Development of Non-Petroleum-Based Binders for Use in Flexible Pavements – Phase II

Final Report
October 2015

ASPHALT MATERIALS &
PAVEMENTS PROGRAM

IOWA STATE UNIVERSITY

Institute for Transportation

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The preparation of this report was financed in part through funds provided by the Iowa Department of Transportation through its "Second Revised Agreement for the Management of Research Conducted by Iowa State University for the Iowa Department of Transportation" and its amendments.

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Iowa Department of Transportation or the U.S. Department of Transportation.

Technical Report Documentation Page

1. Report No. IHRB Project TR-650	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Development of Non-Petroleum-Based Binders for Use in Flexible Pavements – Phase II		5. Report Date October 2015	
		6. Performing Organization Code	
7. Author(s) R. Christopher Williams, Joana Peralta, and Ka Lai Ng Puga		8. Performing Organization Report No. InTrans Project 12-447	
9. Performing Organization Name and Address Institute for Transportation Iowa State University 2711 South Loop Drive, Suite 4700 Ames, IA 50010-8664		10. Work Unit No. (TRAIS)	
		11. Contract or Grant No.	
12. Sponsoring Organization Name and Address Iowa Highway Research Board Iowa Department of Transportation 800 Lincoln Way Ames, IA 50010	Federal Highway Administration 1200 New Jersey Avenue SE Washington, DC 20590	13. Type of Report and Period Covered Final Report	
		14. Sponsoring Agency Code IHRB and SPR Project TR-650	
15. Supplementary Notes Visit www.intrans.iastate.edu for color pdfs of this and other research reports.			

16. Abstract

Bio-binders can be utilized as asphalt modifiers, extenders, and replacements for conventional asphalt in bituminous binders. From the rheology results of Phase I of this project, it was found that the bio-binders tested had good performance, similar to conventional asphalt, except at low temperatures. Phase II of this project addresses this shortcoming and evaluates the Superpave performance of laboratory mixes produced with the enhanced bio-binders.

The main objective of this research was to develop a bio-binder capable of replacing conventional asphalt in flexible pavements by incorporating ground tire rubber (GTR) into bio-oil derived from fast pyrolysis of agriculture and forestry residues. The chemical compatibility of the new bio-binder with GTR was assessed, and the low-temperature performance of the bio-binders was enhanced by the use of GTR.

The newly developed binder, which consisted of 80 percent conventional binder and 20 percent rubber-modified bio-oil (85 percent bio-oil with 15 percent GTR), was used to produce mixes at two different air void contents, 4 and 7 percent. The laboratory performance test results showed that the performance of the newly developed bio-binder mixes is as good as or better than conventional asphalt mixes for fatigue cracking, rutting resistance, moisture sensitivity, and low-temperature cracking. These results need to be validated in field projects in order to demonstrate adequate performance for this innovative and sustainable technology for flexible pavements.

17. Key Words asphalt-rubber—bio-binder—bio-oil—fast pyrolysis—flexible pavements—mixtures—rheology—sustainability		18. Distribution Statement No restrictions.	
19. Security Classification (of this report) Unclassified.	20. Security Classification (of this page) Unclassified.	21. No. of Pages 130	22. Price NA

Form DOT F 1700.7 (8-72)   **Reproduction of completed page authorized**

DEVELOPMENT OF NON-PETROLEUM-BASED BINDERS FOR USE IN FLEXIBLE PAVEMENTS – PHASE II

Final Report
October 2015

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EXECUTIVE SUMMARY

Asphalt is the most common binder material used in road construction. However, the need for more durable and safer pavements requires a better understanding of asphalt in terms of its aging mechanisms and how its characteristics can be improved by the addition of polymers. Although asphalt modified with crumb rubber from used tires has been applied with great success all over the world since the 1960s, the interactions between the asphalt and rubber are not yet fully understood.

Bio-oil produced by fast pyrolysis of organic waste materials has been commercially available for over a decade. This material is mainly used as fuel, in ways similar to petroleum. However, the heavy fractions of bio-oil are similar to those of asphalt, and bio-oil may prove to be an excellent asphalt substitute. From the first phase of this project, it was concluded that bio-oils are viscoelastic materials and can be used after applying a heat treatment. After this treatment, bio-binders have a viscosity and high/intermediate thermal rheological behavior similar to many types of asphalt used in the paving industry. These two characteristics show that this material can be a good alternative to replace asphalt. However, it was found that the low-temperature performance of bio-binders varied significantly compared to bitumen binders. To improve the performance of bio-oil, it was hypothesized that the addition of crumb rubber would change the rheology of the modified bio-oil, making it rheologically similar to conventional paving asphalts. Therefore, two sources of ground tire rubber (GTR) from used tires, from different manufacturing processes, were used to modify the bio-oil. Then, blends were produced by adding 20% (weight/weight) of this bio-binder to two different asphalts, PG58-28 and PG64-22. Chemical characterization of the developed materials was performed to better understand the chemical compatibility between the GTRs and bio-binders.

The overall conclusions from the second phase of this project can be summarized as follows. The addition of GTR produced chemical changes in the structure of the bio-binders, as established by the Fourier transform infrared (FTIR) spectroscopy results. The bio-blends produced had rheological properties similar to those of conventional asphalt, including thermal rheological behavior, aging susceptibility, and separation tendency. According to the performance testing results, the performance of the mixes developed with the bio-blends was as good as or better than conventional asphalt mixes for moisture susceptibility, fatigue cracking, dynamic modulus, flow number, and low-temperature fracture resistance. These results need to be validated in pavement trials, after asphalt plant production, in order to demonstrate adequate performance. Highway agencies can then use higher quantities of bio-oil as an alternative binder material for pavements, which can present technological, environmental, and economic advantages.

CHAPTER 1. INTRODUCTION

Background

Asphalt, or bitumen, is "a black sticky substance that is used for making roads" (MacMillan Dictionary 2013). Although this material is usually associated with the residue from petroleum distillation, the bio-oil from fast pyrolysis of agriculture and forestry residues can also be included in the previous definition when the bio-oil is used as a binder in flexible pavement construction (bio-binder or bioasphalt).

In fact, both crude petroleum and unfractioned bio-oil are the result of the degradation of organic materials, mainly plants, under vacuum. Although petroleum is naturally obtained at ambient temperatures while bio-oil from fast-pyrolysis requires high temperatures, the main difference between them is the amount of time needed to obtain each one of the above mentioned materials. The longer time needed to obtain petroleum has some implications at the chemical level, such as the formation of very big molecules (e.g., asphaltenes). Additionally, the process to obtain paving grade asphalt, either from petroleum or from bio-oil, is also similar; asphalt is the residue of the distillation of petroleum, and bio-oil is the result of the condensation of a fraction of the pyrolysis liquid. Usually, both asphalt distillation residue and bio-oil require some post-treatment to ensure that materials with the adequate characteristics are applied as binders in pavement construction; however, paving grade asphalt can be directly produced after distillation using blowing or deasphalting, and paving grades of bio-oil might be readily obtained from the fractionation process.

In terms of road construction, using mixtures of asphalt with rubber allows the thickness of the asphalt mixtures layers to be reduced (Amirkhanian 2003) and a product with superior performance to be obtained (Thodesen et al. 2009) because these mixtures are structurally and functionally better. These improvements mainly contribute to the reduction of reflective cracks. In addition, the use of asphalt modified with crumb rubber contributes to sustainable development by setting a final destination for waste tires from cars and trucks (Campos 2007) and improving the performance and safety of the pavement (Jeong et al. 2010). As compared to pavements built with conventional asphalt, pavements built with asphalt-rubber (AR) blends have prolonged life (Xiang et al. 2009, Lee et al. 2008).

Additionally, the substantial increase in oil prices over the past five years has been reflected in asphalt prices and has caused a reduction in its supply due to the maximization of fuel production in refineries. In fact, many refineries have installed coking facilities to further increase the production yield of transportation fuels, resulting in a reduction in the supply of asphalt. This has led to the production of a distillation residue that cannot be used as binder in asphalt mixtures. The reduced supply of asphalt has also prompted the substantial product development of alternative sources of asphalt binders, including the fractionation of bio-oil from the fast pyrolysis of biomass, which has the potential for application in asphalt as an additive/modifier/extender, especially in mixtures with polymers (Williams et al. 2009). In fact, bio-oil may even replace asphalt entirely because it presents rheological properties similar to those of asphalt (Raouf and Williams 2010d, Peralta et al. 2012b).

Combining the benefits of recycling waste materials (such as rubber from used tires and residues from agriculture and forestry activities) with asphalt, which is ultimately the residue of crude petroleum distillation, by applying well-known technologies (such as fast pyrolysis and asphalt-rubber production methods) can change the way binders for flexible pavements are envisioned. However, a more profound knowledge of the chemistry of and the interactions between these different materials must be achieved in order to successfully develop an alternative binder that is capable of enhancing pavement performance, safety, and durability.

Because most polymers currently used as asphalt modifiers have a high melting point while bio-oil should be handled at lower temperatures, the use of polymers with bio-oil is restricted. The need to modify bio-oil with polymers for pavement construction is due to the bio-oil poor performance at low temperatures, even after a heat treatment to remove residual water and volatiles.

