RELATIONSHIP BETWEEN PHYSICAL AND CHEMICAL PROPERTIES

OF STRAIGHT AND RECOVERED ASPHALT BINDERS FROM

ONTARIO

by

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Abstract

Thermal and fatigue cracking are the major pavement distresses that contribute to a drastic reduction of the pavement's service life and performance in Ontario. Chemical oxidation and hardening of asphalt binders deteriorates its physical properties since physical properties of asphalts depend on its chemical composition. This thesis is aimed to establish a relationship between physical and chemical properties of asphalt binders. A secondary objective is to show the strong correlation between CTOD and temperature.

All recovered and straight Ministry of Transportation of Ontario (MTO) samples were investigated using conventional Superpave® test method dynamic shear rheometer (DSR) as well as improved MTO test methods such as extended bending beam rheometer (eBBR) and double-edge-notched tension (DENT) test. DENT test was conducted for all Ontario contract samples at three different temperatures based on their performance grade after three hours of thermal conditioning and compared the results in terms of essential work of fracture, plastic work of fracture and CTOD at different temperatures. Good correlation exists between CTOD and temperature according to the DENT data.

X-ray fluorescence (XRF) analysis was conducted to detect the presence of heavy metals such as zinc and molybdenum believed to have originated from waste engine oil. Fourier transform infra-red spectroscopy (FTIR) was performed to determine the abundance of functional groups such as carbonyl, sulfoxides, polyisobutylene, etc. XRF and FTIR analysis confirmed that most of the samples contain waste engine oil and/or oxidized residues, which is believed to be a root cause of premature pavement failures.

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Abbreviations and Acronyms

AASHTO   American Association of State and Highway Transportation Officials

ASTM   American Society for Testing and Materials

BBR   Bending Beam Rheometer

CTOD   Critical Crack Tip Opening Displacement

DENT   Double-Edge-Notched Tension

DSR   Dynamic Shear Rheometer

eBBR   Extended Bending Beam Rheometer

FTIR   Fourier Transform Infrared

HMA   Hot Mix Asphalt

kPa   Kilo Pacsal

keV   Kilo Electrovolt

LS   Laboratory Standard Test Method

mN   Milli Newton

MTO   Ministry of Transportation of Ontario

NSERC   Natural Sciences and Engineering Research Council of Canada

PAV   Pressure Aging Vessel

PG   Performance Grade

PI   Penetration Index

PIB   Polyisobutylene

RTFO   Rolling Thin Film Oven

SBS   Styrene Butadiene Styrene

SHRP   Strategic Highway Research Program

SUPERPAVE®   SUperior PERforming Asphalt PAVEment

TFOT   Thin Film Oven Test

WEO   Waste Engine Oil

WMA   Warm Mix Additives

XRF   X-Ray Fluorescence

Symbols

a   Length of a sharp crack, m

A   Temperature Susceptibility

b   Beam width, 12.5 mm

B   Specimen thickness, m

G^* Complex shear modulus

G'   Elastic modulus

G''   Loss modulus

h   BBR beam thickness, 6.25 mm

L   Ligament length, mm

P   Penetration at temperature T

%   Percent

π Pi (3.14)

S(t)   Creep Stiffness at time, t = 60 seconds

T   Temperature, K

T   Loading time, s

T_g Glass transition temperature

w	Angular velocity
W_e	Essential failure energy, J
w_e	Specific essential work of failure, J/m^2
W_p	Plastic or non-essential work of fracture, J
w_p	Specific plastic work of fracture, J/m^2
W_t	Total energy, J
w_t	Specific total work of fracture, J/m^2
β	Plastic zone shape factor
δ	Phase angle
τ	Shear stress
γ	Shear strain
δ_t	CTOD
σ_n	Net section stress or yield stress (N/m^2)

Chapter 1

INTRODUCTION

In this era, roads are the most important travelled way having stabilized base accessible for public traffic. Roads and highways can be considered as major infrastructure for all the economies in the country. It means, the countries without roads and highways are considered as underdeveloped. In North America, billions of dollars have been spent for the development of the highway transportation system. Canada spends about $10 billion and Ontario government spends about $3.8 billion annually for the construction and maintenance of provincial roads and highways [1].

Asphalt cement is a semi-solid material at normal temperatures, used in road construction, as a binder for aggregates and sand while in roofing industry, it is mixed with fine aggregate and fibers to produce roofing felt and sealing of flat roof [3].Generally, asphalt cement tends to be very stiff and brittle at low temperatures and viscous at high temperatures. Such extreme changes in properties lead to degrade the performance in the pavement. At low temperatures, the binder in the pavement becomes too stiff, resulting in low temperature cracking which is one of the most significant modes of asphalt pavement distress in northern climates. On the other hand, at high temperatures, the binder in the pavement becomes too soft and this causes rutting in the pavement. Rheology is one of the most important tools to ensure the satisfactory performance of the asphalt cement. The rheological characteristics of the asphalt can be determined by its chemical composition and physical arrangement of the molecules in a material. Changes in chemical composition and its structure alters the rheology of the asphalt. Asphalts are generally characterized by their physical properties rather than its chemical properties due to its inadequate

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findings. The detailed composition of asphalt cement is still a topic of interest for researchers. It is most essential to correlate the chemical properties of asphalt with pavement performance characteristics and physical properties as well [2].

1.1 Definition and Origin of Asphalt

Depending on its applications and the origin, asphalt has different names, definitions and descriptions. Asphalt is a black and sticky semi-solid glue used for road paving. In North America, it is called asphalt binder or asphalt cement while in the rest of world, it is called bitumen. According to the American Society for Testing and Materials (ASTM 1998), asphalt cement is defined as a *"dark brown or black cementitious material occurring in the nature or obtained by crude oil refining, where the pre dominate material is mainly bitumen"* [4]. The word "asphalt" originated from the Greek word *asphalto* meaning "secure" or "firm", which passed into late Latin and then into French (*asphalte*) and English "asphalt". It is believed that the expression "bitumen" was originated from the sacred language of Hindus "Sanskrit", in which "*Jatu-Krit*" means "pitch-creating" or "pitch producing" [5].

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"* [6]. According to the American Heritage Dictionary, *"a brownish-black solid or semi-solid mixture of bitumen obtained from nature deposits or as petroleum by-product is termed as asphalt that is used in paving, roofing and water proofing"* [6]. It is also defined by the American Association of State Highway Transportation Officials (AASTHO) as an, *"asphalt*

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based cement that is made from petroleum residues either with or without the addition of non-particulate organic modifiers".

1.2 Sources of Asphalt

1.2.1 Natural Asphalt

Asphalt lakes around the world are the major sources of natural asphalt. The natural asphalts mostly are found in Trinidad, Venezuela, Iraq, Southern California and a few other locations. About 2.7×10^{12} barrels of asphalts including tar sands has been estimated to exist in various locations around the world. About 95% of natural asphalt cement including tar sand is found in Canada, mostly in Northern Alberta [7]. Other sources of natural asphalt are rocks and Gilsonite. Caulking for boats, cement for jewellery, colouring material in paintings, sealing of water tanks and bathing pools, etc. are some of the early applications of naturally occurring asphalts [6]. In the 1860s, builders in Scotland used hot coal tar to bond stone together on roadways reducing dust and maintenance, which was the first modern application of asphalt.

1.2.2 Petroleum Asphalt

It is produced through the refining of petroleum. Petroleum crude oil is a complex mixture of different hydrocarbons. Upon the addition of lower-boiling hydrocarbons in the crude oil, petroleum asphalt can be separated from higher boiling hydrocarbons by precipitation.

The precipitated material consists of asphaltenes having an average molecular weight of 800 to 2,500 g/mol [8]. The synthetic production of asphalt from crude oil was started in the United States in 1902. The methods used to produce and process asphalt materials are as shown in Table 1.1.

Table 1.1: Methods used to produce and process asphalts [9].

Production/Process	Base Material	Product
Atmospheric and Vacuum Distillation	Asphalt-based Crude or Crude Mix	Asphalt Cements
Blending	Hard and Soft Asphalt, Asphalt Cements and Petroleum Distillates	Asphalt Cements of Intermediate Consistency Cutback Asphalts
Air-blowing	Asphalt Flux	Asphalt Cements, Roofing Asphalt, Pipe coating, Special Membranes
Solvent De-asphalting	Vacuum Residuum	Hard Asphalts
Solvent Extraction	Vacuum Residuum	Asphalt Components (Asphaltenes, Resin, Oils)
Emulsification	Asphalt, Emulsifying Agent, and Water	Emulsified Asphalts
Modification	Asphalts and Modifiers (Polymers, Chemicals, etc.)	Modified Asphalts

1.3 Pavements

1.3.1 Asphalt Pavements

Asphalt pavement concrete is also known as hot mix asphalt (HMA) pavement or flexible pavement. It is a mixture of course aggregates, fine aggregates and asphalt binders. HMA are generally produced by heating the asphalt cement to about 160°C and blending it at 5 weight percent with aggregate. The typical thickness of an asphalt concrete pavement is about 4-8 inches but in some cases it is as thick as 20 inches due to a high volume of traffic.

The unique nature of asphalt pavement concrete is its flexibility under loading. Hot mix asphalt are generally applied in 5-10 cm thick layers with the lower part of the pavement supporting the top layer known as the surface course. The aggregates in the lower layer are responsible to prevent rutting and fatigue cracking while the aggregates in the surface course are responsible for their friction properties and durability [10]. Mainly pavement structures contain three components as shown in Figure 1.1, i.e., the foundation, the base, and the surface, which are equally responsible in the overall performance of the road.

| Flexible Pavement | Rigid Pavement |
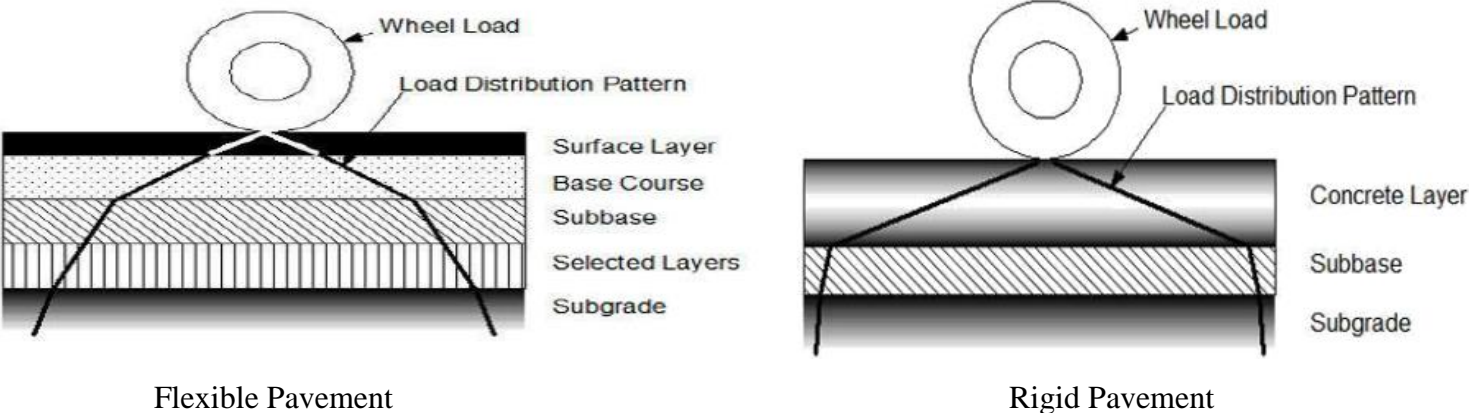
Figure 1.1: Load distribution in flexible and rigid pavements [11].

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1.3.2 Rigid Pavements

As shown in Figure 1.1, rigid pavements are constructed with one layer of Portland cement concrete (PCC). The rigid pavement has a high modulus of elasticity to distribute load over a wide area of subgrade. Excessive deformations due to heavier wheel loads are not recoverable.

1.3.3 Pavement Layers

HMA pavements are flexible pavements. Foundation thickness, performance grading of asphalt binders, aggregate sizes and air voids are the major factors to be considered for a good design of an asphalt pavement. A cross section of a flexible pavement structure is typically made up of several layers such as the surface course, the binder course, the base course, the sub-base and the sub-grade as shown in Figure 1.2.
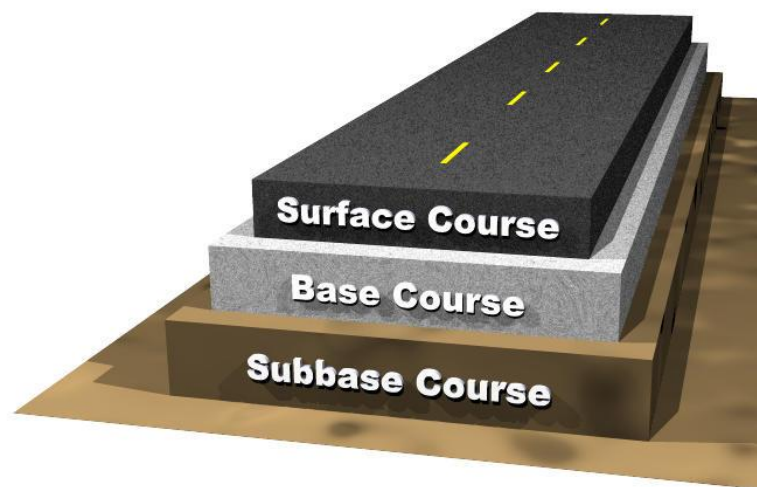
Figure 1.2: Basic flexible pavement structure [12].

1.3.3.1 Foundation

As shown in the Figure 1.2, foundation of the pavement is made up of sub-grade and sub-base. In the pavement system, sub-grade is the compacted soil layer of the foundation. Generally, sub-base layer is used in those areas where the sub-grade soil is extremely weak. Basically, foundation transmits stresses generated by construction traffic to the sub-grade without causing any distress on it.

1.3.3.2 Base

The base is the principle structural component of the flexible pavement. The base course should be designed with sufficient quality and thickness to prevent failure in sub-base or sub-grade. The base layer spreads the wheel load, so that the foundation is not over stressed. The base is said to be good, if it resists permanent deformation, fatigue cracking and can withstand stresses caused by the temperature gradients. The quality of the base course depends on the composition, physical properties and compaction of materials.

1.3.3.3 Surfacing

The surfacing consists of two layer. The upper layer is termed the "surface course" or "wearing course" and the lower layer termed the "binder course". The main function of the binder course is simply to distribute the stresses from the surface course to the base without overstressing. The surface course is made up of a mixture of different aggregates bound together with asphalt cement and visible to the road user. The surface course prevents the penetration of surface water to the base course, provides skid-resistant surface, resists the effects of extreme weather conditions,

deformation by traffic and fatigue, supports the strength of the pavement, and generates an acceptable level of noise.

1.4 Composition of Asphalt

Asphalt is a highly complex chemical mixture of molecules containing saturated and unsaturated aromatic as well as aliphatic compounds with an estimated 100-200 carbon atoms. The composition of asphalt depends on the type of crude oil from which it is derived. Very small amounts of heteroatoms like sulphur, nitrogen, oxygen present in the asphalt and contribute to its unique physical and chemical properties, i.e. sulphur reacts with oxygen easily and gets oxidized [13]. Asphalt contains trace amounts of metal such as vanadium, nickel, iron, magnesium and calcium, which act as finger prints to identify the source of an asphalt cement. However, asphalt consist of,

- Carbon 82-88%
- Hydrogen 8-11%
- Sulphur 0-6%
- Oxygen 0-1.5%
- Nitrogen 0-1%

Generally asphalt contains three basic types of molecules – aliphatic, cyclic, and aromatic. The aliphatic molecules are oily and waxy in nature, having linear, three-dimensional chain-like molecules, also called paraffins. The cyclic molecules are called naphthenics which are three-dimensional saturated rings of carbon atoms with various atoms attached to it. Asphalts can be separated into the following groups [6].

1.4.1 Asphaltenes

Asphaltenes are black and brown amorphous solids containing nitrogen, sulphur and oxygen, in addition to carbon and hydrogen. They are insoluble in n-heptane and considered to be highly polar and complex aromatic materials of a high molecular weight ranging from 1,000 to 100,000 g/mol. The higher content of asphaltenes increases hardness and viscosity of the asphalt, resulting in rheological changes in the asphalt.

1.4.2 Resins

Like asphaltenes, resins contain carbon and hydrogen with a small amount of oxygen, sulphur and nitrogen. They are polar in nature and acts as dispersing agents or peptizers for the asphaltenes. They appear dark brown in colour and are strongly adhesive to the aggregate in a pavement. The proportion of resins to asphaltenes in bitumen governs the sol-gel behaviour of the bitumen. The molecular weight of the resin ranges from 500 to 50,000 g/mol. Resins are soluble in n-heptane.

1.4.3 Aromatics

It contains the lowest molecular weight naphthenic aromatic compounds in the bitumen and provide a dispersion medium for the peptized asphaltenes. The average molecular weight of the aromatics ranges from 300 to 2,000 g/mol.

1.4.4 Saturates

Saturates contain straight and branched chain aliphatic hydrocarbons with alkyl-naphthenes and alkyl-aromatics. They are non-polar in nature, with an average molecular weight ranging from 300

to 2,000 g/mol. It contains both waxy and non-waxy saturates and its fraction forms 5 to 20% of the bitumen.

The fractions of saturates, aromatics, resins and asphaltenes directly affects the rheological properties of asphalt. At constant temperature, the viscosity of asphalt increases as the concentration of asphaltenes increases. Likewise, the constant ratio of resins to aromatics and increasing saturates, soften the asphalt. In contrast, addition of resins content, increases the viscosity of asphalt. The viscoelastic behaviour of asphalt can be explained by spring and dashpot models. All the molecules present in an asphalt contains two functional categories, i.e. polar and non-polar group. The polar molecules form a network and give the elastic behaviour of the asphalt while the non-polar high molecular weight molecules contribute to the viscous properties. It is expected that both polar and non-polar components should be existed in the balance form for the better performance in service [7]. At low temperatures, asphalt with large amounts of high molecular weights (non-polar) molecules may result in brittle failure whereas high polar content of asphalt gives more flexibility to asphalt.

1.5 Properties of Asphalt

Although the physical properties of an asphalt are direct results of its chemical composition, asphalts are generally characterized by its physical properties. But the failure mechanism also can be explained chemically.

1.5.1 Physical Properties of Asphalt

The most important physical properties of asphalt comprises durability, adhesion and cohesion, temperature susceptibility, aging and hardening.

1.5.1.1 Durability

It measures the ability of asphalt to retain its original characteristics in long-term service. Durability of asphalt binders primarily depends on the pavement performance. It can be tested in the laboratory by Thin Film Oven Test (TFOT) and Rolling Thin Film Oven (RTFO) test [10].

1.5.1.2 Adhesion and Cohesion

The tendency of two materials with dissimilar molecules clinging together is known as adhesion. It means adhesion is the ability of asphalt to stick to the aggregate in the paving mixture. Cohesion is the ability of asphalt to hold the aggregate particles firmly in place in the finished pavement. The loss of adhesion and cohesion occurs when water interacts or penetrates the interface between asphalt and aggregate. It can be measured by the ductility test.

1.5.1.3 Temperature Susceptibility

Temperature susceptibility plays a vital role in physical properties of asphalt. Asphalt binders are thermoplastic in nature, i.e. it becomes harder (more viscous) as their temperature decreases and softer (less viscous) on their temperature increases [14, 15].

1.5.1.4 Aging and Hardening

Asphalt binders harden during mixing, transportation, construction and in the pavement in-service. Hardening of the asphalt is the major cause for low temperature cracking in flexible pavement. The primary cause of hardening is oxidation. Physical hardening also takes place at low temperature due to its structural changes such as wax crystallization, asphaltenes aggregation and volume relaxation [16, 17].

1.5.2 Chemical Properties of Asphalt

The internal structure of an asphalt is generally predicted by the chemical constitution of the molecular species present in it. Basically, asphalt is composed of various hydrocarbons, small quantities of heteroatoms and traces of some metals. When asphalt is dissolved in n-heptane, maltenes get dissolved and asphaltenes precipitate out [6]. Maltenes are viscous liquid composed of resins and oils. Usually, resins are dark brown heavy liquids that provide stickiness in asphalt while light coloured oils act as a medium in which the asphaltenes and resins are carried. The change in proportion of maltenes and asphaltenes ultimately alters the properties of asphalt. There are a number of factors which are responsible for changing the proportions of maltenes and asphaltenes:

- High temperatures;
- Exposure to oxygen and light;
- Types of aggregate used in the pavement mixture; and
- Thickness of the asphalt film on the aggregate particles.

The changes occur in the proportion of maltenes and asphaltenes due to the evaporation of more volatile components, oxidation, polymerisation and other chemical reactions [14]. Asphalt can be considered as a colloidal system containing high molecular weight asphaltenes micelles dispersed in a low molecular weight maltenes. It is believed that micelles consist of asphaltenes in addition to an adsorbed sheath of high molecular weight aromatic resins that act as stabilizing solvating layer. There are two types of asphalts, i.e. sol-type and gel-type asphalts.

In asphalts with high quantities of resins and aromatics of adequate solvating power, the asphaltenes are well peptized (dispersed) and the resulting micelles have good mobility [6]. Such asphalts are referred to as sol-type asphalts as shown in Figure 1.3.
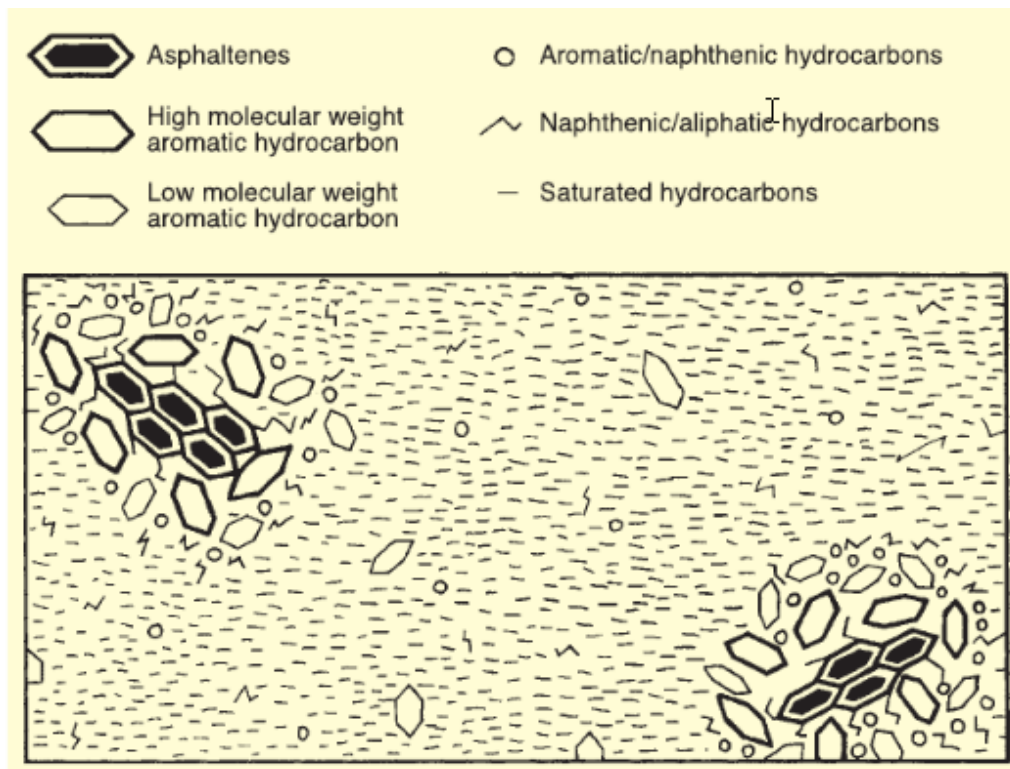
Figure 1.3: Sol-type asphalt [6].

They exhibit high ductility, high temperature susceptibilities, low value of complex flow, little thixotropic behaviour and low rates of age hardening [18]. On the other hand, insufficient quantities of aromatic maltenes fractions, cannot be well peptized with the asphaltenes. As a result, asphaltenes get associated together in the asphalt as shown in Figure 1.4. Such asphalts are known as gel-type asphalts. They have low temperature susceptibilities, significant thixotropic behaviour, low ductility and high rates of age hardening [6, 19]. Sol-type asphalts have better physical properties and resistance to cracking than gel-types.
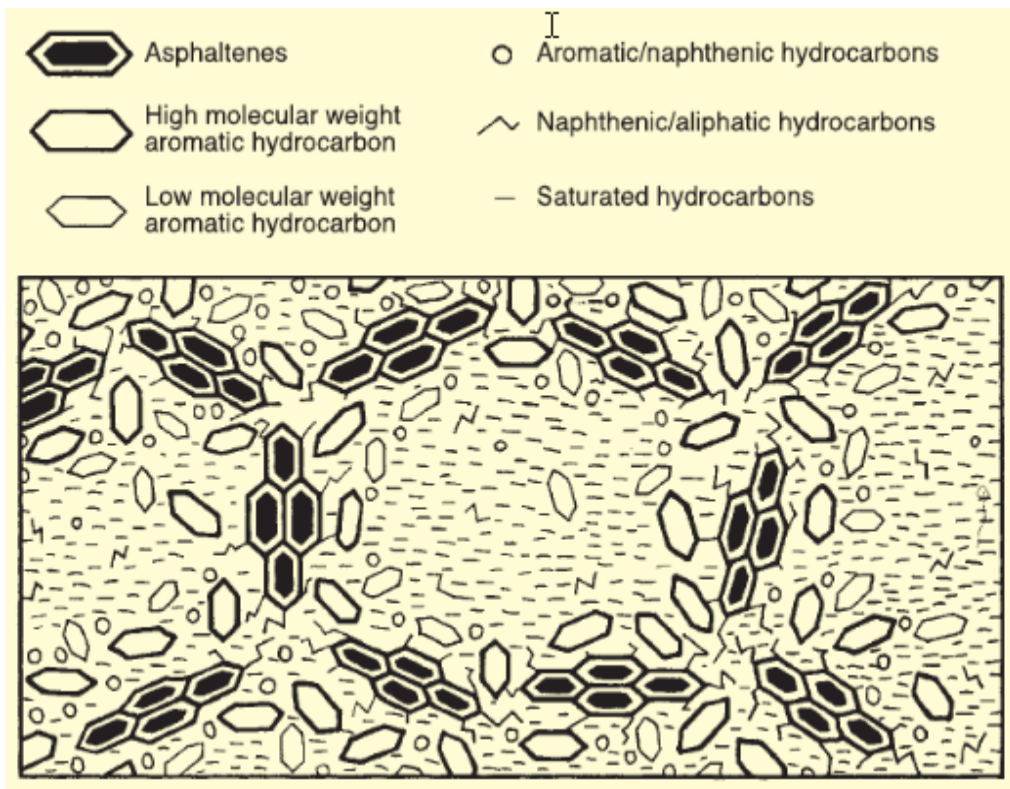
Figure 1.4: Gel-type asphalt [6].

1.6 Deterioration of Asphalt Pavement

The process by which distress developed in the pavement due to traffic loading and environmental conditions is known as deterioration of asphalt pavement. Due to extremely high strength of the

asphalt pavement, it became a widely used material for many pavement applications, like provincial and federal highway projects. Deterioration of constructed asphalt pavement is natural. It might be due to various reasons such as ultraviolet exposure, rain, weather conditions, asphalt mix design, and traffic frequency during construction [11]. The premature deterioration of asphalt pavement occurs due to failures in construction or human error. It is expected that service life of the asphalt pavement is 25 years, if it is constructed and maintained properly.

Factors that cause deterioration of asphalt pavements:

- Sudden increase in traffic loading especially on the new roads designed for lesser traffic.

- Aging or oxidation of asphalt in the presence of sunlight; breaks down and dries out the flexible asphalt that binds the aggregate together. As a result, ravelling and shrinking appear where water easily penetrates the surface.

- The exposure of the chemicals including gas and oils soften the asphalt and lead to break down more rapidly.

- Poor drainage system and lack of proper maintenance, causes the water to penetrate the asphalt and washes out the base underneath it. Hence, the top layer gets detached from the lower layer, and finally it breaks and collapses.

- Temperature variation ranges from below zero to $50^{\circ}C$, causes cracking of the pavement.

