PHYSICAL AND CHEMICAL AGING BEHAVIOR OF ASPHALT CEMENTS FROM TWO NORTHERN ONTARIO PAVEMENT TRIALS

by

AMIT KANABAR

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Queen's University
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Abstract

This thesis documents and discusses the analysis of material properties and pavement performance for Highway 17 and Highway 655 pavement trial sections located in northern Ontario. The object of this work was to compare laboratory-aged material with recovered asphalt cement and to develop an improved chemical aging method that provides asphalt cement that more closely reflects properties after 8-10 years of service. Physical testing of the asphalt cements was done using a bending beam rheometer (BBR) and double-edge-notched tension (DENT) test for laboratory aged material as well as recovered material from the road. The comparison of the regular BBR, extended BBR and elastic recovery test in BBR is also done for the laboratory-aged and recovered material.

Two simple modifications to the regular pressure aging vessel (PAV) aging protocol were investigated as possible ways to improve the correlation between field and laboratory material properties. The length of the PAV aging was doubled to 40 hours and the weight for each pan was halved to 25 grams. It was observed that the presently used RTFO/PAV aging protocol does not produce sufficient aging. Hence, the conditions chosen were more severe and therefore are likely to bring the laboratory aging closer to the field aged condition. It was found that both the increase in time and the reduction in weight were able to accomplish the stated objective for most but not all asphalt cements.

A separate investigation involved the infrared (IR) analysis of asphalt cements recovered from a large number of contracts in eastern and northeastern Ontario. This study indicated that those asphalts with a largely paraffinic structure (low aromatics

index) showed excessive and premature cracking even at lower levels of oxidation (carbonyl index). In contrast, those pavements that were largely spared of thermal distress were constructed with asphalt cements that contained more aromatics (high IR aromatics indices). Aromatics allow the largely aromatic asphaltenes that are formed upon oxidation to remain well peptized rather than flocculated. Peptized asphaltenes allow for good stress relaxation during winter and spring thaw and thus such materials show a reduced tendency for cracking.

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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
LTPPBind®	Long Term Pavement Performance Binder Selection Software
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
NCHRP	National Cooperative Highway Research Program
NMR	Nuclear Magnetic Resonance Spectroscopy
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
XRF	X-Ray Fluorescence Spectroscopy
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
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

Asphalt is a black material and owing to its sticky nature and low price, it is used as the world's largest volume glue in road construction. In North America it is called asphalt, asphalt cement or asphalt pavement while in the rest of the world it is known as bitumen. Road construction plays a vital role in the development of a sustainable infrastructure for all economies. Countries without roads and highways will find themselves underdeveloped and will struggle to attain a level of wealth that is generally reached in the developed world. The construction of roads and highways has been a priority in the western world since Roman times. Countries like the United States and Canada spend billions of dollars to develop and maintain their highway transportation system. The Province of Ontario spends roughly $300 million annually on the purchase of asphalt concrete for the construction and maintenance of provincial roads and highways while cities and municipalities spend a few times this amount on local roads [1]. To minimize the costs of asphalt, it is crucial that proper materials are selected in order to guarantee an optimized pavement life-cycle. It is forecast that the demand for asphalt cement will grow by 2 percent annually through 2013 and that it will reach a yearly volume of just over 100 million metric tons worldwide [2].

1.1.1 Definition of Asphalt

The word "asphalt" is derived from the Greek word "asphaltos" meaning "secure". Similarly the word "bitumen" originated from the Sanskrit word "jatu-krit" meaning “pitch creating” [4]. In ancient times, asphalt was used as a mortar between bricks and stones, for ship caulking and as a water proofing material [3]. It was mainly used for adhesive applications where water-proofing properties were desired.

According to the Oxford English Reference Dictionary asphalt is defined as “a tar like mixture of hydrocarbons derived from petroleum naturally or by distillation and used for road surfacing and roofing” [4]. Asphalts are defined by the American Society for Testing and Materials (ASTM) as “dark brown to black cementitious materials in which the predominant constituents are bitumen that occur in petroleum processing” [5]. According to the American Heritage Dictionary, asphalt is defined as “a brownish-black solid or semi-solid mixture of bitumen obtained from native deposits or as a petroleum byproduct, used in paving, roofing and water proofing” [6].

1.1.2 Sources of Asphalt

The two sources of asphalt are from natural deposits and residues from the petroleum refining process:

(1) Natural asphalt is obtained from nature in that it is found in so called “asphalt lakes” around the world. Pit Lake, Trinidad; Gard, Auvergne, Ain and Haute Savoie in France; Central Iraq; Butin Island, Indonesia, etc are some of the sources for natural asphalt. Further, there is a huge deposit of Athabasca tar sands in northern Alberta which currently produces about 95% of all natural asphalt in the world [7].

(2) Petroleum asphalt is obtained during the refinery process of heavy crude oils. Asphalt used for road construction is mainly produced from the refinery process. Different types and grades of asphalt can be produce by using various operations. Vacuum and

atmospheric distillations are the basic processes used in oil refineries to produce asphalt and other useful products.

1.2.1 Composition of Asphalt

Rheology is the main science to characterize asphalt as it deals with flow and deformation at various rates and temperatures. Rheological properties of asphalt depend on the physical arrangement of the constituent molecules and this change rapidly with temperature. Asphalt is a highly complex material that has yet to be characterized properly. It mainly consists of saturated and unsaturated aromatic as well as aliphatic compounds with up to an estimated 150 carbon atoms. Usually the composition of the asphalt depends a great deal on the type of crude oil from which it is derived. Generally, the molecular compounds within asphalt contain oxygen, nitrogen, sulphur and other heteroatoms. However, asphalt largely consists of ~ 80 percent by weight of carbon, up to 10 percent by weight of hydrogen, and ~ 6 percent by weight of sulphur, small amounts of oxygen and nitrogen, and traces of metals like iron, nickel and vanadium. The constituent compounds possess molecular weights that range from several hundred to many thousands. The detailed composition of asphalt still obtains a significant amount of attention from several research groups around the world.

Due to its complex composition, asphalt is often separated in two different chemical classes of constituents called asphaltenes and maltenes. Maltenes can further be divided in three groups: saturates, aromatics, and resins. In this study, a solvent precipitation method was used to separate asphaltenes and maltenes [8].

1.2.2 Properties of Asphalt

According to Usmani, “Asphalt consists of a unique polymer-type network” [9]. It is mainly a thermoplastic type of material that softens when heated and on cooling regains back its property by hardening. Asphalt also has a visco-elastic nature [4] in that it exhibits the mechanical characteristics of viscous flow and elastic deformation over certain temperature ranges.

Asphalt has traditionally been described as a colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes) [10]. At a microscopic level the micelles are formed from asphaltenes that have an absorbed sheath of high molecular weight aromatic resins attached to stabilize them within the oily continuous phase. Hence, any type of change in the quantity or quality of the resins fraction can directly affect the properties of the asphalt cement [4]. For example, if the quantity of resin is sufficiently aromatic with adequate solvating power, the asphaltenes are better peptized and possess good mobility within the asphalt. This is known as a “sol-type” asphalt as schematically shown in Figure 1. In contrast, if the quantity of resins is insufficient and less aromatic, the asphaltenes will be less mobile and associate together. This can create an irregular open packed structure of micelles in which internal voids are filled with other constitution. This is called “gel-type” asphalt as schematically shown in Figure 2.

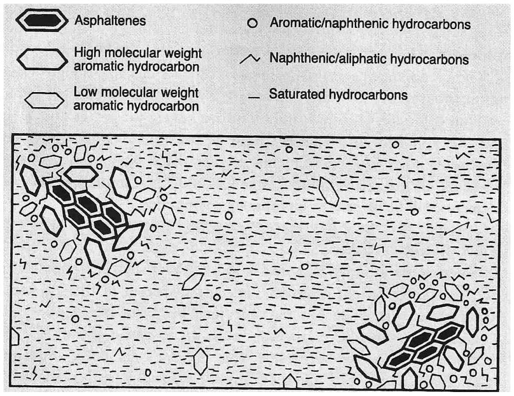

Figure 1. Sol-type asphalt [4].

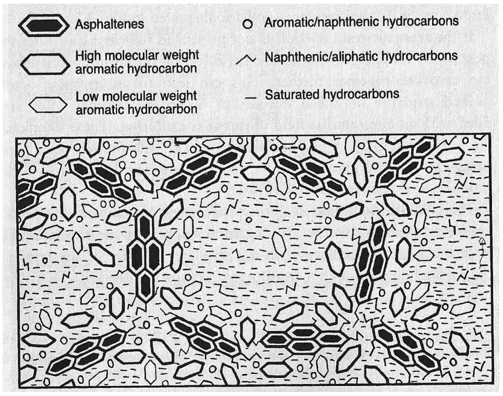

Figure 2. Gel-type asphalt [4].

This state of dispersion of the entire system has a direct influence on the viscosity of the asphalt cement and thus the rheological performance (rutting and cracking resistance). The viscosity of saturates, aromatics and resins depend on their molecular weight distribution. Viscosity increases as molar weight of the maltenes increases. As the saturate fraction increases, it decreases the solvating power of the maltene fraction, as saturates are generally known to facilitate the precipitation of asphaltenes.

1.2.3. Relation between Constitution and Rheology

The following are general observations that have been made about the relationship between constitution and rheology in asphalt cement [4]:

1) At constant temperatures the viscosity increases as the amount of asphaltenes increases in the parent maltenes.

2) Changes in concentration for fractions other than the asphaltenes show changes in the rheological properties of asphalt as follows:

- (i) An increase in saturates with a constant ratio of resins to aromatics, softens the asphalt.

(ii) An increase in aromatics at a constant saturates to resins ratio has less effect on rheology but considerable reduction in shear susceptibility.

(iii) An increase in resins results in hardening of the asphalt and an increase in viscosity.

1.3 Failure Modes in Asphalt Pavements

Pavement designers consider major failure modes which are fracture and permanent deformation. This failure happens due to four different types of distresses:

(1) Rutting: It occurs due to high temperature conditions. In such conditions, strain accumulates in the pavement and permanent deformation takes place. Deformation results as a formation of ruts (tracks) on the surface of asphalt pavement (Figure 3). Heavy loads at low frequencies and/or high temperatures are the major cause of this failure.

Figure 3. Severe ruts in an asphalt pavement [11].

(2) Fatigue: This mode of failure is observed due to the cyclic load of vehicles (especially heavy trucks) until it is cracked (Figure 4). This is often reduced by early repair planning.

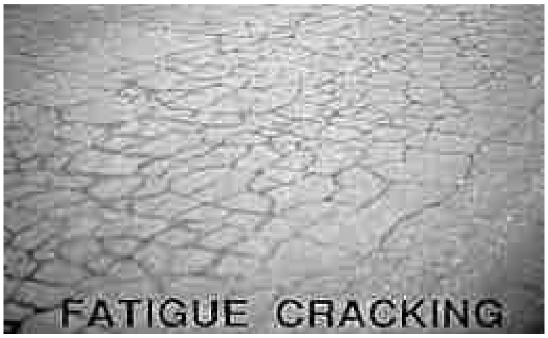

Figure 4. Fatigue cracking in an asphalt road surface [11].

(3) Moisture Damage: Failure due to moisture happens due to the lack of adhesion and cohesion between the asphalt cement and the aggregate and sand fractions. In presence of water, as asphalt is hydrophobic by nature and aggregate is not, the asphalt mastic can let go of the aggregate and sand fractions. This stripping phenomenon is a major cause of failure in many roads. Anti-stripping agents and proper compaction provide a remedy for this type failure.

(4) Thermal Cracking: This type of failure takes place mainly due to the exposure of the road to extremely low temperatures where thermal stresses exceed the strength of the materials. Frequent and long term low temperature exposure during winter can lead to physical hardening which is mainly seen in countries like Canada and the northern part of the United States which have harsh winters for many months in length. Thermal cracking also happens due to repeated thermal stresses below the design limit and this is called thermal fatigue cracking (Figure 5). Another reason for thermal distress is the repetitive loading by heavy traffic during the freeze-thaw cycle in early spring. This cycle develops cracks at the surface and edge of the pavement which can then progress to the full width during the next cold winter. Thick layers will help to prevent this type of distress to a limited degree.

Figure 5. Longitudinal and transverse cracks due to thermal effects [11].

1.4 Aging of Asphalt Materials

As mentioned earlier, asphalt is a complex mixture of organic molecules, so the presence of oxygen in the atmosphere and ultraviolet radiation on its surface, along with changes in temperature, play a significant role in the chemical aging process. Oxidation of asphalt creates changes in the physical and chemical properties of the material. The main outcome of these reactions is that they increase the stiffness of the asphalt cement. It becomes hard and brittle resulting in cracks when loads are applied.

Physical aging is another process by which asphalt cement can stiffen, especially at low temperatures during extended periods of conditioning. The mechanism of the physical aging process varies depending on which literature one considers [12-15]. According to Petersen [16] there are the following three main causes for physical aging:

(i) Amount of composition present in asphalt changes with oxidation reactions.

(ii) Decrease in maltenes content due to volatilization or adsorption.

(iii) Slow crystallization of waxes and rearrangement of asphaltene and resin molecules.

Due to the complex composition of asphalt that changes widely with different sources, it is still an ongoing research subject to identify the exact mechanism behind the physical aging process.

1.5 Scope

Nowadays characterizations of physical properties are the main methods to predict the life cycle of asphalt cement. It has been observed that an extended bending beam rheometer (BBR) method in which the asphalt cement is conditioned for 1 h, 24 h and 72 h prior to specification grading provides a much improved ranking of performance compared to the regular BBR method in which the asphalt cement is only cooled for 1 h prior to testing [17-19]. However, this method is not entirely successful because there are still problems with current laboratory chemical aging protocols. These protocols are known as the rolling thin film oven (RTFO) and pressure aging vessel (PAV) methods and they generally do not age the materials chemically in a manner that is similar to what happens to the asphalt cement in service. Hence, it is important to identify the types of chemical changes that take place in order to develop an improved chemical aging process. This thesis investigates the physical and chemical changes that take place during laboratory and field aging of a series of asphalt cements that were used in a northeastern Ontario pavement trial constructed in 2003 and sampled in 2008 and 2009.

Chapter 2

Background

2.1 Aging of Asphalt

In order to investigate effects on the general properties of binders, particularly at low temperatures, the aging of asphalt has received considerable attention in recent times. The behavior of asphalt binders is dependent on temperature and time such that time and temperature can be used interchangeably. For example, a high temperature within a short time appears to be equivalent to a lower temperature and longer time (time-temperature superposition principle) [20].

During hot mixing, construction, and service the oxidation that occurs in asphalt binders is referred to as asphalt aging. The binder becomes more brittle in nature when the oxidation takes place in presence of organic molecules that are present in asphalt, which leads to an increase in viscosity and results in the pavement distress of the asphalt mixture. The enhancement in oxidative hardening happens with the penetration of air in to asphalt mixtures which have a higher percentage of interconnected air voids. Thus, improperly compacted asphalt pavements have a greater tendency to exhibit oxidative hardening and thus could fail prematurely. The chemical composition of asphalt binders affects the adhesion (interaction) level between the aggregate and modifiers of binders [21] and also plays [22] an essential role in oxidative hardening. Mainly when heat is applied and progressive oxidation takes place, the aging behavior of asphalt can be related to the volatilization of its light components. There are two stages of a pavement's life where oxidation can occur in the field [23]:

1. **Hot mixing and construction:** During the mixing and placement process the asphalt binder is exposed to elevated temperatures and a large contact area with the aggregates which can lead to rapid aging by volatilization and oxidation. The aging mechanism which includes the loss of volatiles and chemical oxidation that result from elevated mixing and placement temperatures falls under the primary process which is followed by oxidation in a secondary process during long term service.
2. **In-service:** The constituent asphalt binder slowly ages as the oxygen from the surrounding environment percolates through the HMA and chemically reacts during the life of an in-service HMA pavement.

In order to evaluate the effect of aging on short and long-term service conditions of the pavement, the aging behavior of asphalt binders has to be simulated in the laboratory. The mechanical and rheological properties on the binders are used to evaluate the effect of aging. The type of aging that occurs in asphalt binders when mixed with hot aggregate (hot-mixed asphalt) is termed short-term aging, whereas the one that occurs after HMA pavement is exposed to environmental conditions and traffic for a long period of time is termed long-term aging [24].

2.2 Laboratory Aging

In the laboratory the aging during mixing and construction is simulated by the RTFO procedure, whereas aging in-service life is simulated using the PAV procedure. Hence, the asphalt binder tests concerned with mix and placement properties like the DSR are carried out on RTFO aged samples, whereas the asphalt binder tests concerned with in-service performance like the DSR, BBR and DTT are done on samples first aged in the RTFO and then in the PAV.

2.2.1 Rolling Thin-Film Oven (RTFO) Test

The key issue investigated by the RTFO is the loss of volatiles in spite of various other factors that contribute to asphalt binder aging. The asphalt's viscosity is increased due to the loss of volatiles from the asphalt binder which mainly occurs during the processes of manufacturing and placement. These processes age the asphalt binder by driving off a substantial amount of volatiles when exposed to elevated temperatures. In-place asphalt binder does not lose a significant amount of volatiles over its life as shown through field investigations [25].

2.2.1.1 Origin of Test and Overview

For the short term asphalt binder aging the RTFO test was developed as an improvement to the Thin-Film Oven Test (TFOT). The asphalt samples were placed in shallow pans and heated in an oven for an extended period of time to accomplish simulated aging during the TFOT process. An improved process over the TFOT is the RTFO because:

- Due to the rolling action, asphalt binder is continuously exposed to heat and air flow.
- Modifiers, if used, usually remain dispersed in the asphalt binder due to the rolling action.
- The duration of the test is of 85 minutes only rather than the 5 hours for the TFOT.

Short-term aging by heating a moving film of asphalt binder in an oven for 85 minutes at 163°C (325°F) is carried out in the rolling thin-film oven (RTFO) test. Determinations of effects by heat and air that incurred in physical properties are measured before and after the oven treatment by other test methods. The asphalt binder sample is poured in a small jar which is then placed in a circular metal carriage that rotates within the oven (Figure 6) in turn creating the moving film.

Figure 6. Rolling thin-film oven test [26].

The Rolling Thin-Film Oven test is embodied in AASHTO T 240 and ASTM D 2872 “Effect of Heat and Air on a Moving Film of Asphalt” standards.

2.2.2 Pressure Aging Vessel (PAV)

Old pavements generally fail through a number of distresses of which cracking through both thermal and load-induced stresses is a critical one. Hence, in the process of predicting various types of distresses a method to simulate in an accelerated manner the long-term aging of the asphalt binder is of utmost importance. The PAV is the currently used method of choice for simulating the long-term aging of asphalt materials. To predict and control fatigue and low temperature cracking resistance, the Superpave® binder specification requires that PAV-aged asphalt binder is tested at intermediate and cold temperatures.

2.2.2.1 Origin of Test and Overview

There were two general approaches considered in developing a procedure to simulate long term aging by oxidation [23]:

- **Oven tests:** Relatively simple, quick and older than pressure tests. Tests are based on high temperatures and thin asphalt films to stimulate the oxidation process. Moreover, the asphalt binder samples lose a valid amount of volatiles during aging process. In-service, the constituent asphalt binders did not lose significant amounts of volatiles was observed by field tests [25].
- **Pressure tests:** This approach has been around for over 40 years in spite of its lower popularity over oven tests. To increase the diffusion rate of oxygen into an asphalt binder sample by using high pressure is the mechanism behind the pressure tests. Thus during aging of asphalt binder, this approach limits the loss of volatiles.

To simulate the effects of long-term asphalt binder aging that occurs as a result of 8 to 10 years pavement service, the pressure aging vessel (PAV) was adopted by SHRP researchers [27]. In rubber product aging, the general concept of the pressure aging vessel had been used for many years prior to Superpave®. The PAV is a combination of an oven and a pressure vessel method which is done using RTFO aged samples that are exposed to high air pressure (300 psi) and temperature (90°C, 100°C or 110°C) on the basis of expected climatic conditions for 20 hours.

The simulated long-term aged asphalt binder for physical property testing is provided by the Pressure Aging Vessel (PAV) as in Figure 7.

Figure 7: Pressure Aging Vessel (PAV) [26].

At Iowa State University the standard asphalt binder PAV was developed for long term aging of asphalt cements which is also a standard method for aging rubber products (as in ASTM D 454 and ASTM D 572) [28].

2.2.2.2 Reasons for PAV Time and Temperature [23]

This process is generally carried out for 20 hours at 90, 100 or 110°C which was more based on practical approach instead of theoretical. Generally this experiment was performed for 6 days at 60°C and 300 psi. The test period was deemed too long and the test results showed up insufficient aging. Hence the test temperature was raised in order to produce shorter test times through increased aging rates. Initially the temperature for the test was chosen as 100°C which during field validation turned out to be too mild for hot climates and overly harsh for cold climates. Thus, three elevated temperatures are used which simulate a different general environmental condition:

Temperature	**Simulation**
194°F (90°C)	cold climate
212°F (100°C)	moderate climate
230°F (110°C)	hot climate

The standard Pressure Aging Vessel procedures are embodied in AASHTO R 28 and ASTM D6521 – 08 “Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)”.

There are still distresses observed within one month to five years of service that are passed through above mentioned standard method [17]. Hence, it indicates that still some space for improvement to predict the long-term aging process especially for cold weather.

2.3 Physical Characterizations of Asphalt Material

The pavement contracts and builds up internal stresses as the surrounding temperature drops. It does not have enough time to relax the stresses if the contraction occurs fast enough and load applies resulting in the formation of cracks in the pavement surface. The resultant of this type of crack which is commonly known as thermal crack could occur on either of two related mechanisms which are as follows:

1. **Single thermal cycle below the critical temperature:** The cause of stress to quickly build up to a critical point that leads to cracking is possible when a severe drop in temperature takes place. The particular temperature related with these critical stresses is called the "critical temperature" and the process is known as "single-event low temperature cracking".
2. **Thermal cycling above the critical temperature:** The stresses could be built up due to repeated thermal contraction and expansion which occur above the critical temperature that leads to cracking.

2.3.1 Bending Beam Rheometer (BBR)

The failure mechanism of asphalt material is actually the same which includes the thermal shrinkage that initiates and propagates flaws or cracks in the asphalt binder portion of the HMA in both the above mentioned cases. The BBR test was developed to measure the stiffness and rate of stress relaxation, commonly known as the m-value, or slope of the creep stiffness master curve asphalt binders which are not too stiff at low temperatures and which are able to relax built up stresses are generally able to withstand cold temperatures without extensive cracking.

2.3.1.1 Overview and Method

A measure of low temperature stiffness and relaxation properties of asphalt is determined on the basis of the Bending Beam Rheometer (BBR) test. An asphalt binder's ability to resist low temperature cracking could be determined on the basis of these parameters. The actual temperatures anticipated in the area where the asphalt binder will be placed determine the test temperatures used, which is the same as other Superpave® binder tests.

Figure 8: BBR beam on its supports [26]

As in Figure 8, a small asphalt beam that is simply supported and immersed in a cold liquid bath in a basic BBR test. The deflection against time is measured when a load is applied to the center of the beam. A measure of how the asphalt binder relaxes the load induced stresses is measured along with the stiffness which is calculated on the basis of measured deflection and standard beam properties. The BBR test, which is mainly software controlled, is performed on the PAV aged asphalt binder samples.

The AASHTO standard M320 provides the specification criteria for passing/failing the BBR test [29]. The testing temperature and conditioning temperature are both the same in this test method. Before testing, the binder samples are conditioned for an hour at room temperature followed by conditioning at -10°C and -20°C in refrigerators for an hour. Above the design temperature of the pavement, the loading of the specimen in three-point bending at a temperature of 10 degrees is carried out on the assumption that the time-temperature superposition is valid, and the 10°C difference reduces the testing duration of the binder sample from 2 hours to 60 seconds [20, 27]. If 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 sample passes the specifications. The material fails the specification if either the stiffness is above 300 MPa or the m-value is below 0.3 and could be used only in a location with warm climatic conditions.