Report Objectives

The main objective of this project was to understand the interaction behavior of asphalt/bio-oil/ground tire rubber (GTR) to effectively replace petroleum asphalt, partially or totally, by using bio-oil from the fast pyrolysis of agriculture and forestry residues and consequently optimize the performance of asphalt mixtures with asphalt-rubber (AR).

Thus, this work aimed to develop asphalt-rubber mixtures with an optimized binder (using petroleum asphalt, bio-oils from fast pyrolysis of biomass, or both in combination), improved performance throughout the life of the pavement, and greater stability during the production and construction stages. This work promotes research, development, and innovation because it should be possible to use this new product in the rehabilitation of the current roadway system, as well as in the construction of new roads and highways, with a substantial reduction in environmental and economic costs.

Overall Report Experimental Plan

The aim of this study was to characterize the different components of the studied binders (e.g., petroleum asphalt or asphalt, bio-oil, and ground tire rubber) in order to understand how the binders change and interact when subjected to different treatments.

Therefore, the first component of the experimental plan was to characterize the unmodified binders (asphalt and bio-oil), which included the characterization of different asphalts and bio oils and the determination of their physical, rheological, and chemical properties. This phase also included the evaluation of the effect of the asphalt's aging, as well as the asphalt's chemical composition and physical and rheological properties during the production of the bio-binders with GTR.

After characterization of the materials (asphalt/bio-oil and rubber), the materials were mixed so that they would interact under predefined conditions. Thus, the characterization of the various

binders was conducted in this stage of the experimental work to evaluate how the asphalt and bio-oil interact with the rubber to produce asphalt-rubber and bio-binder. The objective of this phase was to understand the changes in the rubber caused by temperature and by the rubber's interactions with the asphalt and bio-oil, particularly the degree of rubber swelling and de-vulcanization. At this stage of the work, the researchers also tried to determine the main properties of the modified binders produced with asphalt/bio-oil and rubber.

At present, the commercial production of fractionated bio-oil from fast pyrolysis with suitable characteristics is insufficient for the paving industry to fully replace petroleum asphalt. However, partial replacement might be possible and desirable from an economic and environmental point of view. Therefore, some techniques were developed to design or develop a new binder by blending some of the previously produced bio-binders with two petroleum asphalts currently used in the asphalt paving industry. Several binder blends were produced, and the chemical, physical, and rheological properties were assessed. The binder showing the best properties was selected for use in the following phase.

The binder selected in the previous phase was used to design a new asphalt mixture produced with local aggregates from Iowa, taking into account the impact of the volumetric composition of the mixtures (aggregate, binder, filler, and voids), the conditions to be used for the mixture production (temperature, time of manufacture), and the mixing and compaction temperatures. Specimens for different performance tests were produced using the mixtures previously designed to determine their characteristics and estimate their durability or lifetime under specific traffic levels and weather conditions. The performance tests carried out included dynamic modulus, fatigue cracking, moisture sensitivity, flow number, and fracture mechanics at low temperatures for specimens compacted at 4% and 7% air voids.

Hypothesis

Bio-oil has great antioxidant properties due to its naturally occurring high lignin content. Furthermore, bio-oil also contains significant amounts of furfural, which is beneficial in promoting interactions between asphalt and rubber (Shatanawi et al. 2012). Moreover, regarding ground tire rubber, Wang et al. (2012) reported a reduction in creep stiffness, and thus a decrease of binder performance grade (PG), at low temperatures from -22 to -28 °C by modifying conventional asphalt with 10% ground tire rubber. Therefore, it was hypothesized that the addition of ground tire rubber to the bio-oil may improve its low-temperature characteristics, and the properties of this new bio-binder should be comparable to, and maybe surpass, the properties of conventional asphalt paving binder.

Content of this Report

Chapter 1 presents a brief background, including the main objectives of the study. The essential literature review is presented in Chapter 2, which summarizes the chemical constitution of the materials (asphalt, bio-oil, rubber, and asphalt-rubber), production, interaction mechanisms, and characterization, followed by the rheological and empirical-mechanic characterization methods of the binders for pavements. At last, the mixes behavior and performance literature is revised.

Chapter 3 delineates the experimental methods used throughout the different stages of this study. Chapter 4 describes the chemical study of the bio-oil modification with ground tire rubber to produce a bio-binder suitable for use at a large range of temperatures. Chapter 5 presents the study of the chemical characteristics of the developed bio-oil blends and their comparison with conventional asphalts. Chapter 6 presents the study of the rheological characteristics of the bio-oil blends developed in Chapter 5. Chapter 7 combines the study of several binders (simple binders and blends of bio-binder with asphalt) and presents the results of the mix design and characterization of a paving mixture produced with the best of the studied binder blends. For this chapter, some techniques were developed to design or develop a new binder through the blending of some of the bio-binders previously produced with two petroleum asphalts currently used in the asphalt paving industry. The paving mixture was evaluated by means of performance tests, such as dynamic modulus, fatigue cracking, moisture sensitivity, and fracture mechanics at low temperatures, in order to forecast durability or lifetime under specific traffic levels and weather conditions. Finally, conclusions and recommendations for future research are presented in Chapter 8.

CHAPTER 2. LITERATURE REVIEW

Binder Materials Production and Characterization

Petroleum Asphalt

Asphalt has been known since antiquity and it is considered a complex material. It is a primary engineering material, often employed as binder in road construction and roofing systems, due to its thermoplastic nature, its water resistance and its adhesion with most other substances. Asphalt possesses strong temperature dependent rheological properties, governed by the physicochemical interactions of their individual constituents (Loeber et al. 1998).

Mixing of mineral aggregate and asphalt produces asphalt mixes, also referred to as asphaltic concrete or asphalt mix (Rodriguez-Valverde et al. 2008). Usually, in order to dry the mineral aggregates and obtain adequate fluidity (handling) of the asphalt, both the mineral aggregates and the asphalt must be heated prior to mixing. This is the origin of the term hot-mix asphalt (Rodriguez-Valverde et al. 2008, Youtcheff 2006, Usmani 1997).

Definition of Petroleum Asphalt

Asphalt is a semisolid viscoelastic material, which can be produced by the non-destructive distillation of crude oil during petroleum refining (Rodriguez-Valverde et al. 2008). It can also be found in nature as "natural asphalt" (Redelius 2004). One of the most important surface deposits of "natural" asphalt is located in Trinidad, and is referred to as "Trinidad Lake Asphalt" (Read and Whiteoak 2003).

Studies carried out indicate that asphalt is a complex mixture of a wide variety of molecules: paraffinics, naphthenics, and aromatics including heteroatoms. This complexity makes the prediction of asphalt properties particularly difficult (Michon et al. 1997).

Petroleum Asphalt Production

The overwhelming majority of crude refiners use atmospheric or vacuum distillation to refine crude petroleum. While there is some solvent refining and air blowing utilized, they are clearly of secondary importance (Youtcheff 2006). Upgrading of low-grade asphalt is usually carried out by the air-blowing process to produce oxidized or semi-blown products (Oyekunle 2006).

Asphalt is manufactured from crude oil following the steps described below and presented in Figure 1 (Read and Whiteoak 2003).
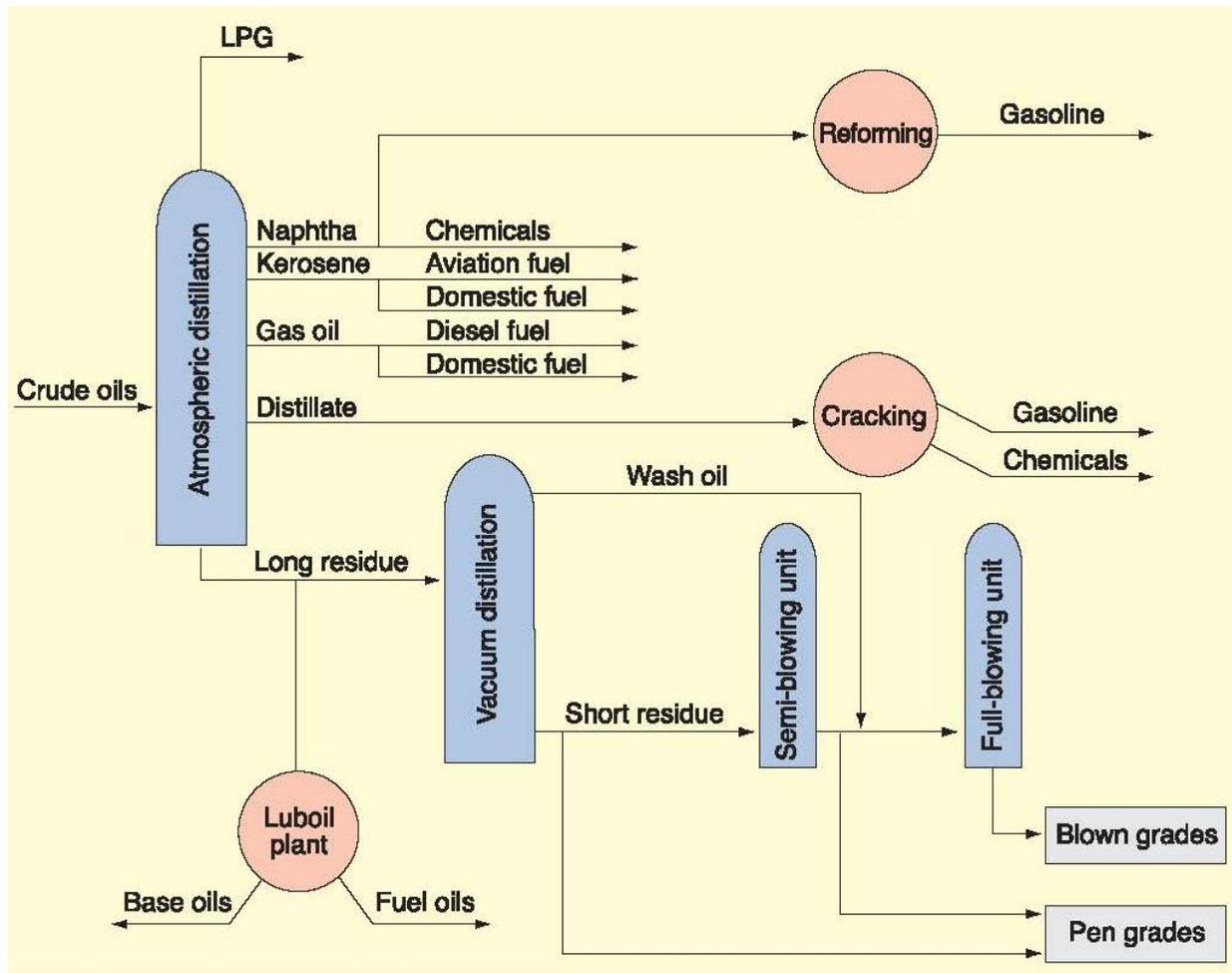
Read and Whiteoak 2003