- Improper temperature of asphalt during mixing leads to pavement failure i.e. overheating of asphalt reduces the binding property and the compaction will not be proper if the temperature is lowered.

1.6.1 Types of Deterioration

- Cracking: There are different types of cracking that shortens the service life of the asphalt pavement. The most common types of cracking are as follows.

  ➢ Fatigue Cracking

  ➢ Longitudinal Cracking

  ➢ Transverse Cracking

  ➢ Block Cracking

  ➢ Slippage Cracking

  ➢ Reflective Cracking

  ➢ Edge Cracking

- Distortion (Surface Deformation): Improper pavement construction leads to surface deformation, which is accompanied by cracking. It might be the major cause of traffic hazard. The main types of distortions are rutting, corrugation, shoving, depressions, and swell.

- Disintegration: The progressive breaking up of the asphalt pavement into loose pieces is known as disintegration. Reconstruction of the pavement should be done if the disintegration is not repaired on time. Potholes and patches are the two common types of disintegration.

  ➢ Potholes: Potholes are the bowl-shaped holes mostly seen in the area of poor drainage, when the pavement disintegrates under traffic loading.

  ➢ Patches: The portion of the pavement that has been removed or replaced is known as patches, which is generally used to cover a utility trench [20, 21].

1.7 Performance Grading of Asphalt Binders and Superpave^{TM} Testing

Generally, asphalt binders are classified according to their performance and physical properties, and depend on the climate and traffic of that location. Performance grade of the asphalt binder can be determined by conventional testing methods such as penetration, softening point, and viscosity tests. These methods cannot predict the low temperature properties of the binder. To overcome such limitations of conventional grading tests, new specification grading system was developed under the Strategic Highway Research Program (SHRP) in USA, known as the Superpave^{TM} (SUperior PERforming Asphalt PAVEments) [22, 23]. It involves the aging of the asphalt binders using RTFO and PAV followed by measuring their properties using DSR and BBR [24]. The purpose of such performance grading system was to correlate the binder properties to pavement performance especially with regards to low temperature cracking, rutting, fatigue cracking, which are the major destresses of the asphalt pavement. Aging behaviour, applied load (stress) and climatic conditions are the factors responsible for the determination of the performance of asphalt binders.

According to the Superpave specification, grades of asphalts can be expressed as Performance Grade (PG) or Performance Grade Asphalt Cement (PGAC) XX-YY. Here, XX represents the high temperature in degree Celsius that the pavement is expected to reach and –YY represents the low service temperature expected. An example, of PG binder designation is PG 64-28. The first number 64 is the high temperature working limit of the asphalt cement and the second number -28 is the low temperature limit based on the Superpave test methods. It is expected that, the asphalt binder will be able to resist rutting at a high temperature limit of 64º and thermal cracking at a lowest minimum temperature of -28ºC. According to Superpave specification, XX can be

determined by DSR at intermediate and high temperature for failure properties like rutting and fatigue. While –YY can be determined by BBR at low temperature for thermal cracking of asphalt.

1.8 Scope and Objectives

Low temperature cracking and fatigue cracking are the major causes of premature failures of asphalt pavements in Ontario. In fact, Ontario government spends huge sums of money annually for the reconstruction and rehabilitation of distressed asphalt-based road networks. In order to reduce the expenditures, and ensure the efficient traffic flow and safety to the road users, distress survey should be performed to determine the type of distress, severity and quantity of distress present on the pavement surface.

The aim of this thesis is to conduct a comprehensive evaluation of physical and chemical properties test methods and to utilize the results to evaluate the resistance to fatigue and thermal cracking of a number of asphalt samples. The main objectives were,

❖ To compare the physical and chemical properties of recovered and straight binder samples.

❖ To use dynamic shear rheometer (DSR), extended bending beam rheometer (eBBR), and double edged notched tension (DENT) tests to assess the low temperature cracking performance and fatigue cracking properties of virgin and recovered MTO samples.

❖ To measure the ductility of 10 Ontario contract samples using double-edged-notched tension (DENT) test at three different temperatures either 5°C, 10°C, 15°C, 20°C or 25°C based on their performance grade, after three hours thermal conditioning under the loading rate of 50 mm/minute until failure takes place. In this test, different PG graded samples were tested at the same temperature of 15°C.

❖ To perform the chemical properties testing methods like Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF) tests. These results were correlated with physical performance of binder samples.

Finally, the results obtained from different physical and chemical testing were correlated to predict the performance of the pavements and its mode of failures.

Chapter 2

BACKGROUND AND LITERATURE REVIEW

2.1 Reversible or Physical Hardening of Asphalt

Physical hardening is a reversible process in which stiffness of asphalt increases during isothermal storage at low temperature due to its structural changes [16]. On the other hand, the physical hardening of asphalt is completely removed, when it is heated above room temperature. Physical hardening in polymers was first reported by Struik [25]. The physical hardening of the asphalt binders maybe affected by the source of binders, modification of binder, glass transition behaviour, thermal history, etc. [26]. When asphalt binders are cooled down from high temperatures, the volume decreases due to the reduction of free volume and finally it attains equilibrium. When it reaches the glass transition temperature, the material continuously shrinks isothermally, reducing the molecular mobility due to decrease in free volume. As a result, the viscoelastic properties change with time, and the material hardens [25, 27]. In the 1950s, Brown et al. described the terms "steric hardening", where hardening process was considered as a slow isothermal sol-gel transformation [28]. From the recent study, it has been reported that the hardening rate also depends on the chemical composition of the asphalt binder such as length of molecular chains, wax content, etc. According to Kriz et al. physical hardening may occur at temperatures well above T_g due to partial crystallization of some components of the asphalt binder [15, 26]. Age hardening is caused by the following factors [21]:

- ❖ Oxidation: Oxidation takes place when oxygen reacts with asphalt binder during hot mixing, construction and in-service periods.

- ❖ Volatilization: During HMA production, the lighter constituents of the asphalt evaporate, which is known as volatilization.

- ❖ Polymerization: Larger molecules formed after polymerization can be considered a cause of hardening of asphalt.

- ❖ Thixotropy: The setting nature of an asphalt binder in unagitated condition is known as thixotropy. It causes an increase in viscosity and eventually hardening the binder. The HMA pavements with little or no traffic are generally affected by hardening due to thixotropy.

- ❖ Separation: The removal of the oily components, resins or asphaltenes from asphalt binder by selective absorption is known as separation.

- ❖ Syneresis: The separation of less viscous liquids from more viscous asphalt binder causes the hardening due to changing its physical or chemical properties.

2.2 Chemical and Physical Aging

Age hardening of asphalt mixtures is an irreversible process, ultimately reducing the durability of the pavements. There are a number of factors that influence asphalt aging like oxidation, volatilization, steric or physical factors, exudation of oils etc. On the basis of such factors aging can be classified into two types; chemical aging and physical aging. Asphalt binders is composed of organic substance, which are directly affected by external influences like oxygen, ultraviolet radiation, and temperature, resulting the changes in structure and composition of the asphalt molecules. Chemical aging occurs when there is an oxidation in asphalt binder during hot-mixing, constructions and in-service periods. The oxidation will make the asphalt binder becoming harder

and less flexible. The degree of oxidation depends on temperature, time and thickness of the film [6]. As already discussed in the previous section, physical aging takes place when the asphalt binder is kept at a low temperature over a long period of time. The fundamental reasons behind chemical and physical aging are as follows [29]:

- Loss of oily compounds by adsorption or volatilization.

- Changes in the chemical composition of asphalt.

- Reorientation of asphalt molecules and slow crystallization of waxes.

Aging of asphalt binders can be classified further into two types, i.e. short-term aging and long-term aging. The aging behaviour of asphalt binders are simulated in the laboratory to evaluate the effect of the short term and long term service condition of the pavement. The aging of asphalt that takes place during mixing, transportation and construction is known as short-term aging. It occurs due to rapid volatilization and oxidation of thermally unstable and volatile components. The short term aging can be simulated in the laboratory by the Rolling Thin Film Oven (RTFO) test. In contrast, the aging of the asphalt takes place when the hot mix asphalt is exposed to different climatic conditions, especially at low-temperatures and heavy traffic volumes between 8-10 years in service is called long term aging. It can be simulated in the laboratory by Pressure Aging Vessel (PAV) test. Asphalt film thickness and void content of the mixture play a vital role for the hardening of asphalt on the road [6, 30].
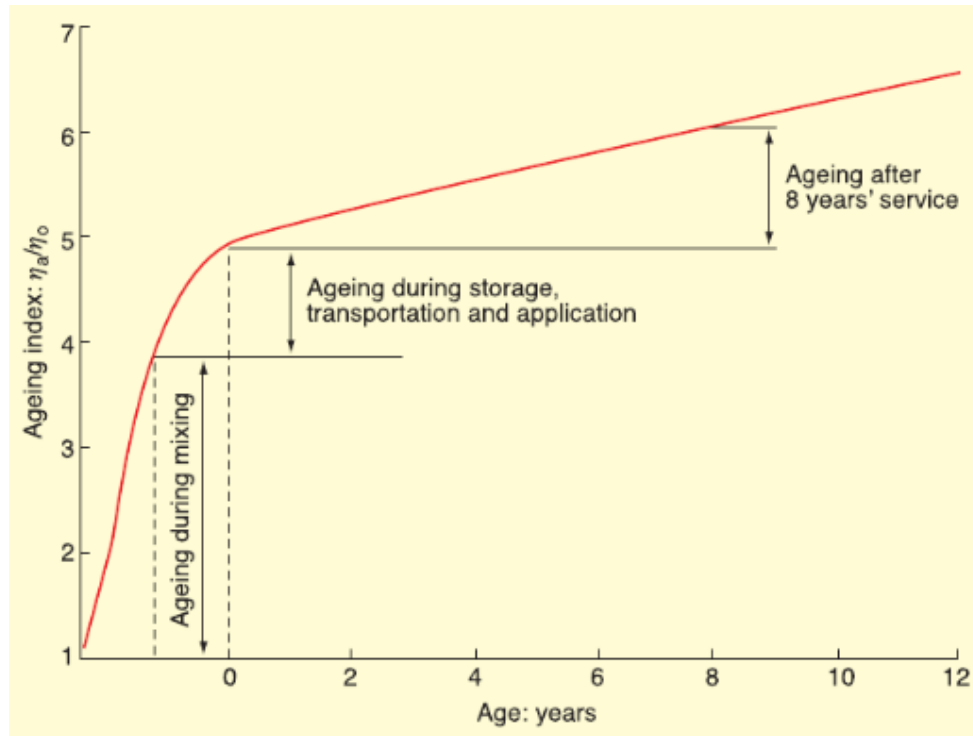
Figure 2.1: Aging of asphalt binder [6].

2.3 Distresses in Asphalt Pavement

The failure modes in asphalt is also known as distresses in asphalt pavement. Generally, it is expected that the asphalt used in the pavement must remain viscoelastic in all weather conditions, but it does not happen practically. During summer, it becomes soft and causes rutting or permanent deformation. While during winter all the neutral molecules in the asphalt arrange themselves into organized structural forms. As a result it hardens and becomes prone to thermal cracking. Mainly, there are two factors responsible for the failure of asphalt pavements, i.e. structural factors and environmental factors. Rain, sunlight, oxygen, chemicals, thermal stresses, disintegrations, and distortions with repeated traffic load over a period of time are the additional factors responsible for the failure of asphalt pavement. The typical life span of flexible asphalt pavement is considered

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to be between 20 to 30 years. Several factors that affect the asphalt pavement lifecycle [31] are discussed below;

- Initial design and construction: The life of the pavement can be significantly reduced by poor quality materials or poor construction procedures. So, pavement structure must be designed to withstand the traffic loading in that particular area.

- Environmental factors: Wet and humid environment ultimately weakens the subgrade load-bearing capacity. In contrast, hot and dry climates accelerate oxidation of asphalt resulting the premature failure of the road.

- Traffic loading: Heavy traffic loading adversely affect the life of pavement structures. But too little traffic loading is also detrimental to the asphalt pavement.

- Upkeep and maintenance: Timely and effective maintenance can increase a pavement's life. Crack sealing and seal coating can slow down the rate of oxidation and prevent water from seeping under the pavement [32].

The common types of pavement distresses are rutting (permanent deformation), fatigue cracking, thermal cracking, and moisture damage [33].

2.3.1 Rutting (Permanent Deformation)

Rutting is a surface depression in the pavement that occurs due to unrecoverable strains coming from repeated heavy traffic loading at high temperature during summer [34]. Insufficient compaction during the construction, improper mix design, and heavy traffic load at low frequency are the major reasons for rutting. It results the formation of ruts or tracks in the asphalt surface layers as shown in Figure 2.2. Ruts filled with water can cause vehicle hydroplaning. Rutting can be dangerous since it pulls vehicles towards rut paths. Hence, rutting not only reduces the pavement service life but it may also affect the safety of highway users. The rutting behaviour of

asphalt binders can be predicted in the laboratory using a dynamic shear rheometer (DSR). The rutting resistance factor, G*/sinδ (where G* is the complex shear modulus and δ is the phase angle), helps to predict rutting behaviour.

Figure 2.2: Permanent pavement deformation [35].

2.3.2. Fatigue Cracking

Fatigue cracking is caused by cyclic loading of vehicles that induce the stress which is more than the fatigue limit of the pavement under moderate and low temperature conditions. It is also known as alligator cracking because it looks like the skin of an alligator. In thin pavements, cracking starts at the bottom of the asphalt surface where tensile stress is the highest, then propagates to the surface. In thick pavements, cracking starts from the top area. After repeated traffic loading, transverse cracks connect with longitudinal cracks forming a pattern the same as an alligator's skin as shown in Figure 2.3. Poor compaction during construction, inadequate structural design, heavy traffic loading, loss of base or sub base due to poor drainage and stripping are the major causes

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responsible for fatigue cracking. Early maintenance of the cracks/potholes is one of the best ways to reduce the fatigue cracking. The fatigue behaviour of asphalt pavements can be predicted by the using fatigue cracking resistance factor, G*x sin δ, obtained from dynamic shear rheometer (DSR) test.

Figure 2.3: Fatigue cracking (alligator cracking) [36].

2.3.3 Thermal Cracking

Thermal cracking is also known as low temperature cracking or transverse cracking. Low temperature cracking is the most prevalent distresses found in Canada and the northern United States. It occurs due to the large drops of temperature. When the temperature drops, the asphalt binder in the pavement tries to shrink. The cracks are formed when the tensile stresses build up to the critical point as shown in Figure 2.4 [37].

Figure 2.4: Thermal cracking [38].

This type of cracking is observed perpendicular to the pavement's central line of the roadway. The existence of transverse cracks leads to the other type of degradation of the pavement structure, i.e. frost heave of the pavement occurred in the winter. Water entered inside the pavement weakens the pavement base and sub-base, resulting in deterioration of the pavement.

When the temperature of pavement is below the glass transition temperature, micro cracks are formed. As a result, stresses build up in the restrained asphalt pavement is greater than the material strength, leading to the formation of transverse cracks along the pavement. These cracks are formed as a result of single event thermal cracking and thermal fatigue cracking [38]. Additional transverse cracking can be observed due to freeze and spring thawing cycle, heavy traffic and

repetitive loading is known as load or thermal distress cracking. Field observations show that the single event thermal cracking is the most significant contributor to transverse cracking.

Cold temperature and faster cooling rates lead to greater susceptibility of the asphalt cement to thermal cracking. The pavements are more susceptible to thermal cracking, as the pavement gets older and it happens due to increase in stiffness of aging in asphalt binder [39]. Good pavement structure geometry factors such as pavement thickness, width and subgrade types help to reduce thermal cracking. Aggregates used in pavements should possess some characteristics such as low-freeze thaw loss, low absorption and high abrasion resistance in order to resist thermal cracking. It shows that factors such as material, geochemical and environmental conditions have a great impact on the ability of a particular pavement to resist low temperature cracking.

2.3.4 Moisture Damage

Moisture susceptibility is a major cause of failure in HMA pavements. In the presence of water, the bond between asphalt binder and aggregate becomes weak, resulting the stripping [40]. As shown in Figure 2.5, the deterioration of asphalt pavement due to loss of adhesion between asphalt binder and aggregate or loss of cohesion within the binder due to water, is known as moisture damage [33]. Stripping causes fatigue cracking after rutting. Poor asphalt binder, air voids, lack of proper compaction, excess dust, lean mixes, poor drainage are the major reasons for moisture damage in asphalt [41]. Moisture damage can be prevented by proper drainage, proper compaction during construction, good quality asphalt binder, use of antistripping agents and aggregates with rough surfaces.

Figure 2.5: Moisture Damage [42].

2.4 Viscoelastic Nature of Asphalt

The performance of asphalt binder in governed by its viscoelastic properties which is characterized using the stress strain behaviour of the materials in response to load. Viscoelastic nature of asphalt binder depends on climatic conditions such as temperature and loading time. Asphalt binder behave like purely elastic material at low temperatures, viscous material at intermediate temperatures. But at high temperatures they have a tendency to flow as freely as other liquids, indicating their viscous nature. A typical response of elastic, viscous and viscoelastic materials with applied stress is as shown in Figure 2.6.

An elastic material has its ability to resist a distorting stress and to return to its original shape when the stress is released. As shown in Figure 2.6 (b), an elastic material experiences recoverable

deformation on applying a constant load. When a constant load is applied to an elastic material the strain of material and the applied stress are related as,

$$\tau = G\gamma \qquad\qquad - - - - - - - - (1)$$

Which is also known as Hooke's law.

Where,

τ = Shear Stress

G = Modulus

γ = Shear Strain

Hence, the stiffness of material or its ability to resist deformation depends on its modulus. In contrast, at constant load, viscous material shows constant deformation until the load is released. But the deformation will not recovered as shown in Figure 2.6 (c), after the load is removed. Viscoelastic materials experiences partial recovery of the deformation resulting from creep loading as shown in Figure 2.6 (d). The immediate deformation is related to the elastic response of material and time-dependent deformation is related to viscous response of materials [43].

(a) Applied stress

Time
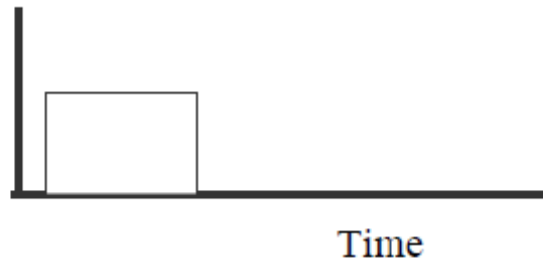
(b) Elastic response

Time
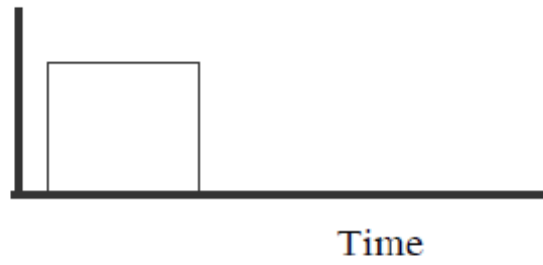
(c) Viscous response

Time
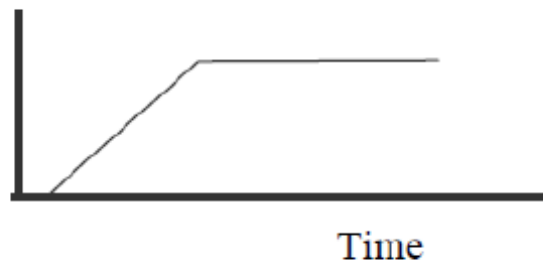
(d) Viscoelastic response

Time
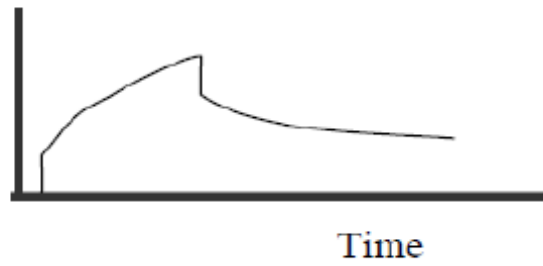
Figure 2.6: Mechanical response of elastic, viscous and viscoelastic materials under constant stress [43].

2.5 Chemical Characterization of Asphalt Binder

Generally, asphalts are characterized by its physical properties. But in reality, physical properties of asphalts depends on the chemical composition of the asphalt. When asphalt is subjected to chemical oxidation, hardening of the asphalt takes place which deteriorates its physical properties. It shows that oxidation of asphalt greatly affects its physical and chemical properties and over time makes the asphalt binders harder and stiffer. When the binders get oxidized, Carbonyl (-C=O) groups are formed that increase the polarity and associate with other compounds. As a result of these associations, a less soluble asphaltenes materials are formed leading the hardening of asphalt. 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 [44].

2.5.1 Oxidation Effect on Fractions of Asphalt

The most widely used fractionation scheme to separate asphalt into generic fractions was developed by Corbett [45]. The four Corbett fractions in order to increase their molecular polarity are saturates, naphthene aromatics, polar aromatics and asphaltenes. The saturate fraction is highly resistant to ambient air oxidation due to its low chemical reactivity. Corbett and Merz observed that during the 18-year service period, no measurable loss of saturates fraction due to oxidation occurred. In contrast, oxidation of other fractions such as naphthene aromatics, polar aromatics and asphaltenes changes from the more non-polar fractions to more polar fractions as oxygen – containing functional groups are formed in the asphalt molecules. During oxidation, a net loss of naphthene aromatics and polar aromatics, result the increase in the asphaltenes fraction. The uptake of oxygen by the generic asphalt fractions and the formation of oxygen – containing functional groups was further studied. King and Corbett found that the saturate fractions was relatively inert

to the reaction with oxygen uptake. The naphthene aromatics showed slight reactivity and aromatic fractions showed no reactivity [46, 47]. But the Corbett polar aromatic fraction and the Knotnerus resin and asphaltenes fractions were highly reactive with oxygen. Peterson et al. [48] ranked the relative reactivity with atmospheric oxygen of saturates, naphthene aromatics, polar aromatics and asphaltenes fractions as 1:7:32:40 respectively. It has been shown that the amount of ketone formed due to oxidation is linearly related to the increases in log viscosity of the asphalt i.e. viscosity of asphalt increases as a function of ketone formation [49].

2.5.2 Oxidation Reaction Mechanism

The types of oxidation products of different asphalt are similar regardless the source of asphalt binders. The mechanism of oxidation of asphalt is complicated. According to Dorrence et al. [50] ketones are formed at the first carbon of an alkyl chain attached to an aromatic ring, which is the benzylic carbon position. The tertiary benzylic carbon is likely to be the most reactive ketone and hydrogen on tertiary benzylic carbon is very reactive and is easily removed during oxidation.

Mill and Tse [51] observed four different asphalts using NMR spectroscopy and concluded that out of the total benzylic hydrogen, 6-11 % is from the tertiary benzylic carbon. The carbon-hydrogen bond of unbranched aliphatic hydrocarbons are less reactive toward oxidation in comparison to carbon-hydrogen methane bond. No measurable amount of esters and only trace amount of new carboxylic acids were found in laboratory or pavement aged asphalts [52]. The hydrocarbon oxidation reaction almost stops with the formation of ketone at pavement aging temperature except for the anhydride formation reaction.
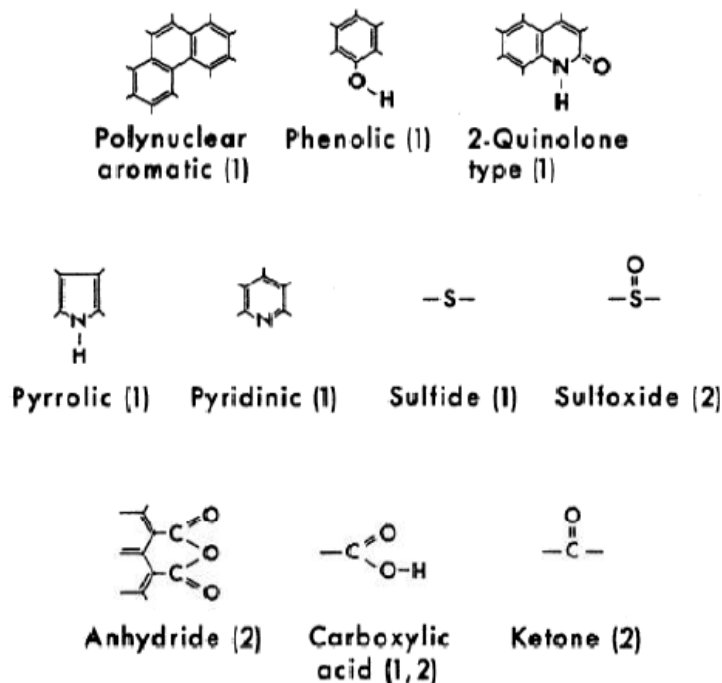
Figure 2.7: Chemical functionalities that are present in asphalt naturally (indicates 1) and formed during oxidation in asphalt (indicates 2) [53].

The chemical functional groups were determined by using Functional Group Analysis (IR Spectroscopy), are carboxylic acids, anhydrides, ketones, 2-quinolone types, sulfoxides, pyrrolic types, and phenolic types [54] as shown in Figure 2.7. Generally sulphur is present in asphalt as sulphides. Alkyl substituted sulphur are more reactive toward oxidative aging to yield sulfoxides [55]. Nitrogen is present in several forms the slightly acidic pyrrolic type to the more basic, strong interacting pyridine type [56]. An oxidative aging, the nitrogen types and cyclic sulphur molecules are unreactive. Hence, ketones and sulfoxides are considered as major products during oxidative aging [57].

2.6 Test Methods

2.6.1 Conventional Test Methods

During the early 1990s, some conventional test methods such as penetration, softening point, and viscosity test were employed to test asphalt binders. Based on these methods, penetration (PEN), viscosity (AC), and aged residue (AR) were used as grading systems. These test methods are not based on the pavement performance, hence, considered as empirical methods [58]. There are four conventional grades which are used to evaluate asphalt binder properties i.e., penetration grade, cutback grade, oxidized grade, and the hard grade [6]. Out of the four, penetration grade is the only one used for paving roads.

2.6.1.1 Penetration Test

The penetration test is the oldest method for grading the asphalt cement. In 1888, H.C. Bowen of the Barber Asphalt Paving Company introduced the penetration test. The basic assumptions of the penetration test is that, the less the viscous the asphalt, the deeper the needle will penetrate under a specified condition of load, time and temperature [59]. In this test, a specified needle is used to penetrate a sample of asphalt at a standard conditions of temperature, time and load with the values of $25^{o}C$, 5 second and 100 g respectively. The unit used for this method is deci-millimeters i.e., 0.1 mm. For example, 70 pen asphalt cement has a penetration of needle at $25^{o}C$ of 7 mm, means 70 times 0.1 mm [60].Thus, the penetration depth is correlated with the performance of the asphalt binder. It has been shown that asphalt binders with a high penetration number are used in cold climates while in hot climates low penetration numbers are used. The consistency of asphalt

binders related to temperature change can be determined by plotting the logarithm of penetration (p) against temperature (T).

$$LogP = AT + k \qquad\qquad\qquad\qquad\text{- - - - - - - - - - (2)}$$

Where,

P = penetration at temperature T

A = temperature susceptibility

K = constant

The penetration index (PI) is related with temperature susceptibility (A) by the following equation,

$$PI = \frac{20(1-25A)}{1+50A} \qquad\qquad\qquad\text{- - - - - - - - - (3)}$$

Here, PI is obtained from penetration measurement at two different temperatures T_1 and T_2 by the following equation,

$$A = \frac{\log(pen\ at\ T_1) - \log(pen\ at\ T_2)}{T_1 - T_2} \qquad\qquad\text{- - - - - - - - - - (4)}$$

The penetration index value can be used to determine the stiffness of asphalt cement at any temperature and loading time [61].

Figure 2.8: Penetration test equipment [62].