The current AASHTO M320 specification has turned out to be deficient through recent investigations on a large number of pavement trials and regular contracts [30, 31, 32, 33, 34]. A vast difference in low temperature fracture performance is shown in the pavements of the exact same low temperature grade [32, 35, 36]. The AASHTO M320 has problems that relate to the absence of a proper chemical aging 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) in addition to the insufficient physical aging/conditioning of the asphalt cement. Thus an improved performance grading method is needed. In Ontario a recently developed LS-308 method on extended BBR testing that includes an increase in the conditioning time prior to three-point bending tests is one approach taken towards the improvement in the method [37].

2.3.2 Improved Low Temperature Specification Testing

In the earlier part of last century the effects of isothermal conditioning on the low temperature rheological properties of asphalt cement have been studied by a significant number of researchers. Measuring rheological properties at low temperatures in asphalt cement [38, 39, 40] cautioned that physical hardening mechanisms need to be taken into consideration. It was stated by Struik [41] that without considering the physical aging phenomenon it is useless to study properties like creep and stress relaxation.

To address the inadequacies of the AASHTO M320 specification, two test methods have recently been developed in Ontario [30, 32, 34, 42]:

- Extended BBR test - LS-308 [38]; and
- Double-edge-notched tension (DENT) test - LS-299 [43].

The physical aging phenomenon was more recently considered in great detail in the research as an important indicator of thermal cracking performance [15, 32, 34]. To study the ductile failure mechanisms in asphalt cement and hot mix asphalt under high strain conditions the double-edge-notched tension (DENT) test [30, 42, 43] has been introduced in Ontario. As determined in the DENT protocol it was found that the approximate critical crack tip opening displacement (CTOD) shows a good correlation with thermal and fatigue distress [30, 42].

Thus in comparison to the regular BBR protocol, LS-299 and LS-308 are the newly developed test methods that give a consistently better ability to predict either good or poor performance.

2.3.2.1 Extended BBR Testing - MTO method LS-308

The experimental section shall consist of a detailed description of the test method. In the extended BBR test protocol conditioning of the samples is carried out for three different times [37] at two different temperatures. The temperature $T_1 = T_{design} + 10$ and $T_2 = T_{design} + 20$ are the two different conditioning temperatures related to the designed temperature of the pavement. As it is expected that the physical aging tendency peaks at very low temperatures, the molecules cannot move while at higher temperatures above T_2, and the thermodynamic tendency for waxes to crystallize and asphaltene molecules to precipitate is absent therefore these two temperatures were chosen over the total 20°C range. The method is designed to provide a high degree of confidence that thermal cracking is prevented completely rather than to perfectly correlate with low temperature cracking distress. Even though cold spell may not occur during the early life of the contract, the roads that spend most of their time at a relatively warm T_2 would need to be protected from a cold spell at T_1. The regular tests are done to check a pass and a fail temperature after one hour of conditioning, one day of conditioning, and three days of conditioning, according to AASHTO M320 criteria where S(60)=300 MPa and m-value (60)=0.3. Thus, the method is termed as an extended BBR test. At the end of each conditioning period, the grade temperature and subsequent grade losses are calculated. The warmest minus the coldest limiting temperature where S reaches 300 MPa or m reaches 0.3 is the worst grade loss. This test method has shown 95% accuracy in separating the good from the poor performing asphalt cements [19].

2.3.2.2 Ductile Failure Testing - MTO method LS-299

In the experimental section the procedure for LS-299 shall be discussed in detail. In the process of the DENT test the pulling of a notched binder sample until it fails in a water bath is carried out [43]. The temperature of 15°C is maintained in the water bath. The distances between the two opposing notches are 5 mm, 10 mm and 15 mm in length. Conditioning was done for 24 hours at 15°C in the water bath prior to testing. The failure energy and the peak force are observed through this test. The crack tip opening displacement (CTOD) is calculated from the peak force at a 5 mm ligament length. The strain tolerance in ductile failure, which should relate accurately to the tendency for cracking distress, is reported from the CTOD value. A lower value of CTOD corresponds to a worse condition of the roads; this test method provides an approximate 85% accuracy [19].

2.4 Chemical Characterization of Asphalt Material

2.4.1 Introduction to Oxidation of Asphalt

To design pavements, the asphalt binder material requires physical properties that provide optimum service performance and durability. The changes in flow properties with time are usually highly undesirable as they often lead to reduced product performance or even failure as the optimum performance properties that are dependent on the flow or more precisely the rheological properties of the asphalt. Asphalt is subject to chemical oxidation by reactions with atmospheric oxygen that leads to the hardening of the asphalt which results into a deterioration of desirable physical properties. As a result, the asphalt oxidation is of pragmatic importance.

The meaning of physicochemical characterization is important to understand further changes in the properties of asphalt material. The chemical forces at the molecular level which are responsible for the physical properties are different in spite of the fact that asphalts have many physical properties that are quite similar to polymers. The composition of a simple polymeric material consists of large molecules of similar chemical composition. With changes in the environmental temperature, the molecular weights of the molecules do not change in the polymer. In comparison with polymer, the asphalt material consists of relatively small molecules. Asphalt ranges from non-polar hydrocarbons, which are similar in composition to waxes, to highly polar or polarizable hydrocarbon molecules consisting of condensed aromatic ring systems that incorporate heteroatoms such as oxygen, nitrogen, and sulfur, thus forming a complex mixture of molecules. Hence, the molecular association of polar components in the asphalt that forms molecular agglomerates at the nano scale level provides the polymeric property to asphalt.

2.4.1.2 Oxidation Effect on Fractions of Asphalt

Although a variety of fractionation schemes have been used to separate asphalts into generic fractions, perhaps the scheme most widely used in the past has been the procedure developed by Corbett [44]. In the order of their increasing molecular polarities are saturates, naphthene aromatics, polar aromatics, and asphaltenes, which were the four fractions produced by the Corbett separation scheme. A light straw-colored oil, primarily hydrocarbon in nature, with little aromaticity and a low heteroatom content, except for sulfur, is the saturate fraction. The saturate fraction is highly resistant to ambient air oxidation due to its low chemical reactivity. During the 18-year service period no measurable loss of saturates fraction due to oxidation was observed by Corbett and Merz [25]. Generally, the changes in the remaining three Corbett fractions on oxidation were observed from the more non-polar fractions to more polar fractions as oxygen-containing functional groups are formed in the asphalt molecules. The result is usually a net loss of naphthene aromatics, and possibly a net loss in polar aromatics, with a corresponding increase in the asphaltenes fraction as the various fractions have different reactivity toward oxidation.

Several investigators have studied the uptake of oxygen by the generic asphalt fractions and the formation of oxygen-containing functional groups formed by reaction with the oxygen so as to provide additional chemical insight. It was shown that saturates fraction was relatively inert to the reaction with oxygen as measured by oxygen uptake through the studies by King and Corbett [45] who used thin films at 150°C, and by Knotnerus [46], using dilute toluene solutions at ambient temperature. There was a slight reactivity shown by the naphthene aromatics [45], while the aromatics [46] fractions showed no reactivity. However, the Corbett polar aromatics fraction and the Knotnerus resins and asphaltenes fractions were highly reactive with oxygen. An immediate reactivity was shown by the Corbett’s asphaltenes fraction. As the two studies used different temperatures and oxidation conditions (film versus solution), different asphalts and different separation techniques, a comparison of the King and Corbett fractions with the Knotnerus fractions is relative. The increase in the reactivity with increasing fraction polarity is shown by the results of both of the studies. The ketone formation on oxidation of Corbett fractions (thin films, 130°C) derived from Wilmington (California) asphalt by

Petersen et al. [47] ranked the relative reactivity with atmospheric oxygen of saturates, naphthene aromatics, polar aromatics, and asphaltenes fractions as 1:7:32:40, respectively, was directly measured. With the viscosity being an important performance-related property, it has been shown [48] that the amount of ketones formed on oxidation is linearly related to the increase in log viscosity of the asphalt from the production of ketones in asphalt. The sensitivity of given asphalt to viscosity increase as a function of ketone formation, however, is highly asphalt source (composition) dependent.

To produce asphalt that is durable and resistant, a proper balance in the amounts of the different chemical components is a must. A reduction in compatibility and asphalt durability is shown by the asphaltenes that are not properly dispersed by the resinous components of the maltenes (the nonasphaltene fraction of asphalt and referred to by Corbett as petrolenes) [49, 50]. The asphaltenes function as thickeners; fluidity is imparted by the saturates and naphthene aromatics fractions which plasticize the polar aromatics and asphaltenes fractions; the polar aromatics fraction imparts ductility to the asphalts, and the saturates and naphthene aromatics in combination with the asphaltenes produce complex flow properties in the asphalt was based on the Corbett's [51] description of the effects on physical properties of the four generic fractions that were separated by his procedure. "Each fraction or combination of fractions perform separate functions with respect to physical properties, and it is logical to assume that the overall physical properties of one asphalt are thus dependent upon the combined effect of these fractions and the proportions in which they are present" was the conclusion given by Corbett.

Hence, the ratios of asphalt fractions might not be an accurate predictor of asphalt durability based only on the weight percent of the fractions as different sources of asphalt have significant differences in chemical composition.

2.4.1.3 Oxidation Reaction Mechanism

By various mechanisms of oxidation, the oxidation of asphalts that dominate at different stages of the oxidation reaction is apparently complicated. The ketones are formed at the first carbon of an alkyl chain attached to an aromatic ring, which is the benzylic carbon position, as observed by Dorrence et al. [52]. The most reactive ketone precursor is likely to be a tertiary benzylic carbon, i.e. one having two alkyl groups and one hydrogen atom attached to the carbon adjacent to aromatic ring. The hydrogen on the tertiary benzylic carbon is very reactive and is easily removed during oxidation. In four different asphalts tested by Mill and Tse [53], it was observed that out of the total benzylic hydrogen, 6-11 % is from the tertiary benzylic carbon, which was found using nuclear magnetic resonance spectroscopy. The carbon–hydrogen bond of unbranched aliphatic hydrocarbons is less reactive toward oxidation in comparison to the carbon–hydrogen methine bond by orders of magnitude. A highly stable dicarboxylic anhydride can result from the oxidation of these adjacent benzylic carbons followed by the condensation of intermediates that would otherwise form ketones [54] on certain aromatic molecules that have two adjacent benzylic carbon elements. Without prior formation of carboxylic acids, these anhydrides could be formed. In laboratory or pavement-aged asphalts, no measurable amounts of esters and only trace amounts of new carboxylic acids have been found [54]. Except for the anhydride formation reaction, it appeared that the hydrocarbon oxidation reaction almost always stops with ketone formation at pavement aging temperatures.

In Figure 9, the sulfur in asphalts (usually ranging from about 1% to 6%) is present primarily as sulfides [55, 56]. Alkyl substituted sulfur, generally accounts for about one-fourth to one-fifth of the sulfur present in the asphalt [55, 56] and is quite reactive toward oxidative aging to yield sulfoxides [55]. The formation of sulfoxides, the other dominant oxidation product, has been shown to result from the oxidation of organic sulfides that are functional elements of many asphalt molecules [55].

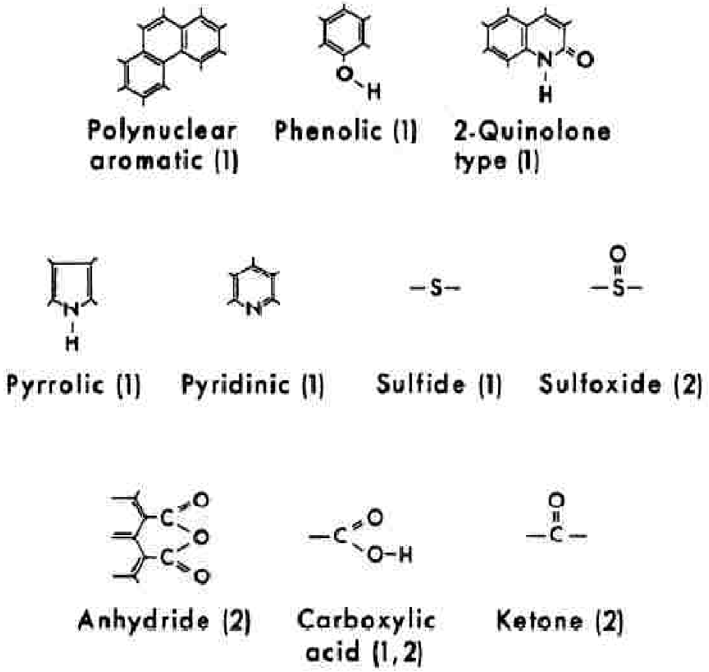

Figure 9: Chemical functionalities that are present in asphalt naturally (indicates 1) and formed during oxidation in asphalt (indicates 2) [16]

Nitrogen is present in several forms from the slightly acidic pyrrolic types to the more basic, strongly interacting pyridine type [57] which occurs in asphalts in concentrations ranging from about 0.2% to 1%. On the oxidative aging, the nitrogen types in asphalt are not known to be significantly altered. The alkyl, cycloalkyl or aromatic [55] may be attached to the sulfur atom as the organic elements. The cyclic sulfur molecules are quite unreactive during oxidative aging and exist primarily as thiophene homologs [56]. The presence of phenolics is noted [57]. Although present in relatively small amounts, the carboxylic acids and 2-quinolone type functionalities are highly polar and strongly associate [56]. There is evidence that ketones and sulfoxides are the major oxidation products formed during oxidative aging as observed in one experiment [58].

2.4.1.4 Oxidation Effect on Physical Properties of Asphalt

The different viscosity sensitivities of the different asphalts to the amount of ketones formed, undoubtedly related to the dispersibility of the asphaltenes and to the dispersive power of the asphalt maltenes fraction, have been observed [48]. The asphaltenes formed on oxidative aging have similar effects on rheological properties as the asphaltenes originally present in the asphalt was shown by Moon-Sun-Lin et al. [59]. With regard to molecular association or aggregation (microstructure) it is instructive to consider further the possible implications of the correlations presented [58]. Both ketones and asphaltenes are related linearly to each other if they are linearly related to log viscosity. The formation of additional asphaltenes is strongly implied by the ketones formed on aging. Hence, by the fact that the polar aromatics fraction shows the greatest mass gain on oxidation, it is likely that most of the ketones are formed on molecules from the Corbett polar aromatics fraction.

Chapter 3

Experimental Methods

3.1 Materials and Recovery

3.1.1 Highway 17 Trial Sections near Petawawa, Ontario

The Highway 17 trial, near Petawawa, Ontario, was constructed in 1996 on both lanes starting some 5.4 km west of the Petawawa River. The 65 mm thick binder course for this trial was constructed in late 1996 whereas a surface course of equal thickness was placed in June 1997.

The Petawawa trial was designed to include one binder with known insufficient low-temperature performance for the location (the PG 58-28). A further two binders were selected with a grade right at the 98% confidence limit for that location of which one was polymer-modified and the other was not (PG 58-34P and PG 58-34NP). Finally, one additional section with an even lower limiting BBR temperature (PG 58-40P) was chosen. Although not apparent, the PG 58-40P had a higher polymer content than the PG 58-34P. Both binders were modified with SB diblock copolymer/sulfur system. Pertinent properties for these materials are listed in Table 1.

Table 1. SHRP Properties for Highway 17 Binders [20, 31]

Hwy 17 Sections	Binder	Modification Type	T, °C	S, MPa (60 s, 300 max)	m-value (60 s, 0.3 min)
2	PG 58-40	SB Copolymer	-30	208	0.333
3	PG 58-34P	SB Copolymer	-24	266	0.307
60	PG 58-28	Unmodified	-18	260	0.316
61	PG 58-34NP	Unmodified	-24	225	0.304

3.1.2 Highway 655 Trial Sections

In Table 2, the details of asphalt cement for the Highway 655 pavement trial are given below, where the Ox stands for oxidized asphalt, PPA stands for polyphosphoric acid and SB stands for styrene-butadiene block copolymer. Also the ^{31}P stands for an additive containing phosphorous (likely PPA and/or zinc dialkyldithiophosphate, which is commonly found in waste engine oils) while RET stands for reactive ethylene terpolymer. The phase lag between stress and strain in a dynamic rheological test is denoted as δ where the complex modulus is denoted as G*.

Table 2. Highway 655 trial section details [19, 34]

Section	Modification Requested	Base AC	Additional Additives Detected	PGAC Grade, ºC
1	RET+PPA	Lloydminister	-	65-36
2	Ox	unknown	SB	65-36
3	SB	unknown	Zn	65-36
4	SB	unknown	Zn + ^{31}P	67-35
5	SB	Western Canadian	-	66-35
6	Ox	unknown	Zn + ^{31}P	59-35
7	-	unknown	Zn + ^{31}P	54-35

3.1.2 Recovery of Asphalt Cements

The separation of the surface layers of the asphalt core samples from the bottom layers was carried out using a diamond-tipped cutting saw. The soaking of each surface layer, weighing about 4 kg, in 4-6 L of tetrahydrofuran (THF) was carried out. A periodic removal of the extract and its storage in a separate container, for particles to settle down at the bottom, was performed. The asphalt cement was washed until the solution was relatively clean compared to the beginning. Using a rotary evaporator, most of the solvent was removed by a condensation method at relatively low temperatures of around 50°C. To ensure complete removal of solvent from the binder, it was then heated at a temperature of 150°C and a vacuum pressure of about 40 mm Hg for an additional one hour. By this method about 180 g of asphalt binder was collected from a total of around 4-6 L of THF. For all of the asphalt binders for all trial sections this was the standard method of recovery that was used.

3.2 Physical Testing

3.2.1 Regular BBR Testing According to AASHTO Method M320

In order to be fluid enough to easily pour, the sample was heated in the oven for approximately 30-45 min at 160°C (sometime modified asphalt takes more time compared to unmodified). After heating, the sample was stirred vigorously to make sure the sample is uniformly liquefied and then poured into aluminum molds greased with Vaseline^{TM} while Teflon strips were placed against the greased face of aluminum mold. After pouring, the sample was cooled for a total of 1 hour. A schematic of the aluminum mold of the asphalt beam is shown in Figure 10. The excess asphalt was trimmed from the top of each mold using a hot spatula after a one hour conditioning time. In a controlled temperature fluid bath, the beam specimen is supported at two points 102 mm apart. Then the loading of the beam at the midpoint, with a load of approximately 1000 mN, for a period of 240 s is carried out.

Figure 10. Aluminum BBR molds [26].

At a loading time of 60 second the beam stiffness usually known as “creep stiffness” (S (t)) and the slope of creep stiffness master curve (m (t)) were calculated. The creep stiffness should not go over 300 MPa at 60 second loading and the m-value less than 0.3 at 60 second loading time, according to the AASHTO M320 specifications. The testing of all of the samples was carried out in duplicate which provided excellent reproducibility. The approximate error in all BBR and extended BBR data is ± 1ºC as determined through round robin tests conducted by the Ontario Ministry of Transportation. A schematic of the bending beam rheometer is shown in Figure 11.

Figure 11: Bending Beam Rheometer Equipment [26].

3.2.2 Extended BBR Testing According to MTO Method LS-308

A total of 12 BBR beams were poured at approximately 150°C for the recovered asphalt. The conditioning of the beams for one hour at room temperature followed by one, 24 and 72 hours at T_{design} + 10 and T_{design} + 20 was done (six beams for each conditioning temperature [37], where T_{design} is the pavement design low temperature for the contract location according to the Long Term Pavement Performance binder selection software). After each conditioning period the beams were tested at two different temperatures. According to regular AASHTO M320 criteria (S (60) = 300 MPa or m (60) = 0.3), the test temperatures were chosen so as to determine a pass and fail temperature. The maximum (worst) grade loss is calculated from the limiting temperatures that were recorded in a table. After three days of conditioning the worst grade is recorded together with the worst grade loss. The determination of the worst grade temperature at -10°C from the warmest limiting temperature where either S (60) = 300 MPa or m (60) = 0.3 was done. The shift of 10°C accounted for the application of the time-temperature superposition principle.

3.2.3 Elastic Recovery Testing

A simple extension of the regular BBR test is the elastic recovery test. Before pouring the recovered samples into BBR molds they are heated for an hour in hot air oven at 150°C. An hour of conditioning at room temperature is carried out for the specimens after that they are placed in three different refrigerators. For this purpose nine specimens are poured. For conditioning, three specimens are placed with appropriate time gaps at each of -30°C, -20°C, and -10°C respectively in refrigerators. Three hours of conditioning is done after which the testing is carried out by placing the samples one by one in the BBR instrument. A similar temperature is maintained for the test as that of the conditioning temperature. Prior to pouring of the sample the BBR is set to -30°C. The specimen is conditioned for at least five minutes prior to testing after calibration. The actual load is applied after a preload is given for 10 seconds for seating of the sample. For a period of 240 s the bending load of about 980 mN is applied after which a load of around 25 mN during a 720 s recovery period is carried out. The measurement of the recovery of the sample in terms of the displacement curve is done. The binder sample recovers due to the elastic components (recoverable and delayed elastic) while the non-recoverable part reflects the viscous part of the displacement at 240 s. The 720 s unloading period was selected to make sure that the displacement no longer changes after this period, i.e. all of the delayed elasticity has recovered. In Figure 12, a typical example of a displacement versus time graph is shown.

For further processing the entire data of force and displacement is exported to an Excel file. The S and m-value at 60 seconds were also noted and used for the purpose of repeatability and reproducibility testing of the previous BBR tests. The specimens were placed back at -30°C after testing. To test the next set of three samples the BBR machine is set to -20°C. The tests were repeated with the same procedure after completing calibration at particular temperature and the changing of temperature takes about 20 minutes. The testing of the samples stored at -10°C was done in an identical way. After testing, the samples are placed back into the respective fridges. The test was repeated on all of those samples after three day conditioning and the recoveries were observed.

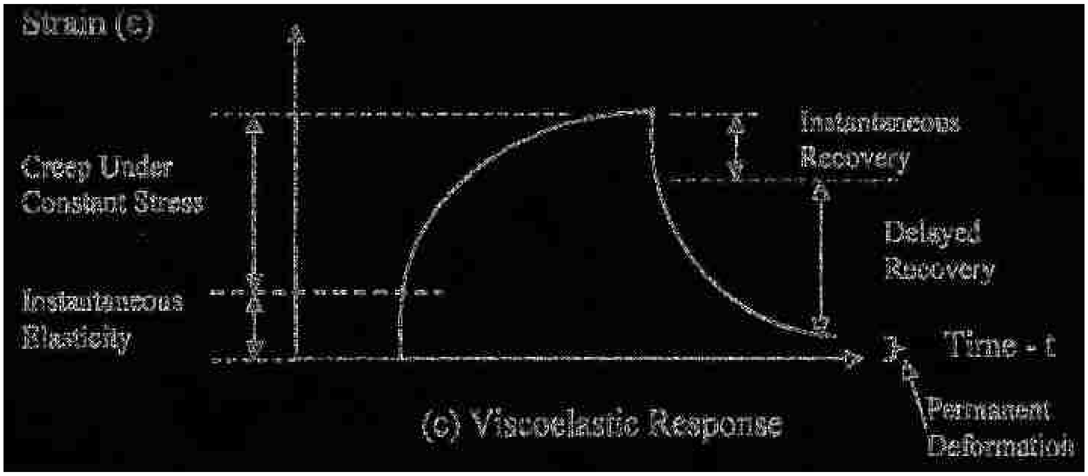

Figure 12. Sample graph of elastic recovery test data [60].

3.2.4 Ductile Failure Testing According to MTO Method LS-299

The asphalt binders were heated for about one hour in oven at 160°C to ensure that the samples (asphalt binders) readily flow when dispensed from the container and then poured into prepared DENT molds.