Figure 1. Schematic representation of the crude oil distillation process

1. Fractional distillation of crude oil at a temperature of 350-380 °C and pressure slightly above atmospheric (in the bottom of the column is taken the heaviest fraction from the crude oil distillation, the long residue).
2. Distillation of the long residue in a vacuum (10-100 mmHg) distillation column at a temperature of 350-425 °C (taken in the bottom of this column is the short residue).
3. Air blowing of short residues by passing air through the short residue, either in a batch or a continuous basis at temperatures between 240 and 320 °C, producing more than 20 different asphalt penetration grades in the range 35 to 300 mm.
4. Beyond blowing process there is another secondary process, called deasphalting which residue is the raw material of asphalt binder.

There are nearly 1,500 different crudes produced throughout the world. Based on the yield and quality of the resultant product, only a few of these are considered suitable for the manufacture of asphalt (Read and Whiteoak 2003).

Chemical treatment of one cut or a blend of different cuts will produce asphalt with special properties that are not imparted by the distillation process. When several processes are applied to one or more crudes, the resultant asphalt blends have properties clearly superior to those obtained when only one manufacturing process is used. Furthermore, the method of production greatly influences the structure and the chemical composition of asphalt, and that determines its rheological properties and the final end uses (Oyekunle 2006).

Chemical Characterization of Petroleum Asphalt

Crude heavy fractions that constitute asphalt are defined as molecules containing between 25 and 150 carbon atoms (C25 to C150), presenting a structural complexity which increases with the boiling point, as well as, the molecular weight, the density, the viscosity, the refractive index (aromaticity) and the polarity (contents of heteroatoms and metals). These fractions are enriched in highly polar compounds, such as resins and asphaltenes. They are composed by various chemical species of different aromaticity, functional heteroatoms and metal contents, when compared to the crude or lighter fractions (Merdrignac and Espinat 2007, Redelius 2004, Read and Whiteoak 2003).

In fact, molecular weight (Mw) wise, asphalt is a mixture of about 300-2,000 chemical components, with an average value of about 500-700 (Stangl et al. 2007, Berkers 2005). The combinations and interactions of these diverse molecules give rise to the characteristics asphalt through the impact on the free volume of the asphalt (Youtcheff and Jones 1994).

At the molecular level, historical studies have shown that there are at least hundreds of thousands of unique molecular species that exist within any particular asphalt (Robertson 1991). Because asphalt is a complex mixture of molecules ranging from nonpolar saturated hydrocarbons to polar polynuclear aromatics. After fractionation of the asphalt by specific solvents, its composition is often conveniently reported in weight percent of saturates (S), aromatics (A), resins (R), and asphaltenes (As), collectively called SARA's (Carbognani et al. 2007, Read and Whiteoak 2003, Loeber et al. 1998, Raki et al. 2000). The aromatics and saturates are the lightest molecular weight group in asphalt. Together, the aromatics and saturates (oily phase) constitute the major portion of the total asphalt (Rozeveld et al. 1997).

Asphalt Models

Nellensteyn (1924) introduced the concept that petroleum residua (e.g., asphalts) are colloidal dispersions of asphaltenes in maltenes (which serve as a solvent phase) peptized by polar materials called resins, which may be isolated from maltenes. Mack (1932) studied rheological properties of asphalts and also concluded that asphalts are colloidal.

Pfeiffer and Saal (1940) suggested that asphalt dispersed phases are composed of an aromatic core surrounded by layers of less aromatic molecules and dispersed in a relatively aliphatic solvent phase. They did not claim that there are distinct boundaries between asphalt dispersed

and solvent phases, as in soap micelles, but that there is a continuum from low to high aromaticity from the solvent phase to the centers of the entities making up the dispersed phase.

Labout (1950) proposed that in asphalts having highly aromatic maltene fractions, asphaltenes are well dispersed (peptized) and do not form extensive associations. Such asphalts were designated sol type asphalts. In asphalts with less aromatic maltene fractions, asphaltenes are not well dispersed and form large agglomeration, which in extreme cases can form a continuous network throughout asphalt. These asphalts were designated gel-type asphalts (Petersen et al. 1994).

Yen et al. (1961) based on X-ray diffraction studies, supported many of the essential features of the colloidal model. They claimed that the predominant interaction in the association phenomena in petroleum residua is the stacking of condensed aromatic molecules to form larger units. Later, Altgelt and Harle (1975) rationalized asphalt rheological behavior based on the stacking of condensed aromatic structures (Petersen et al. 1994).

Donnet et al. (1977) claimed to be able to distinguish between sol type and gel type asphalts. Dwiggins (1978) found evidence for what he termed "colloidal particles" in asphalt crude oils. Ravey et al. (1988) concluded that asphaltenes from several crudes are fairly similar and consist of polydispersed ensembles of thin (about 1 nm) sheets whose diameters range from 1 to 10 nm, in accordance with those calculated by Dwiggins (1978). Based on X-ray studies of asphaltenes and petroleum residua, Herzog et al. (1988) and Senglet et al. (1990) reported evidence of association of molecules into larger structural units (Petersen et al. 1994), as previously suggested by the steric colloidal model of Park and Mansoori (1988). Overfield et al. (1989) claimed to have verified some aspects of the colloidal nature of asphaltenes (in toluene), but they also showed that asphaltenes are neither colloids of fixed size nor assemblages of similar small molecules. It was inferred that the behavior of asphaltenes in deuterated toluene reflects the behavior of the molecules composing asphaltenes in petroleum residua (Petersen et al. 1994). Based on rheological data, Storm and Sheu (1993) claimed that asphaltenes are organized into charged spherical particles of widely distributed sizes that are solvated by resins and dispersed in the surrounding fluid.

The micellar model was accepted as it provided the best available explanation of how asphalts developed the structure that controlled their behavior. In this model, aromatic asphaltenes exist as a discrete phase in the asphalt and are surrounded by the resins. The resins were intermediates in the asphalt, serving to peptize the otherwise insoluble asphaltenes. The resins and asphaltenes existed as "islands" floating in the final asphalt component – the oils. While there have been competing molecular structures proposed throughout the years to explain the viscoelastic behavior of asphalts, the micellar model had held forth for lack of a definitive proof to the contrary (Youtcheff and Jones 1994).

Resins and asphaltenes are known to constitute the polar fraction of crude oil (Speight 1999). Polarity is important in asphalt because it tends to cause molecules to organize themselves into preferred orientations. All of the naturally occurring heteroatoms, nitrogen, sulfur, oxygen, and

metals, contribute to polarity within these molecules. Likewise, oxidation products formed upon aging are polar and further contribute to the polarity of the entire system (Robertson 1991).

Asphalt Aging Chemistry

The chemical composition of asphalt determines its physical properties. However, the chemical composition of asphalts changes during both the short term (handling, pumping, mixing, spraying and compaction) and long term (field service) (Glover 2007).

Asphalt binder aging is one of the main factors that reduce pavement service life (Lima et al. 2006). Oxidation increases age hardening and brittleness of asphalt by contributing additional polar molecules to the structured zones within the asphalt binder (Robertson 1991).

Chemical changes during the mixing/laying operations (Figure 2) reveal an appreciable degree of oxidation and polymerization of the cyclic molecules to form resins, while to a lesser extent the resins have been similarly oxidized and polymerized to form asphaltenes. The content of saturates of some asphalts remain substantially unchanged; whereas, the content of saturates of other asphalts increase with time (Chipperfield et al. 1970).