2.6.1.2 Softening Point Test

The softening point test is also known as Ring and Ball test. As shown in Figure 2.9, asphalt is poured in two shouldered brass rings and allowed to cool down until it solidifies, according to ASTM D36-95 Method [63]. 3.5 grams of steel balls are placed on the top of asphalt in the centre of the rings and heated at a constant rate at $5^{o}C$ per minute in a liquid bath inside the beaker. Distilled water is used as a heating medium for temperature range of 30 to $80^{o}C$, ethylene glycol at 30 to $110^{o}C$ and glycerin at 80 to $157^{o}C$. The arithmetic mean of the temperature at which two rings containing the same sample soften and allow each ball to pass through the asphalt to fall a distance of 25 mm is noted as the softening point [64]. Hence, this method is useful to classify asphalts based on their tendencies to flow at the high temperatures.
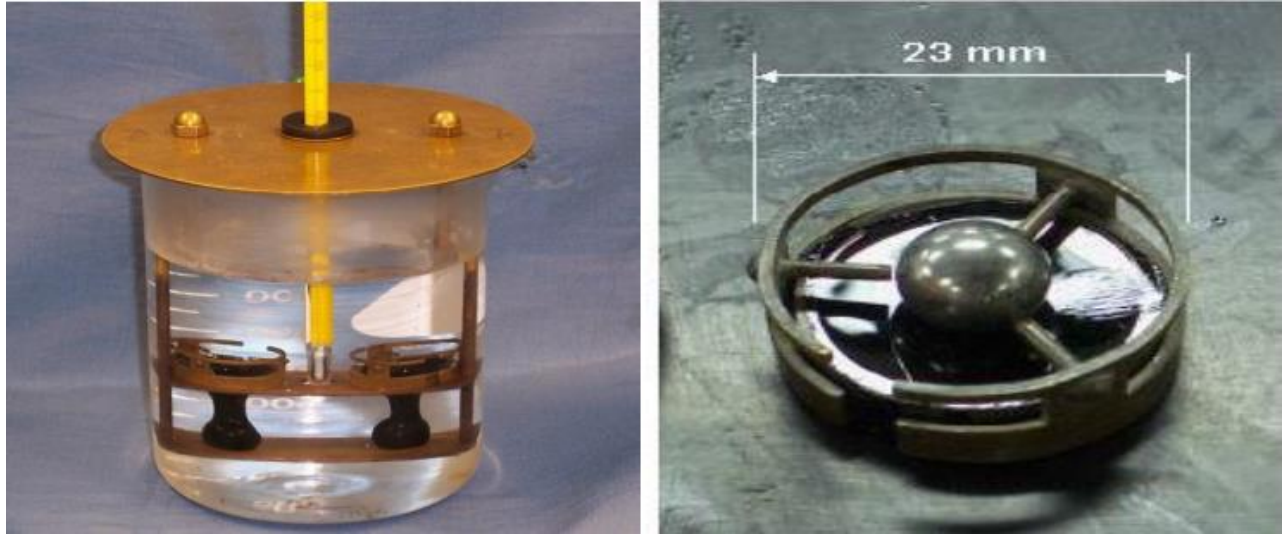
Figure 2.9: Softening point test set up [65].

2.6.1.3 Viscosity Test

Viscosity is a fundamental characteristic of asphalt binder measures the resistance to flow liquids. The viscosity test measures a fundamental physical property of asphalt binder rather than an empirical value obtained from penetration test.

Figure 2.10: Brookfield viscometer and capillary viscometer [67, 68].

Asphalt viscosities are usually measured by Brookfield viscometers and capillary viscometers as shown in Figure 2.10. It measures the time required for the asphalt cement to flow through a calibrated glass tube [66]. Temperature viscosity graphs are used to find the mixing and compaction temperatures for the asphalt mix design.

2.7 Laboratory Aging of Asphalt Cement

There are different laboratory aging procedures designed to simulate aging of asphalt during mixing and pavement in service. RFTO test (short term aging) is done to simulate the aging during mixing and laying, while aging of pavement in service (8-10 years) by PAV test (long term aging). After the aging of asphalt in RTFO and PAV, in service performance of the asphalt can be characterized by DENT, DSR and BBR tests.

2.7.1 Rolling Thin Film Oven Test

The RTFO test provides simulated short term aged asphalt binder for physical properties testing, during mixing and placement of asphalt cement concrete. It is used to measure the volatile lost from the asphalt during aging process quantitatively. It was designed as an improvement over the Thin Film Oven Test (TFOT). RTFO is performed by heating the unaged asphalt binder sample in cylindrical glass bottles and placed in a rotation carriage within an oven at 163°C for 85 minutes [69].

Figure 2.11: Rolling Thin Film Oven (RTFO).

In RTFO test, rolling action are useful for the following,

- It prevents the formation of surface skin on the sample, which may inhibit aging.

- Fresh asphalt binder is continuously exposed to heat and air flow.

2.7.2 Pressure Aging Vessel

In this test, asphalt binder is exposed to heat and pressure to simulate the long term aging of asphalt binder that occurs as a result of 8-10 years pavement service. The RTFO aged samples are exposed to high air pressure of 2.1 MPa and temperature 90-110°C for 20 hours as shown in Figure 2.12. Different temperatures can be used to simulate the different environmental conditions [70]. Hence, PAV test is the best method of choice for researcher to simulate the long term aging of asphalt materials for physical property testing.

Figure 2.12: Pressure Aging Vessel (PAV) [71].

Table 2.1: Elevated temperatures to simulate different environmental conditions.

Temperature	Simulation
194ºF (90ºC)	Cold Climate
212ºF (100ºC)	Moderate Climate
230ºF (110ºC)	Hot Climate

2.7.3 Dynamic Shear Rheometer Test

Based on the Superpave ^{TM} test methods, specification of asphalt grades is done using PG (PGAC) XX-YY, where XX represents the high temperature working limit by DSR and –YY represents the low temperature limit calculated by using bending beam rheometer (BBR) test. DSR is used to quantify the elastic and viscous properties of asphalt binders at intermediate to high temperatures. It determines the rheological properties like complex shear modulus (G*), elastic component (G'), viscous component (G'') and phase angle (δ) of unaged, RTFO, and PAV aged asphalt binders for intermediate and high temperature performance grading. DSR is mainly used to characterize the rutting resistance and fatigue cracking in asphalt binder. The complex shear modulus characterizes the total resistance to deformation when repeatedly sheared, while phase angle represents the lag between the applied shear stress and the resulting shear strain. For purely elastic material, $\delta = 0^o$ and for purely viscous material $\delta = 90^o$, i.e. the higher the phase angle, the greater the viscosity of the material [72, 74]. The ratio of the viscous (loss) modulus to the storage or the elastic modulus is known as phase angle. Mathematically,

$$\delta = \frac{G''}{G'} \qquad \text{- - - - - - - - - - (5)}$$

Where,

G'' = loss modulus (represents viscous behaviour)

G' = elastic modulus (represents elastic behaviour)

Usually, in DSR test sample of asphalt binder is sandwiched between two parallel steel plates. The bottom plate oscillates (10 rad/sec) by a precision motor with a controlled angular velocity (w).

DSR measures the torque and angle of rotation which is used to calculate the shear stress and shear strain of the asphalt binder [73]. The oscillatory strain, γ is given as,

$$\gamma = \gamma^0 \sin wt \qquad ----------- (6)$$

Where γ^0 is the peak shear strain and w is the angular velocity in rad/sec.

The shear stress τ, is given as,

$$\tau = \tau_0 \sin(wt + \delta) \qquad ----------- (7)$$

Where τ_0 is the peak shear stress.

Hence, complex shear modulus can be determined as,

$$G^* = \frac{\tau_0}{\gamma_0} \qquad ----------- (8)$$

According to AASHTO specification, the high temperature and intermediate temperature PG grades should be decided on the following values as in Table 2.2 [74].

The polymer modified asphalt binder shows higher complex shear modulus (G^*) and lower phase angle (δ), indicating the higher stiffness and more elastic behaviour than unmodified asphalt [74].

Figure 2.13: Dynamic Shear Rheometer (DSR) [75].

Table 2.2: AASHTO Specification for DSR Test.

Material (binder)	Value	Specification	Types of Distress
Unaged	$G^*/sin\delta$	≥ 1.0 KPa (0.145 Psi)	Rutting
RTFO Residue	$G^*/sin\delta$	≥ 2.2 KPa (0.319 Psi)	Rutting
PAV Residue	$G^* \cdot sin\delta$	≤ 5000 KPa (725 Psi)	Fatigue Cracking

2.7.4 Bending Beam Rheometer

The bending beam rheometer was developed under SHRP and is used to simulate low temperature cracking of asphalt pavement in the service life. It measures the relaxation properties of asphalt binders and now been accepted in AASHTO M320 protocol. Low temperature cracking is the major distress for asphalts pavements. In this method, asphalt binder samples are conditioned for one hour in an ethanol bath at 10° and 20^oC above the pavement designed low temperature grade; prior to testing. After conditioning, the asphalt beam is simply supported and tested in a cold liquid bath as shown in Figure 2.14.
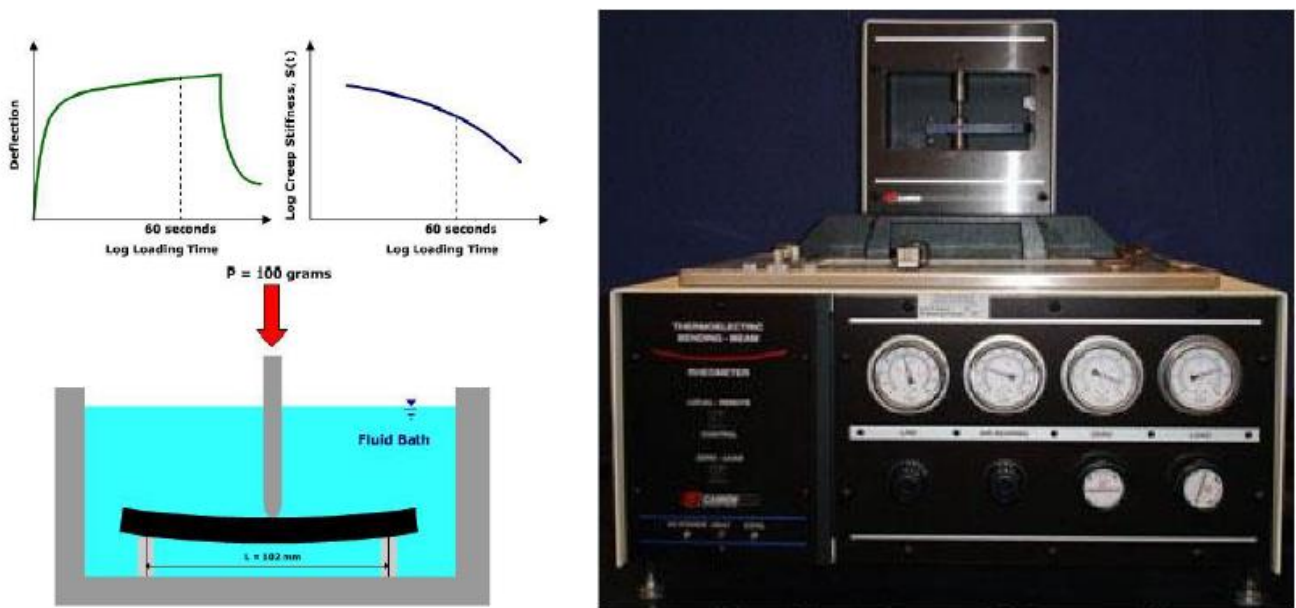
Figure 2.14: Bending Beam Rheometer (BBR) [76].

The graph of load and deflection versus time is plotted continuously, when load is applied to the center of the beam. The creep stiffness of the asphalt (s (t)) can be calculated by the following equation,

$$s(t) = \frac{Pl^3}{4bh^3\delta(t)} \qquad - - - - - - - - - - \ (9)$$

Where,

S(t) = creep stiffness at time, t = 60 seconds

p = applied constant load, 980 mN

l = distance between beam supports, 102 mm

b = beam width, 12.5 mm

h = beam height, 6.25 mm

δ (t) = deflection at time, t = 60 seconds

The specification criteria for passing or failing in the BBR test is according to AASHTO standard M320 protocol [70]. The slope obtained by plotting the logarithm of creep stiffness against logarithm of loading time gives m-value at a specified time. The parameters creep stiffness (s(t)) and m-value, address the low temperature cracking distress. For passing the test, s-value should be below 300 MPa and m-value should be greater than or equal to 0.3. The asphalt cement which failed in the above specification cannot be used in very cold climate location. To overcome the lack of sufficient aging time and high strain testing in regular BBR, a new improved method has been developed.

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

To address the problems facing the AASHTO M320 specification, the Ministry of Transportation of Ontario (MTO) in collaboration with Queen's University has developed a new sets of testing methods;

1) Extended Bending Beam Rheometer (eBBR) test (LS-308)

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

3) Modified Pressure Aging Vessel Protocols (LS-228)

These newly developed methods give a reproducible results and make it easier to predict the quality, either good or poor performance of asphalt cement.

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

In regular BBR protocol, one hour conditioning of the asphalt cannot deal with gradual hardening phenomenon which occurs over periods of days, weeks, and months. In extended BBR, asphalt beams are conditioned for 24 hours and 72 hours instead of 1 hour and then limiting temperature and maximum grade loss is determined after 72 hours. In case of poor quality asphalts containing large quantities of wax and unstable asphaltenes dispersion, lose their ability to relax thermal stress i.e., m-value decreases. The conditioning temperature in extended BBR is 10° and 20^oC above the lowest temperature designed for the pavement before they are tested [78]. Exact grade of pass and fail temperatures are determined by interpolation which involves plotting the grade on a semi logarithmic scale according to AASHTO M320 criteria. The worst grade loss is the warmest minus the coldest limiting temperature. According to LS-308 specification, the maximum grade loss

should be less than 6°C after 72 hours of conditioning which helps to detect very poor quality of asphalt cement. This test provides 95% accuracy and helps to get a high degree of confidence to prevent thermal cracking.

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

The Double-edged-notched tension (DENT) test is used to determine the ductile fracture or failure of asphalt binder at low temperature. It measures not only the essential work of failure but also the plastic work of failure and critical crack tip opening Displacement (CTOD). The test is conducted after thermal conditioning at 15°C in a water bath and loading rate of 50 mm/minute until fracture takes place [78].

Figure 2.15: DENT test setup [93].

The DENT test is based on the essential work of fracture method which was initially proposed by Cotterell and Reddel [80] and was further investigated by Mai et al [81]. It is based on the assumption that total work of fracture at a constant loading rate on a DENT sample can be divided into two regions as shown in Figure 2.16.

1) Essential Fracture Energy – It is responsible for the fracture process.

2) Non-Essential or Plastic Energy – It is responsible for the non-essential or plastic deformation outside the fracture zone.
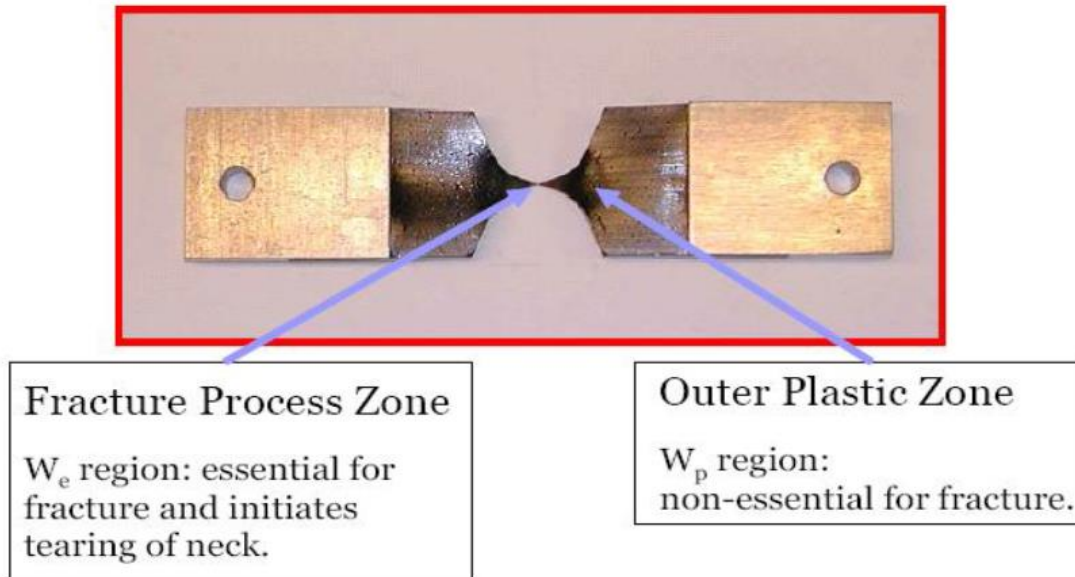
Figure 2.16: Diagram of fracture and plastic zone of asphalt [82].

The total area under the force displacement curve gives the total work of failure (W_t) which is the sum of an essential work of failure (W_e) and a non-essential work of failure (W_p) [83].

i.e.

$$W_t = W_e + W_p \qquad ---------- (10)$$

Here, essential work of failure and plastic work of failure can be determined by the following equation,

$$W_e = w_e \text{ x } LB \qquad ----------- (11)$$

$$W_p = w_p \text{ x } \beta \, L^2 \, B \qquad ----------- (12)$$

Where,

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

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

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

B = the thickness of the sample (m)

β = the plastic zone shape factor

Substituting the values from equation (11) and (12) in (10),

$$W_t = w_e \text{ x } LB + w_p \text{ x } \beta \text{ X } BL^2 \qquad - - - - - - - - - - - (13)$$

Dividing equation (13) by the cross section area of the ligament LB, then;

$$\frac{W_t}{LB} = w_f = w_e + w_p\beta LB \qquad - - - - - - - - - - - (14)$$

Where,

w_f = specific total work of failure (J/m^2)

By plotting the specific total work of failure against the ligament length, a linear graph is obtained. The straight line with y-intercept gives the essential work of failure and the slope gives the product of the plastic zone shape factor and non-essential plastic work of failure. It has been found that essential work of failure helps to predict the fatigue cracking resistance accurately. It is expected that a high value of W_e and W_p will be able to resist fatigue cracking and ductile failure [84]. The ratio of the essential work of failure to the average peak net section stress of the smallest ligament length specimen (5 mm) is known as CTOD. It measures the strain tolerance in ductile state and can be used to rank the performance and determine a high correlation with cracking distress [83].

i.e.

$$CTOD = \frac{W_e}{\sigma_n} \qquad \text{- - - - - - - - - - - (15)}$$

Where,

CTOD = Critical Crack Tip Opening Displacement (m)

σ_n = the net section stress of the smallest ligament length specimen (5 mm) (N/m^2)

Chapter 3

MATERIALS AND EXPERIMENTAL

3.1 Materials

The sample materials used in this study were obtained from various commercial sources. Six samples were obtained from Ministry of Transportation of Ontario and ten contract samples from different parts of Ontario. The detailed information about the sample contracts is provided in Table 3.1 and 3.2.

Table 3.1: MTO Samples

Contract Samples	Highway	PG Grade
M9R	Highway 17	PG 58-34
M12T	Highway 17	PG 58-34
M10R	Highway 127	PG 58-34
M13T	Highway 127	PG 58-34
M11R	Highway 144	PG 58-34 EX
M14T	Highway 144	PG 58-34 EX

Table 3.2: Ontario Contract Samples

Contract Samples	PG Grade
A	PG 58-40
B	PG 52-40P
C	PG 58-40
D	PGAC 58-34
E	PGAC 58-34
F	PGAC 58-34
G	PGAC 58-34P
H	PGAC 58-34P
I	PG 64-34P
J	PG 64-34

3.2 Recovery of Asphalt Binder

The characteristics of asphalt binders in the asphalt paving mixture can be determined by the extraction of asphalt from the asphalt aggregate mixture using a suitable solvent. The properties of recovered asphalt binders may not be exactly similar as the original binder due to aging, contamination, and molecular changes caused by the exposure to heat and solvents. But, it is expected that the recovered asphalt binder's properties has not changed significantly. The recovered asphalt binders can be tested, using the same methods for the original asphalt binder.

Then, the properties of the original and recovered asphalt binders can be compared for quality control and performance evaluation.

Figure 3.1: Rotary Evaporator [85].

The asphalt binder was recovered from HMA (Hot Mix Asphalt) supplied from MTO, through

extraction with toluene. Toluene was preferred as a solvent due to its relatively low flammability.

Chlorine containing solvent such as trichloroethylene, dichloromethane are the least preferred due

to its serious problem for hazardous waste disposal. The HMA sample was crushed into small

pieces and soaked in a solvent overnight. About 4-6 liters of toluene were used to extract

approximately 215 g of asphalt binder from 4 kg of asphalt mixture [77]. The extract was collected

into an empty level bottle and solvent washing was stopped once the aggregate was relatively

clean. The extract in the container was allowed to sediment for 5 hours. A rotary evaporator was used to recover the asphalt cement from the solvent, through condensation process as shown in the Figure 3.1. During this process, solvent was condensed at a temperature of 70-80°C and aspirator pressure of 180 mbar. Finally, the temperature was increased to 150°C and the aspirator pressure at 20-40 mbar for one and a half hour to ensure no trace of solvent in the asphalt binder, and to prevent changes in chemical composition of the asphalt binder.

3.3 Rolling Thin Film Oven (RTFO)

The temperature of the RTFO machine was set to 163°C and the air flow was adjusted to 4 L/minute. The asphalt binder sample was heated in an oven until it changed into fluid enough to pour. The hot sample was stirred with a glass rod to ensure homogeneity and to remove air bubbles in the sample. About 35-40 g of unaged asphalt binder sample was poured in a cylindrical glass bottles and placed into a rotating carriage within the oven. The carriage rotated within the oven at the rate of 15 rpm in order to be oxidative or age hardening of samples for 85 minutes. Then, the RTFO residue was transferred into stainless steel pan for PAV aging and in a small can for DSR testing.
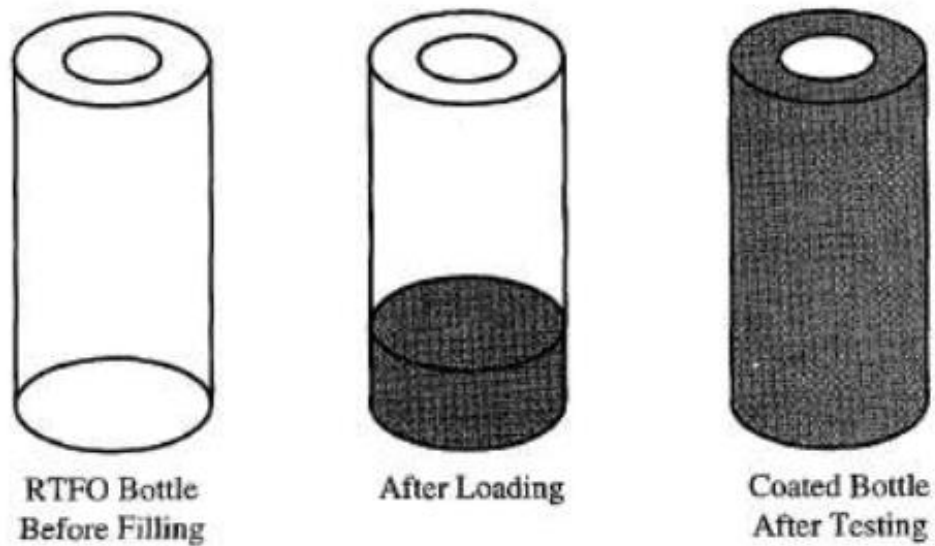
Figure 3.2: RTFO bottle, sample before and after aging.

3.4 Pressure Aging Vessel (PAV)

About 50 g of RTFO-aged asphalt binder sample was poured into a thin stainless steel pan. The pans were kept in a pan holder and placed inside a preheated PAV as shown in Figure 3.3. The samples were then aged for 20 hours in the PAV, with an air pressure of 2.1 MPa, at a temperature of 100ºC. After 20 hours, the pressure gradually decreased, and the pans were removed from the PAV. Finally, the asphalt samples were transferred into another container and used for BBR testing.

Figure 3.3: Pressure Aging Vessels set up [86].

3.5 Dynamic Shear Rheometer (DSR) Test

In this study, DSR was used to evaluate the rutting (permanent deformation) resistance and fatigue cracking resistance of straight and recovered asphalt binders at intermediate and high temperatures. The test was conducted on unaged, RTFO-aged, RTFO + PAV-aged and recovered asphalt binder samples. The sample was first heated in an oven until it was less viscous and hot enough to be poured into the silicon moulds of specified dimensions as shown in Figure 3.4. A gap zero procedure was performed and two parallel plates were heated at 46ºC before mounting the test specimen on the plate. The excess material around the edge of two parallel plates was then trimmed using a heated trimming tool. The test started only after the specimen had been at the desired temperature for at least 10 minutes. The testing parameters like frequency, loading time, test temperature, etc. are given to the software to run the DSR test. The samples were conditioned for

10 cycles at a frequency of 10 rad/second. The range of the phase angle (δ) and complex modulus (G^*) obtained from the DSR test is 50 to 90° and 0.07 to 0.87 Psi respectively.

Table 3.3: DSR Test Geometry [87].

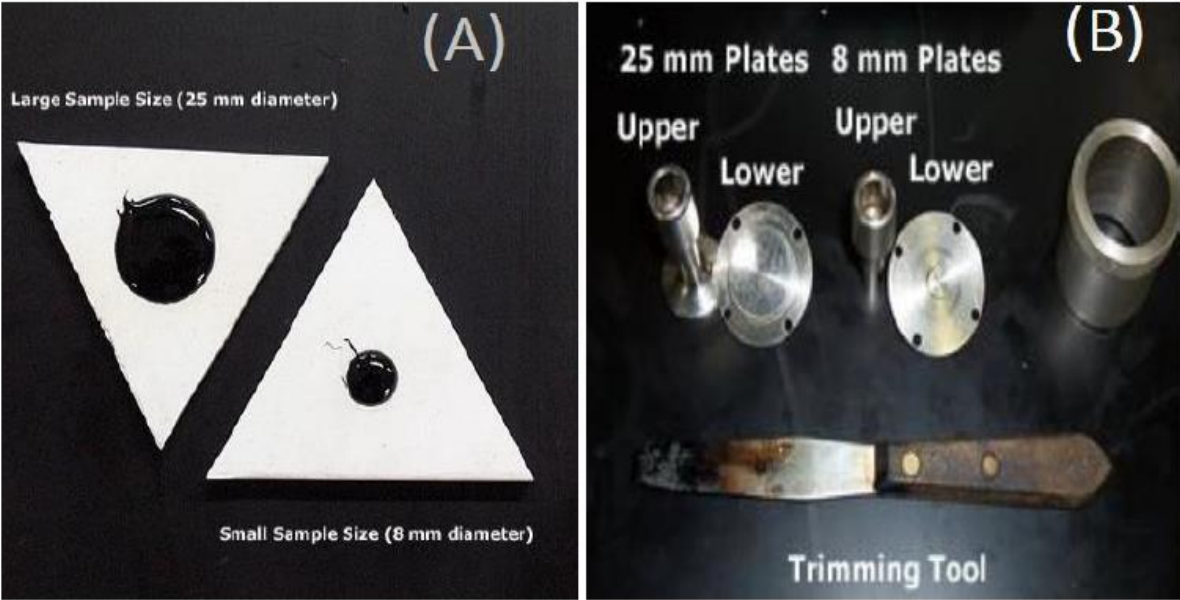| Asphalt Condition	Spindle Geometry	Measuring Gap
Unaged	25 mm	1 mm
RTFO-aged	25 mm	1 mm
PAV-aged	8 mm	2 mm

Figure 3.4: (A) DSR samples and (B) spindles [74].