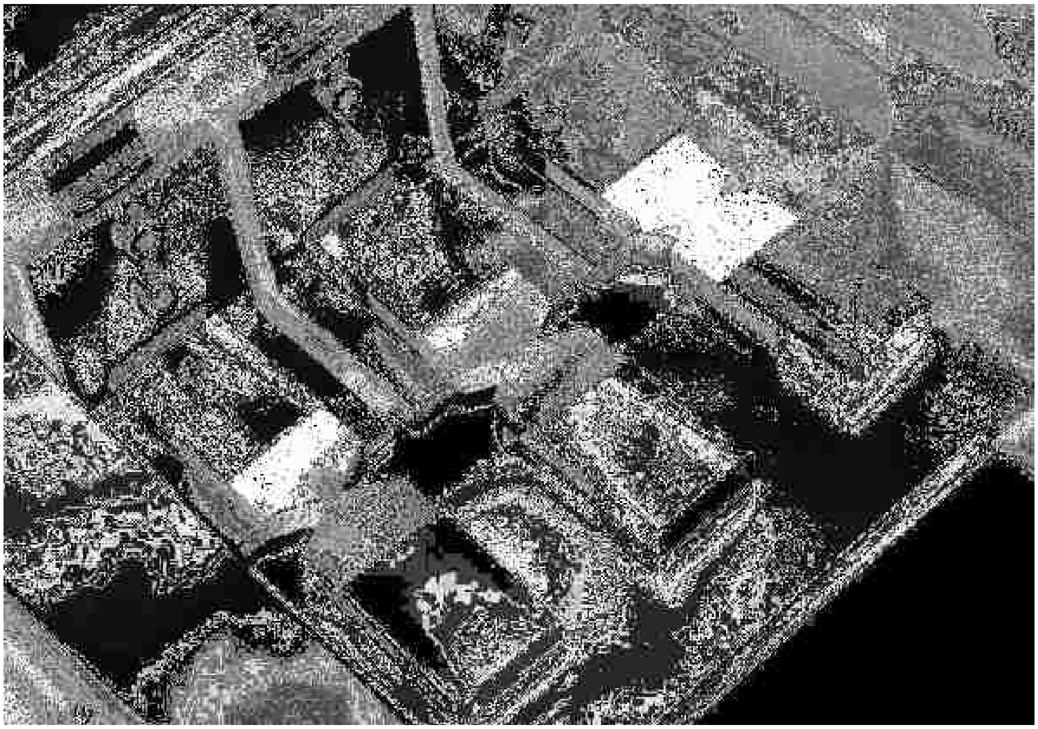

Figure 13. Double Edge Notched Tension (DENT) test set up [19].

Each mold includes three different notch depths (ligaments between notch tips include 5, 10 and 15 mm). The samples were conditioned at ambient temperature for 1 hour before they were loaded into the tensile machine. Subsequently, the samples were conditioned 24 hours at 15°C prior to testing in the bath of the tensile machine. In this study, samples were tested at a speed of 50 mm/min. Figure 13 shows a photograph of DENT test set-up.

3.2.5 Dynamic Shear Rheometer

A small sample of asphalt binder is sandwiched between two plates. Depending upon the type of asphalt binder being tested the test temperature, specimen size and plate diameter varies. Using a specimen 0.04 inches (1 mm) thick and 1 inch (25 mm) in diameter, the unaged asphalt binder and RTFO residue are tested at the high temperature specification for a given performance grade (PG) binder. The PAV residue is tested at lower temperatures; however these temperatures are significantly above the low temperature specification for a given PG binder. The measurement of a small phase angle (δ) is a result of these lower temperatures that make the specimen quite stiff. Hence, to have a measurable phase angle (δ) to be determined, a thicker sample (0.08 inches (2 mm)) with a smaller diameter (0.315 inches (8 mm)) is used. The major DSR apparatus is as shown in Figure 14.

Figure 14. Dynamic Shear Rheometer [61].

For a sample 0.04 inches (1 mm) thick and 1 inch (25 mm) in diameter, test temperatures greater than 115°F (46°C) are used whereas for a sample 0.08 inches (2 mm) thick and 0.315 inches (8 mm) in diameter, test temperatures between 39°F and 104°F (4°C and 40°C) are used (Figure 15).

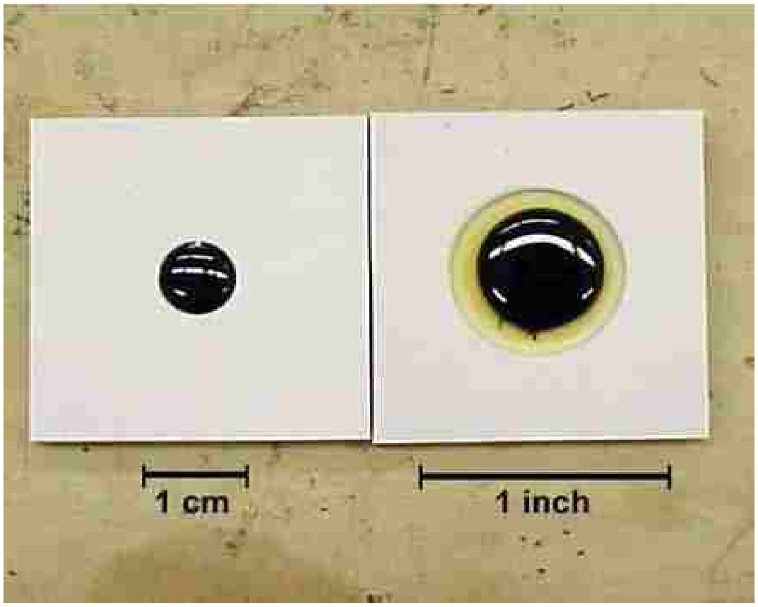

Figure 15. Two different 8 mm and 25 mm diameter sample molds left to right, respectively [26].

The test specimen is kept at near constant temperature by heating and cooling a surrounding environmental chamber. The instrument measures the maximum applied stress, the resulting maximum strain, and the time lag between them while the top plate oscillates at 10 rad/sec (1.59 Hz) in a sinusoidal waveform. The calculation of the complex modulus (G*) and phase angle (δ) is done automatically with the help of the software. Using the test software much of the procedure is automated.

Basic Procedure

At first the asphalt binder is heated until it is sufficiently fluid to pour the test specimens. Then the testing temperature is selected according to the asphalt binder grade or testing schedule. The DSR is set to a particular temperature; this preheats the upper and lower plates, which allows the specimen to adhere to them. The asphalt binder sample is now placed between the test plates. After that, using software, the test plates are moved together until the gap between them equals the test gap plus 0.002 inches (0.05 mm). Due to the compression, excess material will come out which is then trimmed around the edge of the test plates using a heated trimming tool. The test plates moved together to the desired testing gap. This creates a slight bulge in the asphalt binder specimen's perimeter. The specimen is then brought to the test temperature. The test is started up only after the specimen has been at the desired temperature for at least 10 minutes.

Based on the material being tested (e.g., unaged binder, RTFO residue or PAV residue) the determination of a target torque at which to rotate the upper plate is carried out using the DSR software. To ensure that the measurements are within the specimen's region of linear behavior this torque is chosen. The specimen for 10 cycles at a frequency of 10 rad/sec (1.59 Hz) is conditioned using the DSR. The software reduces the data to produce a value for the complex modulus (G*) and the phase angle (δ) once the DSR takes test measurements over the next 10 cycles.

The range of the phase angle (δ), from about 50 to 90°, and while that of the complex modulus (G*), from about 0.07 to 0.87 psi (500 to 6000 Pa), are the typical values obtained from the DSR for asphalt binders. The complete viscous behavior is essentially the δ of 90°. The polymer-modified asphalt binders usually exhibit a higher G* and a lower δ value. Hence, it is meant that compared to the unmodified asphalt cements they turned out to be more elastic and a bit stiffer.

3.3 Chemical Testing

3.3.1 Thin Film Aging at Different Temperature

Aging of asphalt is considered a valuable process which impacts the performance during the service life and therefore the RTFO and PAV methods are implemented for testing before the construction of the road. To understand the chemical changes during the aging process, the thin film aging method was used at different temperatures. There are three different temperatures selected, i.e. 45°C, 65°C and 85°C, to compare the changes in the reaction at different temperature. According to Petersen's presentation [62], this 20 degree temperature drop will lead to a reduction in the reaction speed by ¼ of the speed at 85 degrees. Infrared spectroscopy has been used for the analysis of the chemical changes during aging.

Small containers are used to prepare the thin film with a thickness of 700 microns (which is likely to be best) for aging material in oven; as such films are easy to produce. The asphalt is placed according to containers' diameter that disperses relatively evenly over the base of each can. Since some of the modified asphalt consists of the viscosity that is fairly high at low temperatures, it should soften up by using THF to spread them out. To completely evaporate THF from the samples, they were heated in a vacuum oven at 70-80 degrees for about 15 minutes prior to their placement in the aging oven.

There were at least two containers for each of the test sections being prepared. In the oven, the samples are arranged in rows and they are rotated 180 degrees each time when taken out of the oven for analysis. Two spectra are taken when the samples are analyzed and the results so obtained are averaged out. The samples have been analyzed after 48 hours, 1 week, 2 weeks, 3 weeks, 4 weeks, 8 weeks, 12 weeks and up to 5000 hours using infrared spectroscopy.

3.3.2 Infrared Spectroscopy

Infrared spectroscopy has been used to understand the chemistry of asphalt. For our experiment a Bomem IR instrument was used with 32 scans, over the range of 4000 – 400 cm^{-1}. Data analysis was done using the GRAMS32 software. To analyze the data, integration is done which calculates the area under the curve that covers valley to valley for a particular peak. Integration from 1400 to 1330 cm^{-1} is used for the CH_3 peak (the CH_3 integral was used as an standard since it is relatively inert to oxidative changes). The peaks for carbonyl, aromatics, and sulfoxide are located at 1700 cm^{-1}, 1600 cm^{-1} and 1030 cm^{-1} [58], respectively, hence the integral bounds used are 1760 to 1655 cm^{-1}, 1650 to 1535 cm^{-1} and 1070 to 985 cm^{-1}. The edges of these bands are not always equal, so the integral boundaries sometimes need to be adjusted according to the valley.

To understand chemical changes in asphalt during the aging process, three indices have been followed, which are:

(1) The carbonyl index is defined as the Carbonyl Integral/CH_3 integral.

(2) The aromatics index is defined as the Aromatics Integral/CH_3 integral.

(3) The sulfoxide index is defined as the Sulfoxide Integral/CH_3 integral.

Styrene at 968 cm^{-1} and butadiene at 700 cm^{-1} index are also followed for the sections that are modified with SBS polymer. These are determined as follows; Butadiene is the valley to valley integral from 983 to 955 cm^{-1}, and the index is the Butadiene Integral/CH_3 Integral. Styrene is the valley to valley integral from 710 to 690 cm^{-1}, and the index is the styrene integral/CH_3 integral.

3.3.3 Fraction Separation

Separation of oils and asphaltenes has been carried out using the ASTM D4124 – 09 [8] method in which n-heptane is used to separate the asphaltenes.

Chapter 4

Results and Discussions

4.1 Distress Surveys

4.1.1 Highway 17 Trial Sections near Petawawa, Ontario

The pavement trial on Highway 17 near Petawawa was constructed in 1996 as part of the Long Term Pavement Performance Program (LTPP program), which followed the Strategic Highway Research Program (SHRP) that developed the Superpave® specifications. The Superpave® specifications were to be validated with the data to come out of the LTPP sites. However, the reality has been that many LTPP sites were abandoned after their construction, likely due to a lack of interest and funding.

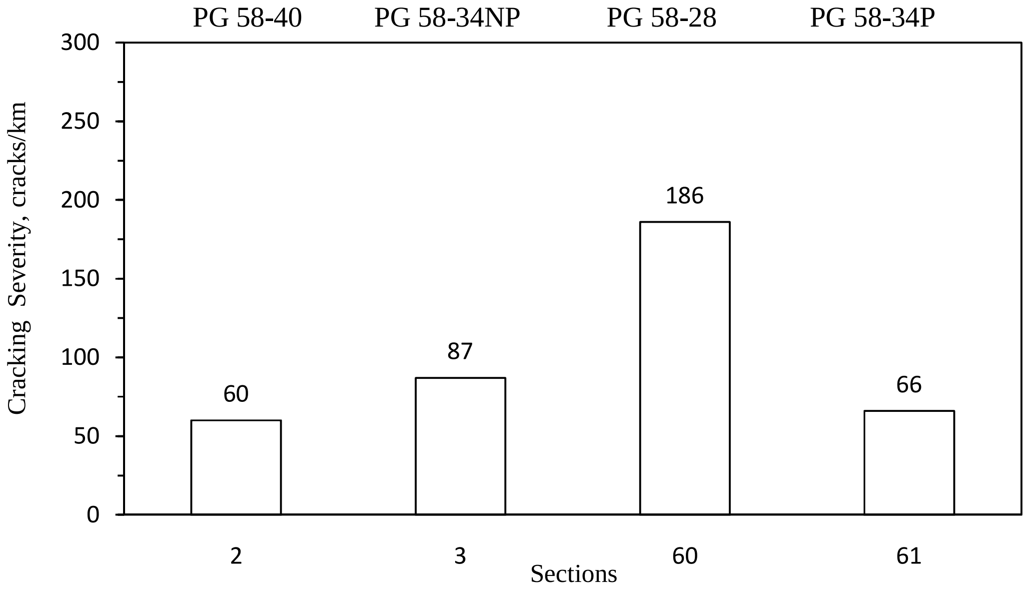

Figure 16. Distress survey for Highway 17 trial sections in 2007 [63].

Figure 16 above shows the cracking distress for the four Superpave® sections on Highway 17. In early 2003, when surface temperature had only reached -27°C, none of the sections should have cracked according to their regular AASHTO M320 grades. However, the distress survey of 2007 shows that there was significant thermal cracking distress in all four sections. The fact that these sections have all cracked at temperatures much warmer than their low temperature grades can likely be attributed to unanticipated physical and chemical hardening processes and poor ductile failure properties. The results for these investigations will be discussed later.

4.1.2 Highway 655 Trial Sections near Timmins, Ontario

The northeastern Highway 655 trial sections were surveyed for cracking distress in 2008 [18]. The results of this survey are presented in Figure 17 below. The bars in the graph represent the total cracking distress in three 50 m stretches surveyed for each 500 m long test section.

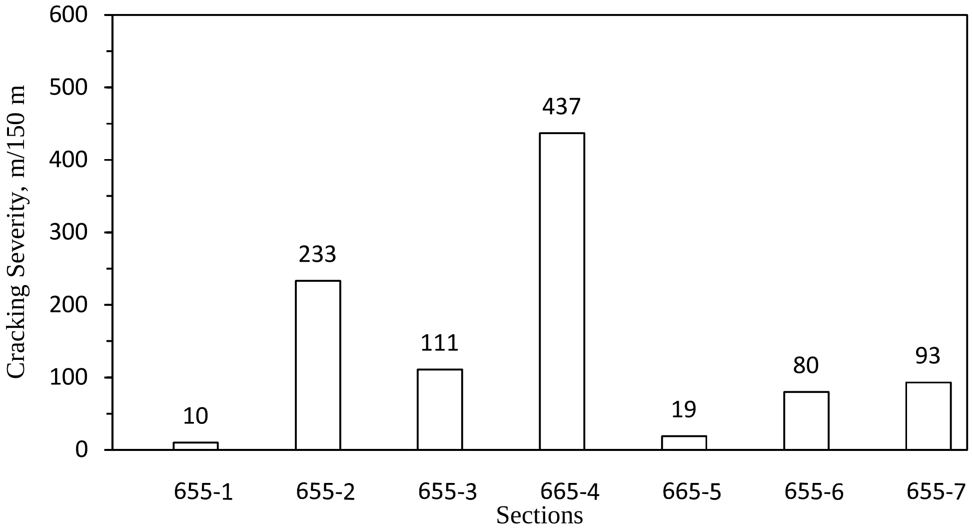

Figure 17. Distress survey for Highway 655 trial sections [18].

The lowest air temperature reached in early 2004 was -48°C with a corresponding pavement surface temperature of -34°C on two occasions. Hence, once more, the fact that five of the seven Highway 655 test sections have cracked by significant amounts indicates that there is an urgent need for improved low temperature specifications that do a better job at correctly ranking the performance. This trial has also shown that it is possible to produce and purchase asphalt cements that do not suffer from premature failure since both the state of Sections 655-1 and 655-5 are satisfactory for a five year old pavement. (Note: The most recent 2010 survey has shown almost no cracking in 655-1 and the start of more significant cracking in 655-5.)

4.2 Physical Testing

4.2.1 Regular Bending Beam Rheometer Testing

Regular bending beam rheometer (BBR) testing was done for Highway 17 and 655 trial section materials. Pressure aging vessel (PAV) materials were compared with materials recovered from the field core samples. The regular BBR method was used to test specimens in three point bending to determine the creep stiffness (S(t)) and slope of the creep stiffness master curve (m(t)-value). This was typically done at pass and fail temperatures according to the criteria set out in the AASHTO M320 standard. The pass and fail data were then used to determine limiting stiffness and limiting m-value temperatures where S(60 s) = 300 MPa, and m(60 s) = 0.3, respectively.

4.2.1.1 PAV Residues

The findings for the Highway 17 trial near Petawawa are provided in Figures 18-20, below.

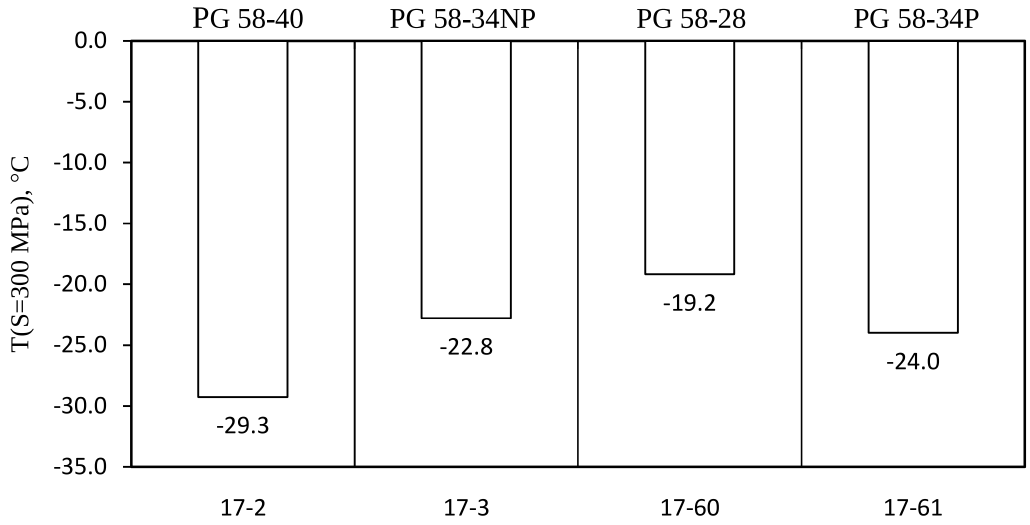

Figure 18. Highway 17 laboratory-aged (PAV) sample grade temperature at which stiffness S(t) = 300 MPa. Note: Approximate errors are ± 1ºC for these and all following BBR grades.

The criteria for the AASHTO M320 method is that creep stiffness should be below 300 MPa. For the Highway 17 trial sections, the temperatures at which the creep stiffness reaches 300 MPa is given in Figure 18. It is observable that the grade of the materials are changed by almost 10°C for all of the trial sections ranging from approximately -19°C (PG-28) to -29°C (PG-40). The commercial PG grade (which reflects the rounded PG grade under which the materials are sold rather than the continuous PG grades) of all sections are given on the top of the graphs for better comparison. In this 'P' indicates polymer modifier while ‘NP’ indicates material without any polymer modifier, but with the same grade.

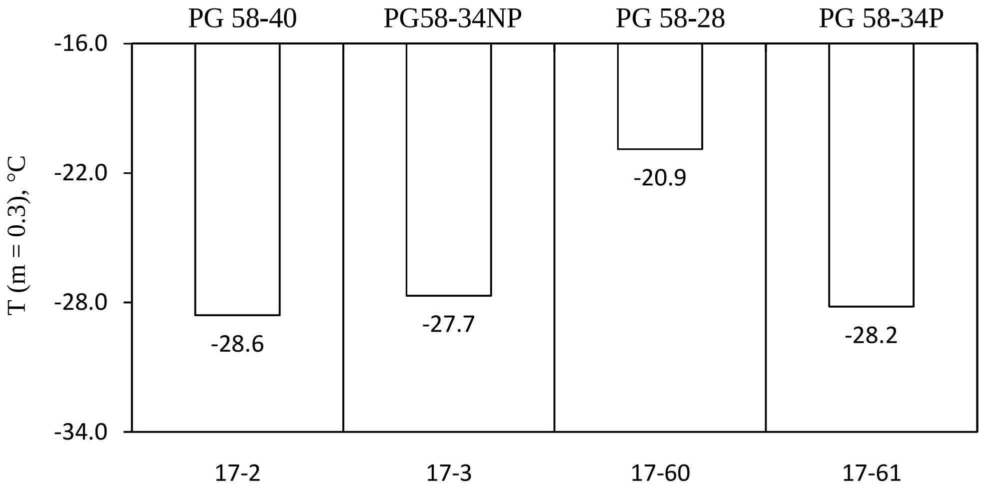

Figure 19. Highway 17 laboratory aged (PAV) sample grade temperature at which slope m-value = 0.3 [31].

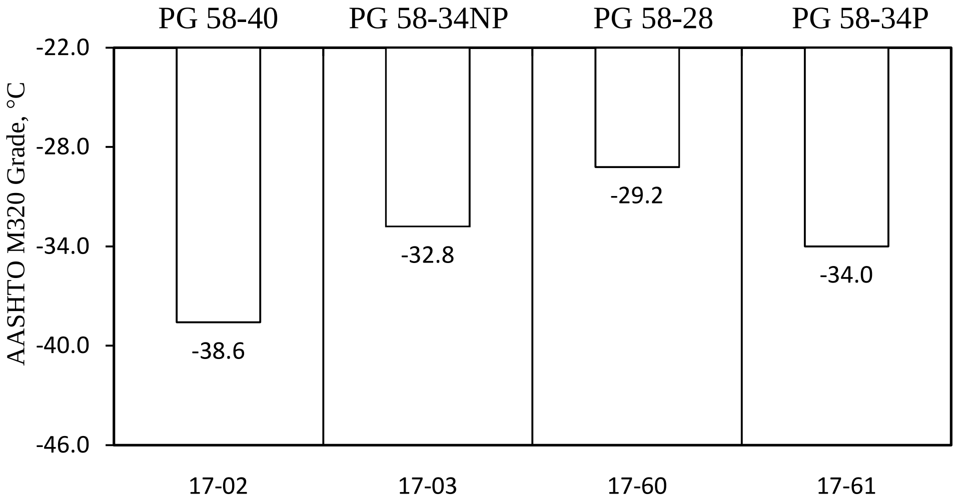

Figure 20. Regular AASHTO M320 specification grades for laboratory-aged (PAV) Highway 17 asphalt cements.

Figure 20 shows the AASHTO M320 grade for the trial sections on Highway 17. In this Section 17-61 has polymer modifier while Section 17-03 is unmodified with the same grade.

The findings for the Highway 655 trial sections are provided in Figures 21-23, below.

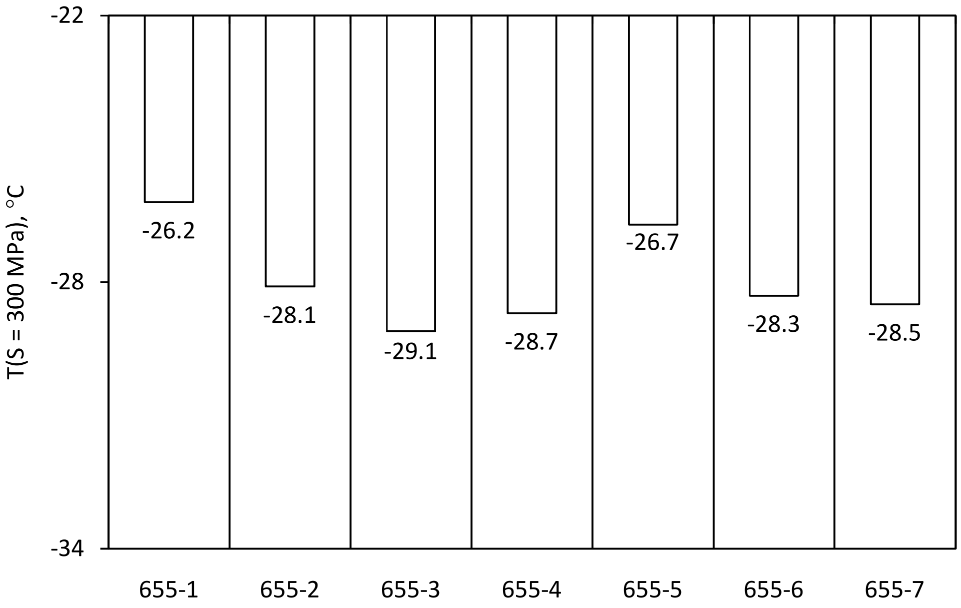

Figure 21. Highway 655 laboratory aged (PAV) sample grade temperature at which stiffness S(t) = 300 MPa [31].