Figure 2. Changes in asphalt composition during mixing, laying, and in service

The principal cause of in-service aging of asphalt binders is the oxidation of certain molecules by oxygen from the air. The oxidation results in the formation of highly polar and strongly interacting functional groups containing oxygen (Mouillet et al. 2007).

During service, asphalt pavement ages, that is, the brittleness of the material gradually increases due to physicochemical changes in the binder. Four principal mechanisms are related to asphalt aging: exudation, evaporation, oxidation, and physical aging. The most important of these is the oxidation.

In asphalt oxidative aging, formation of functionalities containing oxygen, as well as transformation between different binder components, can be observed. Usually, the asphaltene content increases while the content of aromatics decreases. Saturates are inert to oxygen and, thus, slight changes in this fraction may occur only due to volatilization as shown in Figure 3 (Isacsson and Zeng 1997).
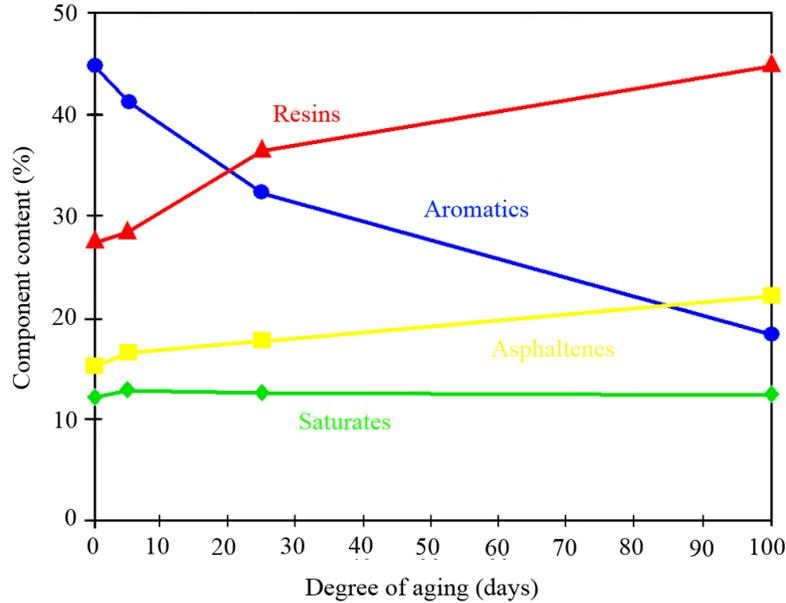
Adapted from Isacsson and Zeng 1997

Figure 3. Effect of aging on chemical composition of a binder recovered from porous asphalt pavement

The aging of conventional asphalts in service results in carbonyl growth. This reaction produces asphaltenes, which then harden the material. The oxidation rate ultimately determines the hardening rate, but the hardening susceptibility, a characteristic of each asphalt, is important for establishing the extent to which oxidation causes hardening (Martinez et al. 2006, Glover et al. 2002).

Bio-Oil

Bio-oils have many advantages over petroleum asphalt as they are renewable, environmentally friendly, provide energy security, and present a great economic opportunity. However, until now, almost no research has been performed on the applicability of utilizing bio-oils as a partial or full replacement alternative of asphalt in the pavement industry. The limited number of references produced on this subject show that this goal might be achieved very soon by the application of a new technology with the incorporation of polymer (Peralta et al. 2012a).

Definition of Bio-Oil

By definition, bio-oils can be described as dark brown, free-flowing organic liquids that are comprised mainly of highly oxygenated compounds (Mohan et al. 2006, Oasmaa et al. 1999). In other words, it is the liquid produced from the rapid heating of biomass in a vacuum condition (Oasmaa et al. 2005). Bio-oils have many synonyms that can be listed as follows: pyrolysis oil, pyrolysis liquid, bio-crude oil, liquid wood, wood oil, liquid smoke, wood distillates, and pyroligneous acid (Mohan et al. 2006, Oasmaa et al. 2005).

Production of Bio-Oil

Bio-oils are produced from plant matter and residues, such as agricultural crops, municipal wastes and agricultural and forestry byproducts (Demirbas and Balat 2006, Mohan et al. 2006). Other biomass sources includes sugar, molasses and rice, corn and potato starches, natural tree and gum resins, natural latex rubber and vegetable oils, lignin, cellulose, palm oil waste, coconut waste, peanut oil waste, canola oil waste, potato starch, dried sewerage effluent and others.

One of the thermochemical processes used to produce bio-oils is fast pyrolysis. The yields from fast pyrolysis are varied with the biomass feed stock and the reactor conditions (Diebold et al. 2008).

Fast pyrolysis is a thermal decomposition process that requires a high heat transfer rate to the biomass particles and a short vapor residence time in the reaction zone (Oasmaa et al. 1999). According to other authors, fast pyrolysis is the rapid decomposition of organic matter (biomass) in the absence of oxygen to produce solids as char, pyrolysis liquid, or oil (bio-oils), and gas (Demirbas 2008, Mullen and Boateng 2008). Another detailed definition of fast pyrolysis is given by Mohan et al. (2006), which describes it as a high-temperature process in which biomass is rapidly heated in vacuum and then decomposes to produce vapors, aerosols, and some charcoal-like char. After cooling and condensation of these vapors and aerosols, a dark brown mobile liquid (bio oil) is formed.

When the organic matter is biomass, which consists of biopolymers (e.g., cellulose, hemicelluloses, and lignin), the produced oils are named bio-oils (Bridgwater and Cottam 1992). Generally, fast pyrolysis is used to obtain high-grade bio-oil. Therefore, fast pyrolysis of ligno-cellulosic biomass leads to extensive de-polymerization and fragmentation of these biopolymers (Mullen and Boateng 2008). Due to the different sources of biomass, the amount of production of the liquid bio-oils, solid char and non-condensable gases vary. For example, fast pyrolysis processes produce 60-75 wt % of liquid bio-oil, 15-25 wt % of solid char, and 10-20 wt % of non-condensable gases (Mohan et al. 2006).

Fast pyrolysis initially starts with slow heating rates, and then involves a rapid heating rate of the biomass, that can reach up to 300 °C/min, but not as fast as flash pyrolysis. According to Goyal et al. (2006) and Luo et al. (2004), fast pyrolysis is most successful with fluidized bed reactors as it offers high heating rates, rapid de-volatilization, easy control, and easy product collection. Fast pyrolysis design variables include, but are not limited to, the following ones reported by Mohan et al. (2006): feed moisture content, particle size, pretreatment, reactor configuration, heat supply, heat transfer, heating rates, reaction temperature, vapor residence time, secondary cracking, char separation, ash separation, and liquid collection.

Chemical Characterization of Bio-Oil

Bio-oils are derived from biomass, which contains oligomeric species that consist mainly of lignin pyrolytic (oligomers from lignin), but also of cellulose and hemicellulose. As

decomposition rapidly occurs, oligomeric species are not vaporized but simply blown apart into aerosols. Thus, these oligomeric species form as part of the aerosols and have varying molecular weights (Mohan et al. 2006).

Due to the variety of forestry and agricultural sources from which bio-oils are derived, bio-oils are a complex chemical mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. Also, bio-oils encompass other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics as reported by Mohan et al. (2006). As a result of the presence of cellulose, hemicellulose, and lignin in forestry and agricultural crops, the production of bio-oils can be described as the rapid and simultaneous depolymerization and fragmentation of these compounds while rapidly increasing the temperature (Mohan et al. 2006).

In the plant kingdom, lignin is present in large amounts in the cell wall of plants, especially in woody tissues. It is known that lignin can have different chemical composition and properties from trees, plants and agricultural crops. Even by operating different extraction methods, the physical and chemical properties are diverse (Dizhbite et al. 2004). Since the scavenging ability of lignin depends on the structural features of the lignin, the same amount of lignin with different structures may react with different amounts of free radicals (Dizhbite et al. 2004). That is to say, the bio-oil with higher amounts of lignin does not have to display better antioxidant effects.

Bio-Oil Applications

Generally, fast pyrolysis does not generate any waste because the bio-oil and solid char can each be used as a fuel and the gas can be recycled back into the process (Mohan et al. 2006). According to Goyal et al. (2006), the bio-oils obtained from pyrolysis methods have many industrial uses that include, but are not limited, to their use as a combustion fuel, a transportation fuel to substitute fossil fuels, a liquid smoke, a preservative, a raw material to produce chemicals and resins, a binder for pelletizing and briquetting of combustible organic waste materials, or an adhesive material that can be used as a binder in the paving industry (Chailleux et al. 2012; Chaiya 2011; Fini et al. 2012, 2011a, 2011b, 2010; Hill 2011; Raouf and Williams 2009). In addition, the char can be utilized in many industrial functions, including the use as a solid fuel in boilers, as briquettes that are mixed with biomass for use as high efficiency fuel in boilers, as a raw material to produce activated carbon or carbon nanotubes, or in the gasification process to obtain hydrogen rich gas by thermal cracking. Bio-char can also be used in the agriculture activity as a soil amendment. Furthermore, pyrolysis gases, which have significant amount of carbon dioxide along with methane, can be used as a fuel for industrial combustion purposes (Goyal et al. 2006).