3.6 Regular Bending Beam Rheometer (BBR) Test (AASHTO M 320)

The sample was heated in the oven for approximately 30-45 min at 160° and then stirred with glass rod to ensure homogeneity and to remove air bubbles present before pouring into the moulds. The samples were conditioned at room temperature for one hour and the excess binder was trimmed. The beams were then conditioned for 1 hour in an alcohol bath prior to testing. The test was performed by loading the beam at the midpoint for a period of 240 seconds with a load of approximately 980 mN. The rheometer software produced the results automatically, creep stiffness (s (t)) and m-value were calculated at a loading time of 60 seconds, according to AASHTO specification, the creep stiffness should be less than 300 MPa and m-value should be more than 0.3 to prevent the low temperature cracking of the asphalt pavement.
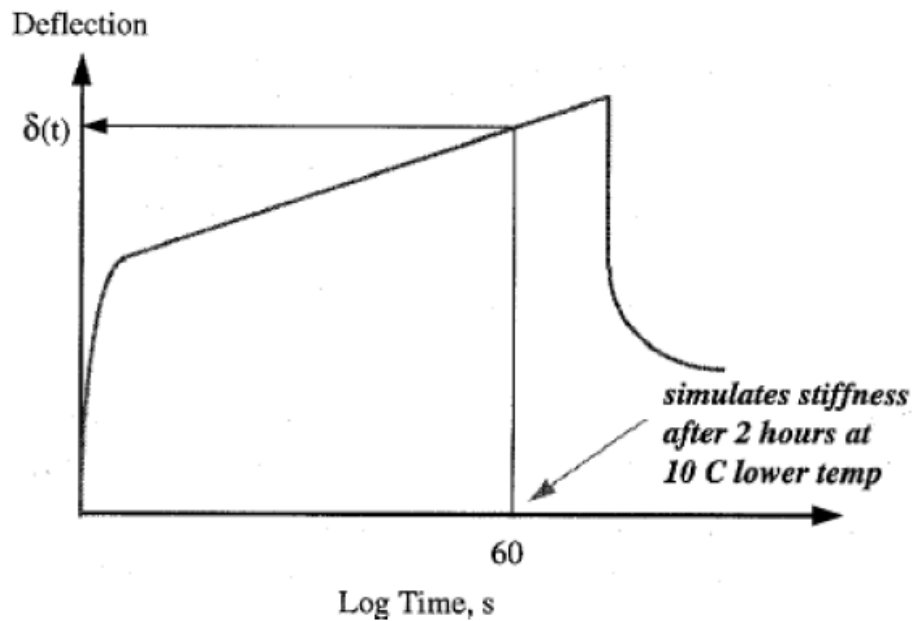

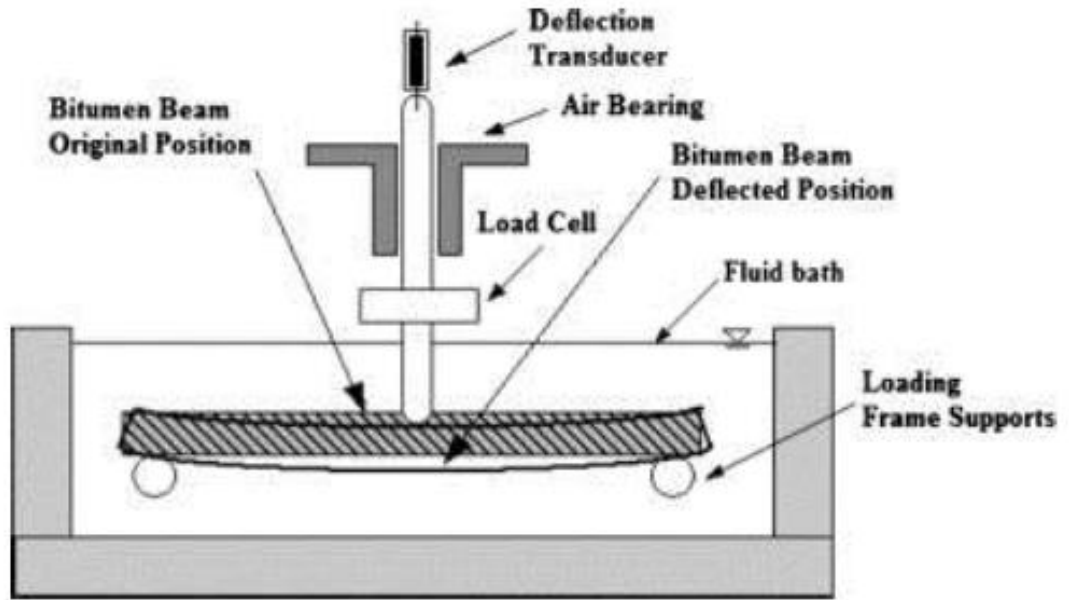Figure 3.5: Deflected asphalt on bending beam test [89].

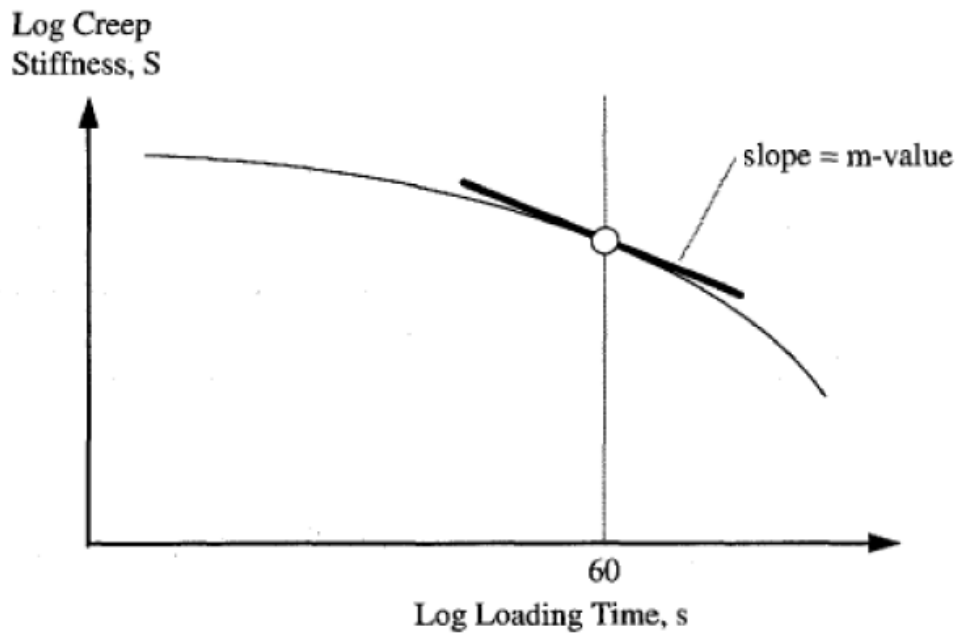Figure 3.6: Creep stiffness of asphalt binder [89].

Figure 3.7: Evaluation of m-values of asphalt binders [89].

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3.7 Extended Bending Beam Rheometer (eBBR) Testing (MTO LS-308)

In extended BBR, asphalt beams were conditioned at 10ºC and 20ºC above the pavement design temperature for 1 hour, 24 hours and 72 hours and tested at two different temperatures. For example, for the samples having PG grade 58-34, the conditioning temperatures were -24ºC and -14ºC, and test temperatures were -24ºC and -18ºC. The m-values and creep stiffness were calculated according to the regular AASHTO M320 protocol. The limiting temperatures and worst grade loss were calculated after 72 hours.

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

The PAV residue of asphalt binder was heated in the oven for approximately 30-45 minutes in an oven at 160ºC and then stirred with a glass rod to ensure homogeneity and to remove any air bubbles present in the sample. The hot asphalt binder was then poured in between two aluminum inserted silicon moulds with three different notch depths having ligaments 5 mm, 10 mm and 15 mm as shown in Figure 3.8. The excess of asphalt binder was trimmed with hot spatula. The water bath was set at 15ºC, prior to the preparation of the DENT moulds. The samples were conditioned at room temperature for 1 hour and 3 hours in water bath at 15ºC before testing [77]. The test samples were carefully removed from the silicon moulds without any distortion or fracture in the specimen and fitted in the testing machine. The samples were tested in DENT bath by pulling at a constant speed of 50 mm/minute at 15ºC until fracture occurred. The test was repeated with a replica for each ligament length to give the reproducible results. The essential work of failure, plastic work of failure and the CTOD parameter were calculated using Excel Spreadsheet.
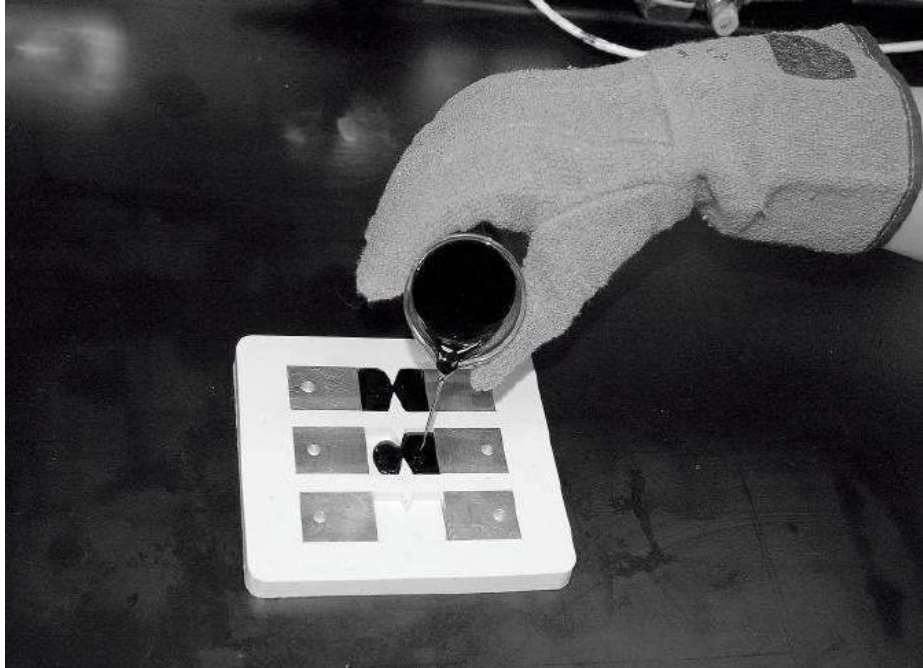
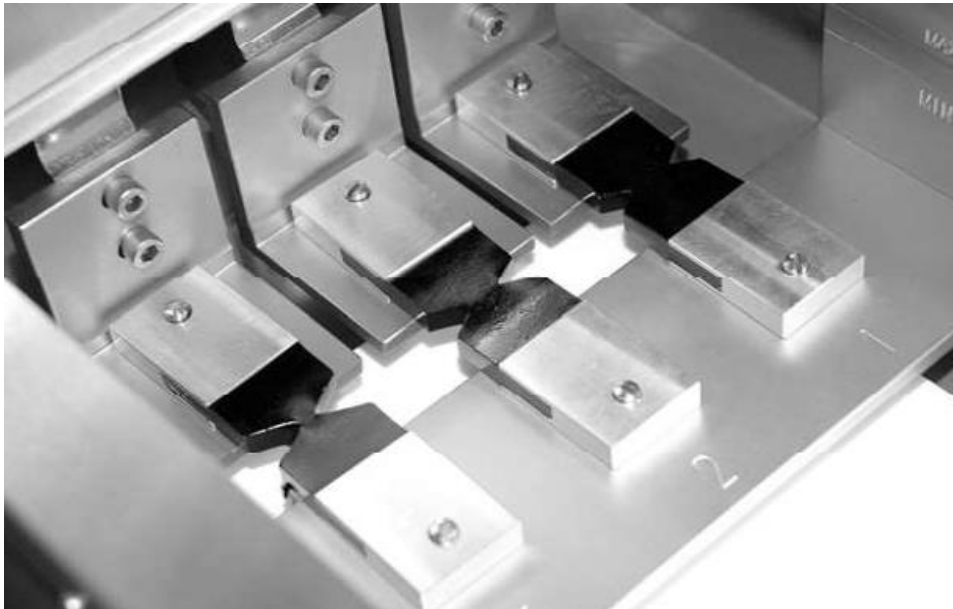Figure 3.8: Sample preparations in DENT test [34].

Figure 3.9: Double-edge-notched tension test set up [34].

3.9 Infrared (IR) Spectroscopy Analysis

Infrared analysis is an extremely valuable tool for investigating the chemical functionality of asphalts. Paving materials characterisation includes identification and quantification of polymers in polymer modified asphalt, analysis of alkali content in concrete, aging and oxidation of asphalt binders etc. [90]. Organic materials exhibit bands in higher wave number range, while inorganic materials generally exhibit their major bands in the wavenumber ranges below 1000 cm^{-1}.

Infrared spectroscopy was carried out by using Perkin-Elmer 400 series FTIR spectrometer. A thin layer of asphalt was placed on a potassium bromide pellet, initially heated at 140°C. Then the IR spectrometer was calibrated by performing background scan and the asphalt coated KBr disk was placed in the spectrometer. Then IR software was used to run the test with 16 scans over a wavenumber range of 400 cm^{-1}. The instrument software analyse the data. It was done by integrating the total area under each peak to find the peak areas for the functional groups of interest. The CH$_2$ was taken as the internal standard because it is relatively inert to oxidative changes compared to CH$_3$ peaks. The integral boundaries essential for the determination of peak areas of the functional groups are given in Table 3.4.

These functional groups selected and analysed are contained in the asphalt which undergoes oxidation in the presence of oxygen and sunlight, significantly influence the physical and chemical aging process. The following functional groups were analysed to understand the chemical change in asphalt during the aging process [9].

1) The sulfoxide index, given as the ratio of the sulfoxide peak area to the CH$_2$ peak area.

2) The carbonic index, given as the ratio of the carbonyl peak area to the CH$_2$ peak area.

3) The aromatic index, given as the ratio of the aromatic peak area to the CH$_2$ peak area.

Table 3.4: Functional groups and their corresponding wavenumber ranges.

Functional Group	Integral Boundaries
Carbonyl	1760 cm^{-1} – 1665 cm^{-1}
Sulfoxides	1070 cm^{-1} – 985 cm^{-1}
Aromatics	1650 cm^{-1} – 1535 cm^{-1}
Butadiene	983 cm^{-1} – 955 cm^{-1}
Styrene	710 cm^{-1} – 696 cm^{-1}
CH$_3$	1400 cm^{-1} – 1300 cm^{-1}
CH$_2$	3121 cm^{-1} – 2746 cm^{-1}

3.10 X-Ray Fluorescence (XRF) Analysis

XRF is one of the best non-destructive analytical techniques to determine the elemental composition of materials. X-ray fluorescence is particularly well-suited for the investigation of heavy metals such as Zn, Mo, Cu, Ca, etc., in asphalt binder. The sample of asphalt binder in a Ziploc bag was placed on an X-ray fluorescence analyser, and scanned. XRF spectra for virgin and recovered asphalt binder were collected and analysed using a hand-held Brucker Tracer III analyser.

Safety Kleen and Newalta samples were taken as a references. When the surface of the asphalt binder was irradiated by high-energy X-ray obtained from the instrument, removal of electrons in

the inner K-shell took place due to the heavy metals present in the asphalt binder. The vacancies produced in the K-shell are then occupied by electrons from the outer L- and M-shells [77]. The descent of electrons from outer shell to inner shell occurred by releasing the fluorescent X-ray, which is the characteristic of the heavy metals present in the sample. The measurement of this energy is the basis of XRF analysis [91]. The emitted radiations are detected by the XRF analyser and a graphical representation of X-ray intensity peaks as a function of energy peaks provides both qualitative and quantitative information on the presence of a range of heavy metals [92]. Generally, peak energy identifies the heavy metals present in the materials. The presence of zinc was determined at 8.64 KeV after 40 seconds using intensity versus X-ray energy graph. In comparison to the reference samples, quantity of zinc present in each sample can be determined.

Chapter 4

Results and Discussion

4.1 XRF analysis

Zinc dialkyldithiophosphate (ZDDTP) and zinc dibutyldithiocarbamate (ZDBC) act as antioxidant and anti-wear additive in engine oils. It is considered that the resistance of the asphalt cement to carbonyl formation due to oxidation, can be improved by the addition of waste engine oil. Unfortunately, waste engine oil residues cause negative effect on the performance of the asphalt cement.

Table 4.1: Relative zinc and molybdenum counts obtained from XRF analysis of MTO samples.

Samples	Relative Zinc Count (%)	Relative Molybdenum Count (%)
M9R	3.51	1.80
M10R	5.49	1.02
M11R	5.91	1.96
M12T	12.47	6.35
M13T	3.45	0.29
M14T	11.77	5.57

Oxidative hardening at high temperature and physical hardening at low temperature can be accelerated due to the presence of high contents of asphaltenes and oily phase [79, 92]. It means,

the asphalt cement containing high amounts of asphaltenes, modified with waste engine oil leads to the formation of gel-type binders. The addition of waste engine oils are the root causes to thermal cracking and premature deformation of the asphalt pavement. Due to highly paraffinic nature of WEO residue, precipitation of asphaltene takes place during oxidation in service, leading to the premature hardening of the asphalt cement.

Table 4.2: Relative zinc and molybdenum counts obtained from XRF analysis of MTO samples.

Sample	Relative Zinc Count (%)	Relative Molybdenum Count (%)
A	13.10	13.35
B	14.41	11.25
C	13.58	11.22
D	0.0	0.51
E	0.23	0.0
F	0.0	0.0
G	10.21	8.97
H	1.21	0.0
I	5.78	4.24
J	8.04	5.89

The straight tank and recovered asphalt cement were analysed using XRF. Two different engine oils (Safety Kleen and Newalta) were used to normalize the peaks at 8.64 KeV and 17.48 KeV for zinc and molybdenum respectively. Tables 4.1 and 4.2 show the relative zinc count (%) and

relative molybdenum count (%) for MTO samples and Ontario contract samples, after 40 seconds scan.
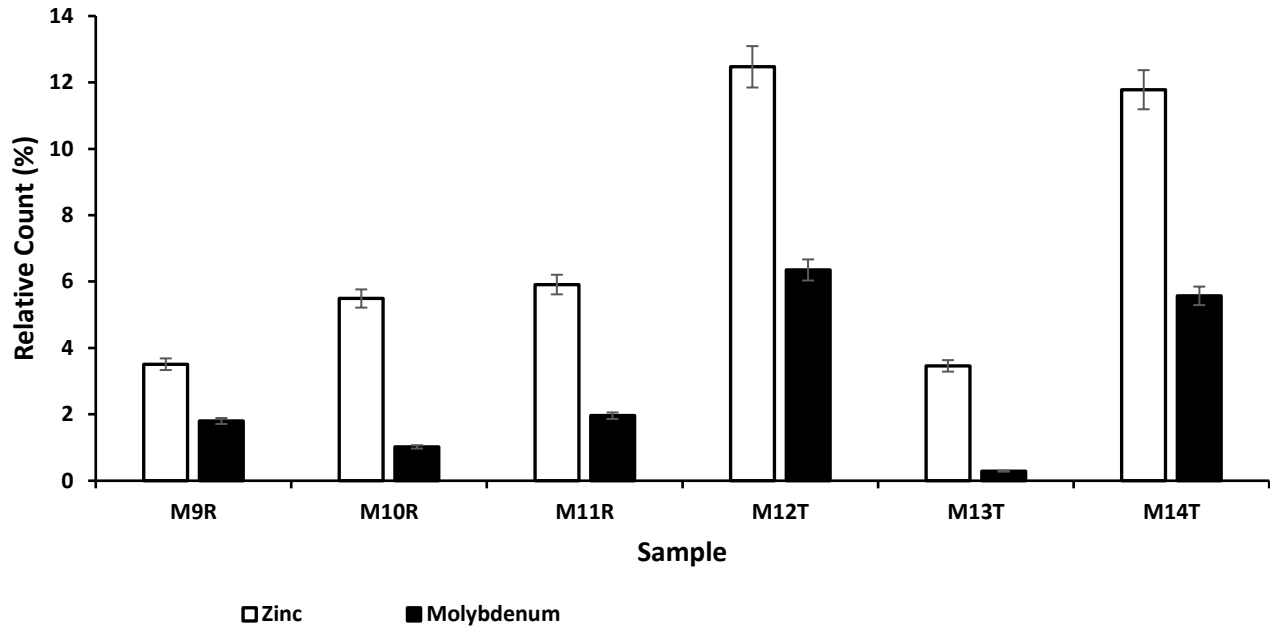

Figure 4.1: Zinc and molybdenum content of MTO samples, relative to Newalta and Safety Kleen waste engine oil residue sample.

Very high amounts of zinc and molybdenum were observed in M12T and M14T samples. Remaining MTO samples (recovered and tank) were also found high amount of zinc and molybdenum. It might be due to the addition of high percentage of waste engine oil as a modifier. The amounts of zinc and molybdenum were found comparatively lower in case of recovered asphalt cement. The instrument limit of error for XRF is 0.5-1.0 %.
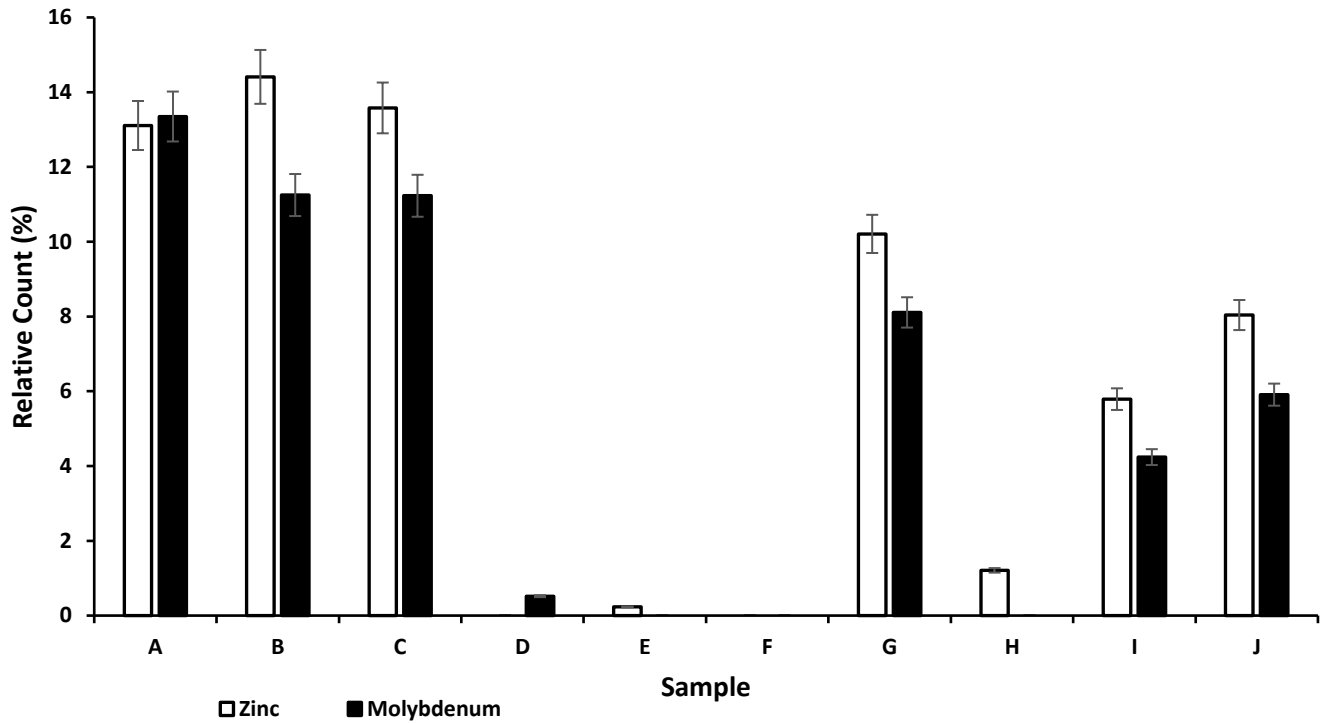
Figure 4.2: Zinc and molybdenum content of Ontario contract samples, relative to Newalta and

Safety Kleen waste engine oil residue sample.

Ontario contract samples A, B, C, G, I and J contains very high amount of zinc and molybdenum.

Such high levels of zinc and molybdenum for these samples are responsible for the poor

performance in the DENT test analysis. Samples A, C and I have a low CTOD value below CTOD

limit. It might be due to the addition of waste engine oil. But samples D, E, F and H contain

insignificant amount of zinc and molybdenum. These samples have a high CTOD value indicating

the best performance in terms of resistance to fatigue cracking. From this survey, it is believed

that, these sections are either free from any pavement cracking or if any, due to other rheological

factors, strain tolerance characteristics, construction issues, etc. It can be concluded from above

observations that, presence of zinc indicates the addition of waste engine oil residues, ultimately

associated with the premature and thermal cracking of asphalt cement pavements.

4.2 FTIR Analysis

FTIR is basically used to determine functional groups present in the asphalt cement. The oxidative hardening of asphalt cement can be determined by monitoring the carbonyl functional groups (wavenumber = 1655-1700 cm^{-1}). The carbonyl compound is the main oxidation product of asphalt cement on exposure to air during construction and in service. The functional groups and its wave length are given in chapter 2. Sulfoxides present in the asphalt cement are the minor oxidation product, which is formed by the reaction of sulfur is asphalt with oxygen.

Most of the asphalt binders are modified using polymer to get better performance in the pavement. Styrene-butadiene-styrene (SBS) is a common polymer modifier used in asphalt cement. So, butadiene and styrene peaks can be observed in case of polymer modified asphalt.

Table 4.3: Relative amounts of carbonyl, sulfoxides, aromatics, butadiene, styrene, methyl and polyisobutylene obtained from FTIR analysis of MTO samples.

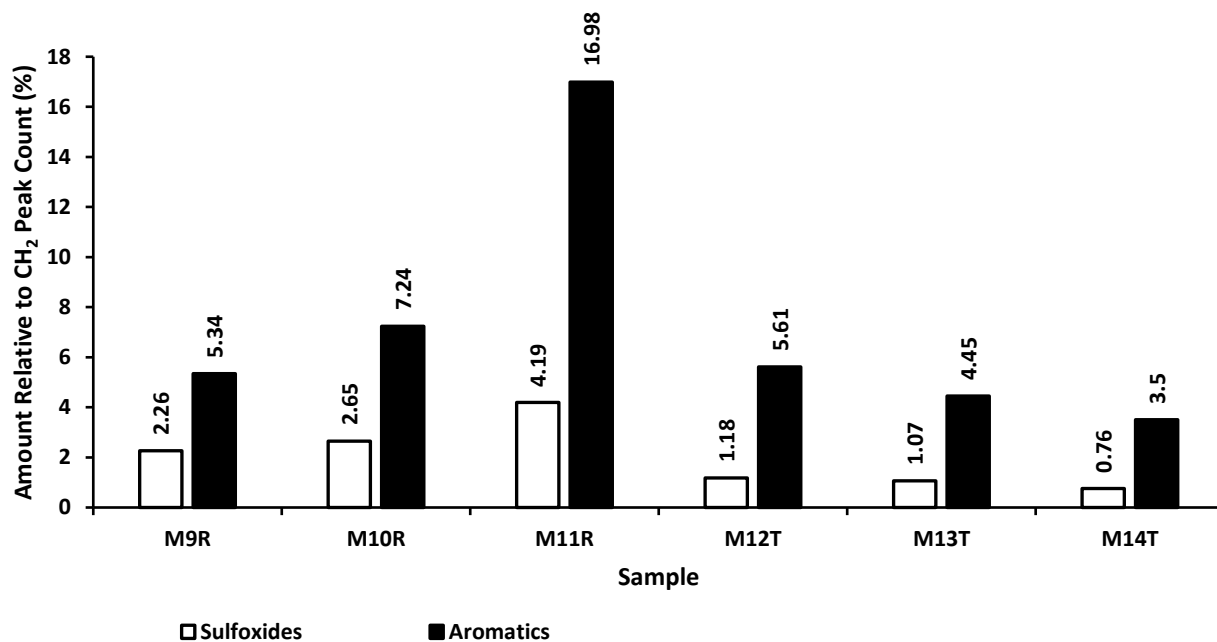| Sample	Relative Carbonyl Content (%)	Relative Sulfoxides Content (%)	Relative Aromatics Content (%)	Relative Butadiene Content (%)	Relative Styrene Content (%)	Relative Methyl Content (%)	Relative PIB Content (%)
M9R	0	2.26	5.34	0.1	0.17	2.39	0
M10R	0	2.65	7.24	0.06	0.17	3.25	0
M11R	0	4.19	16.98	0.16	0.37	3.9	0
M12T	0	1.18	5.61	0.44	0.36	3.52	0.0095
M13T	0	1.07	4.45	0.24	0.17	3.42	0.0040
M14T	0	0.76	3.50	0.29	0.23	2.63	0.0070

Figure 4.3: Sulfoxides and aromatics content of MTO samples, normalized to CH_2 stretch peak
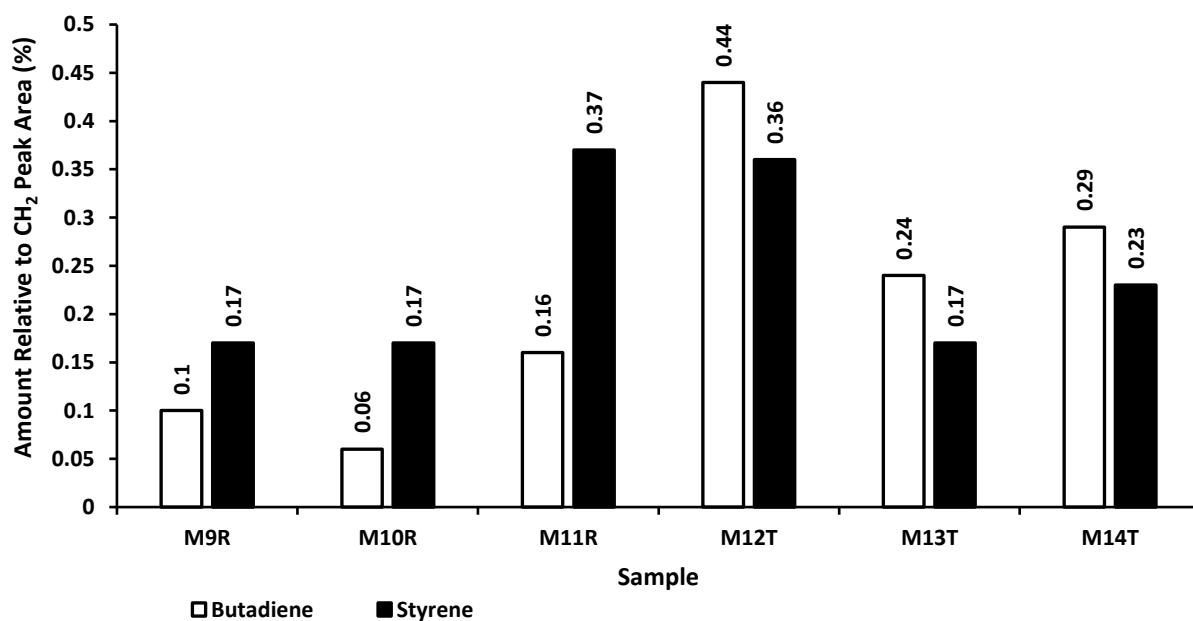
area.