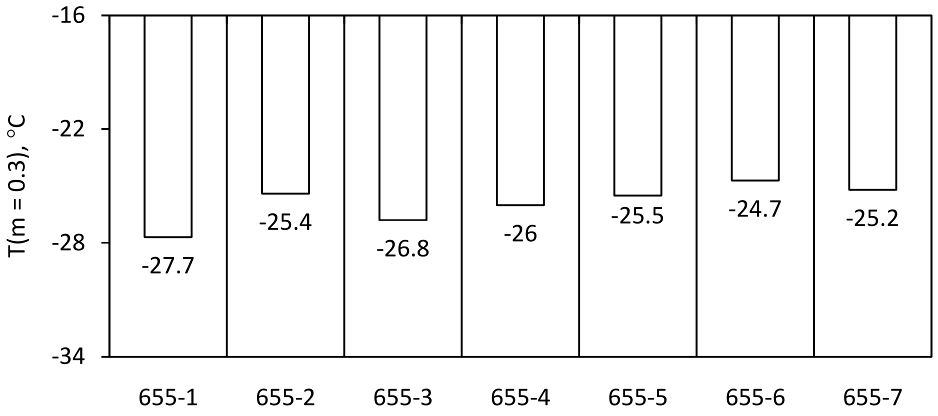

Figure 22. Highway 655 laboratory aged (PAV) sample grade temperature at which m-value = 0.3 [31].

It is obvious from Figure 23 that all materials in this trial had nearly identical low temperature grades. Hence, in light of the serious variation in early cracking for these test sections (see Figure 17 above) there is a need for better performance grading tests.

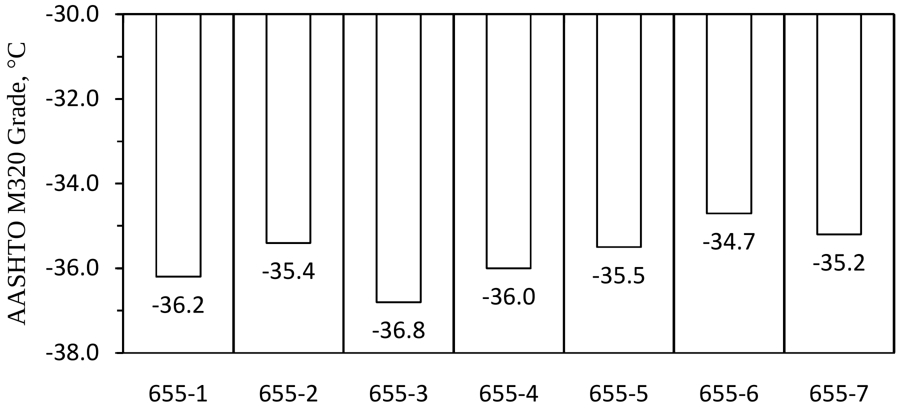

Figure 23. Regular AASHTO M320 specification grades for laboratory-aged (PAV) Highway 655 asphalt cements.

4.2.1.2 Recovered Materials

Similar to the regular BBR tests on PAV residues, the limiting temperatures were determined for the recovered asphalt cements from Highway 17 and Highway 655 materials. Recovered materials of Highway 655 sections are mentioned in alphabets which correlates with the numbers e.g. section 655-1 is the same as 655-A. The findings for this investigation are provided in Figures 24-26 (Highway 17) and Figures 27-29 (Highway 655).

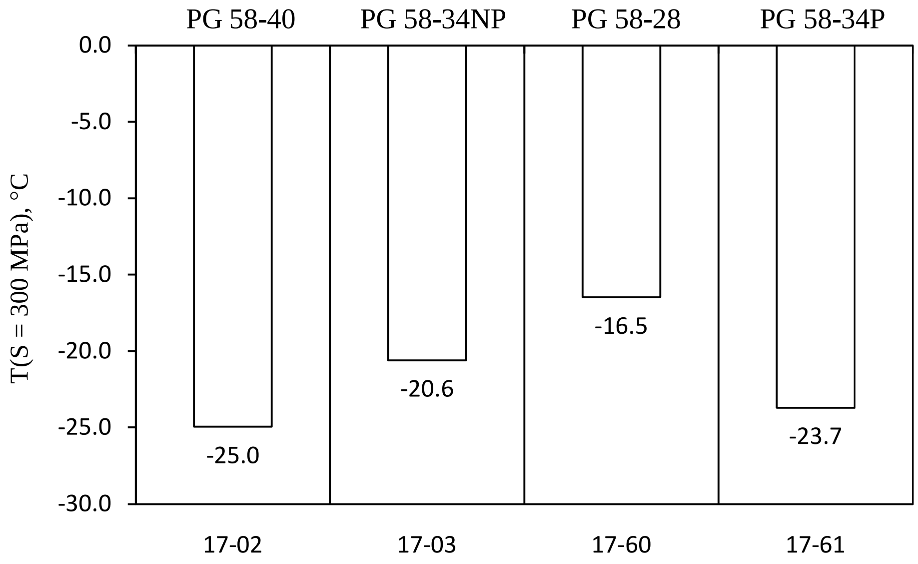

Figure 24. Highway 17 recovered sample grade temperature at which stiffness S(t) = 300 MPa.

The limiting stiffness temperature for the four Highway 17 test sections range from approximately -16°C (PG-28 section) to -25°C (PG-40 section). This already shows clearly that there is a problem for the PAV aging protocol since it should have produced samples that are aged approximately similar to the material which has been in service for

10 years. Sections 17-02 and 17-03 already have limiting stiffness grades (i.e., T(S = 300 MPa)-10) of -35°C and -30.6°C, which is considerable warmer than the -40°C and -34°C predicted by their PAV residues (see Figure 20 above).

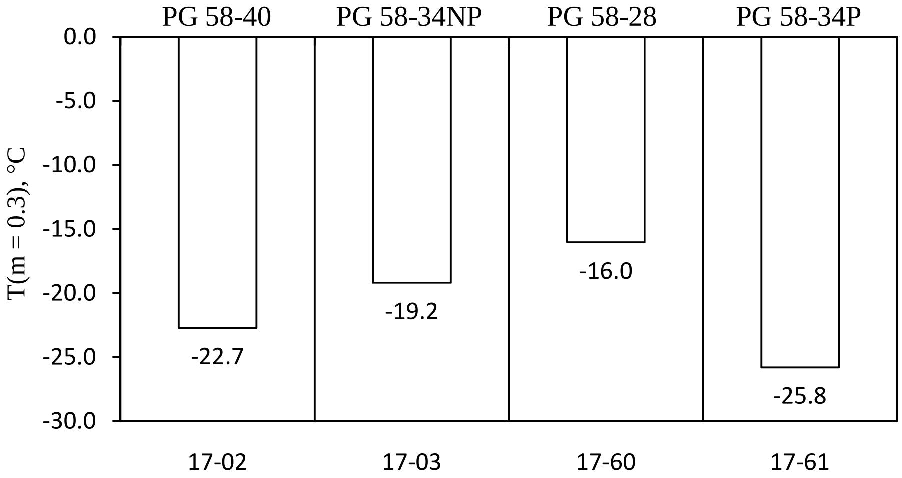

Figure 25. Highway 17 recovered sample grade temperature at which slope m-value = 0.3.

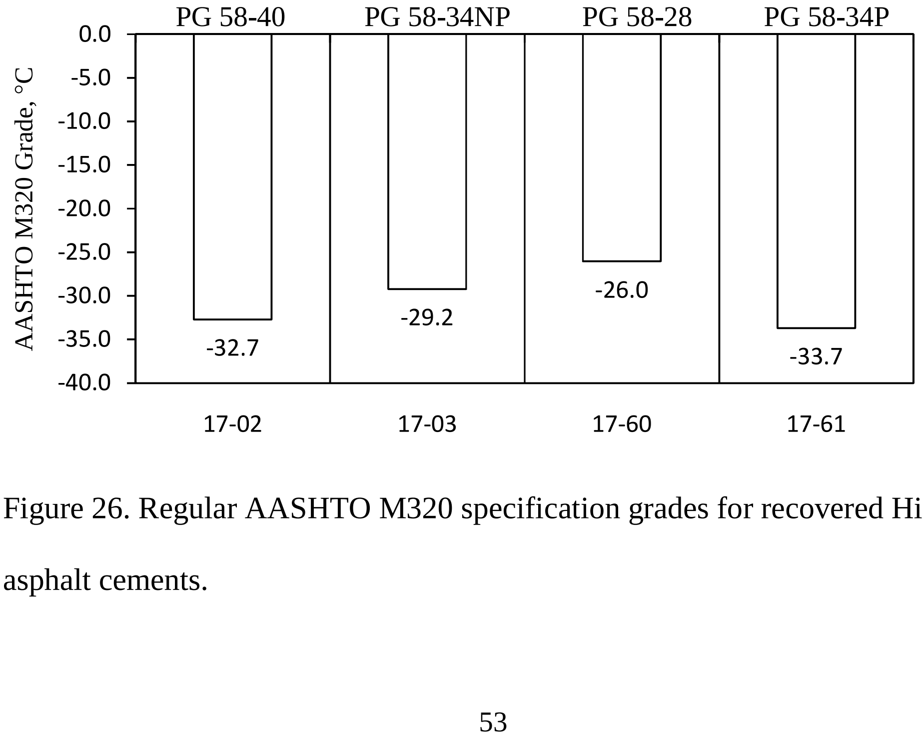

Figure 26. Regular AASHTO M320 specification grades for recovered Highway 17 asphalt cements.

The limiting m-value temperatures as provided in Figure 25 and the limiting grade temperatures as provided in Figure 26 give a similar conclusion compared to the data from Figure 24. Section 17-02 has aged chemically by 7.3°C more than what the PAV predicted (-32.7°C versus -40°C), hence there is a need for improved chemical aging methods that do a better job than the current RTFO/PAV protocol.

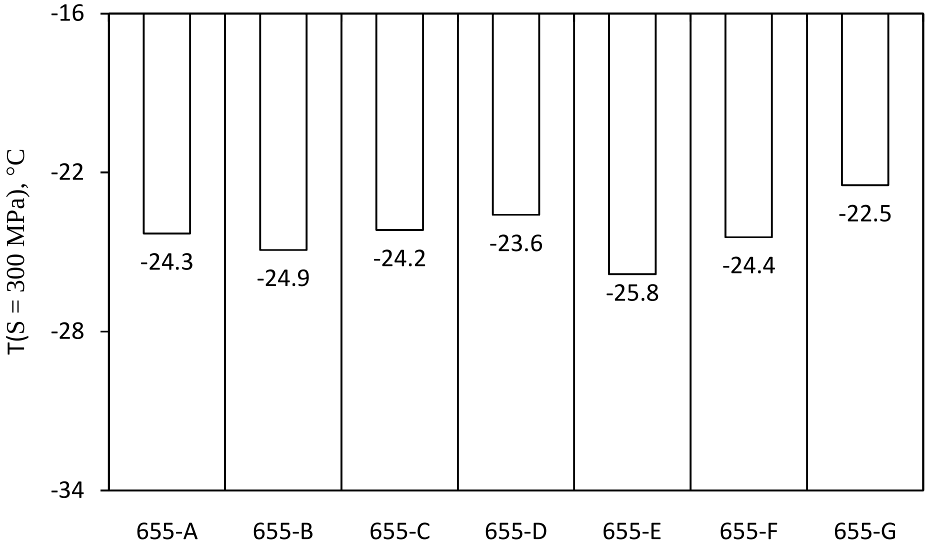

Figure 27. Highway 655 recovered sample grade temperature at which stiffness S(t) = 300 MPa. (Note: Letters represent the respective section numbers but indicate that the material was recovered from field core samples.)

Figures 27 to 29 provide the grades obtained from the regular BBR method for the recovered material of Highway 655 trial sections. Figure 27 shows little variation in the limiting stiffness temperatures so this is likely not a very good specification property given the fact that Section 655-4 has performed very poorly and Sections 655-1 and 655-5 are in relatively good condition (see Figure 17 above).

In contrast, the limiting m-value temperatures for the recovered materials are given in Figure 28 and these results show a reasonable correlation with the field performance (Figure 17). Sections 655-1 and 655-5 have survived largely free of distress and this can be attributed to their good retained limiting m-value temperatures. Section 655-4 has performed worst and this can be attributed to its gel-type and hence warm limiting m-value temperature of -16.7°C. This material is unable to relax shrinkage stresses during winter and is therefore suffering seriously from thermal cracking.

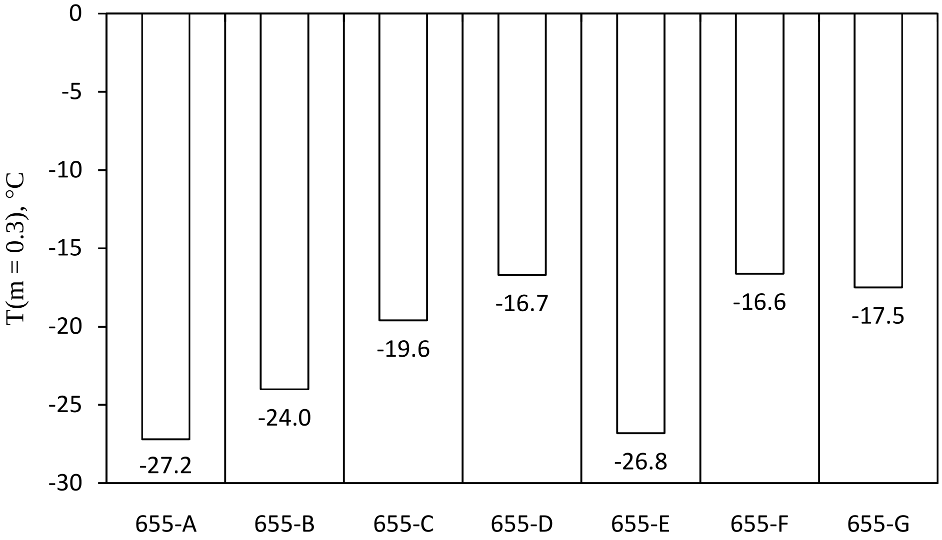

Figure 28. Highway 655 recovered sample grade temperature at which m-value = 0.3.

The AASHTO M320 grades for the recovered materials are shown in Figure 29 where the observable part is Section 655-4 which has a deficit of 10°C compare to PG grade determined on RTFO/PAV residue (Figure 23 above). The actual recovered grade is around -26°C whereas the PAV grade is at -36°C hence there is a problem with the

PAV aging method of around 10°C, which is enormous. Also, Section 655-1 and 655-5 show almost no change in grade.

The results for Section 655-B (i.e., section 655-2 recovered material) shows that even the recovered material does not do a perfect job at predicting which material will do well and which material will do poorly. The section has cracked severely but the grade of -34°C still passes considering this lowest temperature was reached in early 2004. Hence, from this we can conclude that there is more to the problem than just having to develop an improved chemical aging method. The fact that the regular BBR method only conditions sample for a single hour prior to testing causes additional problems with performance specification grading. For this reason the extended BBR method has been developed according to which samples are conditioned for 1 h, 24 h, and 72 h, at two different temperatures above the pavement design temperature, which reflect typical low temperatures at which the road is exposed during most of winter. The extended BBR test results will be discussed next.

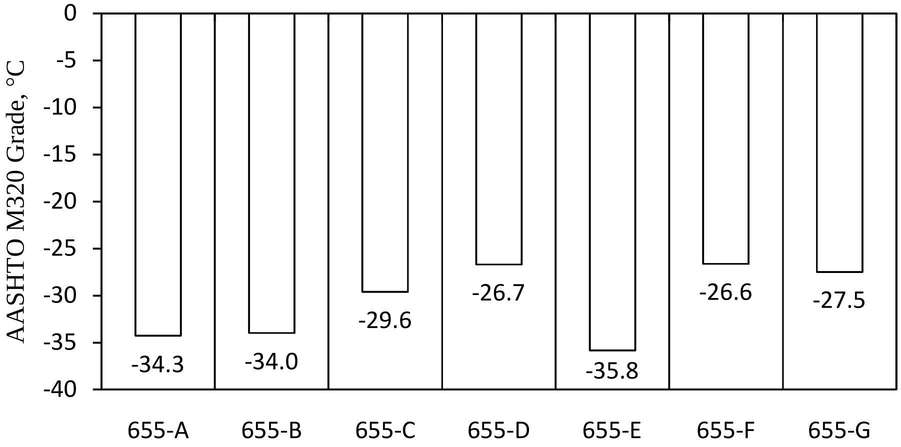

Figure 29. Regular AASHTO M320 specification grades for recovered Highway 655 asphalt cements.

4.2.2 Extended Bending Beam Rheometer Testing

The extended BBR results for both the Highway 17 (PAV and recovered) and Highway 655 (PAV and recovered) materials are given in Tables 3-6.

Table 3. Highway 17 PAV Materials eBBR Results [20]

Sections	Conditioning Temperature, °C	T_S, °C		T_m, °C		T_{Grade}, °C	
		1h	72h	1h	72h	1h	72h
17-2	-30	-30.7	-27.2	-31.4	-28.6	-40.7	-37.2
17-3	-24	-26.4	-24.0	-25.0	-19.2	-35.0	-29.2
17-60	-18	-20.8	-17.5	-20.9	-8.1	-30.8	-18.1
17-61	-24	-25.6	-21.8	-24.6	-18.5	-34.6	-28.5

Table 3 contains data for Highway 17 for extended BBR of laboratory aged material (PAV). It is observed that after conditioning for 72 h, it has a huge variation of 12°C in Section 17-60, which has performed poorest of all, and variations of 6°C in Sections 17-03 and 17-61 that have both cracked prematurely. This is due to the physical aging process after long conditioning that indicates an urgent need for modifications in the laboratory aging RTFO/PAV protocol.

Table 4. Highway 17 Recovered Materials eBBR Results [31]

	Hours	**17-2**	**17-3**	**17-60**	**17-61**
Ts @ -12 °C	1	-26.5	-21.1	-16.6	-24.2
	24	-25.8	-19.8	-15.4	-23.6
	72	-25.6	-19.6	-15.1	-24.3
Ts @ -24 °C	1	-24.8	-20.9	-17.1	-23.7
	24	-23.0	-18.8	-15.1	-22.0
	72	-22.6	-18.0	-14.3	-21.4
Tm @ -12 °C	1	-24.0	-18.9	-16.3	-24.3
	24	-21.3	-13.3	-10.8	-23.0
	72	-19.8	-12.1	-10.8	-21.9
Tm @ -24 °C	1	-23.2	-20.5	-18.1	-25.3
	24	-20.6	-16.9	-14.9	-21.4
	72	-19.9	-15.3	-14.0	-20.6
Grade @ -12 °C	1	-34.0	-28.9	-26.3	-34.2
	24	-31.3	-23.3	-20.8	-33.0
	72	-29.8	-22.1	-20.8	-31.9
Grade @ -24 °C	1	-33.2	-30.5	-27.1	-33.7
	24	-30.6	-26.9	-24.9	-31.4
	72	-29.9	-25.3	-24.0	-30.6

Note: Temperatures indicate conditioning temperature and grade indicates performance grade at conditioning temperature.

Extended BBR tests were also performed for the recovered material of Highway 17 sections according to the LS-308 test protocol. In this, except for Section 17-61 (polymer modified), all of the remaining sections have changes of 8-10°C due to three days of conditioning and chemical aging. Section 17-02, which shows almost no changes in the PAV material results from its grade, has shown a variation of 10°C in recovered material test. This is an indication of the insufficient laboratory aging (physical and chemical) of PAV material compared to the field-aged materials.

Tables 5 and 6 provide the data for the Highway 655 sections for PAV and recovered material, respectively. The extended BBR test results on PAV residues shows that section 655-1 lost the least during 72 h of conditioning and this is reflected in its superior performance (see Figure 17). However, the other sections all lose about the same after three days of conditioning and this suggests that the BBR is not entirely able to predict performance. Section 655-5 has also done very well, but this is likely due to improved failure characteristics at high strain as measured in the DENT test. These results will be discussed later.

Table 5. Highway 655 PAV Materials eBBR Results [31]

	Hours	655-1	655-2	655-3	655-4	655-5	655-6	655-7
Ts @ -22 °C	1	-26.2	-28.1	-29.1	-28.7	-26.7	-28.3	-28.5
	24	-25.1	-26.4	-28.0	-27.4	-25.2	-26.3	-27.0
	72	-24.8	-26.1	-26.9	-26.8	-25.0	-26.0	-26.6
Ts @ -28 °C	1	-25.9	-28.0	-29.2	-28.7	-27.2	-28.7	-28.2
	24	-25.1	-26.2	-27.4	-26.9	-25.4	-25.9	-26.2
	72	-25.7	-25.5	-26.9	-26.2	-24.8	-25.4	-25.8
Tm @ -22 °C	1	-27.7	-25.4	-26.8	-26.0	-25.5	-24.7	-25.2
	24	-25.6	-20.9	-23.2	-22.1	-21.6	-20.8	-20.6
	72	-24.5	-18.4	-22.4	-20.1	-21.3	-18.7	-18.5
Tm @ -28 °C	1	-27.8	-26.5	-27.6	-26.4	-26.3	-25.2	-25.5
	24	-25.5	-22.3	-23.9	-23.2	-22.3	-21.9	-22.2
	72	-24.3	-20.5	-23.1	-21.3	-21.6	-20.9	-20.4
Grade @ -22 °C	1	-36.2	-35.4	-36.8	-36.0	-35.5	-34.7	-35.2
	24	-35.1	-30.9	-33.2	-32.1	-31.6	-30.8	-30.6
	72	-34.5	-28.4	-32.4	-30.1	-31.3	-28.7	-28.5
Grade @ -28 °C	1	-35.9	-36.5	-37.6	-36.4	-36.3	-35.2	-35.5
	24	-35.1	-32.3	-33.9	-33.2	-32.3	-31.9	-32.2
	72	-34.3	-30.5	-33.1	-31.3	-31.6	-30.9	-30.4

Table 6. Highway 655 Recovered eBBR

	Hours	655-A	655-B	655-C	655-D	655-E	655-F	655-G
Ts @ -12 °C	1	-23.9	-25.3	-25.3	-24.4	-26.1	-25.4	-23.6
	24	-23.5	-24.9	-24.6	-22.7	-25.5	-24.6	-21.9
	72	-23.6	-24.2	-24.3	-19.9	-25.4	-23.9	-22.4
Ts @ -24 °C	1	-24.3	-24.8	-24.2	-23.6	-25.6	-24.4	-22.6
	24	-22.4	-22.8	-22.4	-20.7	-23.8	-22.5	-20.3
	72	-22	-22.2	-21.9	-19.1	-23.1	-21.5	-19.9
Tm @ -12 °C	1	-25.9	-22.2	-19.3	-15.5	-25.2	-15.5	-16.5
	24	-24.2	-16.6	-12.6	-9	-22.5	-8.0	-9.3
	72	-23.4	-16.2	-10.8	-8.7	-22.1	-7.7	-7.5
Tm @ -24 °C	1	-26.4	-24.0	-21.3	-20.1	-25.8	-19.9	-20.1
	24	-22.5	-19.2	-17.7	-16.3	-21.8	-25.3	-16.3
	72	-22	-18.2	-16.3	-17.2	-21.0	-14.1	-16.2
Grade @ -12 °C	1	-33.9	-32.2	-29.3	-25.5	-35.2	-25.5	-26.5
	24	-33.5	-26.6	-22.6	-19	-32.5	-18.0	-19.3
	72	-33.4	-26.2	-20.8	-18.7	-32.1	-17.7	-17.5
Grade @ -24 °C	1	-34.3	-34.0	-31.3	-30.1	-35.6	-29.9	-30.1
	24	-32.4	-29.2	-27.7	-26.3	-31.8	-25.3	-26.3
	72	-32	-28.2	-26.3	-27.2	-31.0	-24.1	-26.2

Note: Temperatures indicate conditioning temperature grade indicates performance grade at conditioning temperature.

