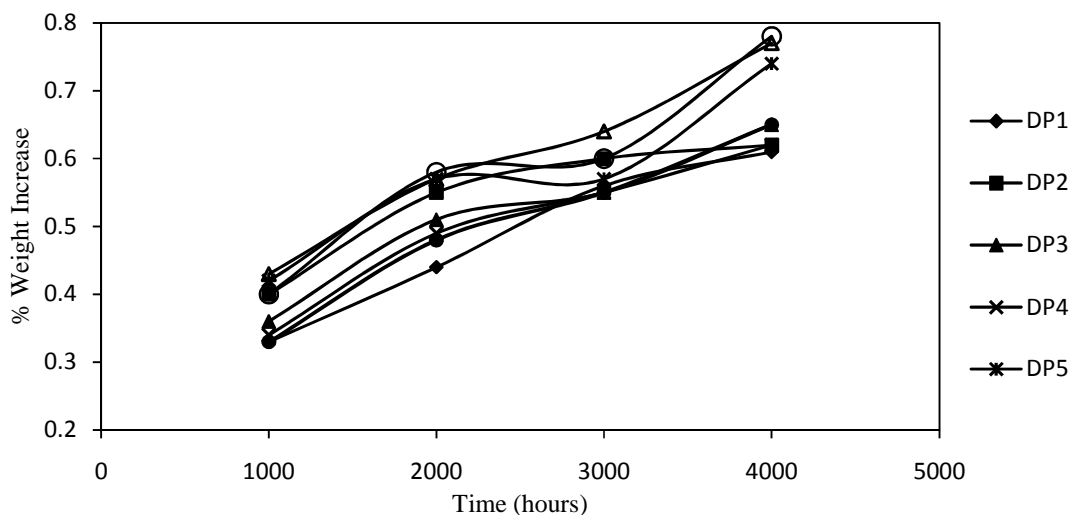


Figure 70. Percentage weight increase for Cold Lake 80/100 material at 45°C after aging for different time.

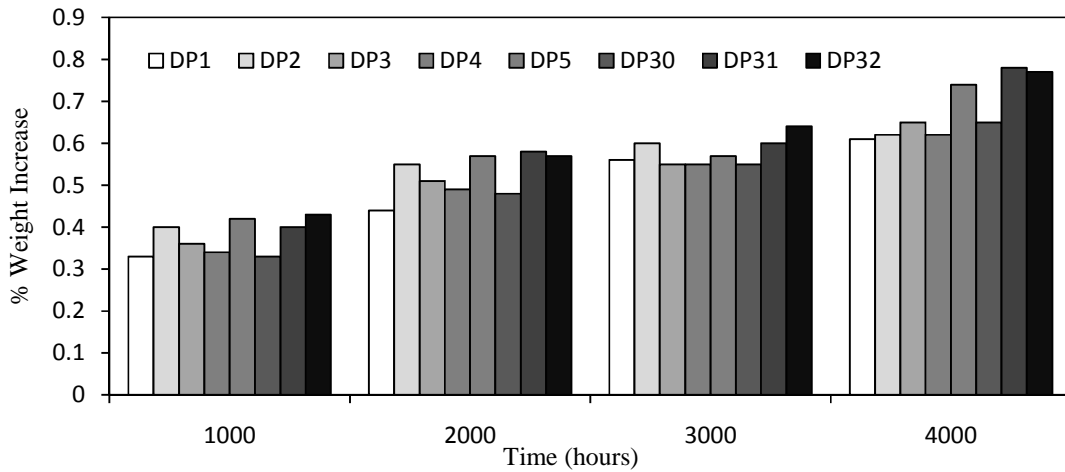


Figure 71. Percentage weight increase for Cold Lake 80/100 material at 45°C after aging for different time.

It is shown in Figures 68 and 69 that the weight changes for different samples are relatively constant. Minor differences occur relatively early on during the aging process but it is not entirely sure how significant this effect is.

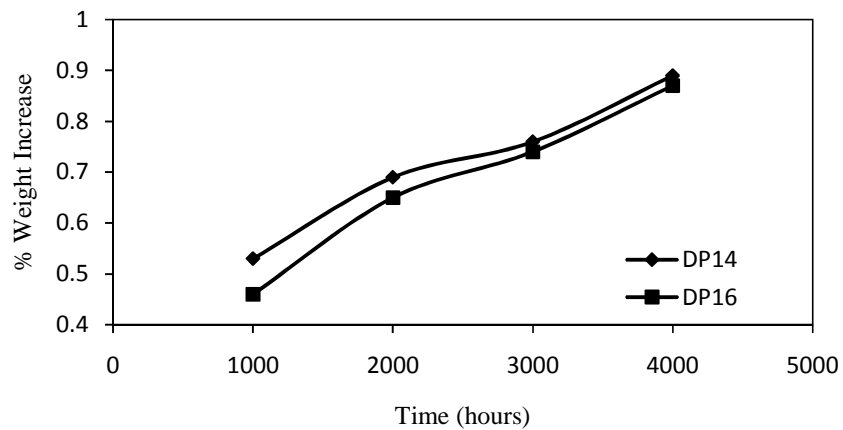


Figure 72. Percentage weight increase for PG 58-28 material at 45°C after aging for different time.