Bio-fuel production plants produce liquid co-products that are high in lignin content. Due to that, bio-oils have been used in many traditional uses which include but are not limited to concrete admixtures, binders, well drilling mud, dust control, vanillin production, and dispersants (Williams et al. 2009). Lignin, which is a biological polymer, is known as an antioxidant compound due to the presence of large amounts of phenolic structures. Due to its dark color, lignin has not been utilized in many industries. However, this is not an issue when it is used in

asphalt binders (Williams et al. 2009). Due to the results of some investigations, it has been found that lignin can be utilized as an extender in asphalt to help reduce the use of petroleum with no adverse effects on performance (Williams et al. 2009, Kandhal 1994, Sundstrom et al. 1983).

Ground Tire Rubber (GTR)

Rubber Definition and Production

According to ASTM D 6814-02 (2002), rubber is a natural or synthetic elastomer that can be chemically cross-linked or vulcanized to enhance its useful properties. There are two types of rubber: natural and synthetic. Natural rubber latex is obtained from the rubber tree called Hevea braziliensis. The raw rubber molecule is a long straight-chain isoprene hydrocarbon. The physical appearance of this hydrocarbon is of a spongy, flocculent nature. At temperatures below 100 ºC this spongy rubber becomes stiff and hard; whereas, when warmed above 100 ºC, it becomes flexible, soft and transparent (Rahman 2004).

Synthetic rubbers are made from petroleum products and other minerals and are produced in two main stages: the production of monomers (small unit molecules) and the polymerization to form a rubber. There are multiple types of synthetic rubbers available for different applications. Some of them are as follows: styrene-butadiene rubber (SBR, used in asphalt, tires, among others), silicon rubber (used in gaskets, seals, among others), fluorocarbon rubber (resistant to heat and chemical attack), and epichlorohydrin rubber (jackets, hose, cable, packing, among others) (Rahman 2004).

In demanding uses, such as in tires, engine mounts, and springs, rubbers are used exclusively due to their better elasticity, resistance to set, and durability (Hamed 1992).

The selection of appropriate additives and fillers is critical to the rubber performance. General purpose elastomers are hydrocarbon polymers. They include styrene-butadiene rubber (SBR), butadiene rubber (BR), and polyisoprene rubber – both natural (NR) and synthetic (IR). These "diene" rubbers contain substantial chemical insaturation in their backbones, causing them to be rather susceptible to attack by oxygen, and especially by ozone. Additionally, they are readily swollen by hydrocarbon fluids. The primary application of these elastomers is in automobile and truck tires (Hamed 1992).

Natural rubber (NR) contains double bonds that promote sulfur vulcanization. Because NR macromolecules are configured identically (stereoregular), they pack together spontaneously as crystallites standing at low temperatures, with a maximum rate at temperatures of about -25 ºC. Natural rubber also crystallizes upon straining. In fact, strain-induced crystallization imparts outstanding green strength and tack, and provides vulcanizates with a high resistance to cut growth at severe deformations. However, NR macromolecules are susceptible to fracture on shearing. High shearing stresses and oxygen promote the rate of molecular chain scission (Hamed 1992).

Synthetic polyisoprene rubber (IR) is produced both anionically and by Ziegler Natta polymerization. IR compounds have lower modulus and higher breaking elongation than similarly formulated NR compositions. This is due, at least in part, to less strain-induced crystallization in IR, especially at high rates of deformation (Hamed 1992).

Polystyrene is a tough hard plastic, and this gives styrene-butadiene-styrene rubber (SBS) its durability. Polybutadiene is rubbery, and this gives SBS its rubber-like properties. In addition, the polystyrene chains tend to clump together. When one styrene group of one SBS molecule joins one clump, and the other polystyrene chain of the same SBS molecule joins another clump, the different clumps become tied together with rubbery polybutadiene chains. This gives the material the ability to retain its shape after being stretched (Polymer Science Learning Center 2005).

Rubber Vulcanization

Straight out of the tree, natural rubber latex (polyisoprene) is not good for much. It gets runny and sticky when it is warm, and it gets hard and brittle when it is cold (Polymer Science Learning Center 2005). However, when sulfur is added to the rubber, it forms bridges amongst the rubber molecules, which tie all the polymer chains in the rubber together. This process is called crosslinking. Bridges made by short chains of sulfur atoms tie one chain of polyisoprene to another, until all the chains are joined into one giant supermolecule. An object made of a cross-linked rubber is in fact one single big molecule (Polymer Science Learning Center 2005).

As a result of crosslinking, rubbers do not dissolve in solvents and do not flow at high temperatures. Cross-linked polymers are usually molded and shaped before they are cross-linked. Once crosslinking has taken place, usually at high temperature, the object can no longer be shaped (Polymer Science Learning Center 2005).

The mechanical behavior of an elastomer depends strongly on its crosslink density (Hamed 1992). The modulus and hardness increase monotonically with crosslink density and the network becomes more elastic. Fracture properties such as tear and tensile strength attain a maximum as crosslinking increases (Rahman 2004).

Tire Production

The tire manufacturing process is similar to the manufacture of other rubber products. The main difference between the two processes is that the building process for manufacturing tires is generally more complex because there are many rubber components (EPA 2005).

A tire is made up of three main materials: elastomeric compound, fabric, and steel. The fabric and steel form the structural skeleton of the tire with the rubber forming the "flesh" of the tire in the tread, side wall, apexes, liner, and shoulder wedge. The tire skeleton consists of beads made of steel or fabric depending on the tire application, which form the "backbone" in the toe of the tire. The beads are designed to have low extensibility and provide reinforcement for the rubber

tire. The tire has a series of reinforcing cords or belts that extend from bead to bead transversely over the tire (Rahman 2004).

The belts are made of nylon fabric or steel but more commonly both types are used. The rubber treads then cover the belts providing the contact area for the tire on the pavement. This rubber contains carbon black, which is an additive that provides additional reinforcement and also acts as antioxidant in the tire against effects of ultraviolet (UV) light. The objective of the skeleton is to reinforce the tire to allow it to perform well without greatly deforming (Rahman 2004).

Rubber from car tires is mainly a combination of styrene-butadiene rubber and natural rubber (Gawel et al. 2006). To improve the mechanical and chemical properties of rubber (e.g., tire), additional compounds and additives are blended into the raw rubber: activators (e.g., ZnO_2), accelerators (e.g., MgO, fatty acids, amines), aging retardants (e.g., metal-oxides, polychloroprene), fillers (e.g., $BaSO_4$, $MgCO_3$, $CaCO_3$), and others. Generally, metal-oxides, fatty acids, amines and different glycols are used as activators and accelerators (Miskolczi et al. 2008).

The proportion of natural and synthetic rubber varies according to the size and use of the tire. The generally accepted rule of thumb is that the larger the tire and the more rugged its intended use, the greater will be the ratio of natural to synthetic rubber (Rahman 2004). In general, truck tire rubber contains larger percentages of natural rubber compared to that from car tires (Artamendi and Khalid 2006).

The most important component of a tire is the elastomer (NR and SR). The second most important component of a tire is carbon black. Carbon black is mainly used to enhance rigidity in tire treads (to improve traction, control abrasion and reduce hydroplaning) and to add flexibility and reduce heat buildup in sidewalls (Shulman 2000). The particle size of the carbon black, as defined by its specific surface area and structure, impacts upon its integration and utilization in compounding (Rahman 2004).

Crumb Rubber Production

The lifecycle of a consumer product is defined as the time span of the product serving the purpose for which it was created. The life span for a tire is nearly five to seven years during which time a tire can be retreaded. It comprises three principal periods: new, continued use (continued chain of utility), and consignment to a waste treatment system (end of life). A post-consumer tire, which may not have a structurally sound casing or residual tread depth suitable for further road use, will be discarded or consigned to another use, such as scrap tires for road construction (Rahman 2004).

Once the tire is permanently removed from a vehicle, it is defined as waste (or scrap tire). A scrap tire can be usable in different forms, such as a whole tire, a slit tire, a shredded or chipped tire, or as a ground tire rubber (GTR) product (Rahman 2004).

Ambient Scrap Tire Processing: The initial step in the production of ground scrap tire rubber is shredding. Scrap tire rubber is delivered to rubber processing plants either as whole tires, cut tires (treads or sidewalls), or shredded tires, with the last being the preferred alternative. As scrap, the rubber is processed, the particle sizing is reduced, steel belting and fibers are separated and removed, and further size reduction is then accomplished (Chesner et al. 1998).