Table 6 contains the data obtained from the extended BBR test for recovered material of Highway 655 sections. These results are much more similar to the performance of the sections on the road. Sections 655-1 and 655-5 are the best of all and lose around 4°C in grade, while Section 655-4 is worst and has a 10°C loss in grade. Sections 655-2, 655-3, 655-6 and 655-7 are also disappointing after only 5-6 years of service.

Finally, we can conclude from the PAV and recovered data that results obtained from the extended BBR test are closer to the actual performance of the sections compare to the regular BBR test due to the insufficient conditioning time at low temperatures in the regular test. Further, the results also show that the PAV provides insufficient chemical aging even for materials that have been in service for only 5-6 years.

4.2.3 Elastic Recovery Testing at Low Temperatures

The same materials were also tested for their elastic and viscous properties at low temperatures in the BBR by unloading for 720 s after the 240 s of loading. These tests allow the viscous and elastic deformation to be separated and the obtained data are analyzed in Figures 30-45, below.

The general observation we can make is that the elastic recovery does not seem to be a very good indicator for performance in any of the materials investigated (PAV and/or recovered). Figures 30 to 32 are for Highway 17 and Figures 34, 36, 38, 42 and 44 for Highway 655 show that all samples have very similar elastic recoveries while they have performed vastly different in terms of cracking in service. The exception is given in Figure 40, which shows that the elastic recovery for Sections 655-1 and 655-5 is marginally less than the rest (i.e., they are less elastic and thus would retain less thermal stress during winter), which agrees with their superior performance in service.

Similarly, the viscous compliance does not do a very good job at distinguishing the good from the poor performers in PAV residues (Figures 33, 35, 37 and 39). In contrast, the viscous properties in the recovered materials show a strong correlation with performance with Sections 655-1 and 655-5 outperforming the rest by a large margin (see Figure 41 and 43) although at the very low temperature of -30°C they all again appear similar.

It may therefore be once more stated that the RTFO/PAV aging deficiencies are in large part to blame for the premature and excessive cracking in some of these test sections and in numerous paving contracts around Ontario.

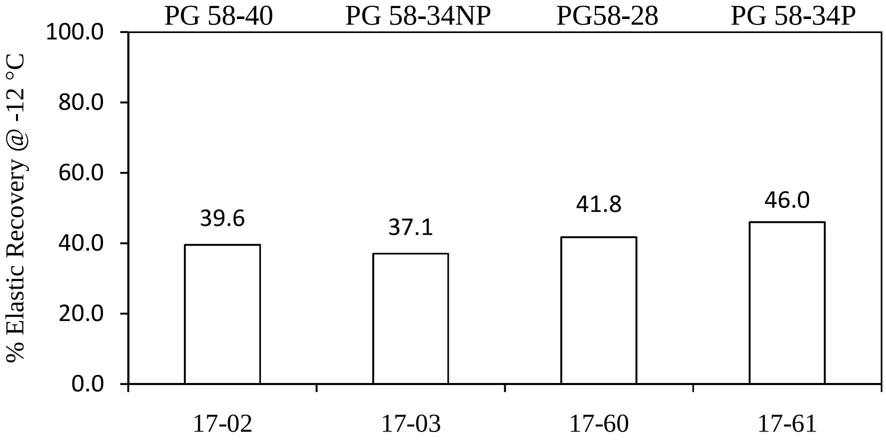

Figure 30. Elastic recovery of laboratory-aged (PAV) Highway 17 sections at -12°C.

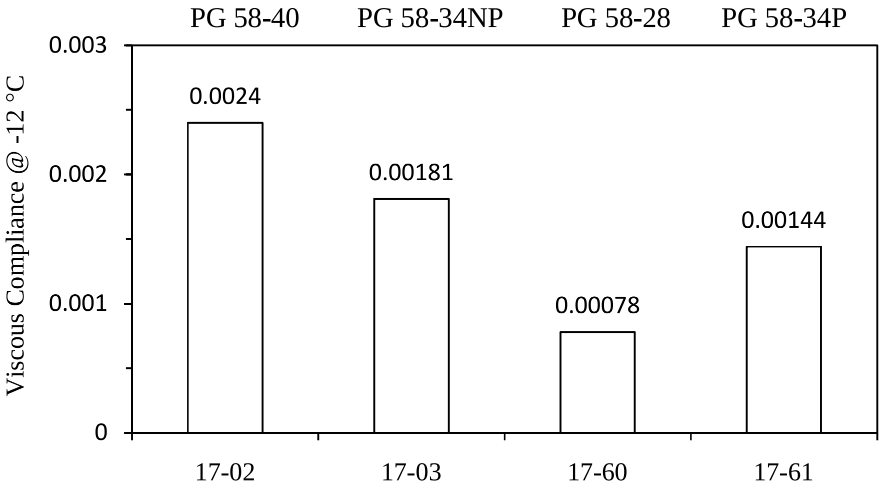

Figure 31. Viscous compliance J(v) of laboratory-aged (PAV) Highway 17 sections at -12°C.

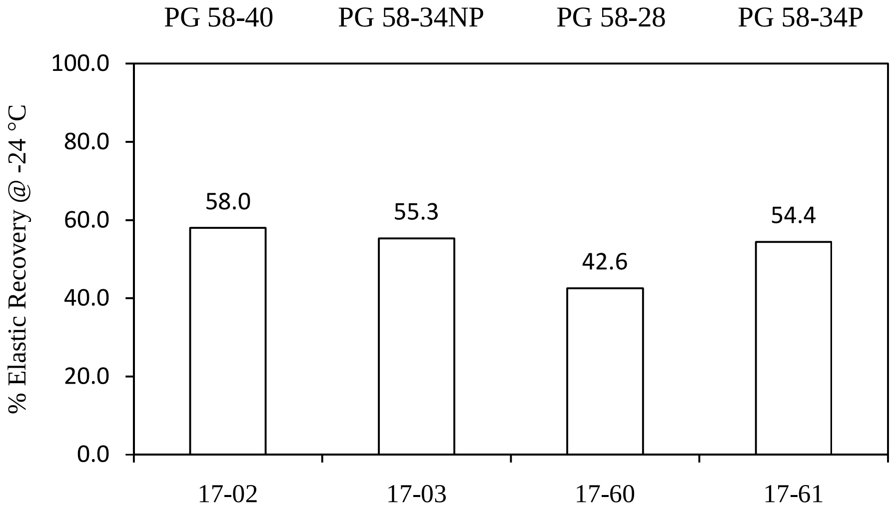

Figure 32. Percentage elastic recovery of laboratory-aged (PAV) Highway 17 sections at -24°C.

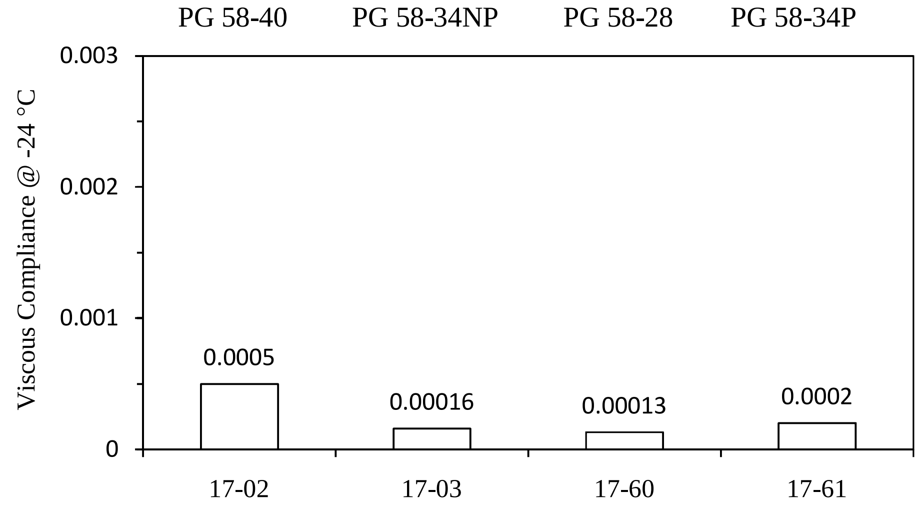

Figure 33. Viscous compliance J(v) of laboratory-aged (PAV) Highway 17 sections at -24°C.

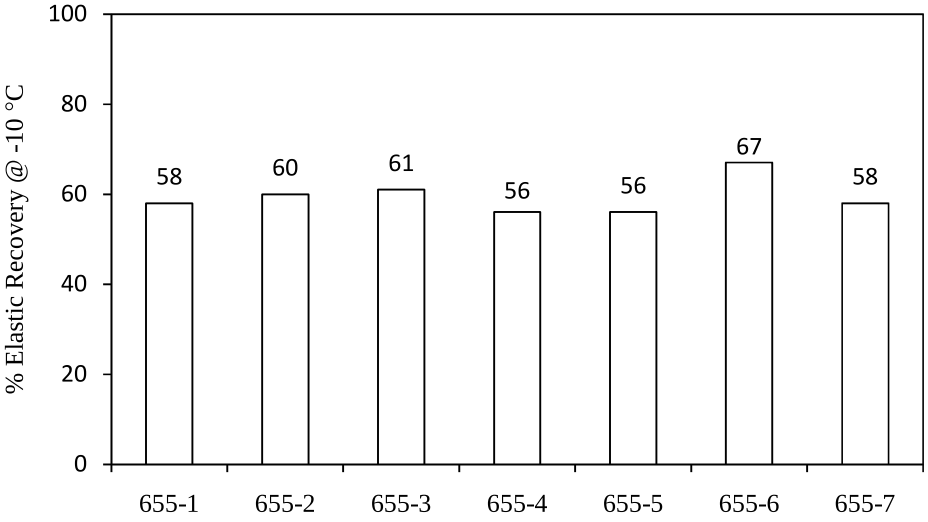

Figure 34. Percentage elastic recovery of laboratory-aged (PAV) Highway 655 sections at -10°C.

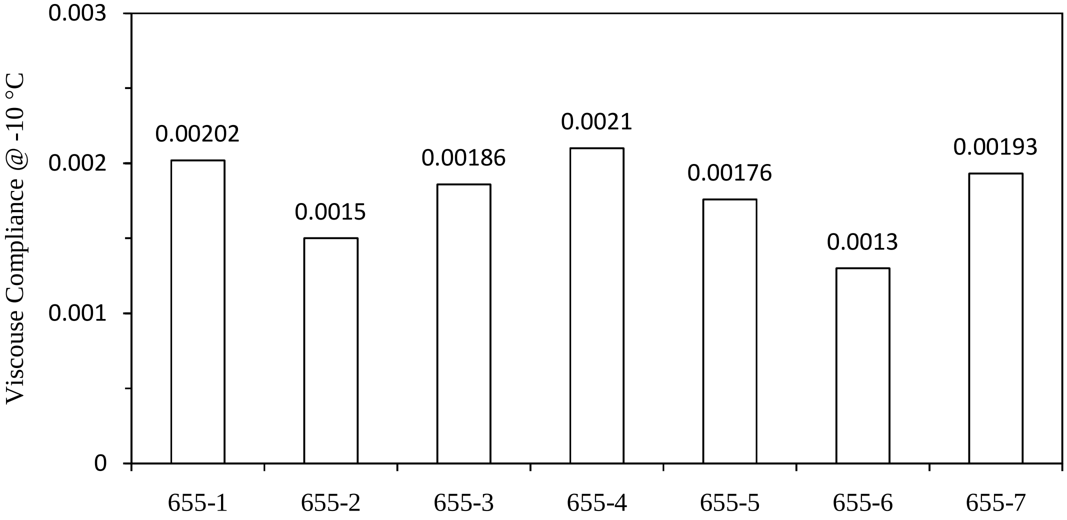

Figure 35. Viscous compliance J(v) of laboratory-aged (PAV) Highway 655 sections at -10°C.

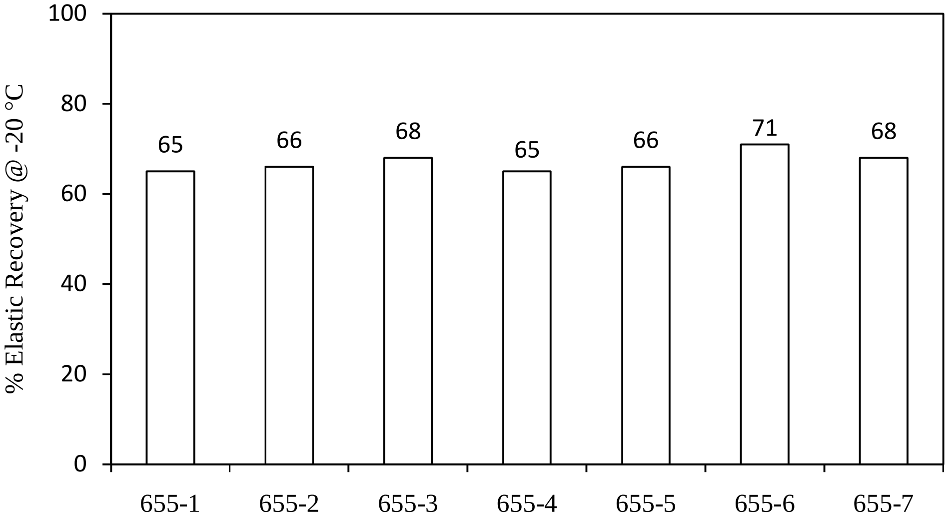

Figure 36. Percentage elastic recovery of laboratory-aged (PAV) Highway 655 sections at -20°C.

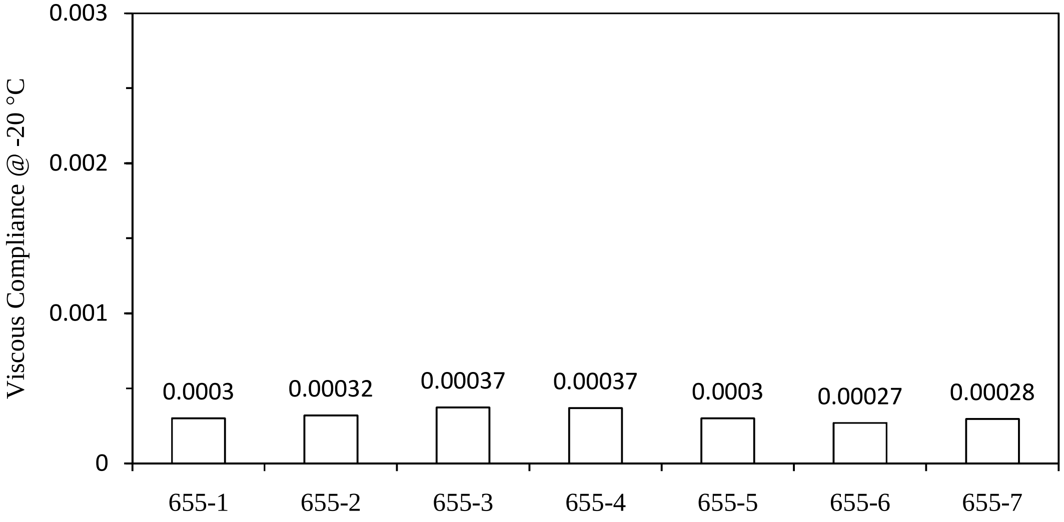

Figure 37. Viscous compliance J(v) of laboratory-aged (PAV) Highway 655 sections at -20°C.

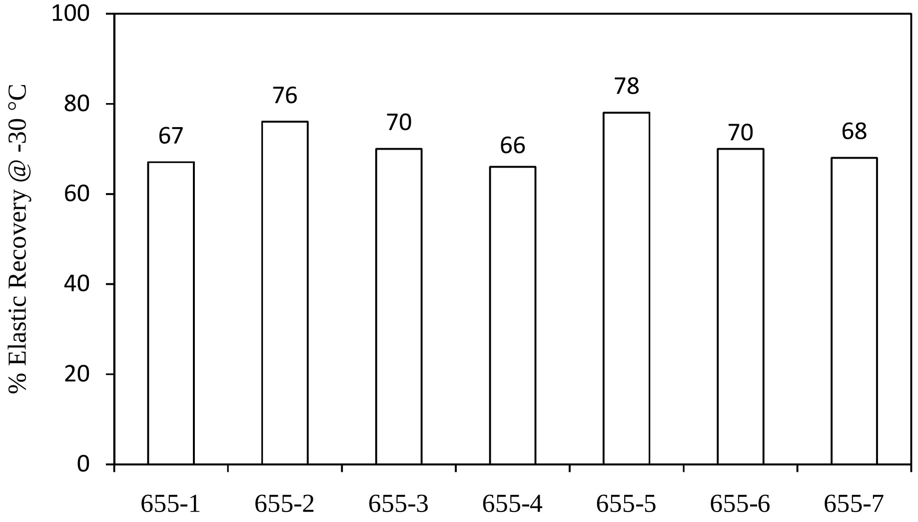

Figure 38. Percentage elastic recovery of laboratory-aged (PAV) Highway 655 sections at -30°C.

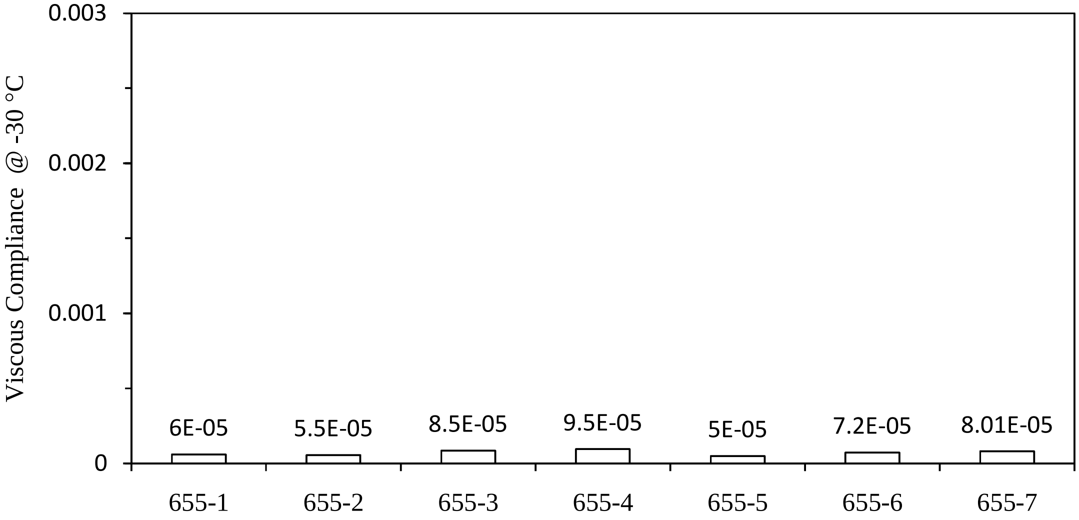

Figure 39. Viscous compliance J(v) of laboratory-aged (PAV) Highway 655 sections at -30°C.

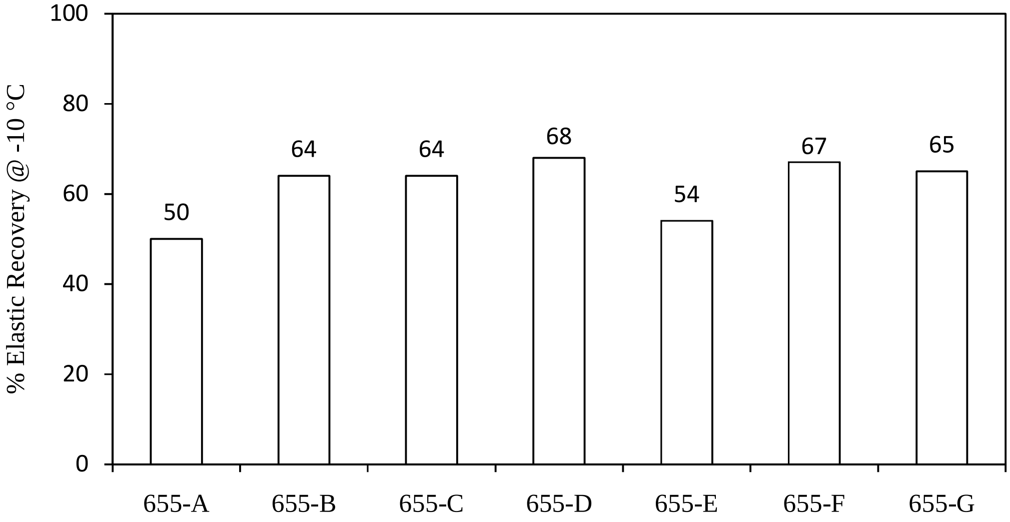

Figure 40. Percentage elastic recovery of Highway 655 recovered materials at -10°C.

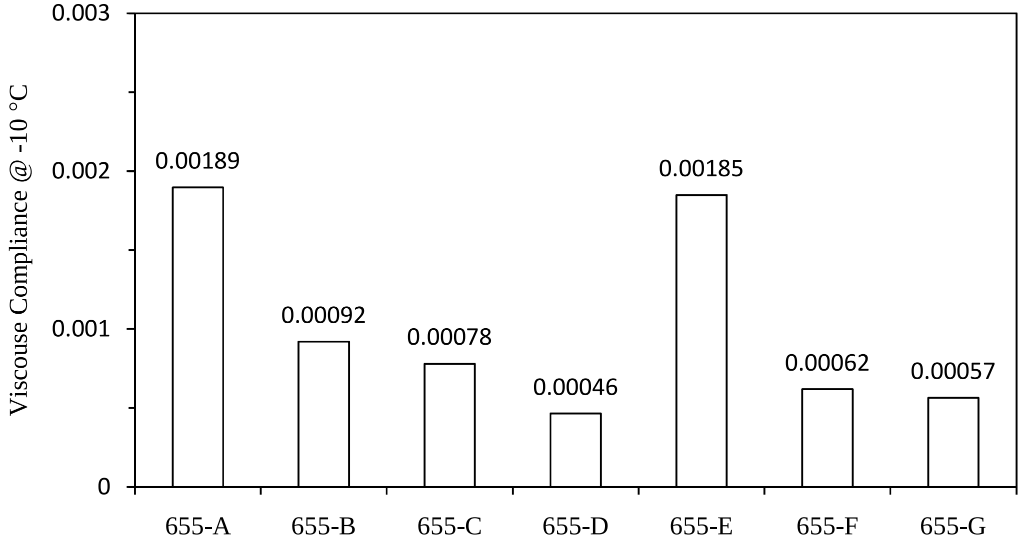

Figure 41. Viscous compliance J(v) of Highway 655 recovered materials at -10°C.

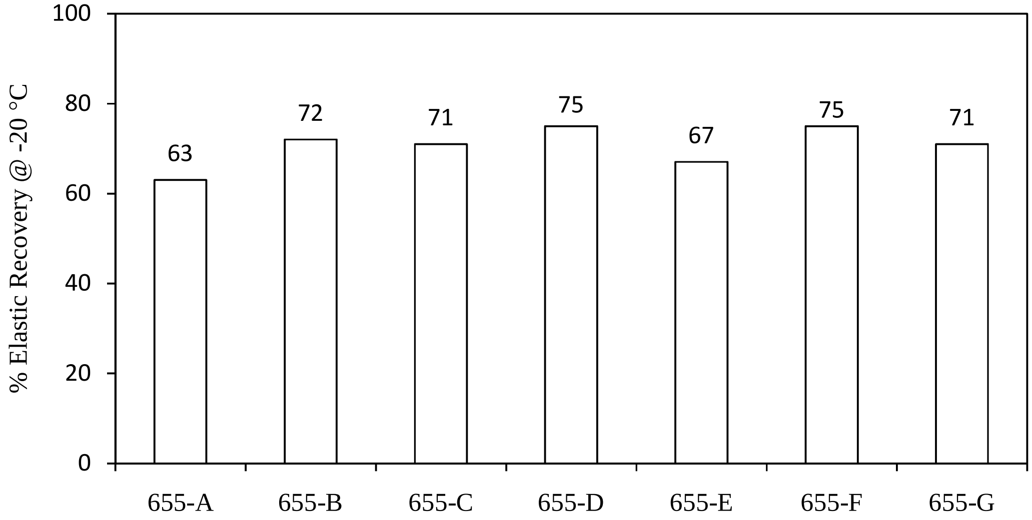

Figure 42. Percentage elastic recovery of Highway 655 recovered materials at -20°C.