Figure 4.4: Butadiene and styrene content of MTO samples, normalized to CH_2 stretch peak area.
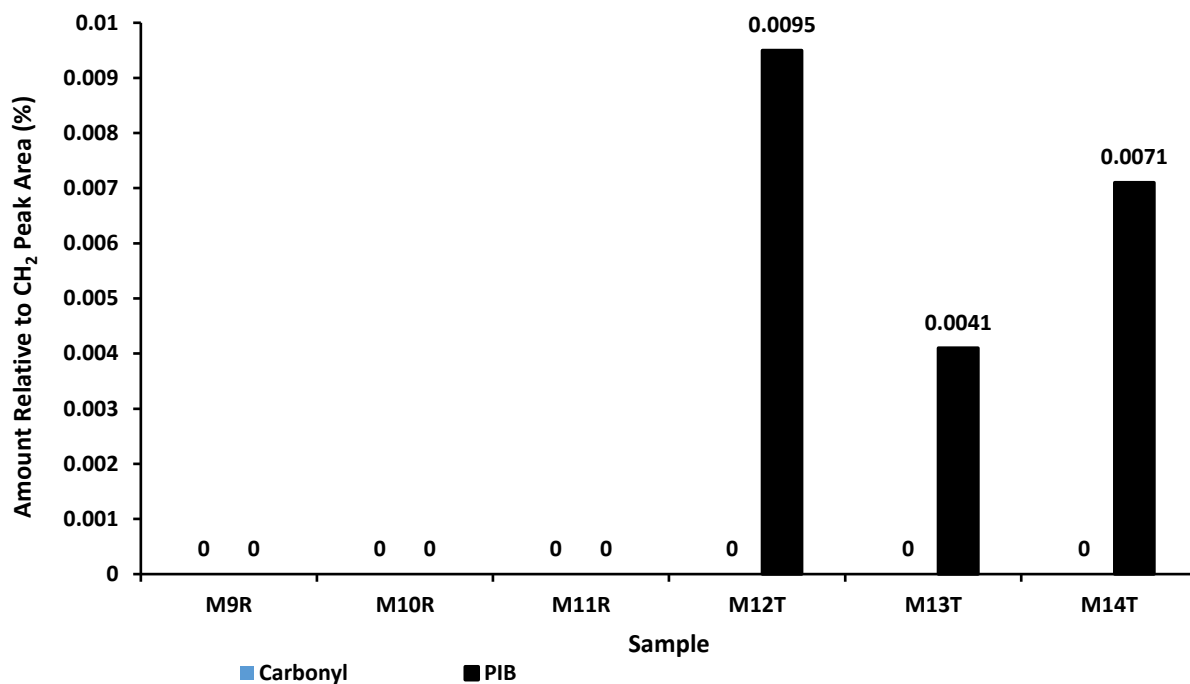
Figure 4.5: Carbonyl and polyisobutylene content of MTO samples, normalized to CH_2 stretch peak area.

The presence of the polyisobutylene indicates the addition of WEO residue in the asphalt cement. The aromatics present in the asphalt cement play an important role in its performance properties in service. The aromatics properties of asphalt binder is independent with time and temperature, Most of the aromatic oils act as a peptizer to disperse asphaltene in the asphalt binder. As a result, the asphalt binder can easily relax the thermal stresses. The relative amount of carbonyl, sulfoxides, aromatics, butadiene, styrene, CH_3 and PIB are summarized in Tables 4.3 and 4.4 for MTO samples and Ontario contract samples respectively.

The relative carbonyl contain in the MTO samples were found nil. However, M9R and M10R failed the DENT test analysis with a CTOD 18.1 and 16.4 mm. It might be due to the presence of 20% recycled asphalt. As shown in Figure 4.3, the recovered samples contain greater level of

sulfoxides as compared to tank samples which contain minor amounts of oxidation product. It could be due to oxidation in the pavement in the field. Butadiene and styrene levels in recovered asphalt is lower than straight tank samples as shown in Figure 4.4. It might be due to the presence of WEO and recycled asphalt, which ultimately degrades or ages SBS based polymer. Very small amount of PIB were observed in all tank samples, further suggesting the addition of WEO in the sample. During the recovery process, PIB might not be obtained because it sticks very strongly to the aggregate. It might be the reason behind the absence of PIB in the recovered asphalt samples.

Table 4.4: Relative amounts of carbonyl, sulfoxides, aromatics, butadiene, styrene, methyl and polyisobutylene obtained from FTIR analysis of Ontario contract samples.

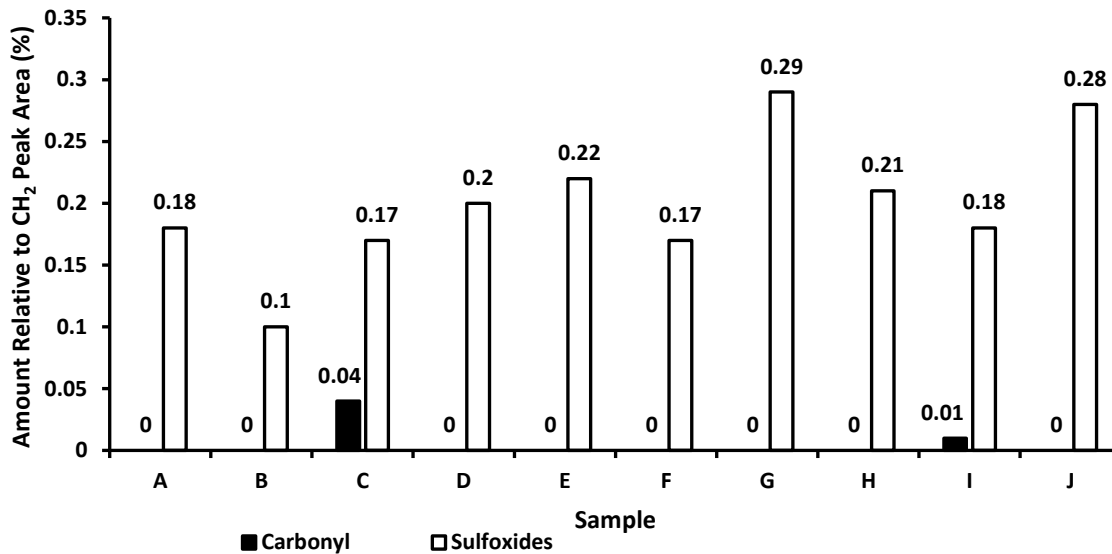| Sample	Relative Carbonyl Content (%)	Relative Sulfoxides Content (%)	Relative Aromatics Content (%)	Relative Butadiene Content (%)	Relative Styrene Content (%)	Relative Methyl Content (%)	Relative PIB Content (%)
A	0	0.18	1.3	0.09	0.07	1.0	0
B	0	0.1	0.36	0.03	0.02	0.54	0
C	0.04	0.17	0.55	0.06	0.05	0.59	0
D	0	0.2	1.42	0.09	0.07	1.0	0
E	0	0.22	2.38	0.07	0.06	1.01	0
F	0	0.17	1.14	0.01	0	0.86	0
G	0	0.29	1.31	0.09	0.07	1.15	0
H	0	0.21	1.94	0.05	0.04	0.71	1.72
I	0.01	0.18	0.54	0.07	0.06	0.73	0
J	0	0.28	2.3	0.29	0.22	2.1	0

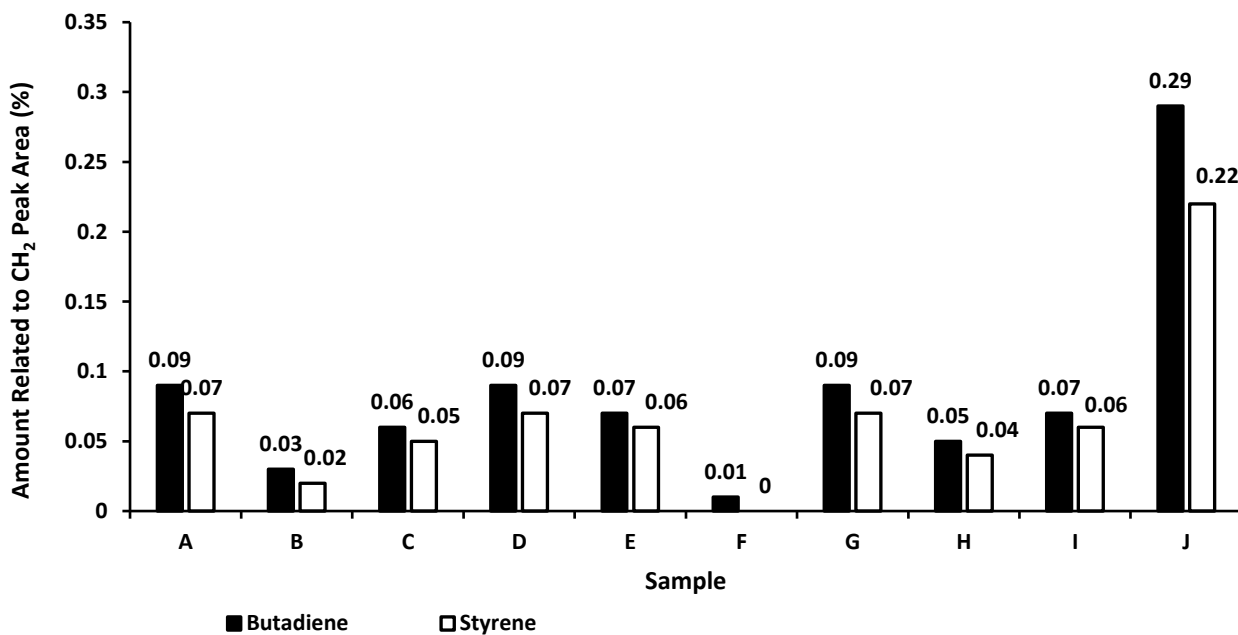Figure 4.6: Carbonyl and sulfoxides for Ontario contract samples.

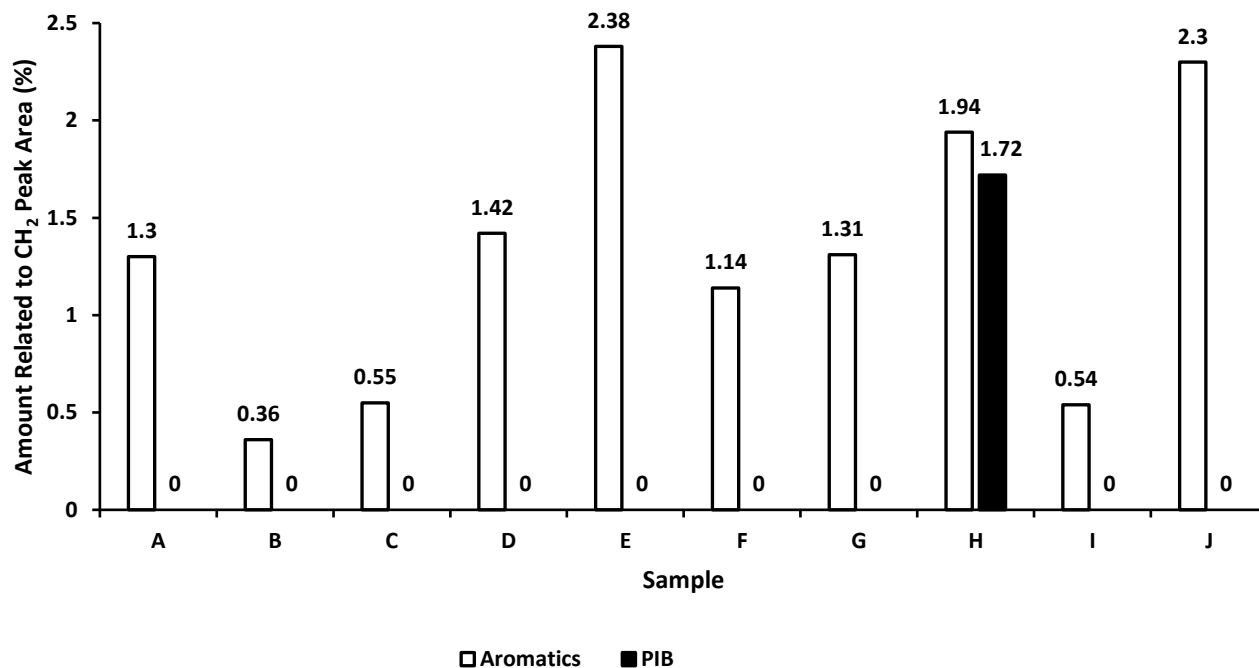Figure 4.7: Butadiene and styrene for Ontario contract samples.

Figure 4.8: Aromatics and polyisobutylene for Ontario contract samples.

From Figure 4.6, it can be clearly observed that samples C and I contain carbonyl group with a percentage of 0.04 and 0.01 respectively. The CTOD value of sample C is 29.5 and sample I is 17.1 mm which is below the CTOD limit. It might be due to the oxidative and chemical hardening in these samples. No carbonyl group were observed in case of remaining samples. The significant proportion of sulfoxides can be observed as shown in Figure 4.6. Samples D, E, H and J contains a high percentage of aromatics which are the positive indicator for better performance in service.

All the Ontario contract samples contain styrene and butadiene, suggesting the SBS based polymer modification. Sample J contains a high amount of styrene and butadiene as compared to the remaining samples. It might be due to the presence of WEO, which probably degrades the polymer. All the samples contain no polyisobutylene except sample H. The level of PIB in sample H is quite significant with a percentage of 1.72. However, it shows almost insignificant amount of zinc and

molybdenum as compared to other samples from XRF analysis, which gives an unclear picture. This needs to be further investigated.

4.3 eBBR Analysis

In eBBR test, beam of asphalt samples were conditioned for 1 hour, 24 hours and 72 hours at $+10^o$ and $+20^o$C above the actual grade temperature i.e. -14^oC and -24^oC. After conditioning, samples were tested at -18^oC and -24^oC. The limiting temperature were determined at $m(60)=0.3$ and $s(60)=300$ MPa, according to AASHTO M 320 standard protocol. The grade loss was determined after 72 hours of conditioning, which reflects on the actual performance of the asphalt pavement.

A lower grade loss indicated a lower tendency to physical hardening at the conditioning temperature i.e. asphalt cement will be able to relax thermal stresses, resulting in better performance in service. So, grade losses of more than 6^oC are considered as indicating poor binders for its durability i.e. it failed. The extended BBR results for MTO samples are given in Table 4.5. The LS-308 data for recovered and tank samples are represented by Figure 4.3.

Table 4.5: Limiting temperature at different conditioning temperature for MTO samples.

Sample	Low Temperature Grades (ºC) @ 1 Hr Conditioning	Low Temperature Grades (ºC) @ 72 Hr Conditioning	Grade Loss (ºC)
M9R	-35.5	-30.0	5.5
M12T	-39.7	-37.9	1.8
M10R	-34.8	-32.0	2.7
M13T	-38.9	-37.2	1.8
M11R	-36.0	-35.0	1.3
M14T	-43.0	-39.0	4.0
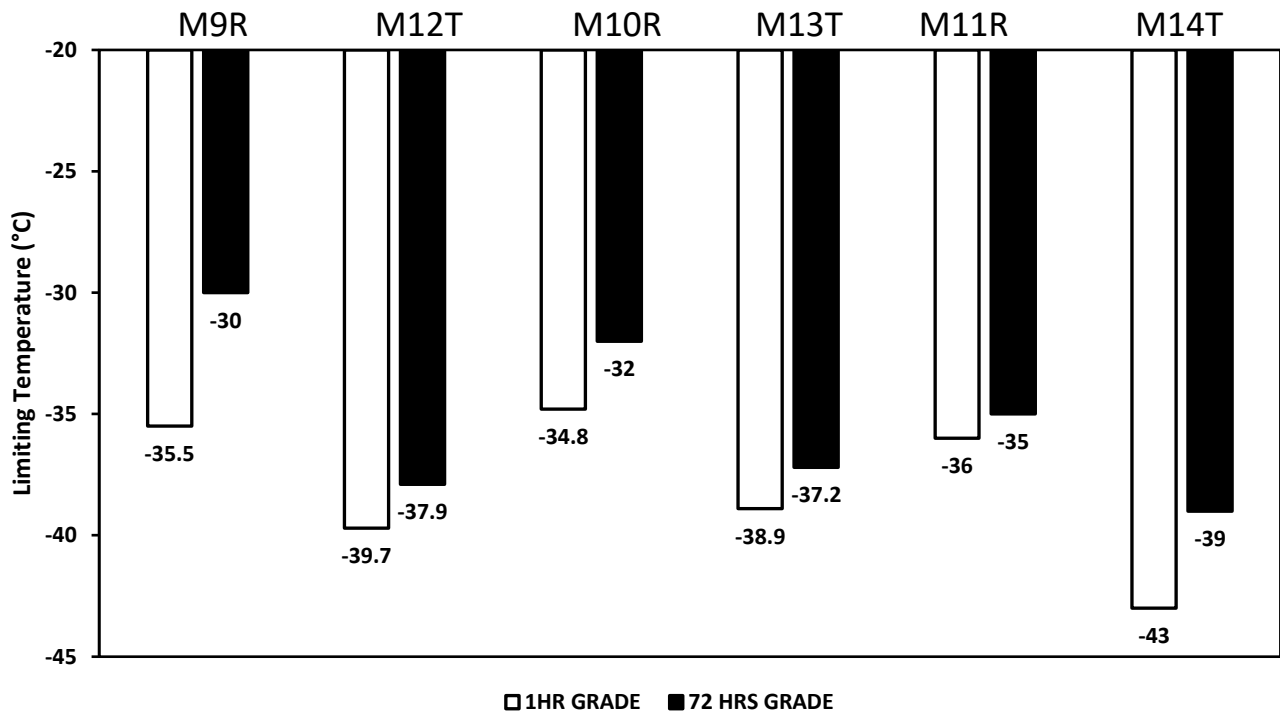
Figure 4.9: Low temperature grades of MTO samples.

As shown in Figure 4.9, all recovered and tank asphalt samples, except M9R and M10R, passed the eBBR test. It is observed that the limiting temperature for all binders become warmer at 72 hours conditioning than 1 hour conditioning. The binders reduced their performance at low temperature conditioning rather than at high temperature conditioning. It is due to the physical hardening of the binders at low temperature and extended time. The one hour grade temperature for all samples were found to be above the minimum grade temperature, indicating a good resistance to thermal cracking. In contrast, of all the binders become warmer at 72 hours, which significantly affects the performance of the binders. It can also be seen from Table 4.5 that M9R and M10R have limiting temperatures about 4°C and 2°C warmer, respectively, than their minimum temperature grade. Thus, it is obvious that these pavements have serious problems when winter temperatures fall below the minimum temperature grade. For instance, M11R shows better performance than the other recovered samples. In comparison to recovered samples, tank samples show better performance to relax thermal stresses. The poor performance at low temperature might be due to the addition of WEO and recycled asphalt.
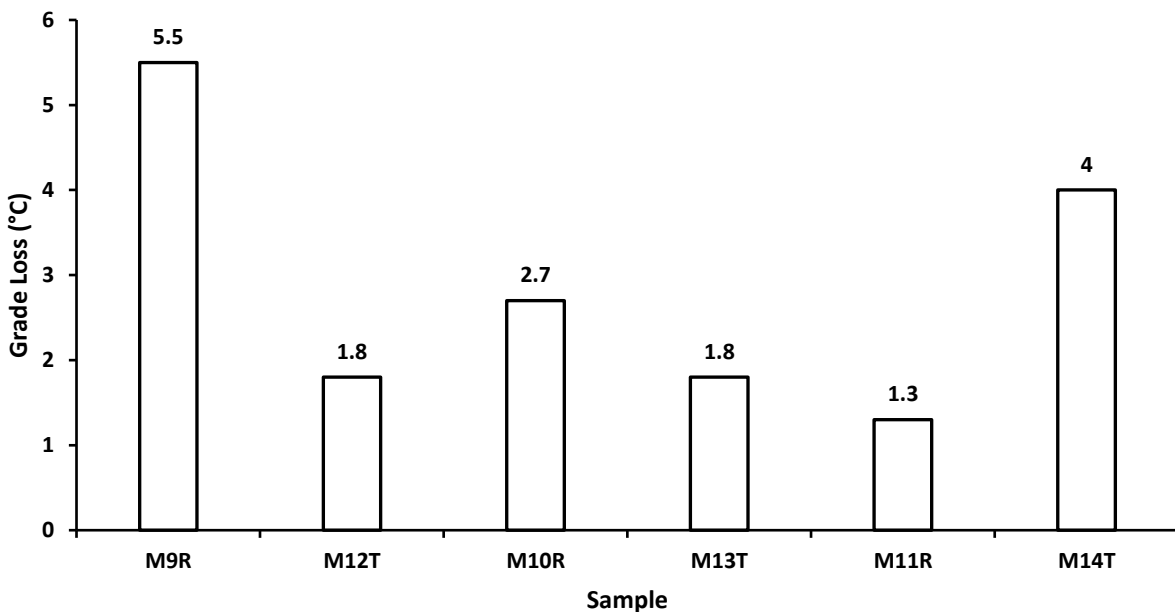

Figure 4.10: Low temperature grade loss of MTO samples.

As shown in Figure 4.10, the grade loss observed in MTO tank samples is quite low except M14T. The sample M9R lost 5.5°C, that means it is either borderline or may pass the test according to LS-308 specification. It can be observed that sample M10R, M11R, M12T, M13T and M14T lose only 2.7°C, 1.3°C, 1.8°C, 1.8°C and 4.0°C, respectively. This shows that these binders have no significant cracking at low temperature.

4.4 Dynamic Shear Rheometer Analysis

4.4.1 High Temperature Superpave Grading

The high temperature Superpave performance grades of unaged and RTFO residues of recovered and tank asphalt cements were determined using TA Instruments AR 200 ex DSR. The high temperature grades measure the rutting (permanent deformation) resistance of asphalt pavement at high temperature.
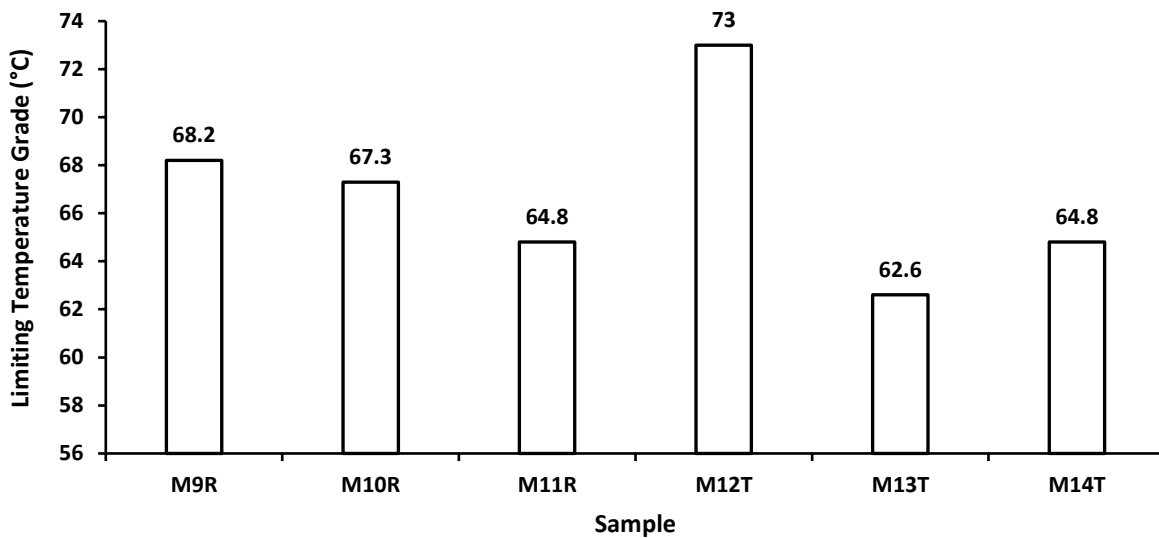
Figure 4.11: Limiting high temperature grades of recovered and tank asphalts.

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The rutting resistance factor, G*/sinδ were used to predict the rutting behaviour of the asphalt pavement. G*/sinδ should be a minimum of 1.0 KPa and 2.0 KPa for unaged and RTFO samples respectively. The limiting temperatures for all recovered and tank samples were summarized in Figure 4.11.

It was observed that sample M12T has higher limiting temperature as compared to others. Essentially high value of the limiting temperature indicates that they have better resistance to rutting at high temperature. It might be due to the presence of high content of elastic components and low content of viscous components in the asphalt binder.

Moreover, asphalt binder should be stiffer and elastic to resist rutting in the pavement. The rutting behaviour of asphalt binder at high temperature can be improved by the addition of additives. Higher limiting temperature of the binder could be due to the presence of additives.

4.4.2 Intermediate Temperature Superpave Grading

The PAV residue were tested to determine the intermediate grades of recovered and tank MTO samples. The fatigue resistance factor G*x sinδ, were used to predict the fatigue behaviour of the asphalt cement. According to the AASHTO M 320 specification, G*x sinδ should be a minimum of 5,000 KPa for PAV aged samples. The limiting temperatures for all recovered and tank samples are summarized in Figure 4.12.

Recovered asphalt binders have high limiting temperature as compared to tank samples. One important conclusion that can be deduced from Figure 4.12, is that tank samples are least susceptible to fatigue cracking.