The schematic in Figure 4 is an example of a typical ambient scrap tire recycling plant. The process is called ambient because all size reduction steps take place at or near ambient temperatures, e.g., no cooling is applied to make the rubber brittle and easier to be processed (Reschner 2008).
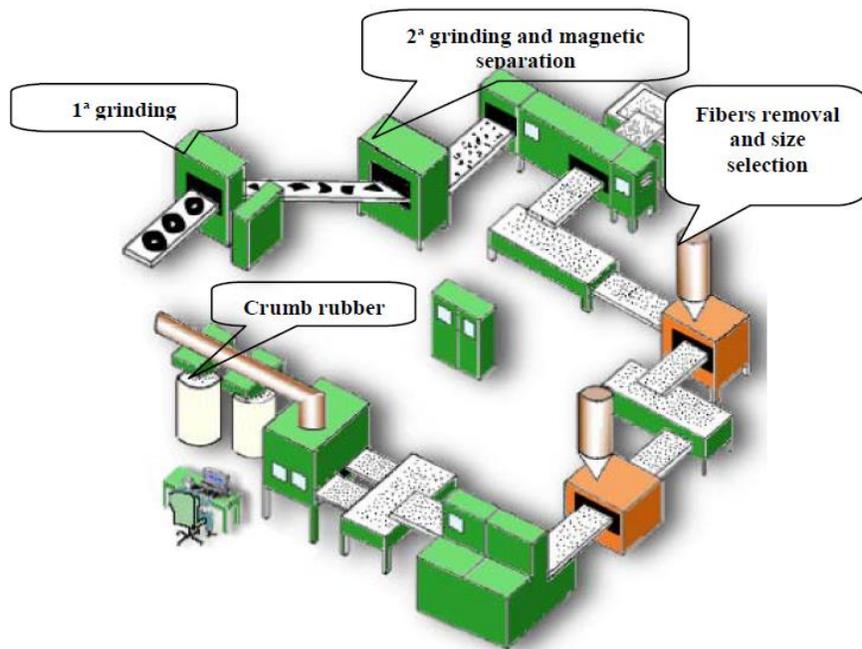
Neto et al. 2006

Figure 4. Ambient scrap tire processing plant

GTR can be produced by one of three processes. The granulator process produces cubical, uniformly shaped particles ranging in size from 9.5 mm (3/8 in.) down to 0.4 mm (No. 40 sieve), which is called granulated GTR. The cracker mill process, which is the most commonly used, produces irregularly shaped torn particles sized from 4.75 mm (No. 4 sieve) to 0.42 mm (No. 40 sieve), referred to as GTR. The micro-mill process produces a very fine GTR, usually ranging from 0.42 mm (No. 40 sieve) down to as small as 0.075 mm (No. 200 sieve) (Epps 1994).

In this plant layout, the tires are first processed into chips of 2 in. (50 mm) in size in a preliminary shredder. The tire chips then enter a granulator. In this processing step the chips are reduced to a size smaller than 3/8 in. (10 mm), while liberating most of the steel and fibers from the rubber granules. After exiting the granulator, steel is removed magnetically and the fiber fraction is removed by a combination of shaking screens and wind sifters (Reschner 2008).

Cryogenic Tire Processing: This process is called cryogenic because whole tires or tire chips are cooled down to a temperature of below -80 ºC. Below this "glass transition temperature," rubber becomes nearly as brittle as glass and size reduction can be accomplished by crushing and breaking (Reschner 2008).

The crumb rubber industrial process takes place in three stages (Recipneu 2013):

- Shredding of the raw material
- Cryogenic processing
- Bagging and storage

Shredding of the raw material consists of fragmenting light and heavy tires into small, homogeneously cut pieces, e.g., the chips (Recipneu 2013).

Cryogenic processing (Figure 5) performs the complete and individualized separation of rubber, steel, and textiles without noticeable waste or losses in material. This is a continuous, automatically controlled process that takes place under an inert nitrogen atmosphere (Recipneu 2013).

A - Preliminary Shredder
B - Freezing Tunnel
C - Hammer Mill
D - Steel and Fiber Removal
E - Dryer
F - Classifier
G - Secondary Grinding Step
H - Product Storage Silos
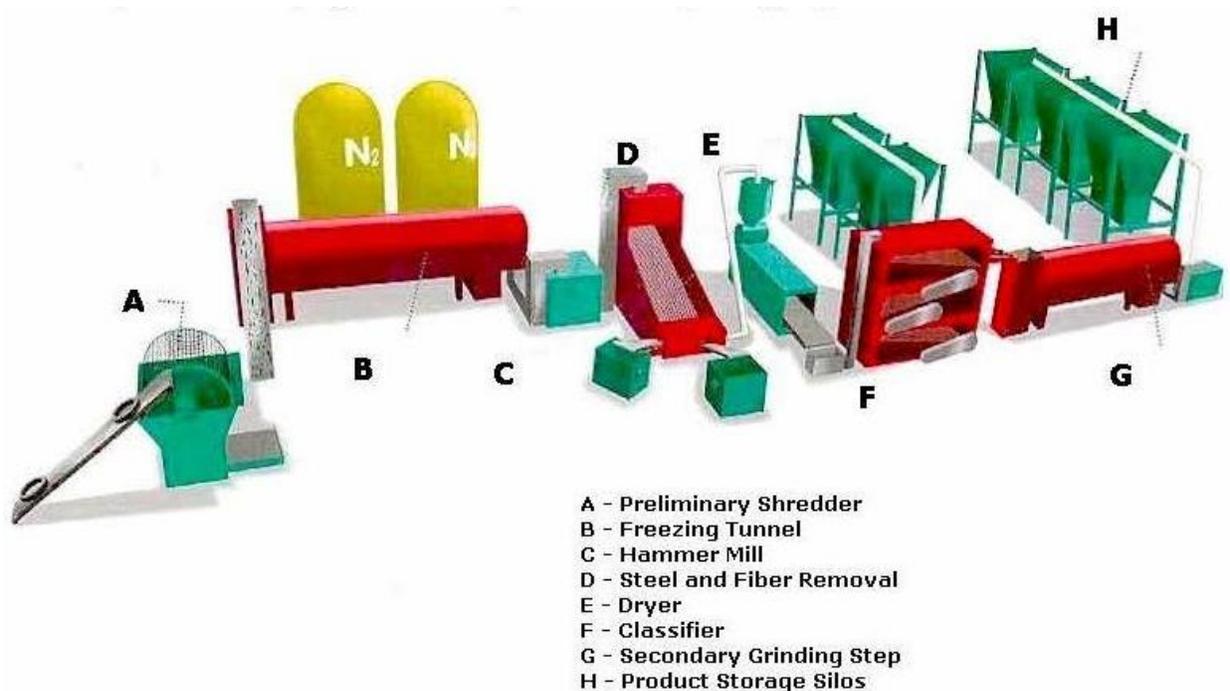
RTI Cryogenics Inc., Canada

Figure 5. Schematic of a cryogenic scrap tire processing plant

In the cryogenic cooling, tire chips with 2 in. (50 mm) are dropped into a long continuously operating freezing tunnel, and are cooled down by the action of liquid nitrogen at about -196 ºC, resulting in a cold exchange between the chips at room temperature and the liquid nitrogen.

When the chips are cooled to a temperature lower than -80 ºC, the glass transition point (Tg) is reached for all the rubber polymers of the tire, and the rubber presents a glass-like behavior (Recipneu 2013).

In general, cryogenic scrap tire processing is more economical if clean and fine mesh rubber powder is required (Reschner 2008). In the cryogrinding process the equipment cost is less, operating costs are lower, productivity is increased, and the product has better flow characteristics than ambient ground rubber (Adhikari et al. 2000).

GTR Specifications for AR Production: Crumb rubber used in hot-mix asphalt normally has 100 percent of the particles finer than .19 in. (4.75 mm). Although the majority of the particles used in the wet process are sized within the 1.2 mm to 0.42 mm range, some crumb rubber particles may be as fine as 0.075 mm, thus being more adequate to use the cryogenic technology for this utilization of GTR. The specific gravity of crumb rubber is approximately 1.15, and the product must be free of fabric, wire, or other contaminants (Chesner et al. 1998).

Crumb rubber is classified with a number depending on its quality and size. However, crumb rubber materials produced in industry should maintain certain quality requirements with respect to their grades. ASTM D 5603-96 and ASTM D 5644-96 are the two most widely used standards for ground tire rubber grading (Rahman 2004).

Asphalt Rubber Production and Characterization

Asphalt-rubber (AR) has been successfully used by several transportation organizations worldwide, especially in the US. The addition of rubber to asphalt changes the asphalt rheology, improving its characteristics, and therefore the asphalt mixes' performance when used in a flexible pavement system (Kuennen 2005).

Rubber Addition into Asphalt Binders

The existing technologies to add GTR into asphalt mixes are the Dry Process and the Wet Process. The main differences between these two processes are the following (Roberts et al. 1989):

- The particle size (the dry process can use coarser rubber particles)
- The amount of GTR added (the dry process uses higher quantities)
- The role of the GTR (in the wet process the rubber is part of the binder, while in the dry process it is part of the aggregate)
- The ease of the GTR incorporation in the asphalt mixture (the dry process does not require specific equipment while the wet process implies the use of special blending tanks and pumps)

Dry Process: In the dry process the rubber is used as a fine aggregate in the asphalt mixture. The rubber (usually between 1% and 3% of the aggregate total weight in the mixture) is added into the mixture before the asphalt introduction, and it can be applied into gap graded, dense graded and open graded mixtures (Heitzman 1992a).

In 1975, the California Department of Transportation (Caltrans) began conducting laboratory experiments with asphalt-rubber to be applied in sealing cracks and repairs, obtaining generally positive results. In 1978, the first application of Caltrans using the dry process in a pavement layer was conducted on Highway SR 50, in Myers Flat, California (Caltrans 2006).