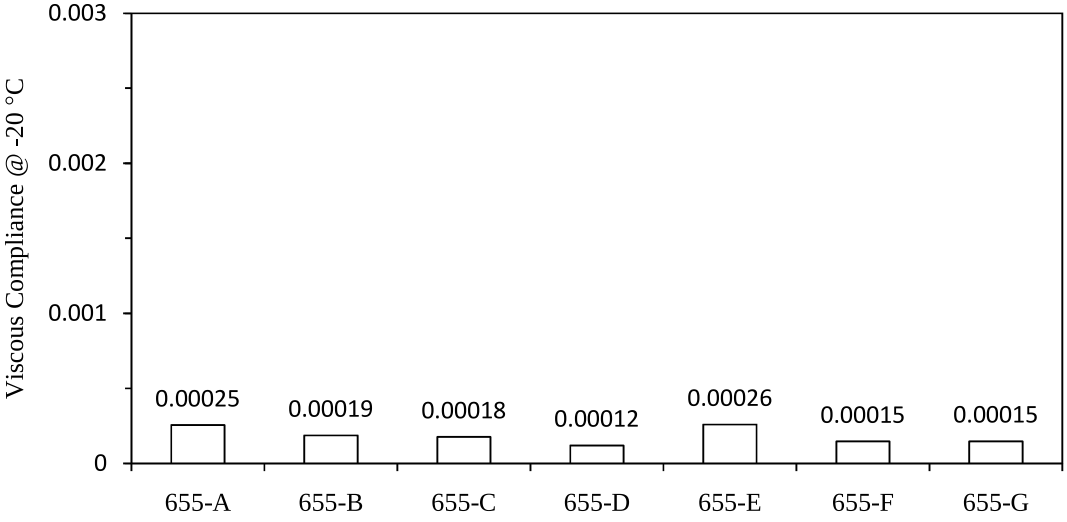

Figure 43. Viscous compliance J(v) of Highway 655 recovered materials at -20°C.

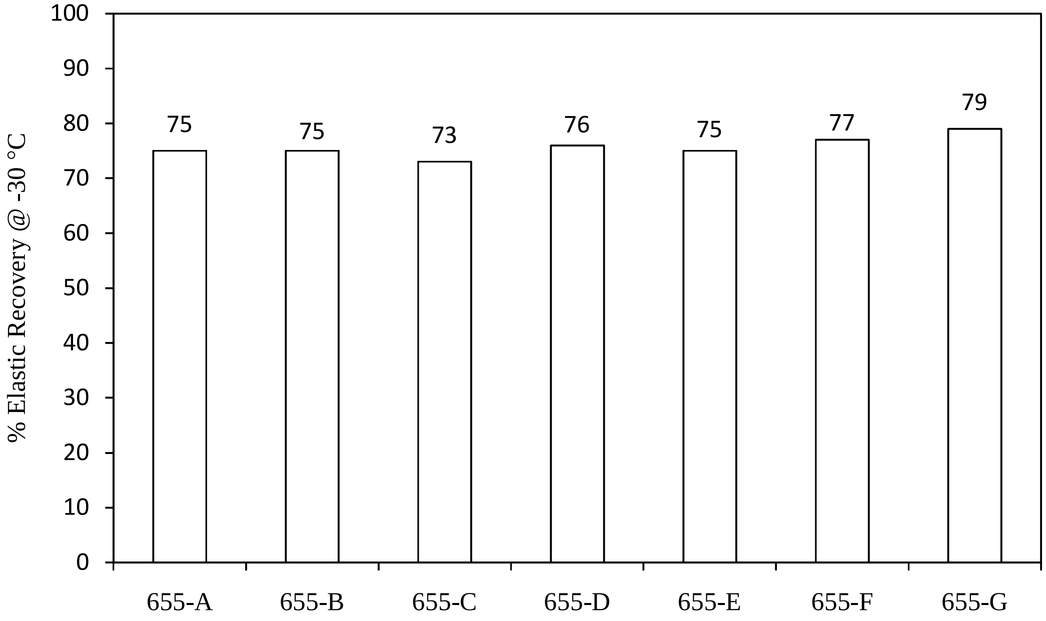

Figure 44. Percentage elastic recovery of Highway 655 recovered materials at -30°C.

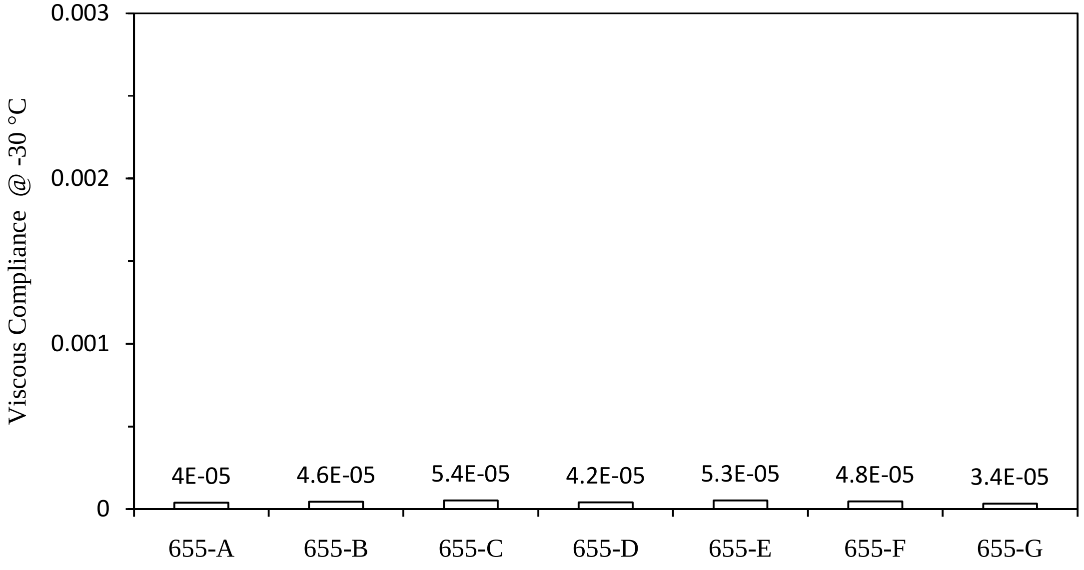

Figure 45. Viscous compliance J(v) of Highway 655 recovered materials at -30°C.

4.2.4 Double-Edge-Notched Tension Testing

The evaluation of the recovered asphalt cement materials was also done according to the LS- 299 double-edge-notched tension test protocol [37]. The approximate critical crack tip opening displacements for binders of Highway 17 and 655 are shown in Figure 46 and 47, respectively.

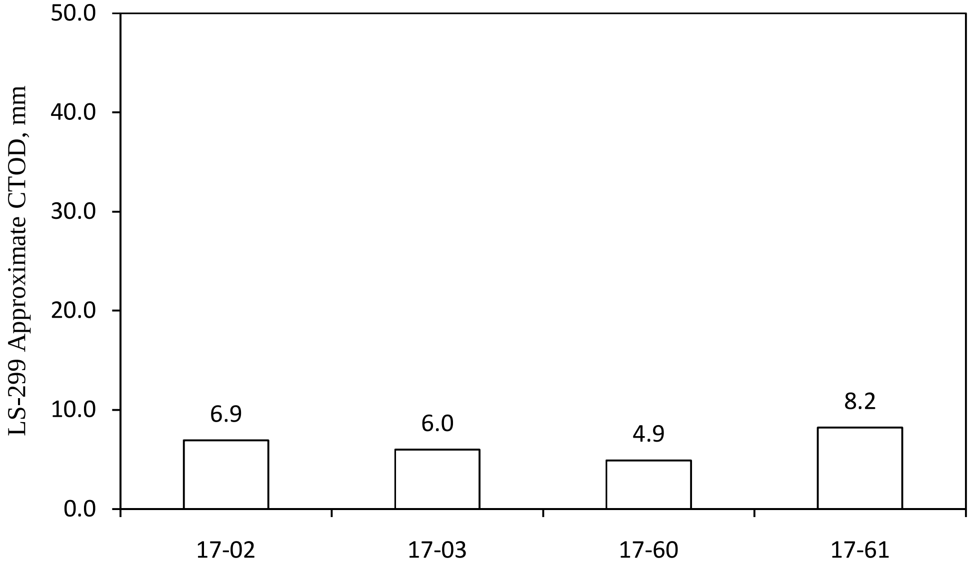

Figure 46. The approximate critical crack tip opening displacements of recovered samples of Highway 17 Sections 17-02, 17-03, 17-60 and 17-61.

The distress surveys taken in 2002, 2003, and 2007 (Figure 16) have shown that Section 17-60 has the most distress at 186 cracks/km followed by 87 cracks/km for Section 17-03 while Sections 17-02 and 17-61 have almost the same amount of distress at around 60 cracks/km [63] in 2007 survey. When these results are compared with the approximate CTOD values in Figure 46 it shows that Section 17-61 has highest value and section 17-60 has lowest value out of this. This correlation indicates that DENT test could be useful for identifying service performance of asphalt binders. However, it should also be noted that these results are all rather poor. Typically the CTOD should be around 10 mm for a PG-28, 14 mm for a PG-34, and even higher for a PG-40 grade.

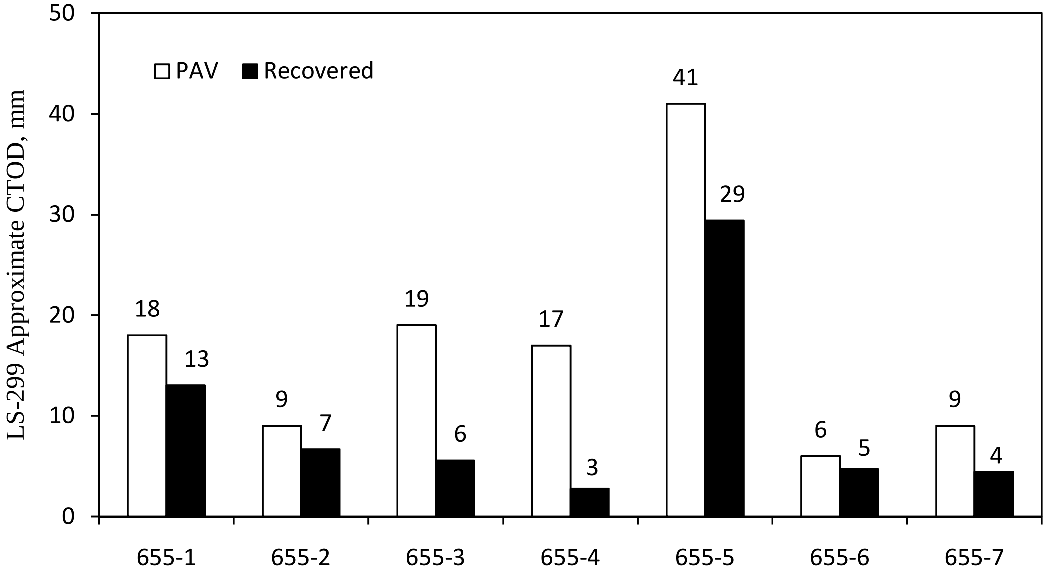

Figure 47. The approximate critical crack tip opening displacements for recovered samples of Highway 655 sections.

Figure 47 shows that the CTODs for recovered Sections 655-3 and 655-4 are dramatically reduced compared to their PAV values. Sections 655-2, 655-6 and 655-7 also have low 4-7 mm CTOD values. The noticeable point is that Sections 655-1 and 655-5 have retained rather good CTODs at 13 mm and 29 mm compared to the remaining sections. These have already performed better in service [18].

This results shows the CTOD value and service performance have much more correlation. As mentioned in the materials chapter, a few of these trial section asphalts were tested with X-ray fluorescence and tested positive for the zinc metal (Sections 655-3, 655-4, 655-6 and 655-7) and also traces of phosphorous (Sections 655-, 655-6 and 655-7) which is observed using ^{31}P nuclear magnetic resonance (NMR) spectroscopy [18]. The presence of zinc and phosphorous in these, as well as in numerous poorly performing eastern and northeastern Ontario contracts, indicates the presence of waste engine oils, with or without the use of polyphosphoric acid (PPA). PPA is found to lower the ductile strain tolerance [64] and waste engine oils are thought to weaken the asphalt cement-aggregate interface [65] and to promote the physical hardening process [15], and hence, these additives could be a strong reason for the observed poor performance.

4.3 Infrared Spectroscopy Study of Asphalt Cement Recovered from Eastern Ontario Paving Contracts

A separate investigation for this thesis involved the infrared spectroscopic (IR) analysis of the asphalt cements recovered from a series of 20 contracts in eastern and northeastern Ontario. These had earlier been investigated for thermal cracking and it was found that 11 performed satisfactorily with almost no cracking for extended periods while 9 had cracked prematurely and excessively in their first few years of service [17].

Table 7. Eastern Ontario Paving Contracts [17]

Number	Highway	Location	Age	Cracking Severity
1	6	Little Current	2000	Excessive
2	11	Cochrane	1999	Mild
3	11	Smooth Rock Falls	1998	Mild
4	17	Petawawa	1996	Excessive
5	28	Burleigh Falls	1993	Mild
6	28	Lakefield	1997/1998	Mild
7	33	Conway	1998	Mild
8	35	Lindsay	1997	Mild
9	41	Dacre	2000	Mild
10	41	Denbigh	1996	Excessive
11	41	Kaladar	1999	Excessive
12	41	Northbrook	2000	Severe
13	41	Vennachar	1997/1998	Mild
14	60	Bat Lake	1998	Severe
15	60	Wilno	1994	Excessive
16	62	Bannockburn	1997	Excessive
17	62	Bloomfield	1993	Mild
18	138	Cornwall	2000/2001	Mild
19	138	Monkland	1998	Excessive
20	416	Spencerville	1999	Mild

Infrared spectroscopy has long been used to study the chemical hardening of asphalt cements through the monitoring of the carbonyl functional group around 1700 cm^{-1}, which is the main oxidation product [59]. The other chemical group that is often followed, since it is also a product of the asphalt cement's reaction with oxygen, is the sulfoxide [59]. A final functional group that is of interest is the aromatic index as measured from the peak around 1600 cm^{-1}. A summary of all findings is provided in Figures 48-50, below.

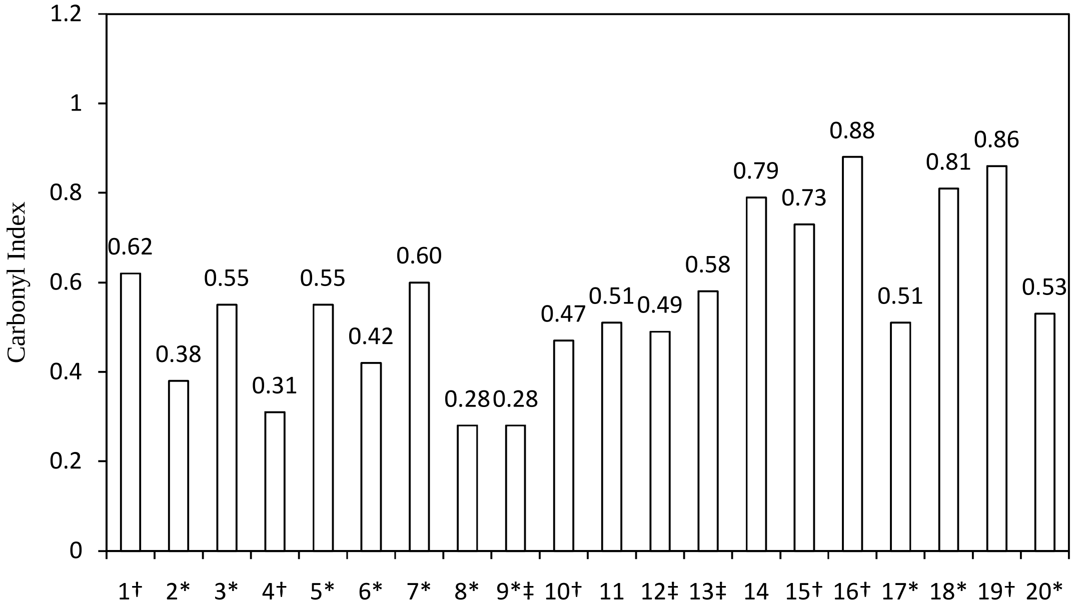

Figure 48. Carbonyl indices for eastern Ontario paving contracts (see Table 7 for contract details). <u>Note</u>: * Indicates minor cracks found during the survey after 7-15 years of service where, † indicates excessive and premature cracks, ‡ indicates polymer found in the infrared spectroscopy analysis.

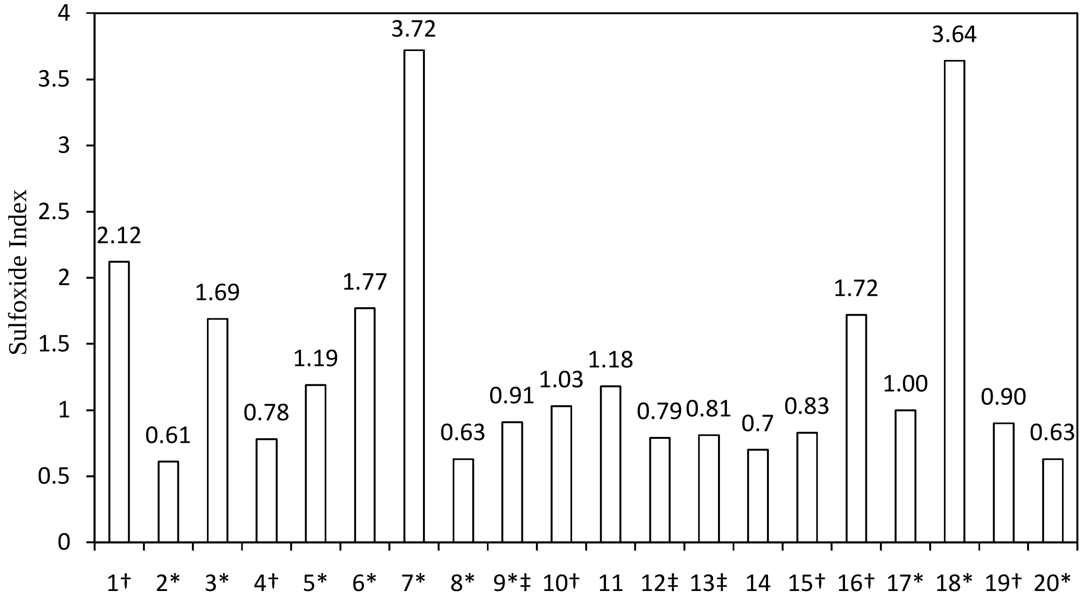

Figure 49. Sulfoxide indices for eastern Ontario paving contracts.

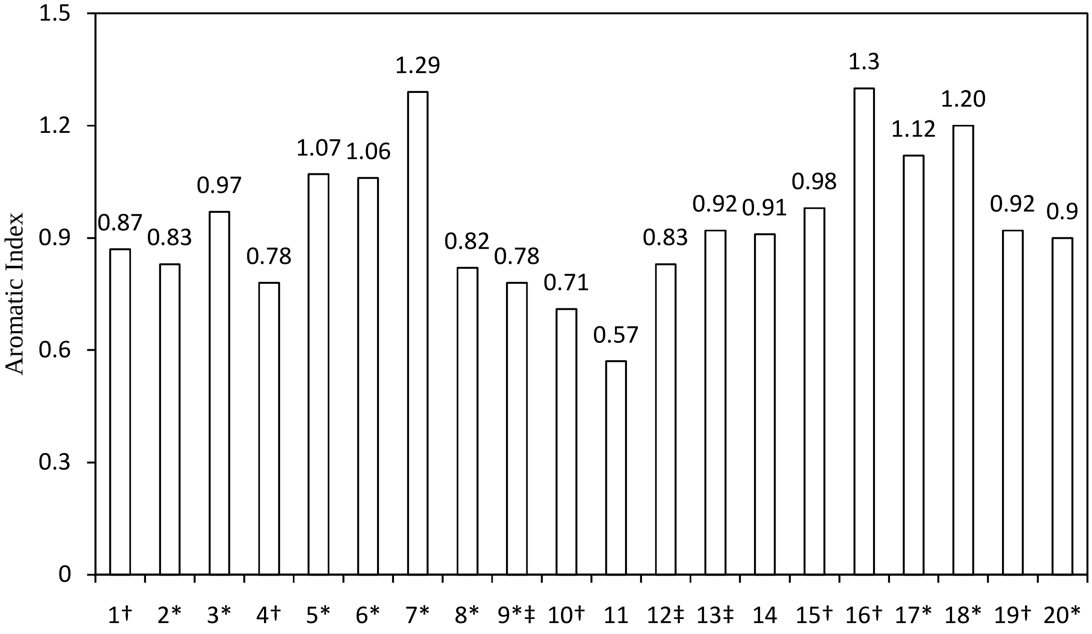

Figure 50. Aromatics indices for eastern Ontario paving contracts.

The data are interesting in several ways. First, the carbonyl index is a rather poor predictor of performance. While some contracts such as Sites 8 and 9 show a low carbonyl index and have performed well, others such as sites 18 and 19 shows opposite performance for rather high and nearly identical carbonyl indices.

This analysis shows that it is not only the addition of asphaltenes (carbonyls) that is of importance for low temperature cracking but rather also the way in which such additional asphaltenes harden the asphalt cement. In highly paraffinic oils, the asphaltenes produced upon oxidation will easily form a gel structure which is unable to relax thermal stresses. In contrast, more aromatic oils will allow the asphaltenes to remain better peptized and thus able to relax thermal stresses.

This conclusion is best illustrated with an example from the graphs above. Highway 138 has a very good performing contract from Cornwall to Monkland (Site 18) adjacent to a very poor performer north of Monkland (Site 19). The extracted asphalt cements have carbonyl indices of 0.81 and 0.86, respectively (see Figure 48). For all intents and purposes these can be considered to be the same and at the high end of the spectrum. The difference in performance can be explained by the data given in Figure 50. The Site 18 material has an aromatics index that is about 30% higher than what was found for Site 19. Aromatics are better at peptizing the asphaltenes and thus this pavement was able to survive as many winters as the one to the north that failed miserably.

Similarly, Sites 11 and 17 have the exact same carbonyl index (0.51) but Site 11 has cracked excessively in early life whereas Site 17 has remained largely free of distress. This can again be explained through the difference in aromatics index with the latter being about twice as high as the former (0.57 versus 1.12).

There are also anomalies to this general trend and this is likely due to the nature of the asphaltenes formed during oxidation. Those asphalt cements that have asphaltenes that are lower in aromaticity will likely stay compatible with saturated oil for longer periods of time and are thus able to withstand more oxidation. Hence, it must be concluded that we not only need to consider the spectroscopic properties but also the rheological properties when developing an improved chemical aging method for asphalt cement.

4.4 Chemical Testing

4.4.1 Thin Film Aging at Different Temperature

Thin film oven-aged specimens were tested for their infrared spectra in order to monitor the changes in functional groups related to the oxidation of the asphalt cement (carbonyl, sulfoxide, and aromatics). The results of the investigation are provided in Figures 51-58 below.

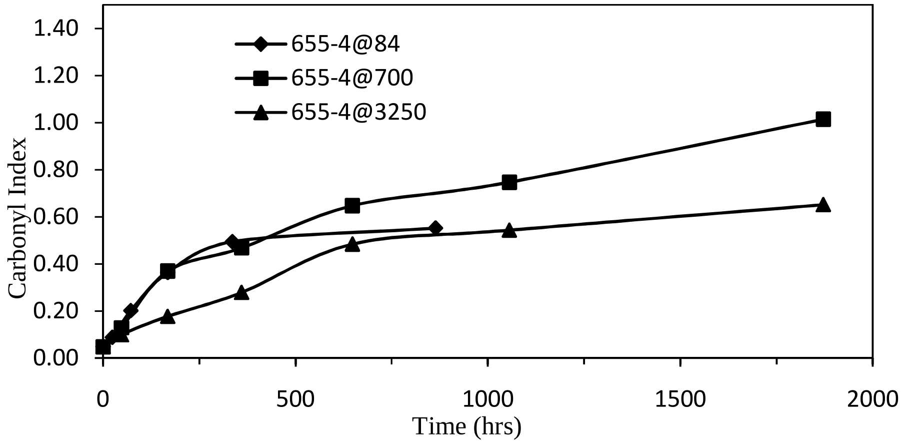

Figure 51. Carbonyl indices of Section 655-4 with different film thickness (in µm).