It is considered that, the asphalt binder should be less stiff and more elastic to resist the fatigue cracking. The fatigue cracking of asphalt binder in service might not be correlated with its loss modulus $G^* \times \sin\delta$. But CTOD is able to measure fatigue cracking resistance of asphalt binders accurately, since it has a high correlation with fatigue cracking. However, there is no correlation observed between loss modulus $G^* \times \sin\delta$ and CTOD.
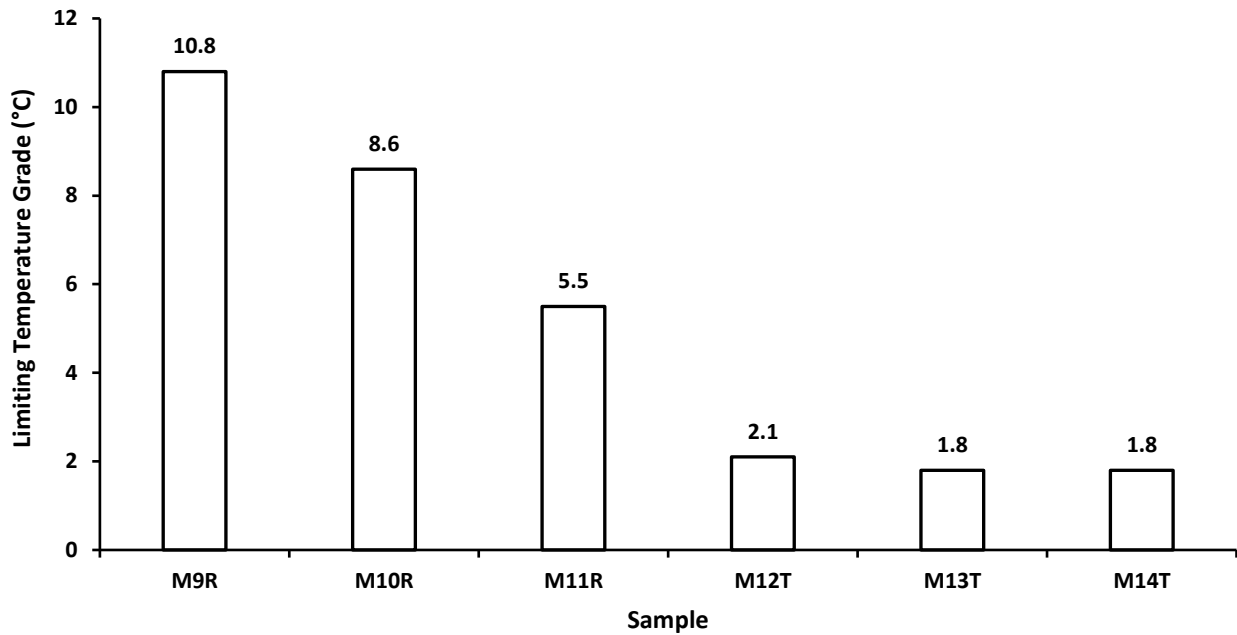
Figure 4.12: Limiting temperature of intermediate temperature grade of recovered and tank asphalts.

4.4.3 Black Space Diagrams

Rheology is the study of deformation and flow of matter. The rheological properties of asphalt binder can be studied using DSR test. The Black space diagrams are used to characterize the rheological properties of asphalt binders. It is used to distinguish between a single phase asphalt

binder with a homogeneous composition and a multiple phase asphalt binder with a heterogeneous composition. Asphalt binders having a single phase system are considered to behave rheologically simple, i.e. there is a smooth progression of curves at different temperatures. In contrast, asphalt binders having two or more phase systems are considered rheologically complex, i.e. no smooth progression of curves at different temperatures, which might be due to the phase separation.

The graphical representation of Black space diagram helps to determine the change in phase angle with the complex modulus at different temperatures. It is believed that, a high phase angle at high stiffness reduces thermal cracking whereas a low phase angle at low stiffness prevents rutting in asphalt cement. The Black space diagrams at high and low temperatures of the recovered and tank asphalt binders are shown in Figures 4.13 to 4.18.

As temperature increases, the phase angle should decrease to resist the rutting behaviour of the asphalt at high temperature grading. However, such trend were not observed in this experiment. It might be due to experimental error or sample preparation error. Samples were displaying different trends as the test was conducted on one frequency. They might be rheologically complex as there would be a lot of phase transitions going on because of polymer modification.
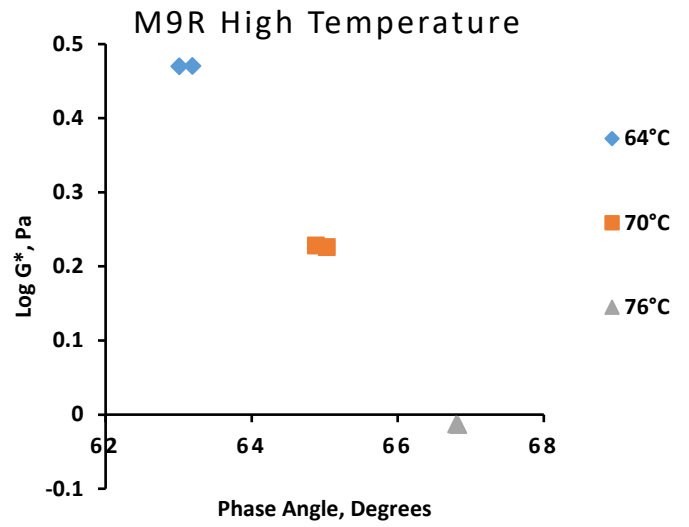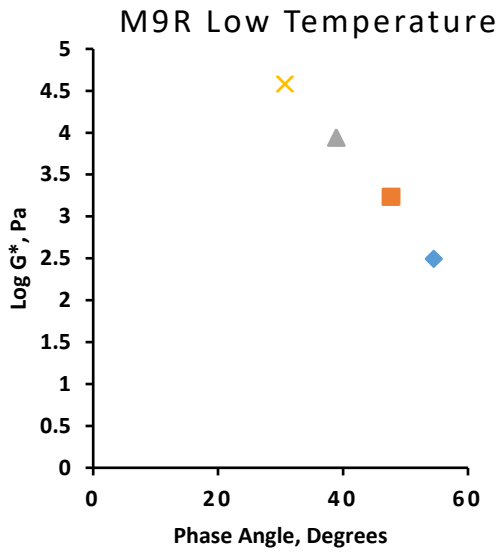
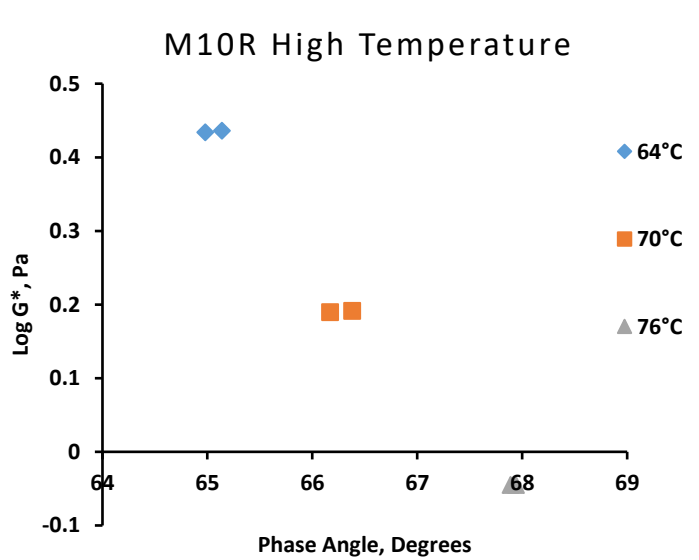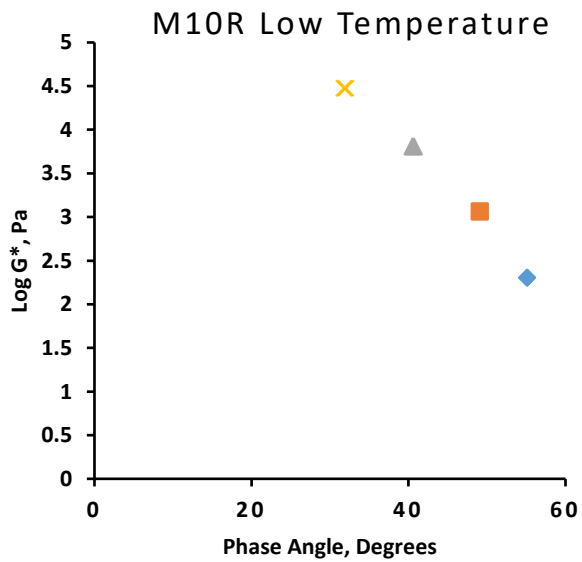Figure 4.13: Black space diagrams for MTO sample, M9R at low and high temperature.

Figure 4.14: Black space diagrams for MTO sample, M10R at low and high temperature.
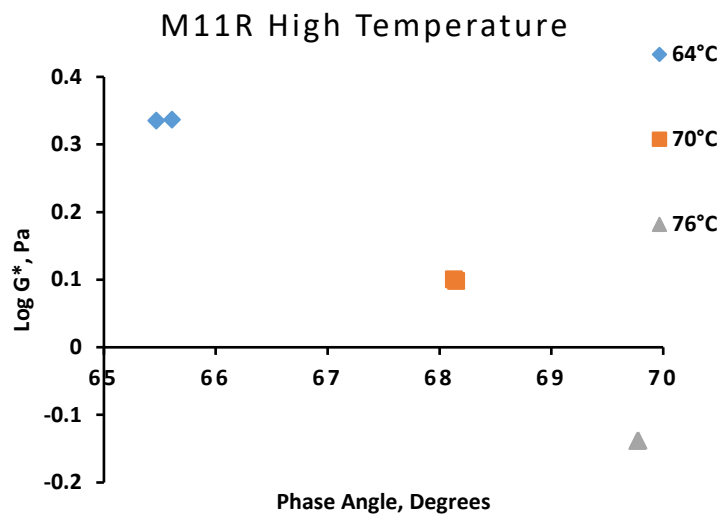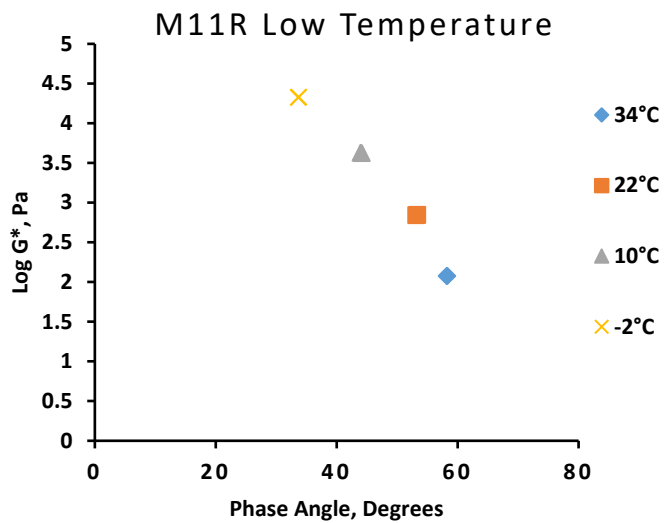
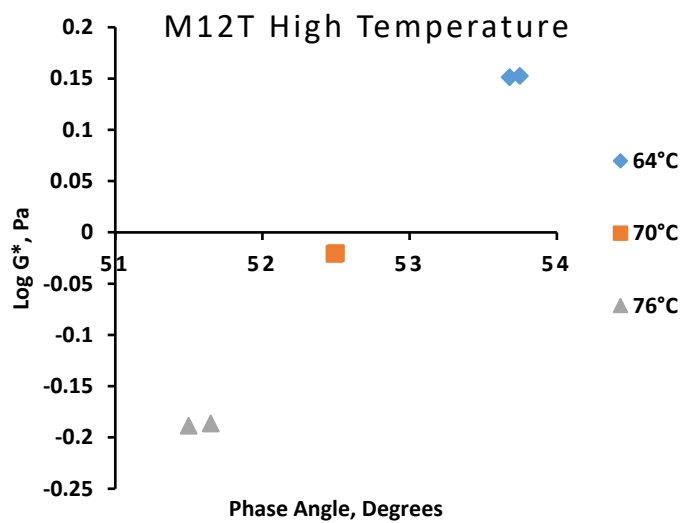Figure 4.15: Black space diagrams for MTO sample, M11R at low and high temperature.
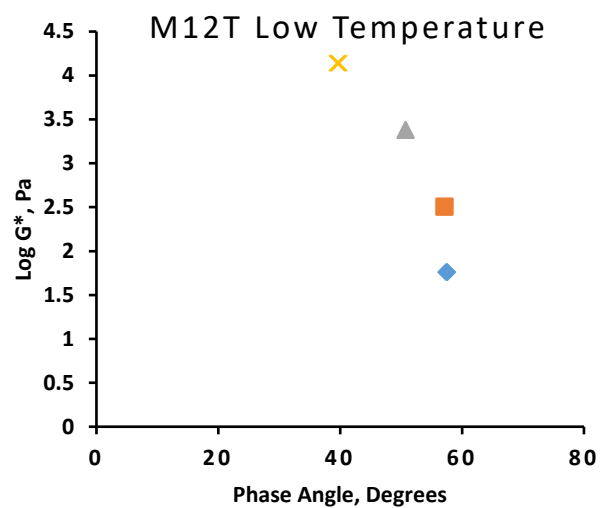

Figure 4.16: Black space diagrams for MTO sample, M12T at low and high temperature.
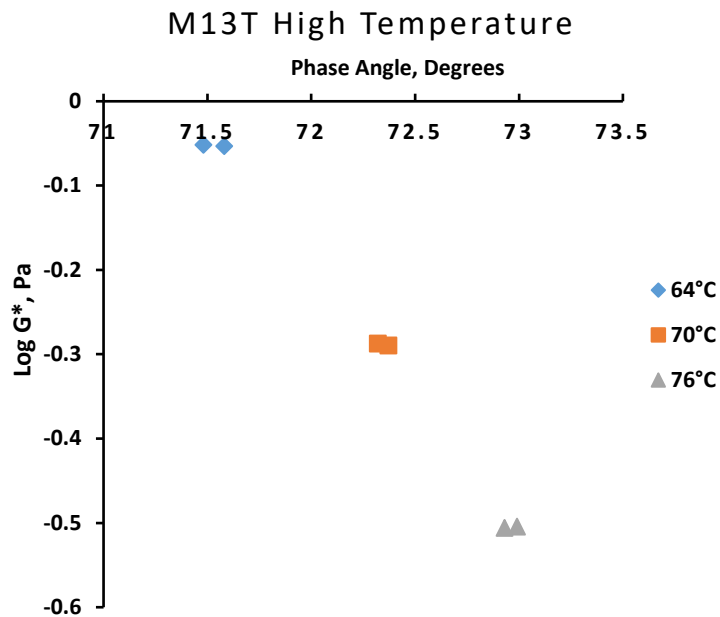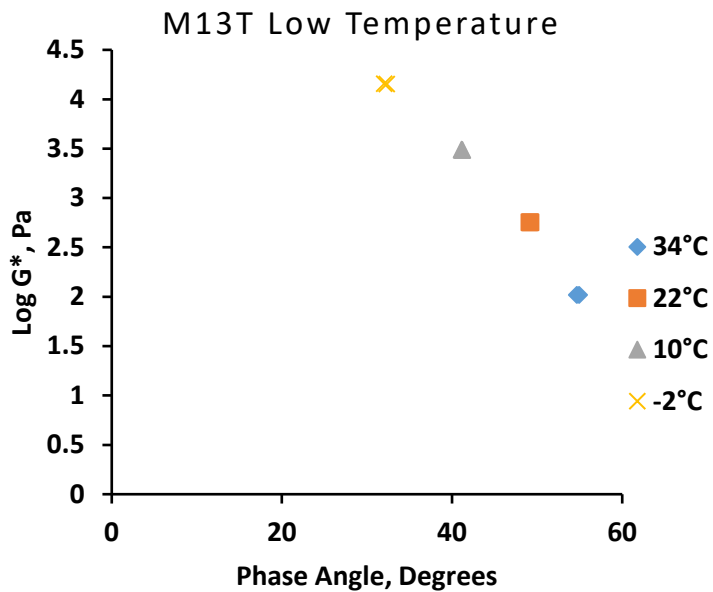
Figure 4.17: Black space diagrams for MTO sample, M13T at low and high temperature.
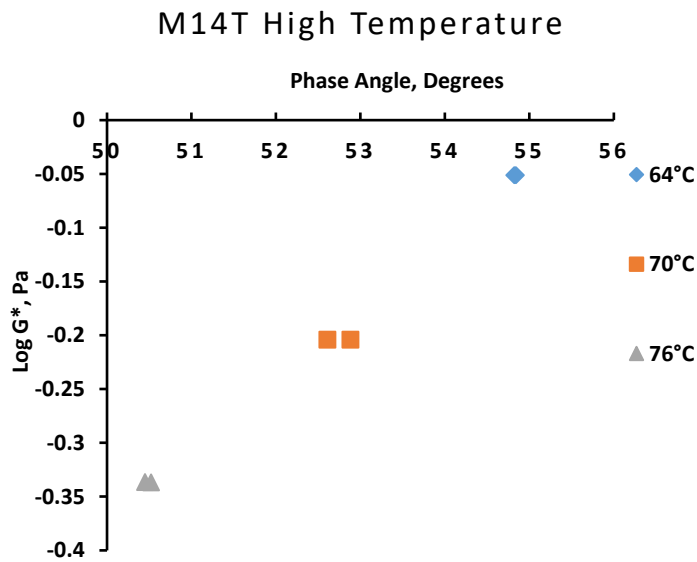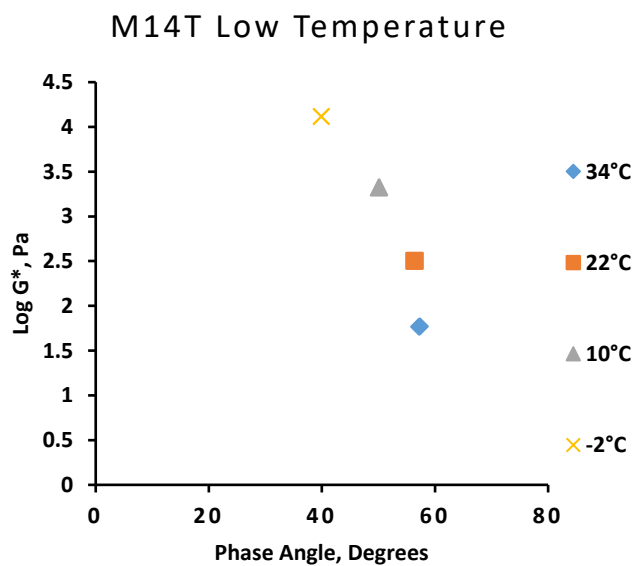

Figure 4.18: Black space diagrams for MTO sample, M14T at low and high temperature.

By observing Black space diagrams from Figure 4.13 to 4.18, it is clearly seen that all samples are rheologically simple at low temperature. However, all samples are rheologically complex except M12T and M14T at higher temperature i.e. a diagram shows discontinuity at different temperatures. At high temperature, the phase separation takes place in these samples might be due to the addition of polymers or waste engine oil. It can be observed that the phase angle decreases with complex shear modulus at high temperature for M12T and M14T indicating their good performance at higher temperature. These binders have high resistance towards rutting and perform very well in service.

Generally, it is believed that asphalt binders should have lower values of phase angle at high temperatures and higher values at low temperatures to perform better in service. For samples M9R, M10R, M11R and M13T it is seen that phase angle increases and complex modulus decreases at higher temperature. It might be due to the shear thinning type of behaviour of asphalt binder at higher temperature.

4.5 Double-Edge-Notched Tension (DENT) Analysis

The strain tolerance and the failure properties of asphalt cement in its ductile state can be determined by DENT test. Moreover, it has been successfully used for ranking the asphalt binders in term of performance and to distinguish superior quality binders from poor quality binders. The test was conducted after thermal conditioning at 15°C in a water bath and loading rate of 50mm/minute until fracture occurred, according to the LS-299 standard. The duplicates force against displacement curves for DENT samples having ligaments 5mm, 10mm, and 15mm can be represented in Figure 4.19.
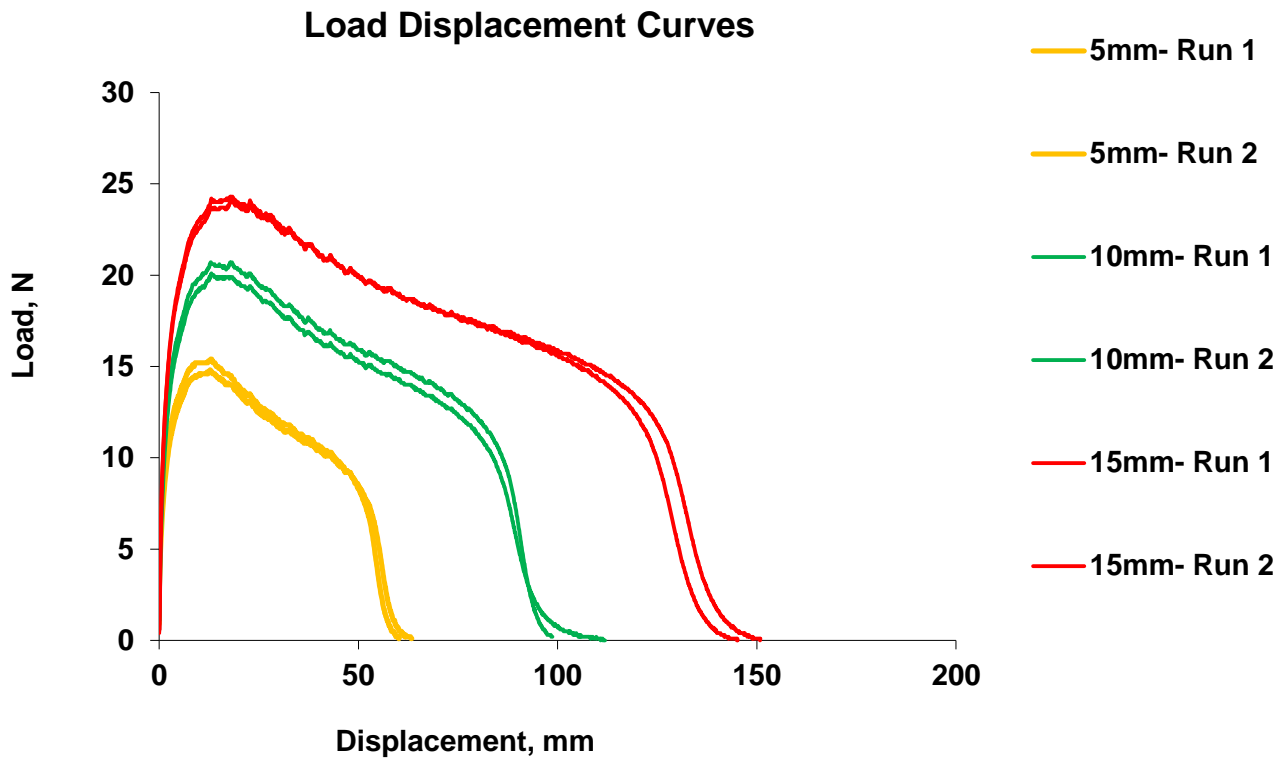
Figure 4.19: Representative force-displacement data for DENT test (Sample H).

It can be observed that the test method is highly reproducible. The sample specimens of different ligament lengths show similar behaviour in terms of necking, yielding and tearing but differ significantly from one binder to another. The integrated area under the force displacement curve gives the total work of failure which is the sum of the essential and plastic work of failure. By plotting the specific total work of failure against the ligament length L, a straight line is obtained. The y-intercept at L=0 gives essential work of failure and the slope gives the product of the plastic zone shape factor and the plastic work of failure. The regression coefficient of the straight line is 0.95, indicating the highly reproducible and accurate results.
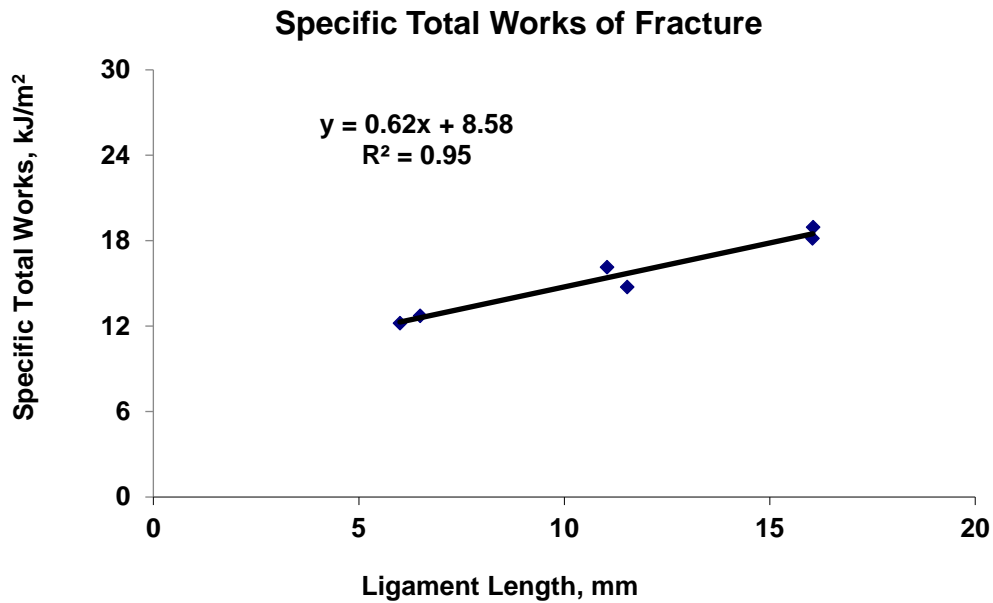
Specific Total Works of Fracture

y = 0.62x + 8.58
R² = 0.95

Y-axis: Specific Total Works, kJ/m²
X-axis: Ligament Length, mm

Figure 4.20: Specific total work of fracture versus ligament length for sample M12T.

4.5.1 DENT Test Analysis for MTO Samples

4.5.1.1 Essential Work of Failure

During the ductile failure of asphalt binder, EWF method is basically concerned on an energy analysis during the yielding, necking and tearing processes [83]. EWF is a material property which is independent to the geometry of the asphalt binder. The fatigue properties of asphalt binder in ductile state can be determined by using EWF methods. It is considered that, high value of essential work of fracture is good for resistance to fatigue cracking i.e., the higher the values of essential work of fracture, the greater the strain tolerance of the pavement [9]. The essential work of fracture for recovered and tank MTO samples are given in Figure 4.21.
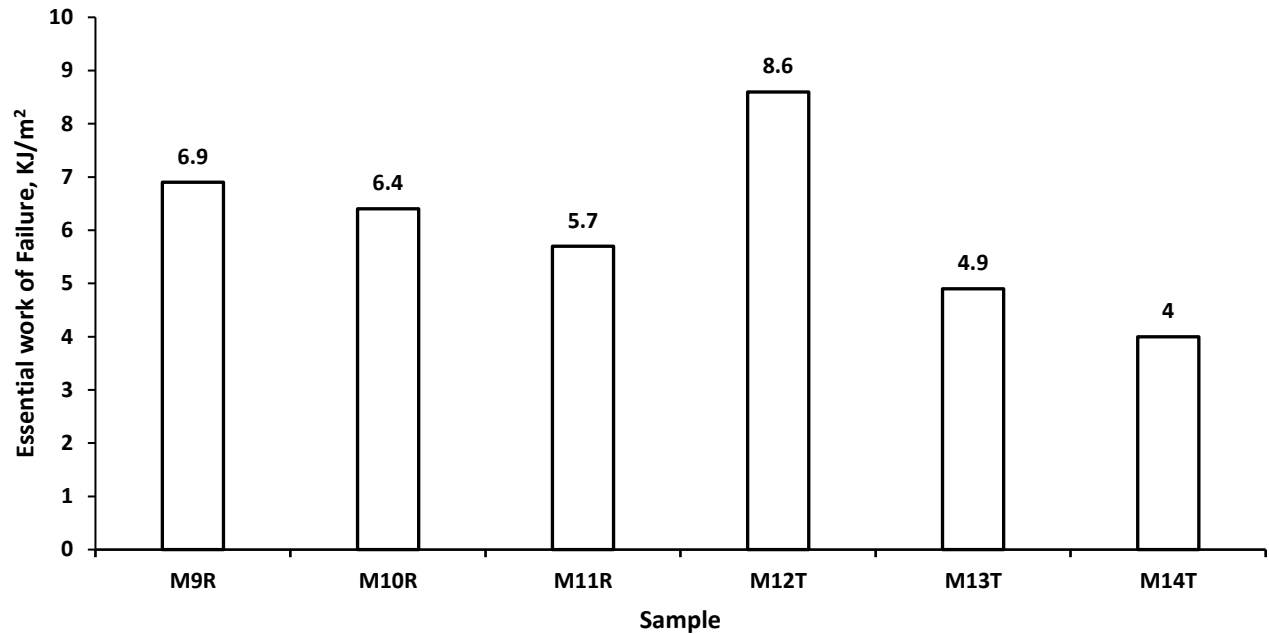
Figure 4.21: Essential work of fracture for MTO contract samples.