According to Caltrans (2006), the dry process should only be used for producing HMA and has not been suitable for other types of asphalt pavement layers such as surface treatments. This restriction to the dry process is supported by other authors, such as Heitzman (1992b) and Epps (1994).

When the crumb tire rubber is used as a part of the aggregate in the asphalt mix (dry process), the resulting product has the name Rubber-Modified Asphalt Concrete (RUMAC). The dry process (Figure 6) was originally developed in the 1960s in Sweden, being marketed in this country with a patented technology (tradename PlusRide) of Enviro Tire (Zanzotto and Svec 1996).
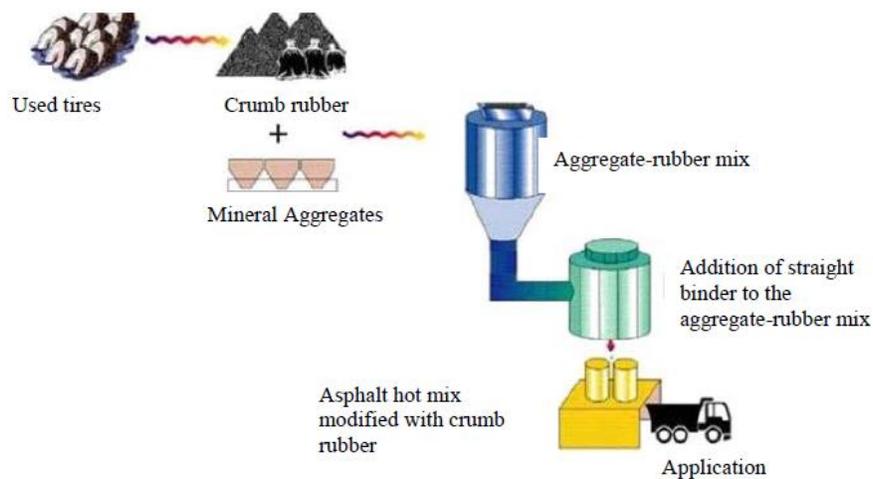
Neto et al. 2006

Figure 6. Asphalt mixtures production with GTR incorporation by the RUMAC dry process

In the case of the PlusRide technology, 1 to 3 wt% of rubber is added as an aggregate, with sizes ranging between 2.0 mm and 4.2 mm. The air voids volume of the asphalt mixture is 2% to 4% and the percentage of asphalt ranges from 7.5% to 9.0% (TFHRC 2005, Baker et al. 2003).

Between the 1980s and the 1990s a generic dry process technology was developed in the US to produce mixtures of dense graded type, which consists in incorporating rubber as aggregate (coarse or fine) in the mixture, in view of improving the process through a pre-reaction, and a

pretreatment using a catalyst. In this system, the amount of rubber should not exceed 2 wt% of the total mixture. The dry process technology was applied in experimental test sections in Florida, New York and Oregon (Epps 1994).

According to TFHRC (2005), in both the dry and wet processes the crumb rubber is called a modifying agent because its use modifies the properties of the resulting product, which is an asphalt mixture. However, this statement is not shared by other authors, who mention that the term asphalt-rubber is not appropriate when used in the dry process (Visser and Verhaeghe 2000, Takallou and Takallou 2003), since the rubber is first incorporated into the aggregate at high temperatures (at about 200 ℃ for 15 minutes or more, to achieve a homogeneous blend between the mineral aggregate and the rubber) to be later mixed with the asphalt (Fontes 2009).

Visser and Verhaeghe (2000) stated that the rubber melting into the asphalt does not occur in the dry process. Takallou and Takallou (2003) also ensure that no reaction occurs between the materials (rubber and asphalt) in this process, so that the rubber works as an additive and not as a modifying agent.

Research conducted by Hunt (2002) in the Oregon Department of Transportation with the dry process (RUMAC and Ride Plus) resulted in poor performance, in which the asphalt mixtures showed premature degradation. Moreover, the cost was 50% to 100% higher than the application of a conventional asphalt mixture.

The results of investigations conducted in the State of Illinois revealed that the experimental test sections with asphalt mixtures using the dry process had lower performance than the sections where conventional asphalts were applied (Volle 2000).

Wet Process: The wet process consists in the incorporation of the ground tire rubber with the asphalt prior to mixing the binder with the aggregates. The result is a modified asphalt that has significantly different properties than the original one. The asphalt blended with the rubber reacts and forms a so-called asphalt-rubber, and some additives may be incorporated to adjust the viscosity of the blend (Oda 2000).

In accordance with ASTM D 8 (1997), asphalt-rubber in the wet process is a blend of asphalt, ground tire rubber and certain additives, in which the rubber is at least 15 wt% of the blend that reacted with the asphalt at a temperature sufficiently high to cause swelling of the rubber particles (Figure 7).
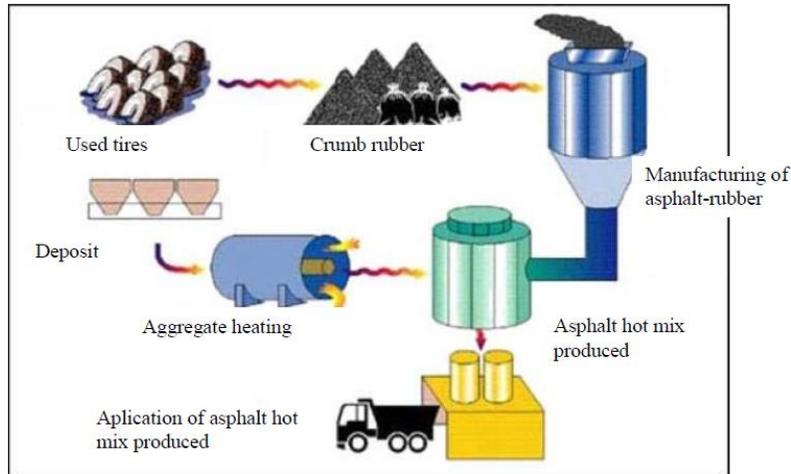
Figure 7. Asphalt mixtures production with GTR incorporation by the wet process

The physical characteristics of asphalt-rubber are specified by ASTM D 6114 (1997) for the regions where the material is expected to be applied.

In the wet process, since the GTR is previously added to the conventional asphalt, it is modified permanently. In this process, the actual transfer of polymers and chemical components of tires to the asphalt results in a binder with greater elasticity and resistance to aging (Morilha and Greca 2003).

According to Hicks and Epps (2000), the properties of asphalt-rubber are substantially different from conventional asphalts, depending on the characteristics of conventional asphalt and rubber used, which must be previously evaluated.

The production of asphalt-rubber in the wet process involves the evaluation of its principal components (asphalt, rubber, and additives) (Hicks and Epps 2000):

- Properties of the blend (asphalt-rubber) for a range of interaction times and temperatures of manufacture
- Stability of the mixture over time
- Percentage of the components to obtain the desired properties of the new binder

Typical temperatures for the asphalt-rubber production range from 160 °C to 205 °C. In general, asphalt-rubber maintains its physical properties for at least 24 hours after production at temperatures up to 175 °C. At higher temperatures rubber depolymerization can occur within three to six hours (Hicks and Epps 2000).

The agitation intensity between the asphalt and rubber during the interaction time can influence the properties of the asphalt-rubber. This intensity can range from low speed agitation, to keep the rubber particle in suspension, to high speed agitation, which may lead to mechanical

disruption of the rubber particles (Hicks and Epps 2000). Various extender oils and additives can be added to the asphalt-rubber to modify the properties of the binder. Aromatic oils or naphthenic oils are usually used. These materials tend to soften the binder at low temperatures (Hicks and Epps 2000).

State transportation agencies in the US usually specify the use of conventional asphalt for use in asphalt-rubber, according to the climate (Fontes 2009). In the wet process, GTR is normally used with the McDonald technology and very fine GTR is used with the Florida technology (Chesner et al. 1998).

Asphalt Rubber Production Systems

The wet process comprises two production systems that are the continuous blend and the terminal blend. The interaction between asphalt and rubber may be performed in separate trucks or tanks in the continuous blend system, or in industrial units or terminals (terminal blend system).

Continuous Blend: The first applications of the continuous blend system were based on the technology developed by Charles McDonald in the 1960s. However, during the 1980s, in Florida, another continuous blend system was developed using rubber particles with a diameter of 0.18 mm, which was named Florida continuous blend process (Fontes 2009).

The asphalt-rubber of the continuous blend system can be made in the asphalt mixing plant introducing additional equipment on stationary vehicles intended for this purpose. The steps to produce rubber-modified asphalt in continuous blend are the following:

1. Transfer of the conventional asphalt to a heating tank to be heated to the desired temperature
2. Addition of the heated conventional asphalt to the mixer
3. Addition of the crumb tire rubber into the mixer
4. Mixing the conventional asphalt with the rubber
5. Stirring of asphalt mixed with rubber during the predetermined digestion time
6. Digestion vessel may be replaced by a tank fitted with a rotating blade to maintain the horizontal shear mixing of the asphalt and rubber
7. Pumping of the AR into the asphalt mixing plant for the mixtures production

In the continuous blend system, the percentage of rubber is generally expressed by the amount, by mass, of the entire asphalt-rubber and/or the percentage, by weight, of conventional asphalt. For example, 19.0% of rubber by mass of AR corresponds to 23.5% of rubber by weight of conventional asphalt (Fontes 2009).