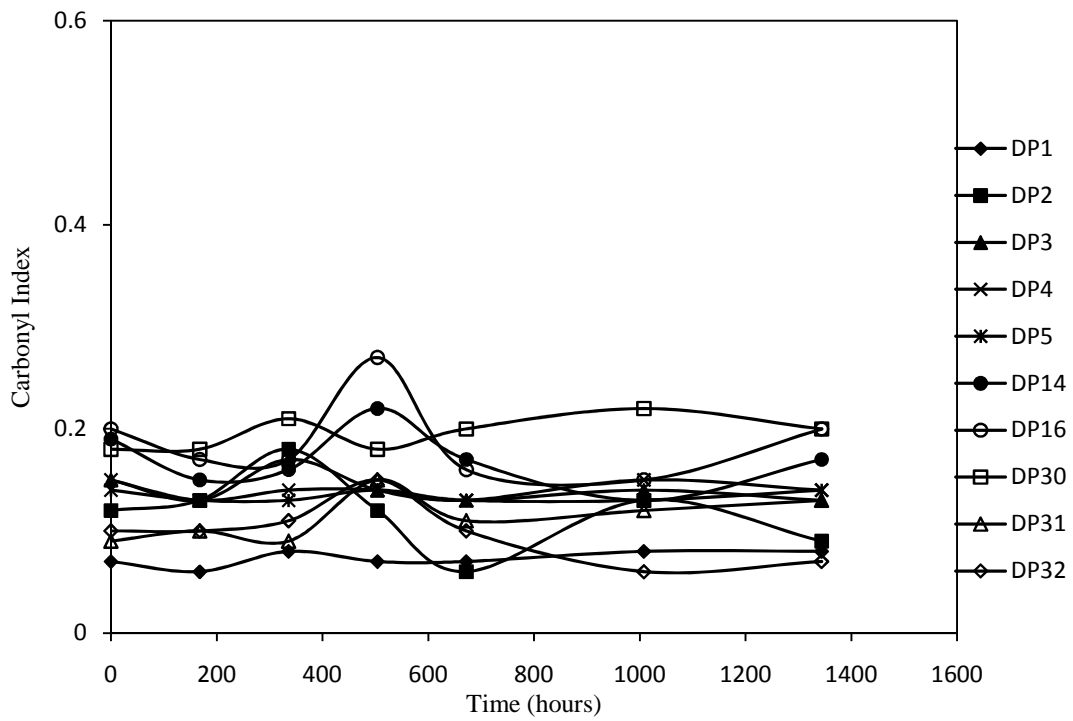


Figure 73. Carbonyl index for different asphalt samples at 45°C after aging for different time.

The changes in carbonyl index are also relatively minor although the length of time for which this was monitored was likely insufficient. Longer times may provide additional insights.

Chapter 5

Summary and Conclusions

Given the results presented and discussed in this thesis, the following summary and conclusions are given:

- All of the polymer, acid, and acid/polymer hybrid modifiers were able to increase the Superpave® performance grade span by significantly increasing the high temperature rutting parameter $G^*/\sin\delta$, while leaving the BBR parameters, $T(S = 300 \text{ MPa})$ and $T(m = 0.3)$, largely unchanged.
- Elvaloy® modifiers were able to reduce the intermediate Superpave® grade temperature by significant amounts in the PG 58-28 base asphalt. This shows a likely improvement in fatigue cracking resistance. The improvements for Elvaloy® were greater than those for pure PPA or SBS type modification. Improvements in Cold Lake 80/100 for this parameter were of lesser magnitude.
- All polymer modifiers were good at improving the ductile strain tolerance as measured in the double-edge-notched tension protocol while acids typically reduced the strain tolerance due to a gelation of the asphaltene phase. Modification with SBS polymers leads to the most impressive gains in strain tolerance for RTFO residues but for the PAV residue this advantage largely disappears. Addition of PPA to Elvaloy® systems improves strain tolerance.
- Black space diagrams and Cole-Cole plots are changed by only minor amounts due to the addition of polymers, acids, and acid/polymer mixtures.

- The Multiple Shear Creep Recovery (MSCR) test passes almost all of the straight and modified samples except those with poor compatibility (SBS blended with Cold Lake without sulfur, Elvaloy® systems without acid catalyst, pure PPA modified systems), which lack the elastic recovery at high levels of non-recoverable compliance.
- All systems show largely similar elastic recovery and viscous (non-recoverable) compliance in the BBR test at low temperatures.
- Minor improvements in the viscous creep compliance at -14°C were noted for Elvaloy®-modified Cold Lake 80/100 and to a lesser degree PG 58-28. The SBS-modified Cold Lake 80/100 did not show such improvement.
- All systems show largely similar chemical aging tendencies as measured by weight gain and carbonyl formation.
- Currently ongoing pavement trials will have to shed further light on the relative benefits of these modifiers.

Chapter 6

Future Work

Further work in this area should focus on the following areas:

1. Chemical aging experiments should be extended to longer times and the produced residues should be tested for both carbonyl formation and rheological properties in a dynamic shear rheometer (DSR). Such experiments will provide more conclusive evidence whether certain modifiers are better than others from a chemical aging perspective.
2. Asphalt mixture tests should be conducted in order to investigate how the various modifiers affect interfacial strength and how this could positively or negatively affect the long term pavement performance. Different aggregate sources should be investigated to see if the type of aggregate has an impact on performance.
3. Asphalt pavement trials should be constructed to investigate how the various modifiers stand up in service. Such trials could shed light on what processes are most important with respect to the various distress mechanisms (thermal cracking, rutting, fatigue cracking, and moisture damage).

Once the above investigations are complete it will allow user agencies of asphalt cement to make a better informed decision on what types of modification technology to promote for use in newly constructed asphalt pavements. This research has the potential to save hundreds of millions and billions of dollars in tax payer money by extending the life cycle of pavements and by preventing the premature and excessive failures in asphalt pavements as seen all around Ontario and other northern jurisdictions.

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