As shown in Figure 4.21, essential work of fracture for samples M9R, M10R, and M12T is comparatively high, indicating that they have a high tolerance to resist low temperature cracking and fatigue cracking. In contrast, samples M13T and M14T have low values of W_e, indicating that they have a low strain tolerance and show poor performance in service. But M11R is in borderline in terms of strain tolerance.

4.5.1.2 Plastic Work of Failure

The energy necessary for the plastic deformation outside the fracture zone is known as plastic work of failure [83]. It is considered that, plastic work of fracture is not material property which is related to mixture design, asphalt binder and air void. High content of the asphalt binder in the mixture contains higher plastic work of fracture indicating higher resistance to cracking [9]. It is believed that, higher the plastic work of fracture, lower the fatigue cracking. The plastic work of fractures for all MTO samples are summarized in Figure 4.22.
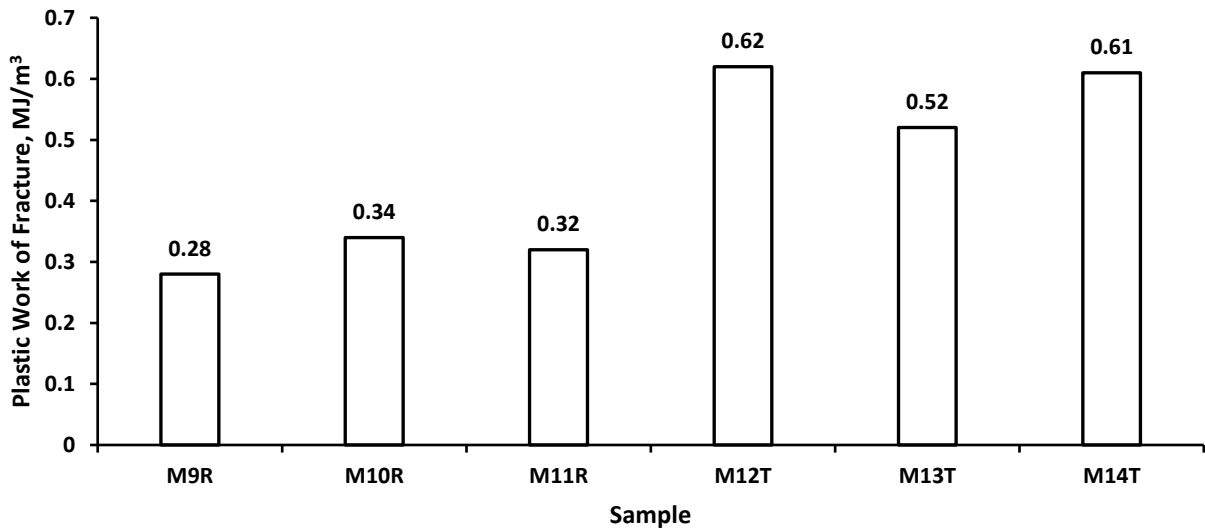
Figure 4.22: Plastic work of failure for MTO samples.

It can be observed that, MTO tank samples have comparatively higher plastic work of fracture as compared to recovered samples. Thus, the recovered binders are more sensitive to the pavement distresses as compared to tank samples in terms of plastic work of failure.

4.5.1.3 Critical Crack Tip Opening Displacements

The ratio of essential work of the fracture to the net section stress or yield stress (σ_n) determined from 5mm ligament length of the DENT mould is known as CTOD. It measures the strain tolerance in ductile state and can be used to rank the performance and determine a high correlation with cracking distress [83]. According to LS-299 specification, CTOD should be 15mm for asphalt cement of PG-28, 20mm for PG-34, and 30mm for PG-40. The asphalt binders having CTOD value below CTOD limit are considered as failed. The CTOD values of MTO samples are summarized in Figure 4.23.
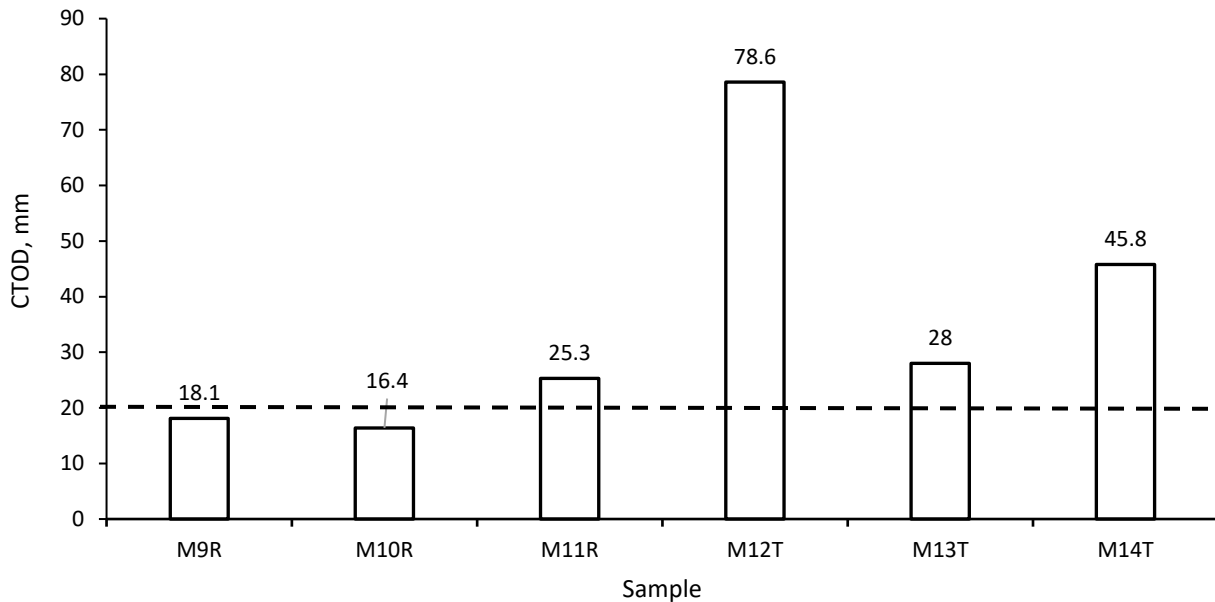
Figure 4.23: CTOD values for all MTO samples. (The dashed black line indicates CTOD limit for a binder PG-34.)

As shown in Figure 4.23, the tank samples M12T, M13T, and M14T have higher CTOD, indicating the higher strain tolerance in the ductile state. Sample M12T has the highest CTOD value i.e. 78.6 mm, which could be due to SBS based polymer modification. In contrast, recovered samples M9R and M10R are failed. It means that they are more susceptible for premature cracking in service. However, M11R has a better resistance to fatigue cracking.

The main aim of this study was to compare the properties of recovered and straight tank samples supplied from MTO. From the above comparison it has observed that recovered samples perform poorly as compared to tank samples in terms of essential work of failure, plastic work of failure and CTOD.

4.5.2 DENT Test Analysis for Ontario Contract Samples
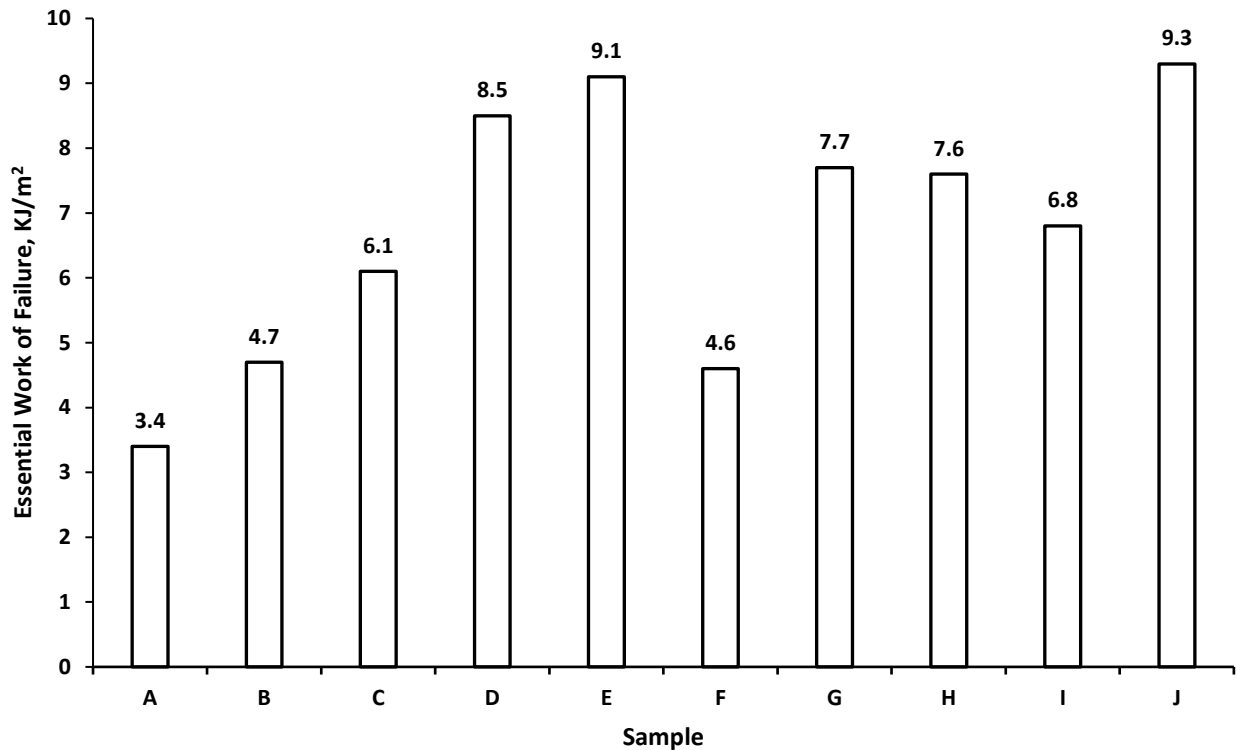
4.5.2.1 DENT Test Analysis at 15ºC

Figure 4.24: Essential work of fracture for Ontario contract samples at 15ºC.

It can be observed that the essential work of fracture for Ontario contract samples J, I, E, D, H, and G indicating the high strain tolerance to resist fatigue cracking. The contract samples A, B, and F with low values of W_e indicate that they have low strain tolerance and they might be performing poorly in service. The remaining contract samples are not so bad.
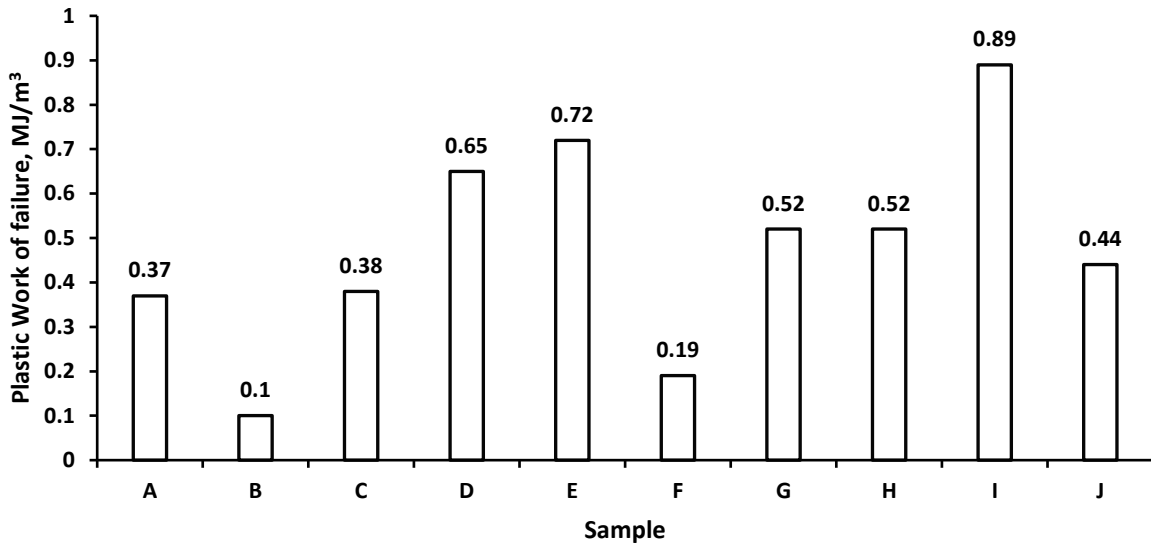
Figure 4.25: Plastic work of failure for Ontario contract samples at 15°C.

It can be observed that, Ontario contract samples D, E, and I have higher plastic work of fracture, indicating high strain tolerance as compared to others.
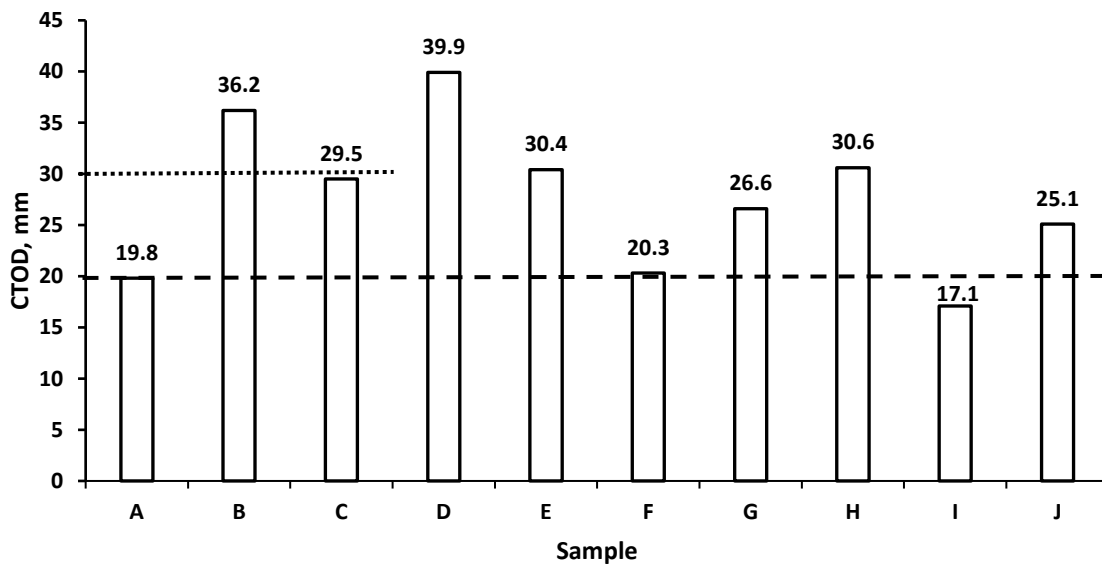

Figure 4.26: CTOD values for all Ontario contract samples at 15°C. (The dotted black line indicates CTOD limit for binder PG-40 and the dashed black line indicates CTOD limit for binder PG-34.)

Eventually, the correlation existing between fatigue properties and CTOD are higher than the essential work of failure and the plastic work of fracture. It has been observed that, contract samples D, E, G, H, and J have high CTOD, indicating high strain tolerance in the ductile state, as shown in Figure 4.26. But the contract samples A, C and I have low CTOD (below CTOD limit), showing its low strain tolerance in ductile state, thus it is more susceptible to premature cracking in service.

4.5.2.2 DENT Test Analysis at 5°C

Figure 4.27 and 4.28 Show a comparision of essential and plastic work of failure at 5°C. It can be observed that, sample C has the higest essential and plastic work of failure. As already mentioned in previous section, it is generally expected that samples with higher values of essential and plastic work of fracture provide better resistance to fatigure cracking. However, CTOD explains more clearly about fatigue cracking then essential work of fracture. As shown in Figure 4.29, CTOD values for all three samples are quite low which is below the CTOD limit.
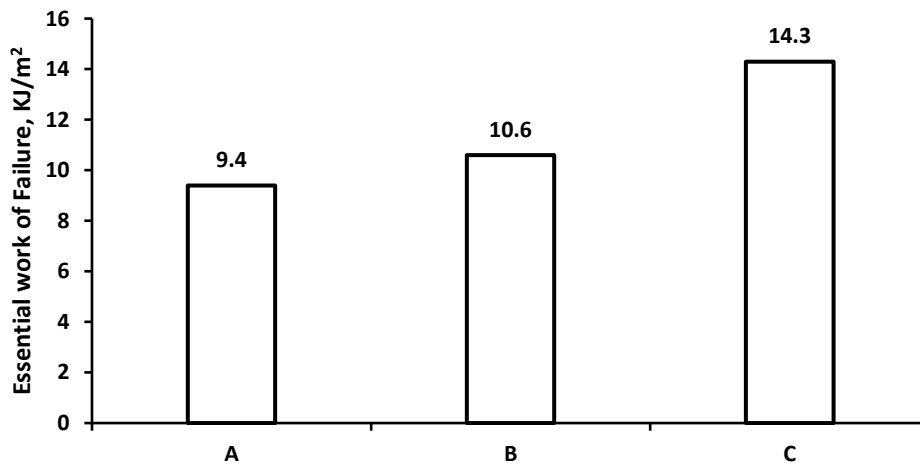

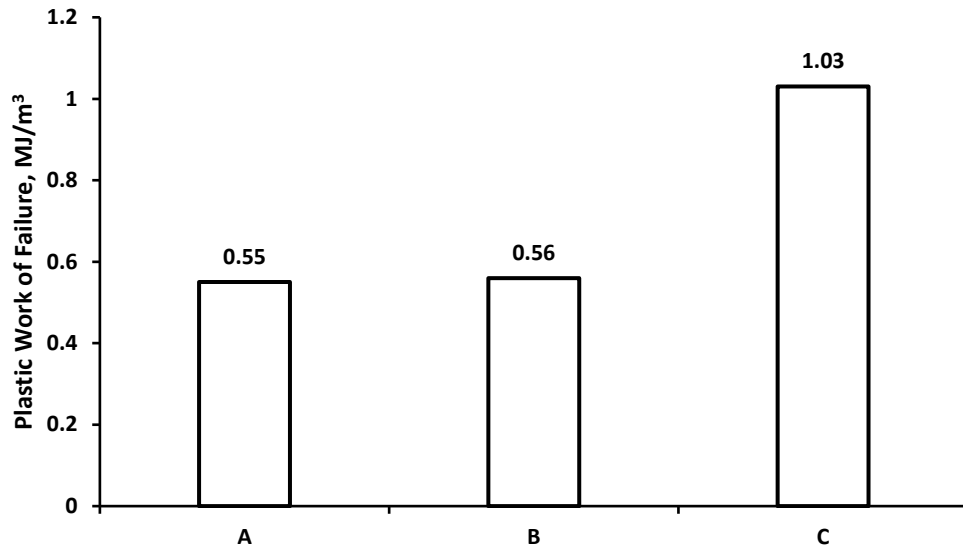Figure 4.27: Comparison of essential work of failure at 5°C.

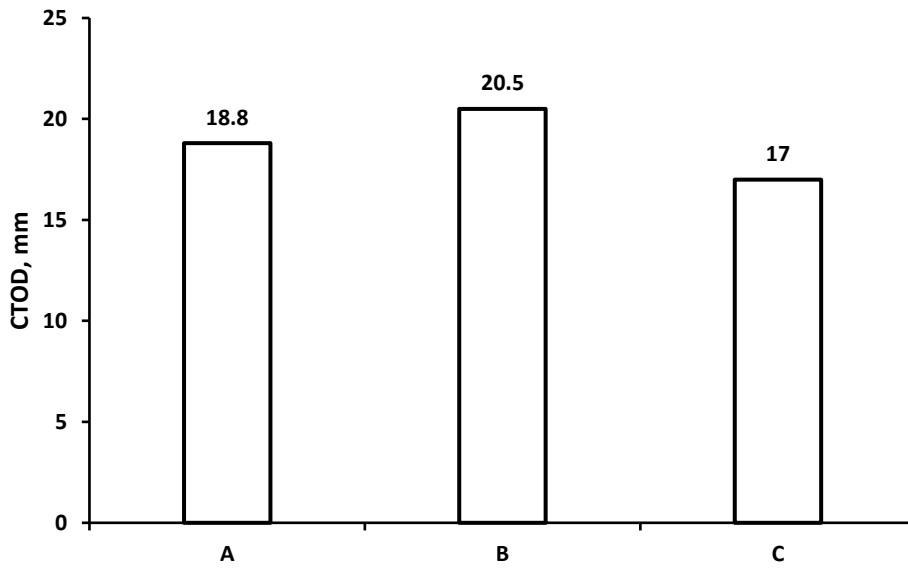Figure 4.28: Comparison of plastic work of failure at 5℃.

Figure 4.29: Comparison of CTOD at 5℃.

4.5.2.3 DENT Test Analysis at 10ºC

Figure 4.30: Comparison of essential work of failure at 10ºC.

Figure 4.31: Comparison of plastic work of failure at 10ºC.

Figure 4.32: Comparison of CTOD at 10°C.

Figures 4.30, 4.31 and 4.32 show a comparision of essential work of failure, plastic work of failure and CTOD. The samples D, H and I have a higher essential and plastic work of frailure as compared to other samples. It is quite evident that sample D and H have high CTOD value as well as essential and plastic work of failure, indicating high strain tolerance and better performance in service. Sample G barely passed the CTOD limit and the remaining samples have low CTOD (below CTOD limit), showing their low strain tolerance in ductile state, thus it is more susceptible to premature cracking in service.
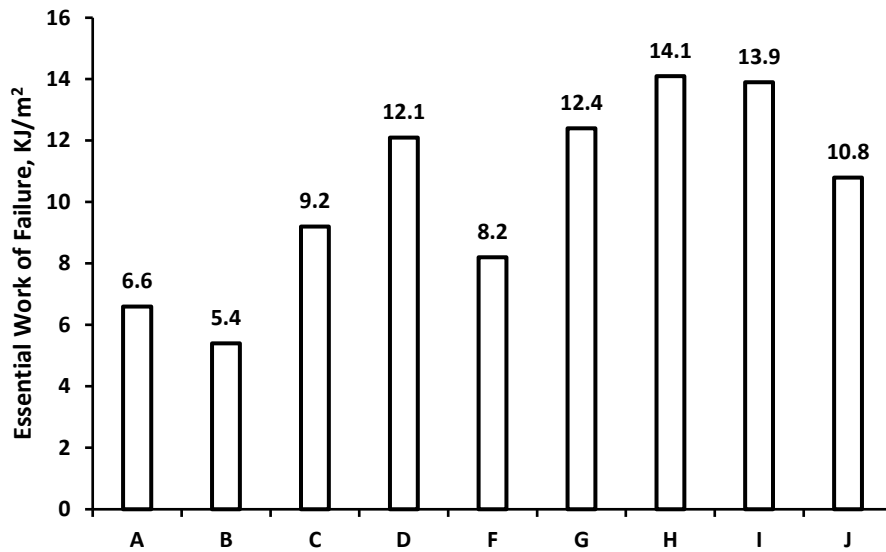
4.5.2.4 DENT Test Analysis at 20ºC

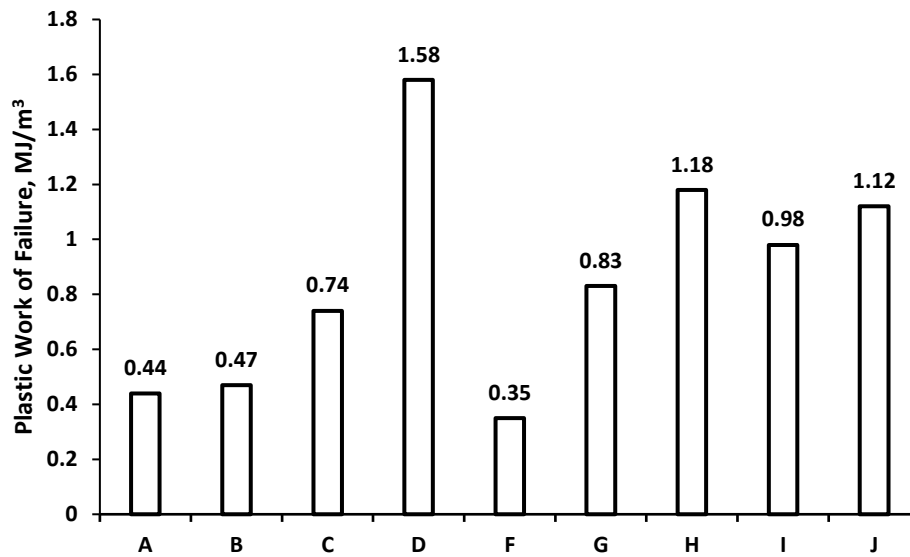Figure 4.33: Comparison of essential work of failure at 20ºC.