Figures 51 and 52 show that the film thickness affects the oxidation rate as measured by the carbonyl index for film thicknesses of 3250 µm but not for those of 700 µm and below. This is likely due to the limiting factor being the diffusion of oxygen into the thicker films. The oxygen disappears faster than the rate at which it is able to diffuse into the film. Hence, the remaining tests were all done with films of 700 µm. This thickness provided sufficient material for further testing in both IR and DSR protocols. The above mentioned film thickness are for aging material in oven.

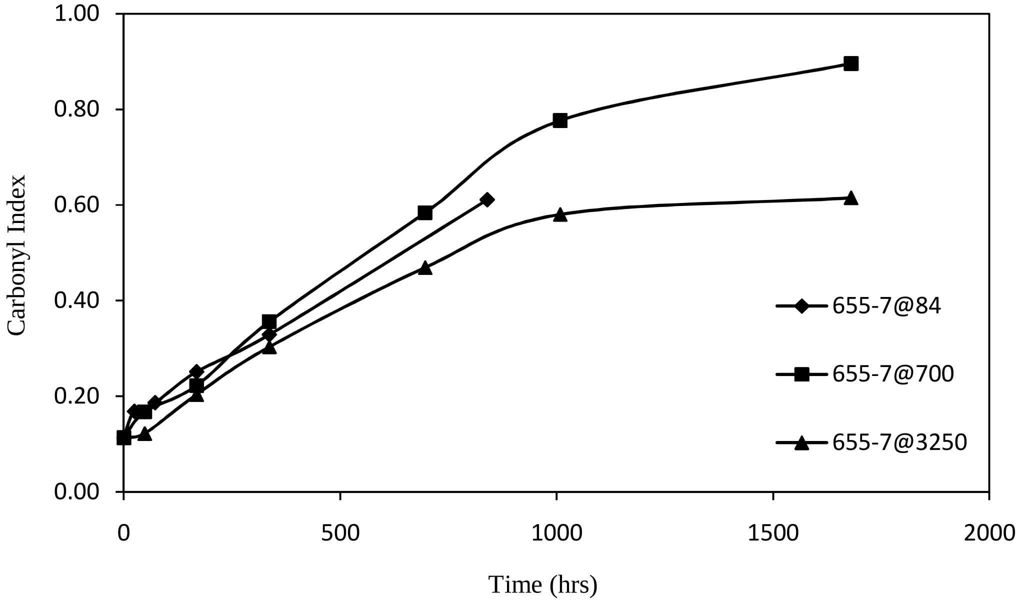

Figure 52. Carbonyl indices of Section 655-7 with different film thickness (µm).

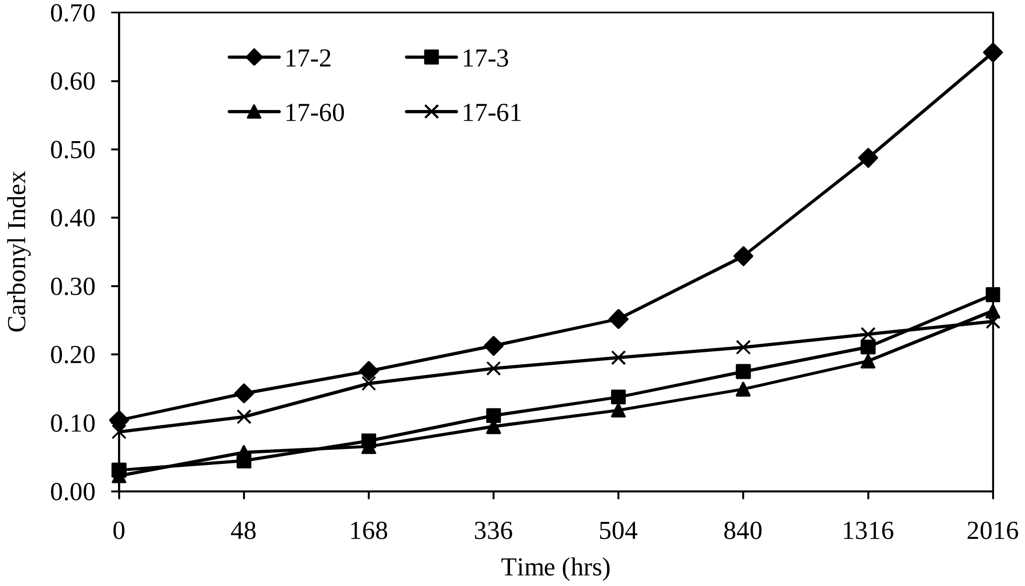

Figure 53. Carbonyl indices of Highway 17 test sections at 65°C.

The results for Highway 17 show that the oxidation rates for Sections 17-03, 17-60 and 17-61 are similar for up to 2000 hours while that for Section 17-02 is slightly higher. These data agree with the results presented in Figures 20 (PAV residues) and 26 (recovered). There Section 17-02 loses more than the three others. However, Section 17-61 loses only 0.3°C in service compared to the PAV which is likely due to a higher compatibility between the asphaltenes formed and the oils in that base asphalt.

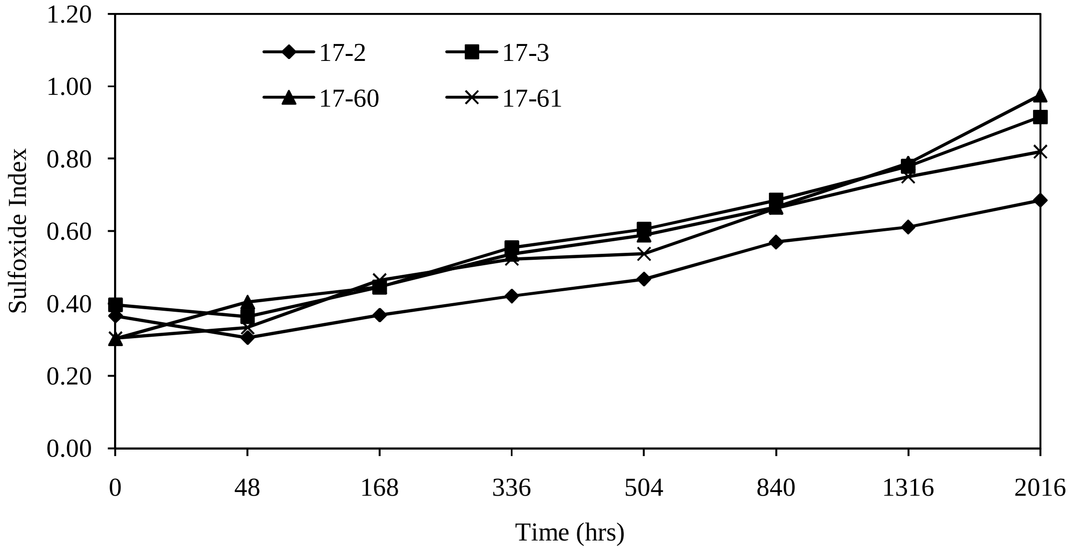

Figure 54. Sulfoxide indices of Highway 17 test sections at 65°C.

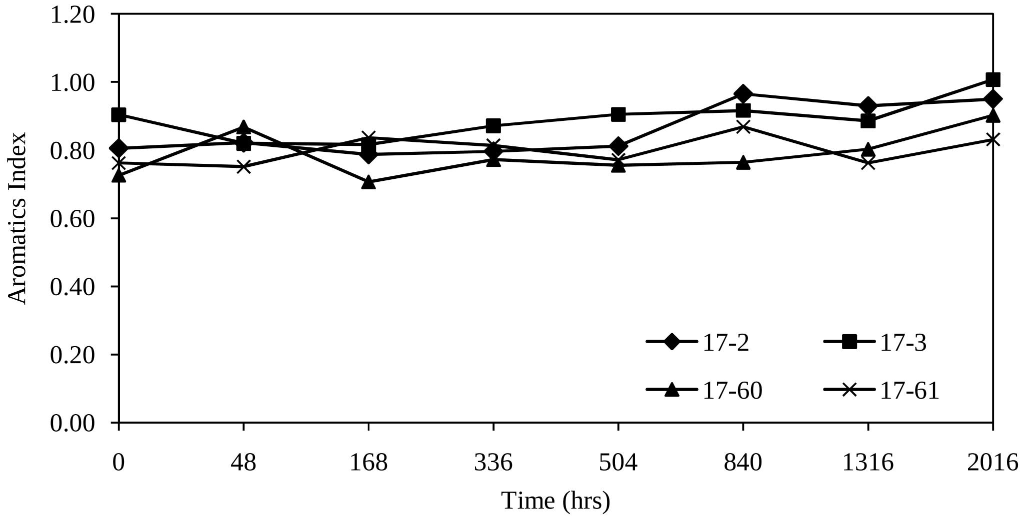

Figure 55. Aromatics indices of Highway 17 test sections at 65°C.

The results for Highway 655 thin film oven aged materials are provided in Figures 56-59 and they are also in reasonable agreement with the findings from the field extracted materials and the field performance. Note that the material from Section 655-1 starts high because it has a reactive ethylene terpolymer with acrylate groups that absorb in the same region as the ketone formed through oxidation. If the value is subtracted then this material ages least followed by Section 655-5 material. Sections 655-4 and 655-7 are the only outliers, which is likely due to the presence of waste engine oils in these materials. These waste oils are highly paraffinic and therefore precipitate the asphaltene that is formed in a more forceful manner, thus reducing the m-value and increasing the thermal cracking beyond what is predicted from just the carbonyl index.

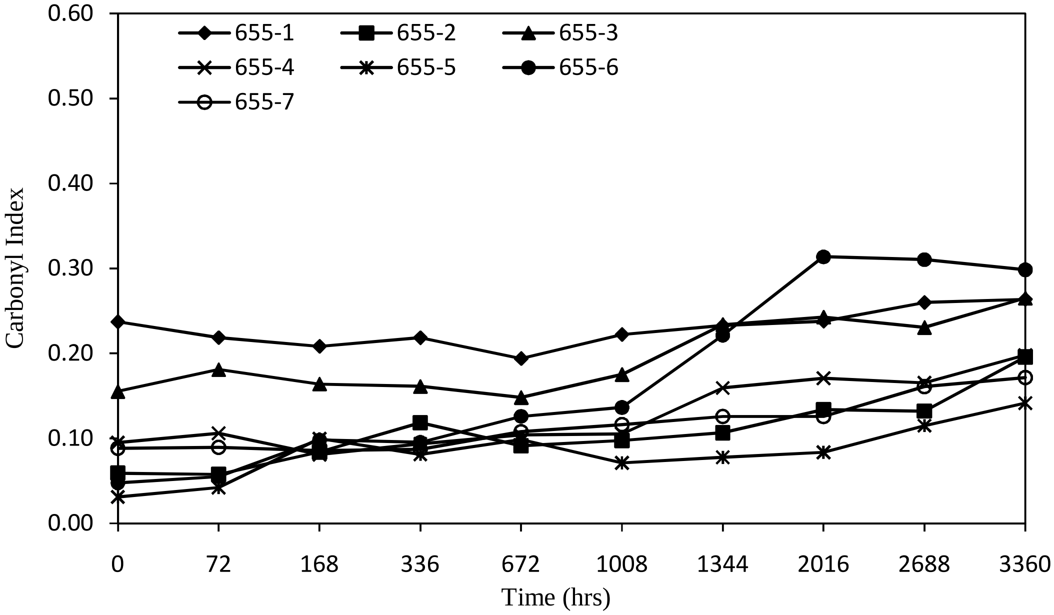

Figure 56. Carbonyl indices for Sections 655-1 to 655-7 at 45°C.

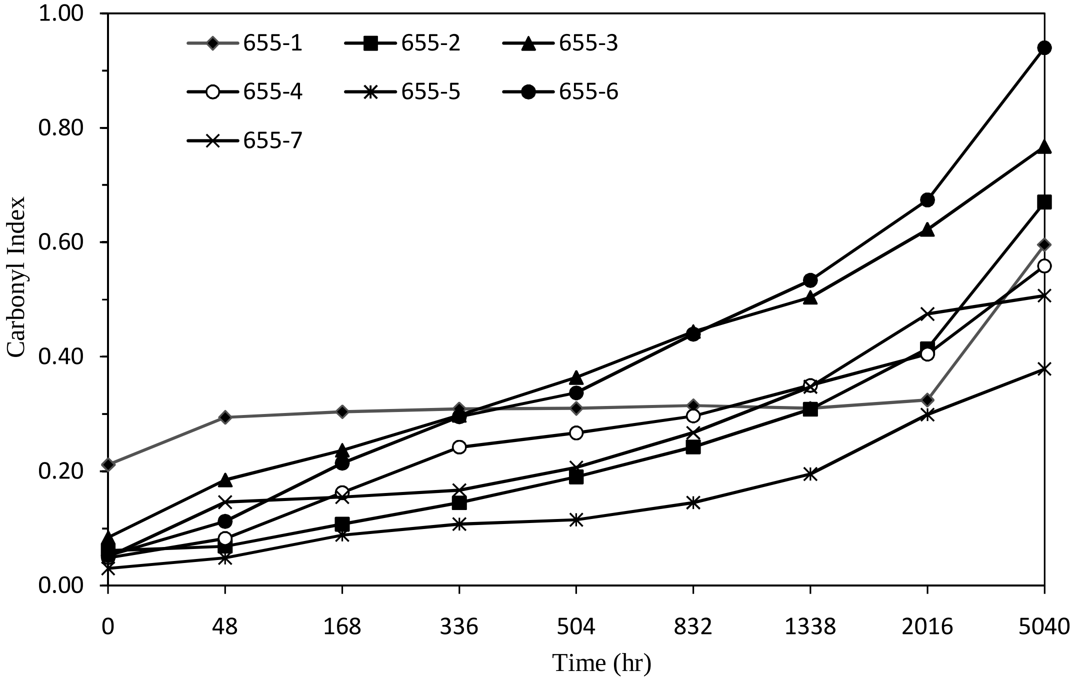

Figure 57. Carbonyl indices for Highway 655 Sections 1-7 at 65°C.

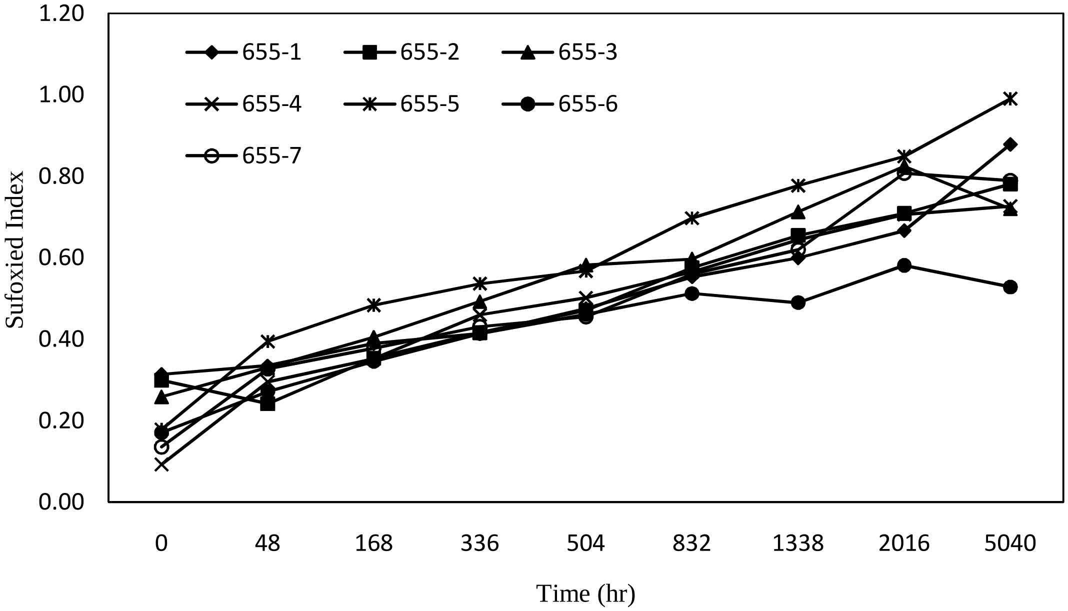

Figure 58. Sulfoxide indices for Highway 655 Sections 1-7 at 65°C.

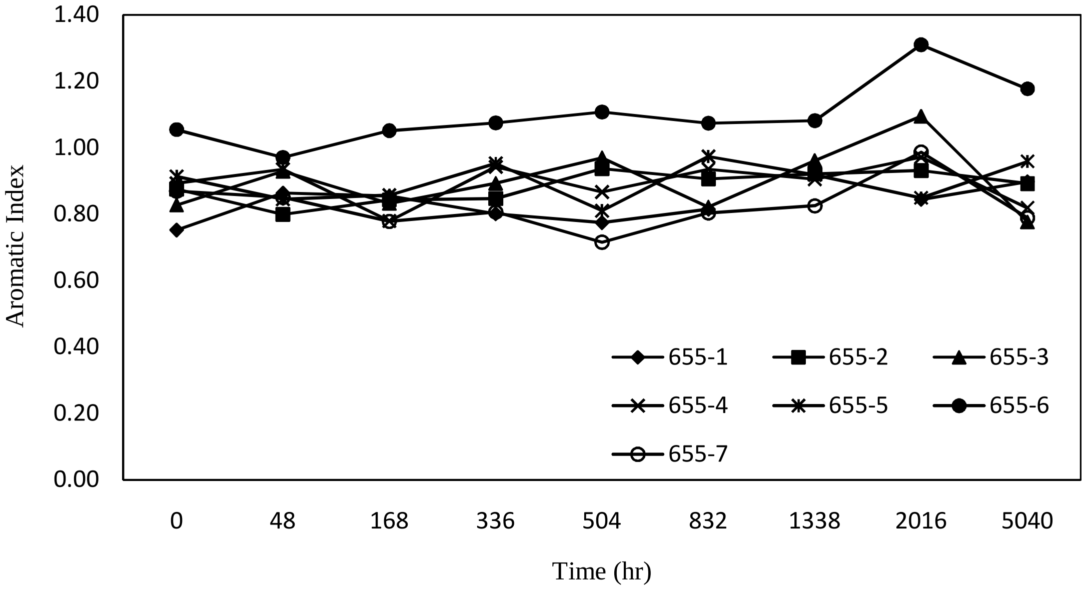

Figure 59. Aromatic indices for Highway 655 Sections 1-7 at 65°C.

4.5 Improvements for the Current RTFO/PAV Protocol

Since it was shown that the current RTFO/PAV protocol does a poor job at replicating the field aging for both the Highway 17 and Highway 655 trial sections, it was decided to investigate simple modifications to see if they would improve the chemical aging method. The PAV test was conducted for twice the length, 40 h versus the regular 20 h, and with half the weight in each pan, 25 g versus the regular 50 g, for the same length of time. The results of these experiments are provided in Figures 60-70 below.

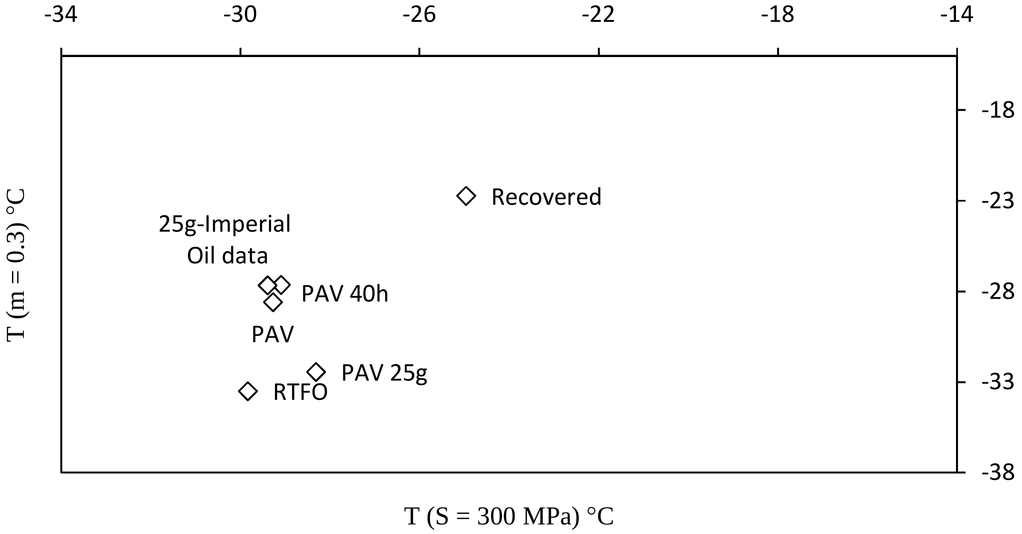

Figure 60. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 17 Section 02.

Note: Imperial Oil data were obtained at their company lab in Sarnia, Ontario.

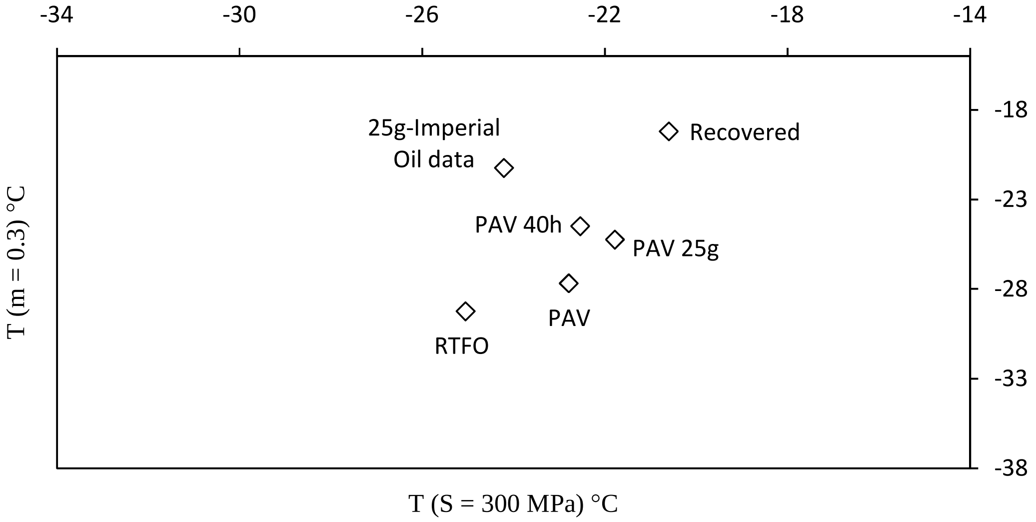

Figure 61. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 17 Section 03.

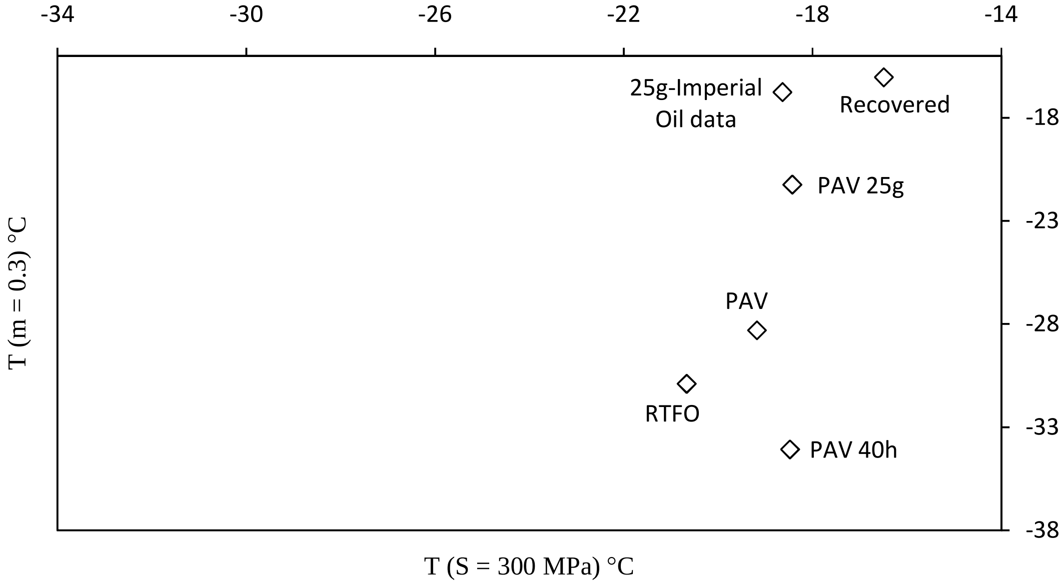

Figure 62. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 17 Section 60.