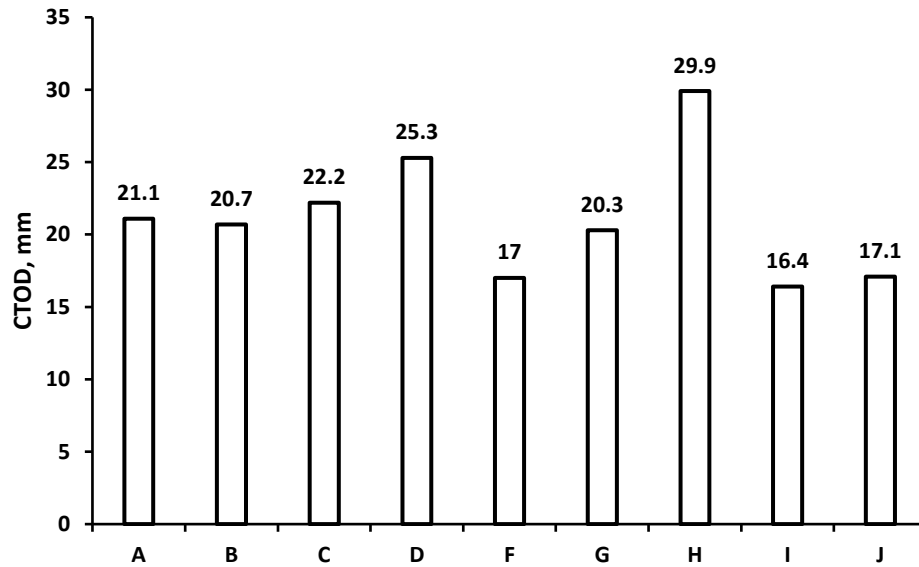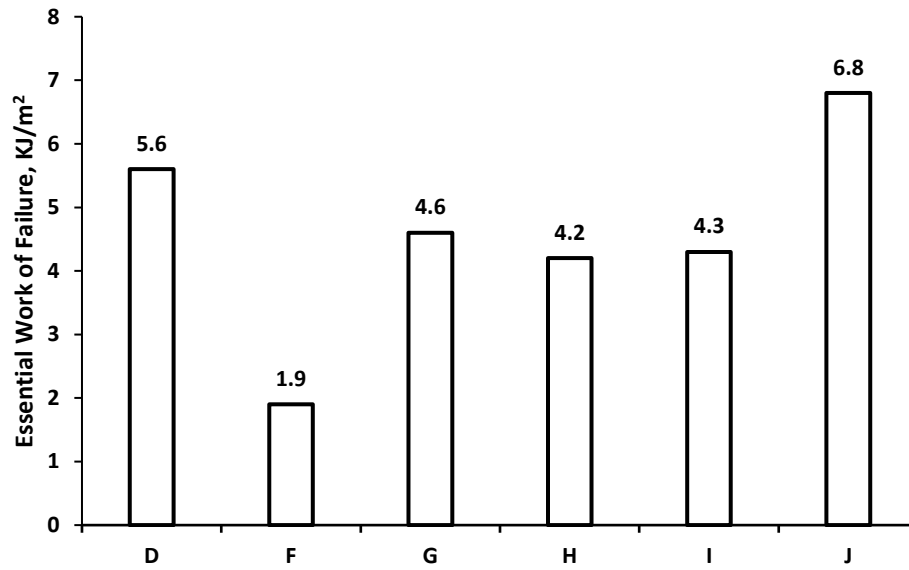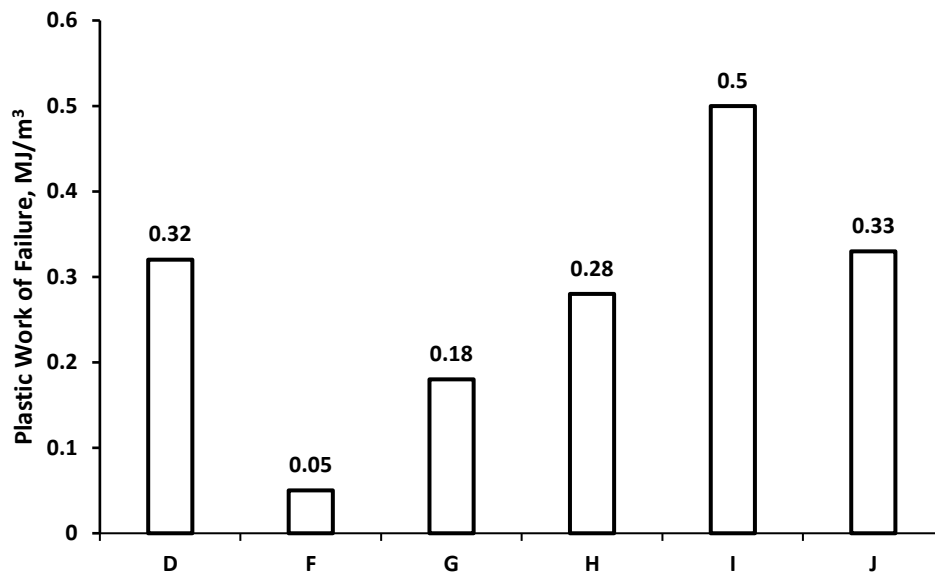Figure 4.34: Comparison of plastic work of failure at 20ºC.
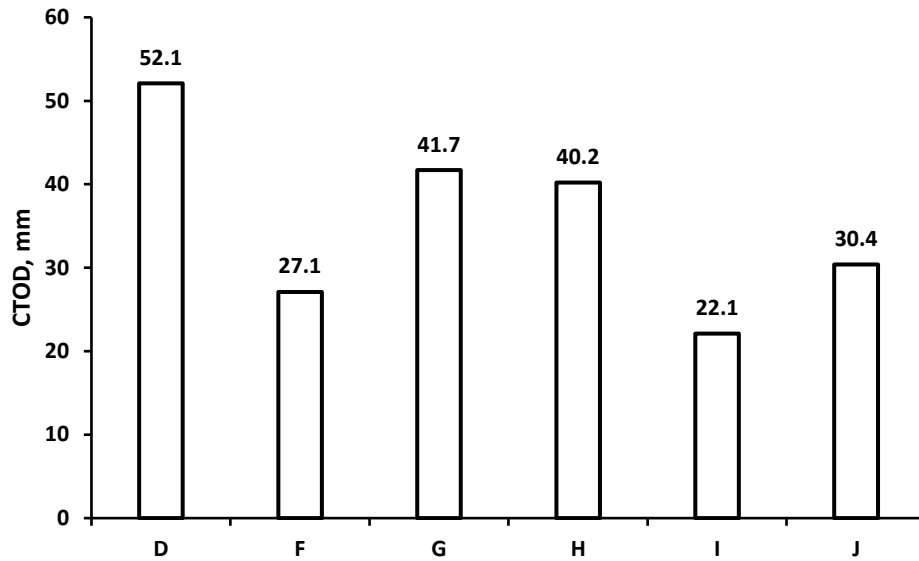
Figure 4.35: Comparison of CTOD at 20°C.

Figures 4.33 and 4.34 show the comparision of essential and plastic work of fracture a 20°C. Sample D and J have a higher strain tolerance in terms of essential work of fracture whereas sample F has the lowest strain tolerance. Sample D, I and J have a higher plastic work of fracture in comparision to remaining samples. Sample F is most susceptible to fatigue distress in terms of plastic work of fracture. The comparision of CTOD values at 20°C is shown in Figure 4.35.

It can be observed that sample D has the highest CTOD value which shows the best performance in terms of resistance to fatigue cracking. Remaining samples pass the CTOD limit. In order to draw reasonable conclusions with respect to the effect of temperature on the performance of binder in terms of fatigue distress, a comparative study was performed on essential work of fracture, plastic work of fracture, and CTOD. Higher CTOD value for sample G, H and I might be due to the addition of polymer modifiers to improve the performance based properties of the asphalt cement.

4.5.2.5 CTOD Analysis at Different Temperatures

The ductility of the different Ontario contract samples were measured using DENT test at three different temperatures, either 5°C, 10°C, 15°C, 20°C, or 25° based on their performance grade. One of the most important part of this thesis is to study different grades at 15°C and to investigate the application of CTOD requirements at different temperatures, other than 15°C.
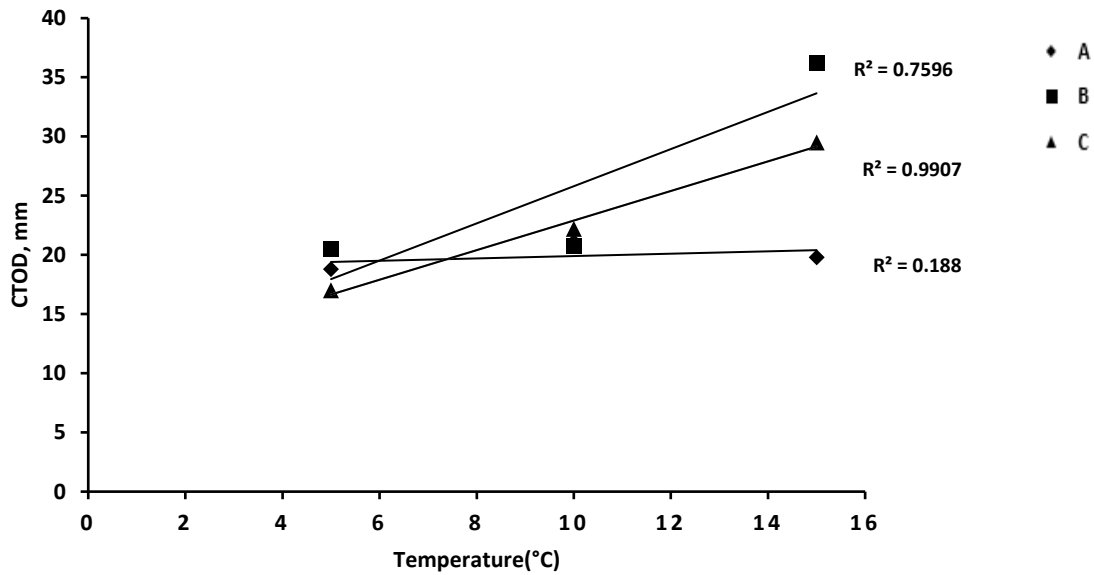
Figure 4.36: CTOD versus temperature at different temperatures.

As shown in Figure 4.36 and 4.37 the variation of CTOD with temperature was studied to show their correlation. The regression coefficient of these straight lines for all samples were observed. The R^2 value ranges from 0.80 to 1.00 expect for samples A and B, conclusively indicating that the CTOD values are strongly correlated with temperature. The extremely low R^2 value for sample A might be due to experimental errors or inadequate conditioning time.

						$R^2 = 0.9973$		×	D
						$R^2 = 0.9466$		✳	F
						$R^2 = 0.8007$		●	G
						$R^2 = 0.9864$		+	H
						$R^2 = 0.9615$		-	I
						$R^2 = 0.8405$		—	J
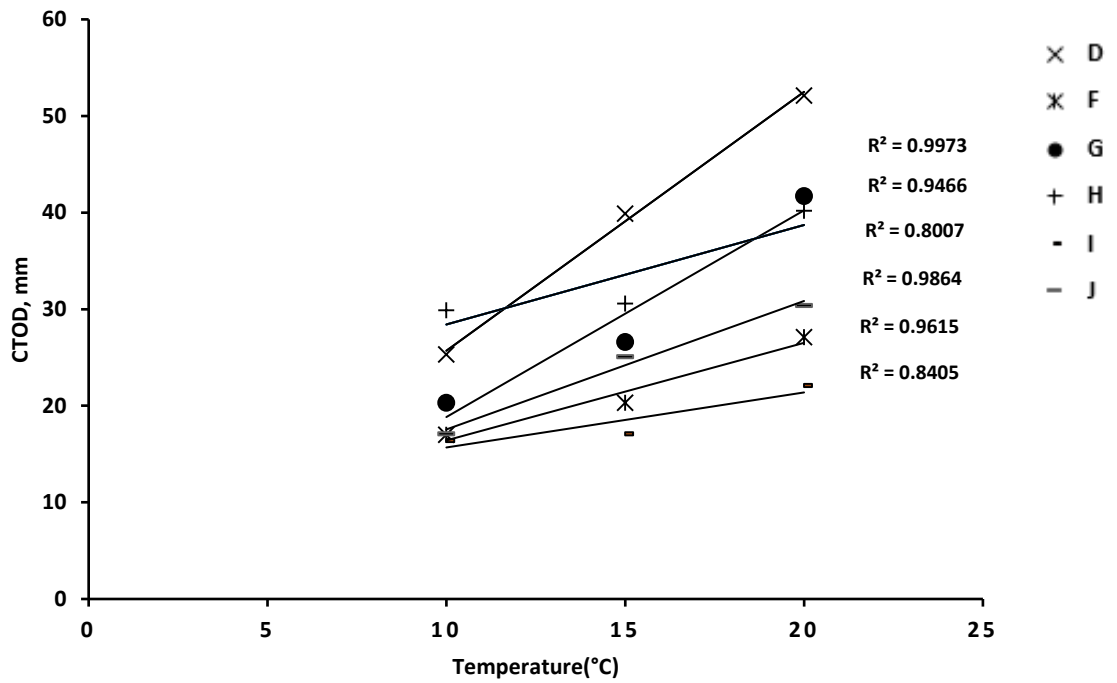
Figure 4.37: CTOD versus temperature at different temperatures.

4.5.2.6 Comparison of DENT Results at Different Temperature
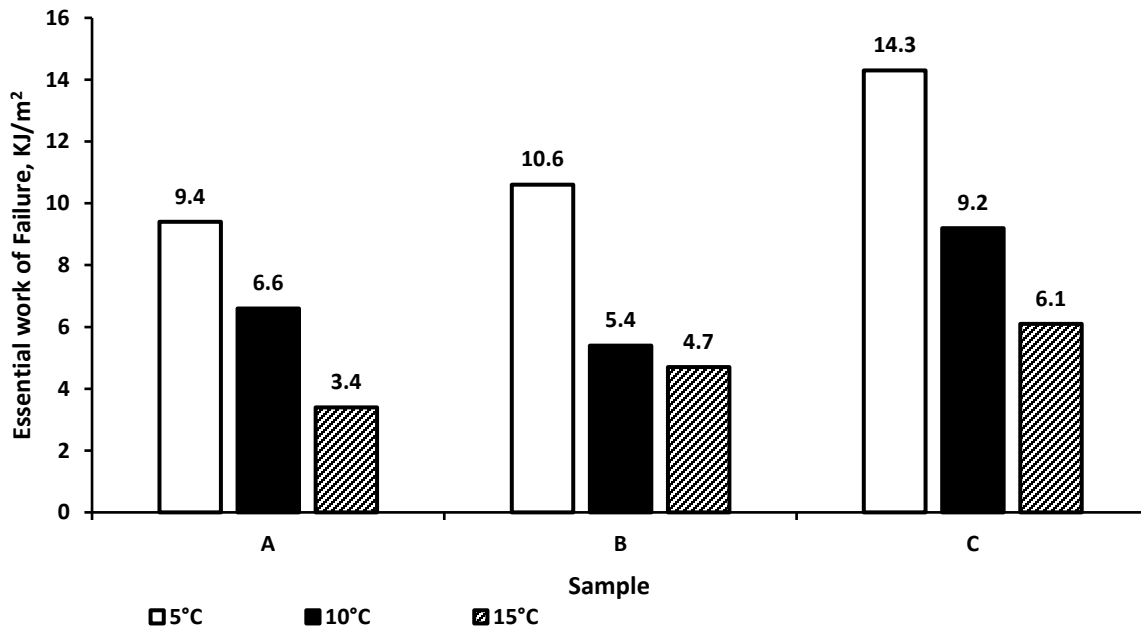
Figure 4.38: Essential work of fracture for Ontario contract samples at different temperatures.
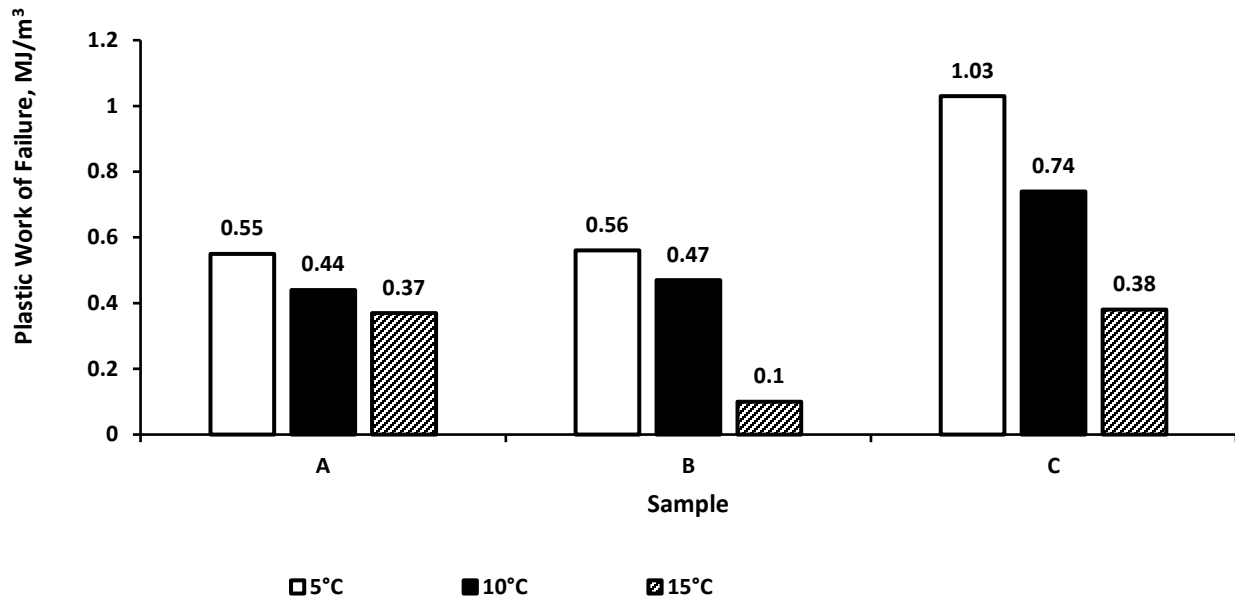
Figure 4.39: Plastic work of fracture for Ontario contract samples at different temperatures.
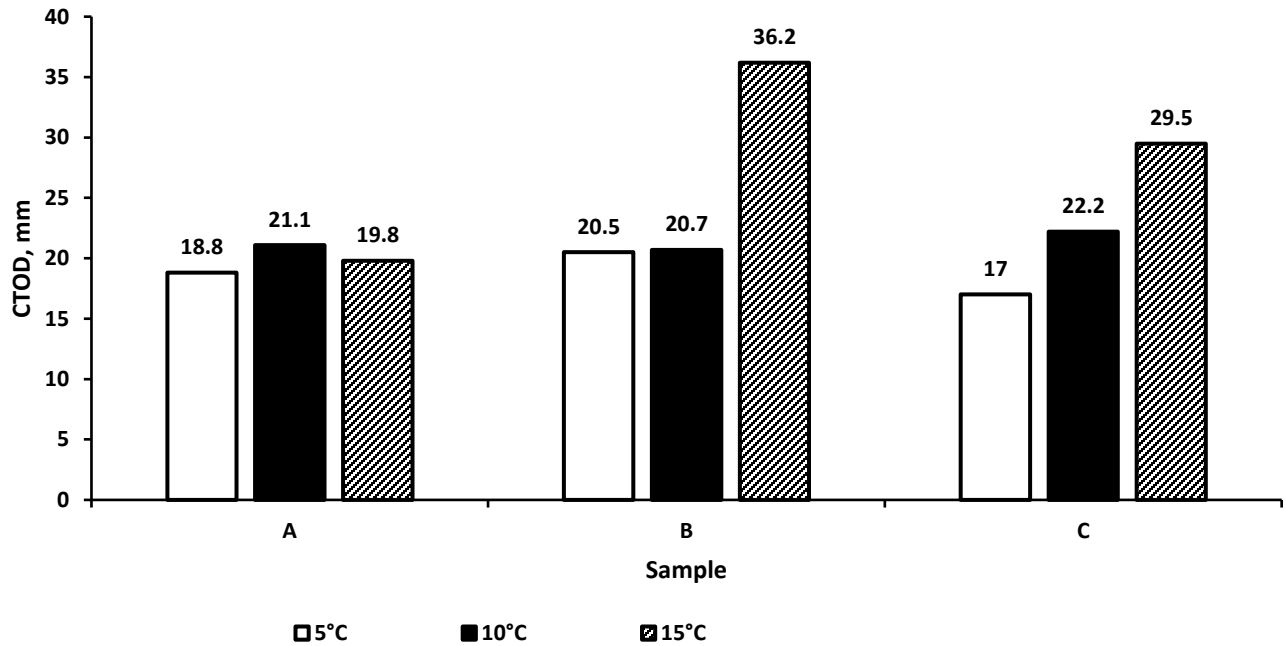
Figure 4.40: CTOD values for Ontario contract samples at different temperatures
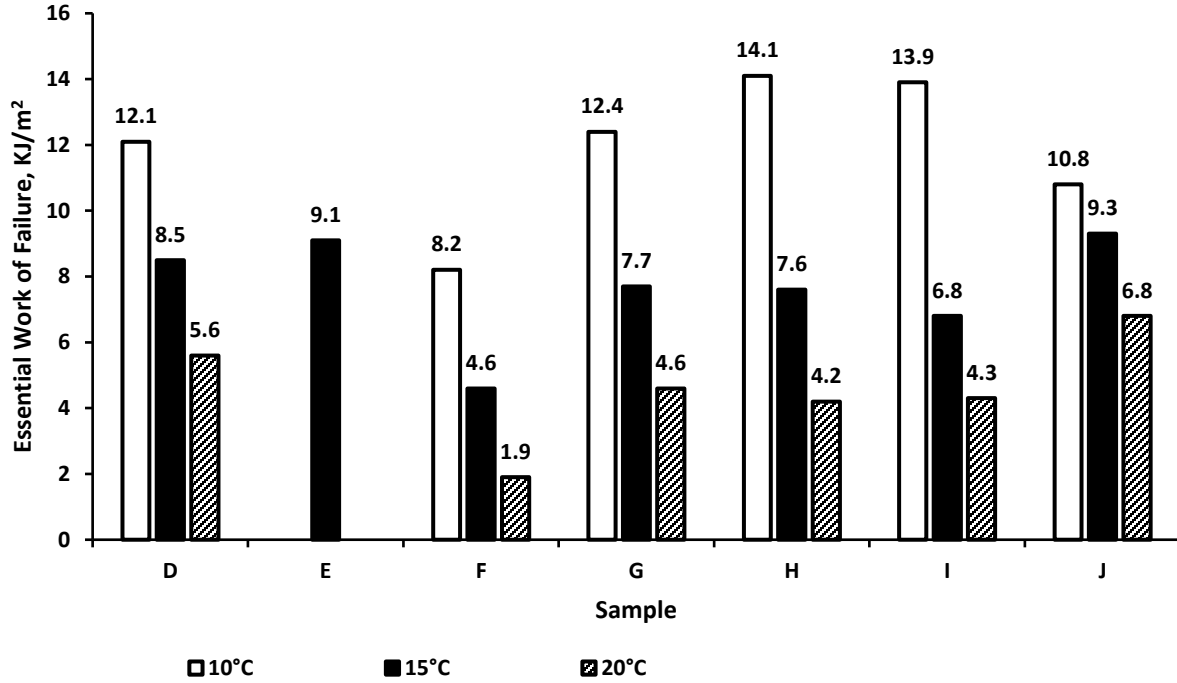
Figure 4.41: Essential work of fracture for Ontario contract samples at different temperatures.
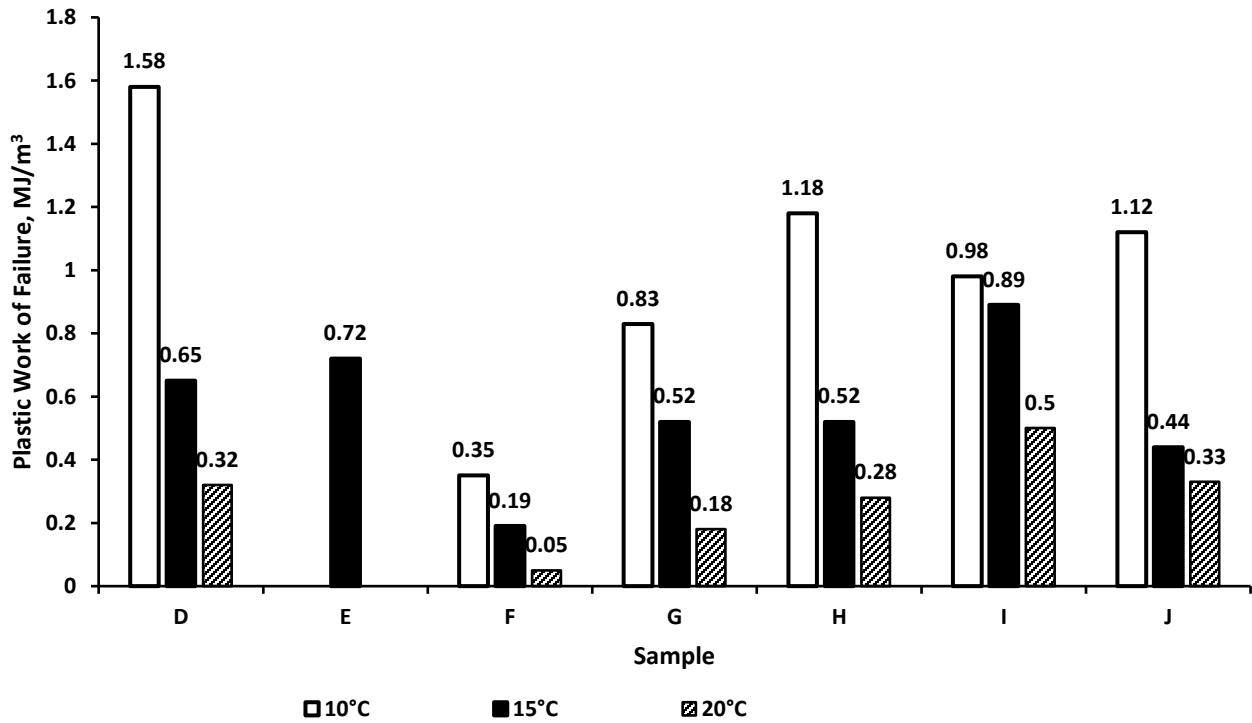
Figure 4.42: Plastic work of failure for Ontario contract samples at different temperatures.
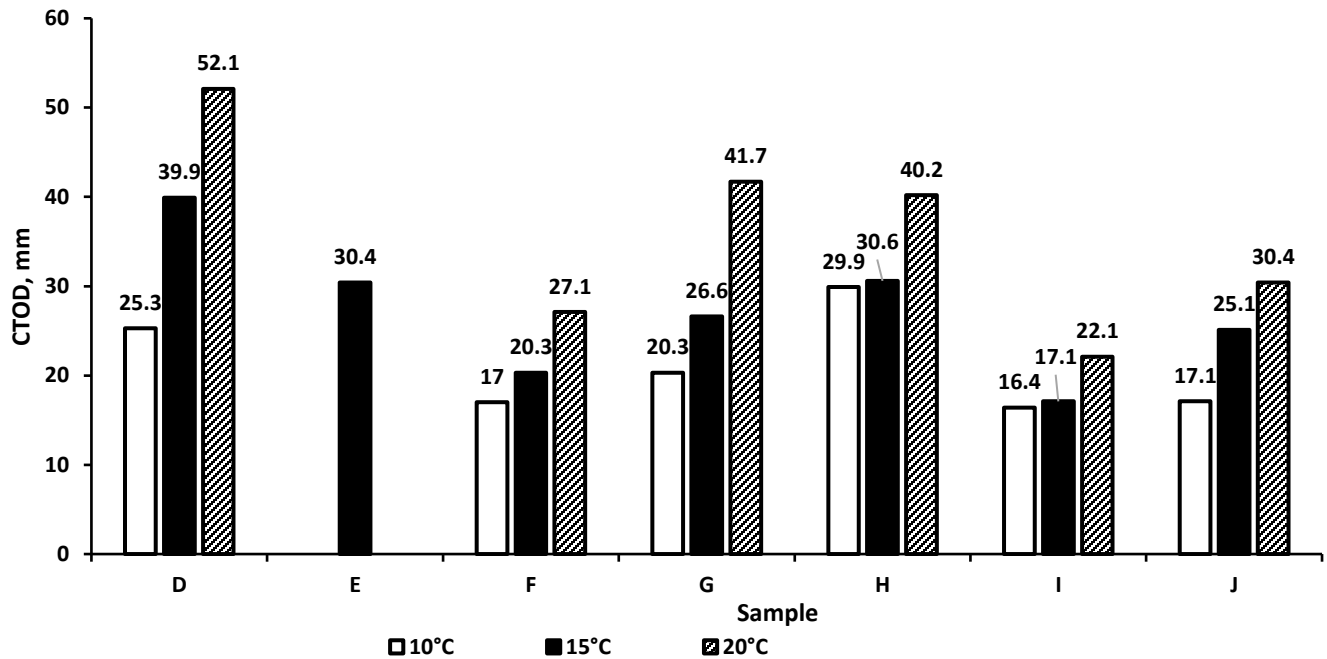
Figure 4.43: CTOD values for Ontario contract samples at different temperature.

Figures 4.38 to 4.43 show the essential work of failure, plastic work of fracture, and CTOD for all Ontario contract samples at different temperature. The data give the relationship between essential work of failure, plastic work of fracture, and CTOD with temperature. It can be observed that essential and plastic work of fracture decrease as temperature increases. On the other hand, CTOD value increases with the temperature. The lower CTOD value in case of sample A at 15°C might be due to experimental errors.

Chapter 5

SUMMARY AND CONCLUSION

The following conclusions can be drawn on the basis of the background, experimental procedures, results and discussions of this thesis:

- Based on the DENT and eBBR results, tank samples have better performance in service as compared to recovered samples. Tank samples cannot be considered as representative of the samples from the pavement in the field because unknown changes may have happened during construction.

- XRF and FTIR are effective tools to detect detrimental chemical contents in the asphalt binder. Chemical oxidation and hardening of asphalt binders deteriorates its physical properties, since physical properties of asphalts depend on its chemical composition. Detection of carbonyl and polyisobutylene in FTIR, and zinc and molybdenum in XRF, indicates the presence of waste engine oil residue in the asphalt binders. It causes premature hardening due to the precipitation of asphaltenes that are formed during oxidation in service. FTIR analysis showed the likely evidence of oxidized residues in Ontario contract samples C and I.

- CTOD is such a parameter which provides better correlation with the field performance at the time of ductile failure in the asphalt pavement. It was observed that sample M12T had the highest CTOD, essential and plastic work of fracture. This sample might be modified with Styrene-Butadiene-Styrene (SBS) and can perform better in service, as evident in FTIR analysis.

- The CTOD values are strongly correlated with temperature. Thus, current CTOD requirements at 15°C in LS-299 DENT test protocols can be applied at other temperatures.

- The Black space diagrams showed that all samples are rheologically simple at low temperatures. But at high temperature, these samples are rheologically complex, except M12T and M14T. It might be due to the phase separation at high temperature.

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