It is observed that in all the test sections at least either one of the modified test results are closer to recovered materials compare to regular PAV aging method. In Section 17-02 (Figure 60) the recovered material results are far from all the aged materials. Results for Section 17-03 (Figure 61) has more clear picture where both the modified test has similar results and closer to recovered material.

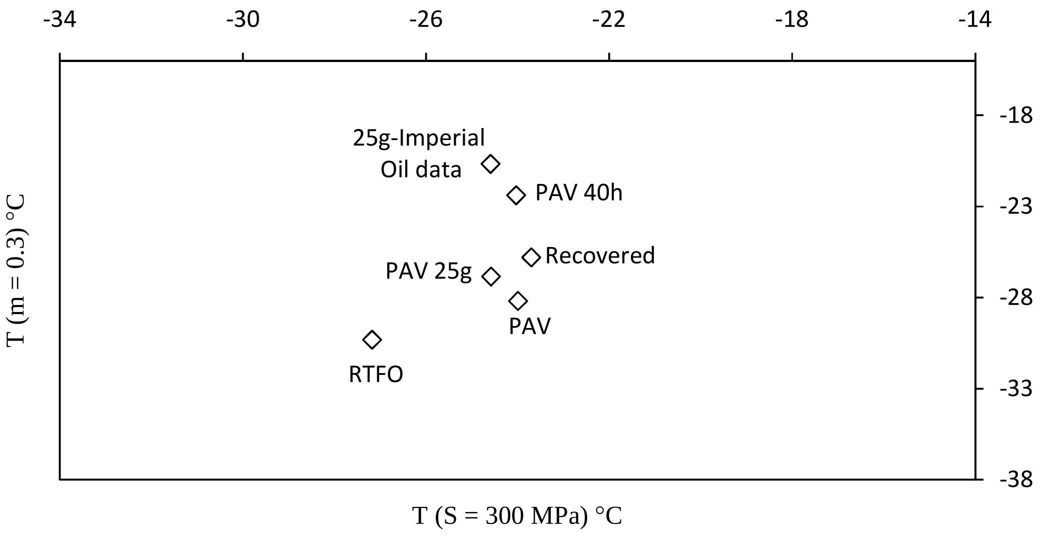

Figure 63. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 17 Section 61.

The observation for section 60 (Figure 62) is important as this section has poorest performed out of all four. In this PAV method modified with film thickness is closest to the recovered material while regular PAV and modified PAV with time length is far from it. In Section 17-61 (Figure 63) time length modified PAV and regular PAV are closer to recovered in terms of thickness while film thickness modified method is closer in m-value as well.

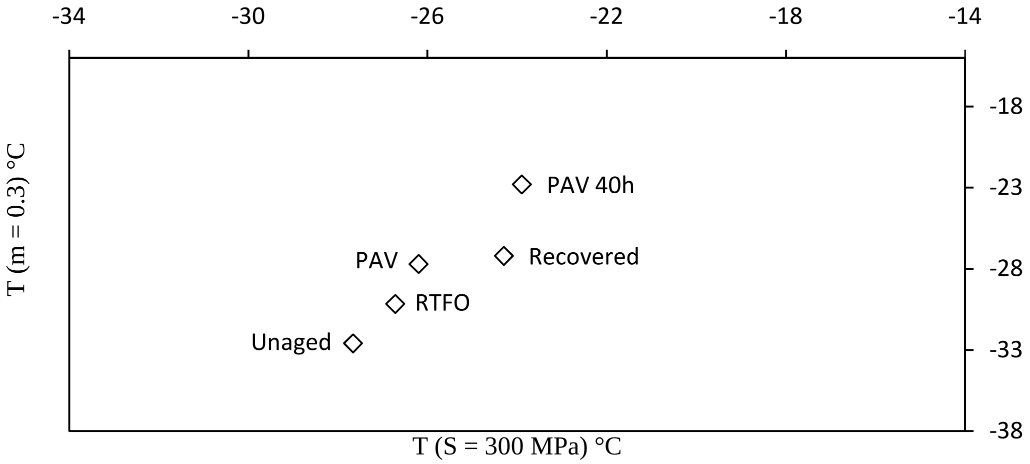

Figure 64. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 655 Section 1 [18]. Note: some of the data are courtesy of Imperial Oil Ltd.

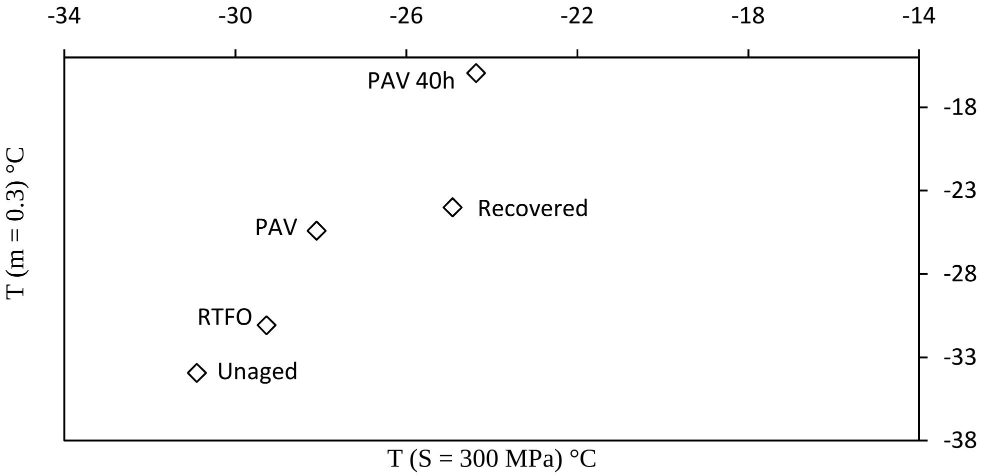

Figure 65. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 655 Section 2 [18]. Note: Some of the data are courtesy of Imperial Oil Ltd.

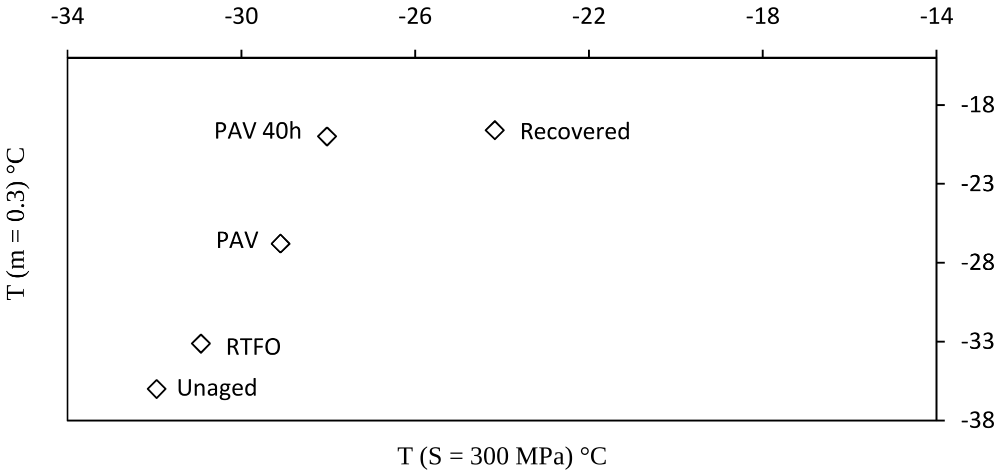

Figure 66. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 655 Section 3 [18]. Note: Some of the data are courtesy of Imperial Oil Ltd.

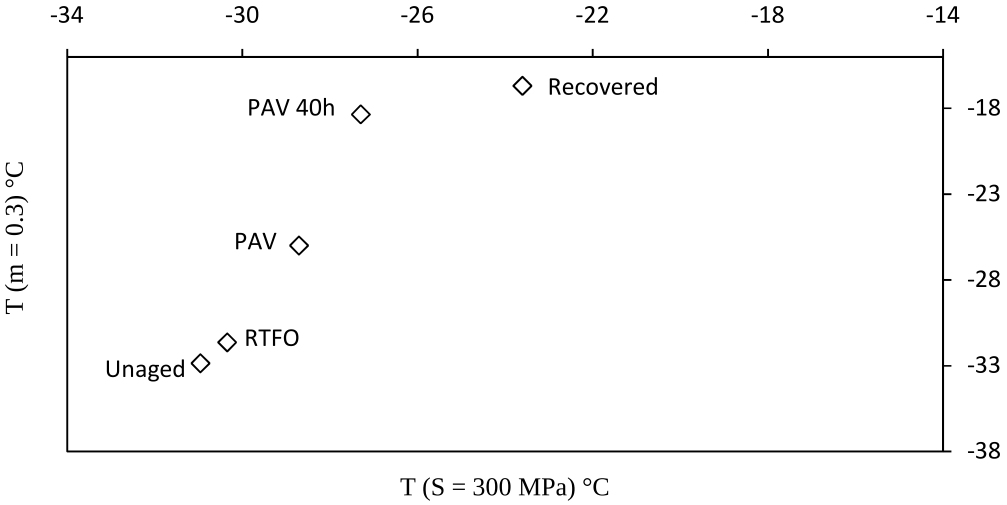

Figure 67. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 655 Section 4 [18]. Note: Some of the data are courtesy of Imperial Oil Ltd.

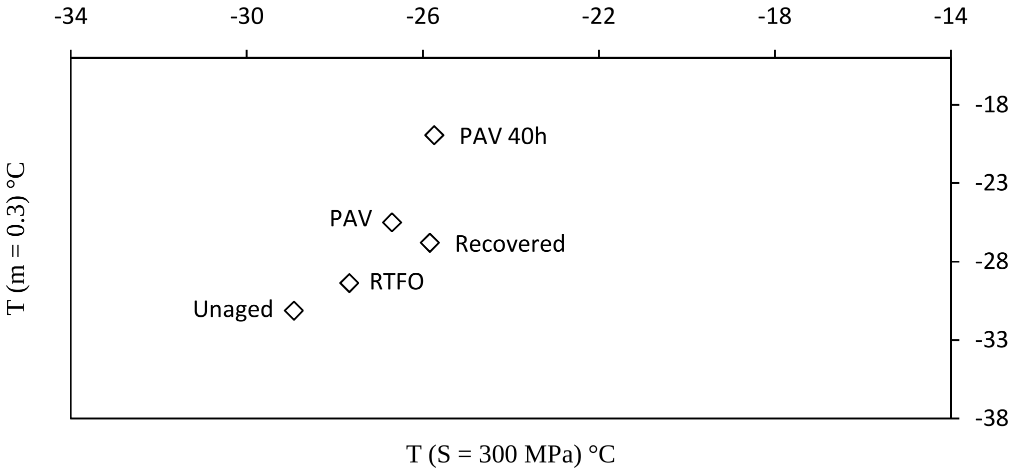

Figure 68. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 655 Section 5 [18]. Note: Some of the data are courtesy of Imperial Oil Ltd.

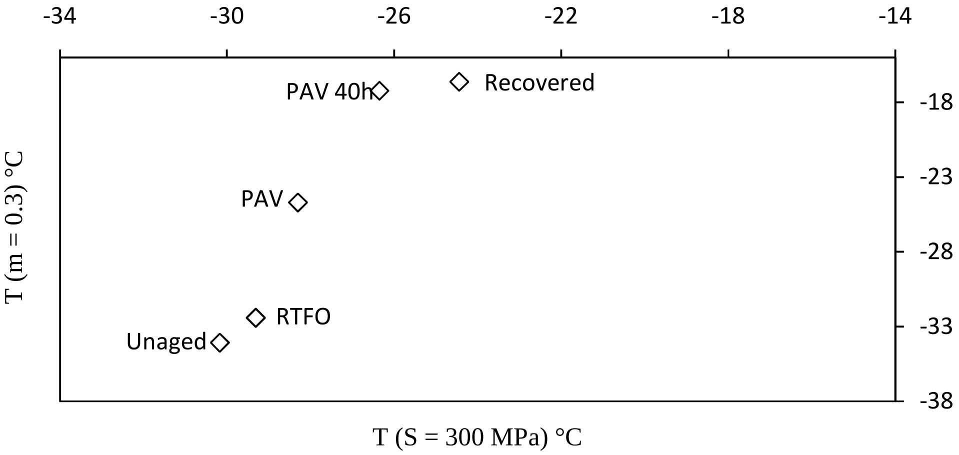

Figure 69. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 655 Section 6. Note: Some of the data are courtesy of Imperial Oil Ltd.

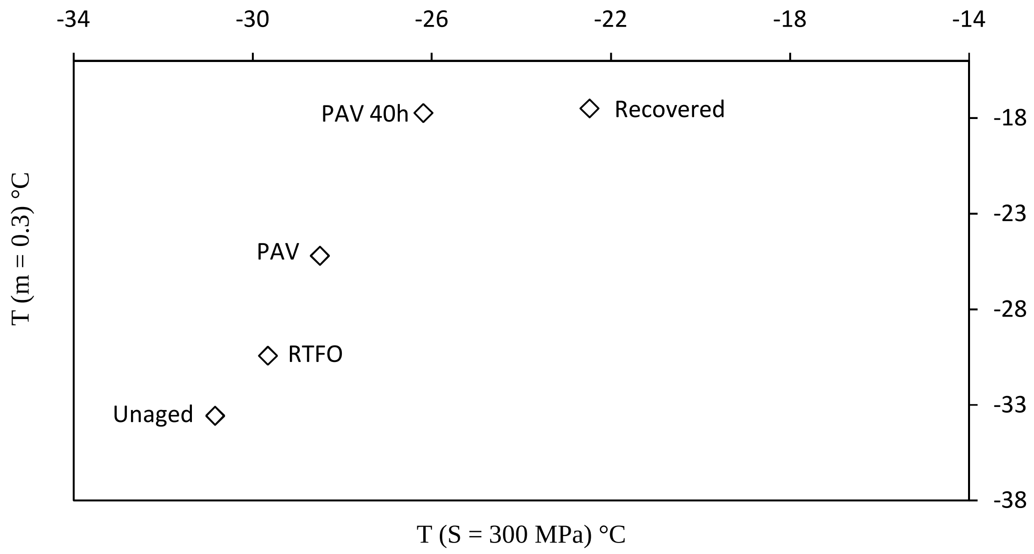

Figure 70. Temperature at which stiffness S = 300 MPa vs. temperature at which m-value = 0.3 of different aged asphalt cement for Highway 655 Section 7. Note: Some of the data are courtesy of Imperial Oil Ltd.

The results for Highway 655 show that nearly all the materials except the one for Section 655-1 are penalized rather harshly by the extended aging period losing anywhere from 4°C to 8°C from their regular Superpave® grade. The material from 655-1 loses a mere 2°C and this is likely the reason for why it has performed so well in service. This asphalt was produced with a base crude from Lloydminster known to have good resistance to oxidation and physical hardening due to a high content of naphthenes (branched saturates) and asphaltenes that are relatively compatible with their oils.

4.6 Fraction of Asphalt (Asphaltenes)

Asphalt contains mainly two constituents, asphaltenes and oils. Basically asphaltenes float in oils [4] and so the rheological property of asphalt also depends on the percentage of these fractions. The aging process has affect on the content of the fractions and so in this part the percentage of asphaltenes is calculated for available different aged asphalt cement. The purpose of this experiment is to compare the percentage of asphaltenes with all different aged materials which includes laboratory-aged as well as recovered material from the road. The error bars included provide the 3 percent of experimental error. All the samples are performed in duplicates that are reproducible and the average is used to plot the graphs.

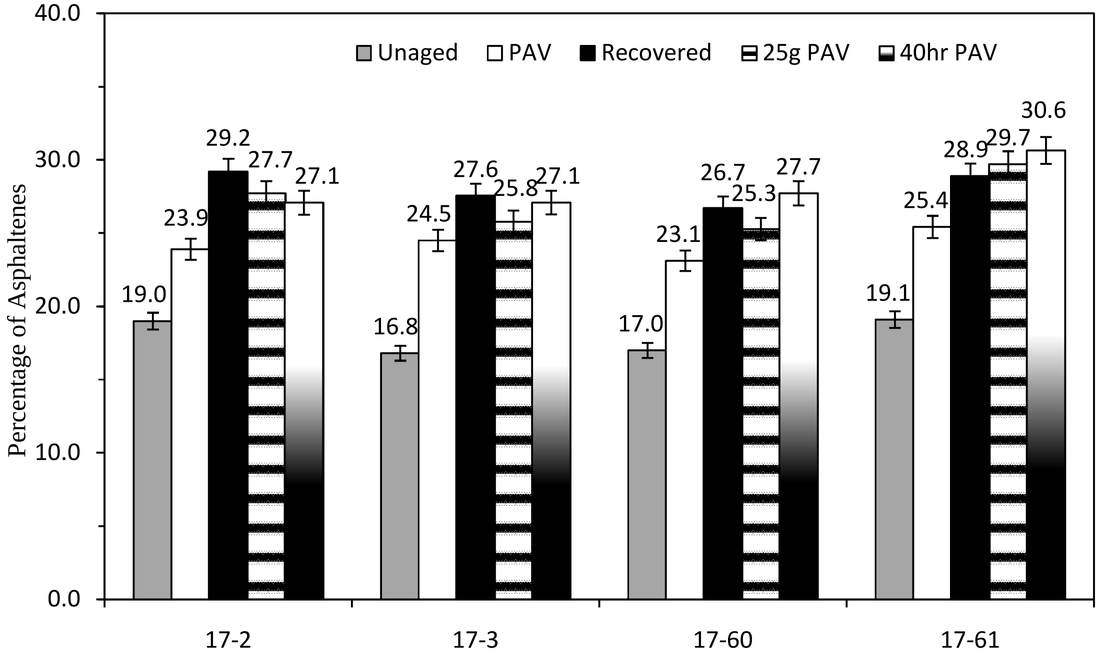

Figure 71. Comparison of asphaltenes percentage for Highway 17 test sections with 3 percent variation bar.

There are five different types of aged samples available for Highway 17 including the modified aging process of PAV. Figure 71 shows that percentage of regular PAV aged material is far from the recovered material from the road. It is an indication that regular

PAV method is insufficient to provide aged material that is similar to the service life. The percentage (asphaltenes) of either one of the modified PAV materials is closer to the recovered asphalt cement. Neither one of has shown consistency in all four sections and so it is hard to conclude which one is more effective. More work is needed to get further an understanding as to which one serves better or maybe other modifications are required to produce material that works for at least 8-10 years of service life.

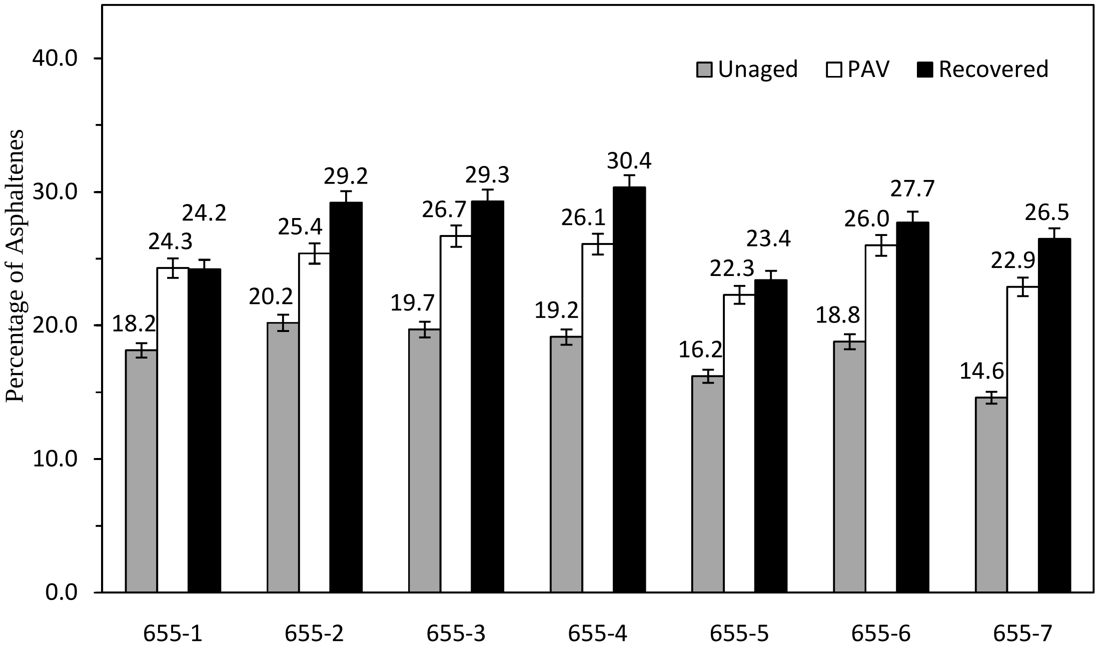

Figure 72. Comparison of asphaltenes percentage for Highway 655 test sections with 3 percent variation bar.

Figure 72 shows the percentage of asphaltenes for the Highway 655 sections with different aged asphalt. In this it is clearly shown that Sections 655-1 and 665-5 have almost similar percentages with the PAV material and these sections have performed well in service. But the interesting point is Section 655-4 which has the highest variation in percentage in PAV and recovered. The Section 655-4 is worst out of all the trials. The point here that one has to keep in mind is that all sections have the same PG asphalt cement.

The difficulty with all of these studies of the asphaltene contents and the carbonyl indices involves the fact that the construction variability is not considered because it is not certain that selected materials were not overheated during the production of the hot mix asphalt and the construction of the pavement. Another confounding factor is presented by the air voids content in the various locations. Higher air voids will provide conditions that are conducive to accelerated chemical aging due to the fact that oxygen can enter more easily. The air voids contents were not measured for these sites so that is another unknown that could have affected the findings.

Notwithstanding, the general trend for the aging at twice the length and half the film thickness is that the grades come closer to the recovered materials. Even an improvement of only 3°C means that future pavements can be constructed much closer to their intended 98% confidence level such as what was accomplished for Section 655-1. The potential savings from the implementation of improved chemical aging methods are in the hundreds of millions and billions of dollars in Ontario alone. Most northern pavements fail due to low temperature exposure and if this is better controlled the benefits to society can be enormous.

Chapter 5

Summary and Conclusions

Given the finding that are presented in this thesis, the following summary and conclusions may be given:

- The currently used RTFO/PAV aging protocol fails to age asphalt cements to a sufficient degree and produces materials that pass the grading criteria but have a tendency to fail in service.
- The currently used 1 hour conditioning time in the BBR fails to replicate the conditioning that asphalt cements experience in service and hence the specification criteria pass unstable asphalt cements that have a tendency to fail in service.
- The double-edge-notched tension (DENT) test appears to do a reasonable job at separating the good from the not-so-good asphalt cements.
- The chemical hardening tendency of asphalt cements is reasonably monitored by the carbonyl functional group except for those asphalts that have an incompatible phase structure (i.e., those with high paraffin oil contents will harden more rapidly than their carbonyl indices suggest).
- Increasing the PAV aging time to 40 h and/or reducing the weight per pan to 25 g would provide significant improvements to the current RTFO/PAV protocol which uses 20 h and 50 g.

The above findings should be further investigated with well controlled field trials and laboratory experiments.

Chapter 6

Further Work

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

1. Extraction of asphalt cement: Different solvents can have varying effects on the properties of the recovered asphalt cements.
2. Degradation of styrene-butadiene type polymers: The PAV does not appear to chemically age butadiene in any way as severely as this happens at more modest temperatures in service. This issue needs to be further investigated and modified protocols may need to be developed to improve the match with service aging.
3. Thinner films need to be investigated to see if volatilization is an issue in certain asphalt cements. Films with 25 g per pan are still significantly thicker than what is the typical film thickness in service (10-20 μm). Such thin films may be more prone to hardening from volatilization.
4. Oil exudation needs to be investigated in order to better replicate hardening in hot mix asphalt that has inferior quality, porous aggregate. Hence, experiments with finely dispersed aggregate should provide valuable insights into how this process can vary between different asphalt sources and aggregate types.

Once the above issues are dealt with the expectation is that user agencies of asphalt cement can do a much improved job at selecting the asphalt cement for a particular contract. The current service life of 20-40 years can easily be extended by a significant amount and premature failures where roads start to crack within their first few winters can be avoided.

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