Roberts et al. (1989) recommended a maximum storage time for the continuous blend asphalt-rubber of 16 hours after its production. Kandhal (1992) indicated that the asphalt rubber should not be stored, but used immediately after production.

Terminal Blend

The terminal blend system facilitates the "digestion" of the rubber by the asphalt at high temperatures in an industrial unit (terminal). This process has been used since 1989 in the state of Texas, and is characterized by using a fixed amount of rubber (less than 10%) clearly lower than that employed in the continuous blend system (15% to 22%) (Takallou and Takallou 2003).

According to Baker et al. (2003), the terminal blend system represents an advance in the technology by making possible to incorporate smaller amounts of rubber in the asphalt than those used in the traditional continuous blend system. The system developed in Texas uses a rubber percentage (by weight of asphalt-rubber) of 10% and an optimum percentage of binder in asphalt mixes between 5.5% and 8.5%.

The asphalt-rubber blend produced through the terminal blend system, in the same way as in continuous blend system, consists of incorporating crumb rubber from tires in the asphalt using suitable equipment. However, the rheological and physicochemical modification of the binder is carried out in a conventional industrial plant (terminal) via a suitable blending process by means of well controlled mechanical stirring and heat, resulting in a uniform and stable binder (Morilha and Greca 2003).

The concept of a terminal blend system adopted by Caltrans is a wet process in which the rubber is added to the asphalt at high temperatures, requiring constant stirring of the asphalt-rubber, which is produced in an industrial plant. In this system it is possible to keep the rubber particles uniformly distributed in the asphalt (Caltrans 2005a), with the advantage of being stored for long periods of time (TRHRC 2005).

Takallou and Sainton (1992) stated that one of the problems of using the asphalt rubber was its low storage stability. However, currently this is not a difficulty when using the asphalt-rubber from the terminal blend system (Hicks 2002).

In summary, the wet process comprises of two systems which are the continuous blend and the terminal blend. Through the two systems, conventional asphalts can be modified by the addition of ground tire rubber. In the continuous blend system, the modification of the asphalt is carried out in tanks (on trucks) or in the asphalt mixing plant itself (or in a laboratory, as in the case of this study) by varying the percentage of rubber and the digestion time at a given temperature. In this system, the asphalt-rubber should be used within four hours after its production (Fontes 2009).

In the terminal blend system, the asphalt-rubber is produced in a terminal facility, whose main feature is the incorporation of rubber into asphalt through powerful shear mills with well controlled time (usually 6 hours) and temperature. The terminal blend asphalt-rubber has good storage stability and can be transported to the asphalt mixing plant without losing its features, but requires the adaptation of the tanks (Fontes 2009).

Asphalt Rubber Interaction Mechanisms

When crumb rubber is blended with asphalt at high temperatures to produce a modified binder, e.g., wet process, the two materials interact as asphalt components migrate into the rubber causing it to swell. Initially, the interaction between GTR and asphalt is a non-chemical reaction where the rubber particles are swollen by absorption of the asphalt's aromatic oils (Heitzman 1992b). Absorption of asphalt components by the rubber inevitably depletes the asphalt of the absorbed components and, consequently, modifies its properties making it stiffer and more brittle (Artamendi and Khalid 2006).

In addition to traditional oxidation of asphalt at high temperatures, the residual asphalts experience further changes in their chemical composition as a result of the crumb rubber-asphalt interaction and the absorption, by the rubber, of the lighter, more volatile fractions of the asphalt (Rahman 2004). Furthermore, the rubber particles may also suffer some form of degradation, mainly devulcanization and depolymerization, when mixed with asphalt at high temperatures for long periods of time (Artamendi and Khalid 2006).

The extent of these two processes, e.g., swelling and degradation, depends on the nature of the rubbers, the chemical composition of the asphalt, and the mixing conditions (time, temperature and degree of agitation). Moreover, these processes will determine the mechanical properties of the final crumb rubber–modified binders (Artamendi and Khalid 2006).

The literature reports three stages of interaction that have been evaluated with regard to asphalt rubber binder (Jensen and Abdelrahman 2006):

- An early stage that occurs immediately after mixing crumb rubber with asphalt
- An intermediate storage stage during which the binder is held at elevated temperatures for up to a few hours before mixing with aggregate
- An extended (storage) stage when asphalt rubber binders are stored for extended periods before mixing with aggregate

The effects of crumb rubber on asphalt rubber binders can be separated into interaction effect (IE) and particle effect (PE). The IE is the effect of the lighter fractions of the binder diffusing into the crumb rubber particles. The PE is the effect of the crumb rubber particles acting as filler in the binder (Putman and Amirkhanian 2006):

- The IE is greatly influenced by the crude source of the binder and could potentially be used as an indicator of a binder's compatibility with GTR (higher IE would indicate a more compatible binder)
- The PE is most significantly affected by the GTR content of the binder, higher GTR contents result in greater PE values
- The effect of GTR size on the PE follows the same trends as either the viscosity or complex modulus ($|G^*|$) of the asphalt-rubber binders

Rubber Swelling: Crosslinked materials can absorb solvents and became a gel *(Polymer Science Learning Center 2005)*. Therefore, rubbers in contact with fluids will swell. The properties of the rubbers under swelling are also subjected to dynamic or continuous changes (Kumnuantip and Sombatsompop 2003).

The swelling process is fully reversible and there is no change in composition (such as removal of non-crosslinked or oligomeric components) of the rubber occurs (Kariyo and Stapf 2004).

From the point of view of molecular dynamics, swelling of networks should be fully equivalent to dilution of the uncrosslinked species in a solvent, as long as fast motions are regarded, which are not yet affected by the presence of fixed points. The addition of solvent molecules reduces the interchain interactions and lubricates the chain motion, until the concept of a polymer tube loses its meaning and the individual chains move relatively freely in the solvent (Kariyo and Stapf 2004). The mechanical response of swollen rubbers changes qualitatively in going from low to high crosslink densities (Douglas and McKenna 1993).

Frenkel (1940) and Flory and Rehner (1943) introduced some fundamental hypotheses relating to the swelling of rubber and the changes of rubber elasticity associated with this swelling, that is: (1) the free energy of mixing and the elastic free energy in swollen networks are additive, and (2) the elastic strain energy density function is "invariant" to swelling (Douglas and McKenna 1993).

The swelling of dry polymer networks is a rather unique phenomenon. Lightly cross-linked dry networks can absorb large quantities of certain fluids and increase their volume by orders of magnitude without appreciable change in shape. The cross-links give these highly swollen materials a remarkable rigidity (Douglas and McKenna 1993). Swelling changes the number of cross-links per unit volume and stretches the chains. In this view, swelling is like any other kind of deformation (a stretch is a stretch, regardless of its mechanical or thermodynamic origins).

Compatibility of the swelling liquid and the rubber may be assessed by comparing the solubility parameters of the components. The Hildebrand solubility parameter for rubber ranges from 17.8 to 20.8 MPa$^{1/2}$ (Gawel et al. 2006).

Rubber Swelling due to Interaction with Asphalt: There are several factors that play a role in the crumb rubber-asphalt interaction. On the part of the asphalt, the interaction depends on the amount of the aromatic fraction, the temperature, and the viscosity. The properties of the GTR that can affect the interaction include production method (ambient or cryogenic grinding), particle size, specific surface area, and chemical composition (e.g., amount of natural rubber) (Putman and Amirkhanian 2006).

The interaction between asphalt and rubber, according to Heitzman (1992a), is not chemical in nature. It involves absorption of aromatic oils from the asphalt cement into the polymer chains, which are the key components of the asphalt. Heitzman (1992b) reported that the rubber changes do not result from melting of the crumb rubber into the asphalt cement. Rather, rubber particles

are swollen by absorption of the asphalt's oily phase at high temperatures, 160 to 200 °C, to form a gel-like material (Jensen and Abdelrahman 2006).

During the interaction process, rubber particles swell over time and depend on the temperature, which results in a reduction in the interparticle distance, thereby increasing viscosity. Once the rubber has swelled, if the temperature is maintained too high or for a long a period, the rubber begins to disintegrate into the asphalt by partial depolymerization. This depolymerization causes a reduction in viscosity. Change in the viscosity of the asphalt rubber binder has traditionally been used to indicate the progress of the interaction between asphalt and rubber (Jensen and Abdelrahman 2006).

Equilibrium swelling and the diffusion coefficient are related to the grade and source of the binders as well as the type of rubber (Artamendi and Khalid 2006). The swelling rate and equilibrium of rubber penetration with the selected asphalt components were found to be dependent on these components and the rubber content in asphalt. At fixed conditions of stirring of asphalt with rubber, the equilibrium swelling value decreases with the increase in rubber content (Gawel et al. 2006).

The wide variation in asphalt-rubber interactions underscores the importance of considering this fact in choosing an asphalt for use with GTR (Billiter et al. 1997a).

The kinetics of swelling indicated a faster rate of asphalt absorption by truck tire rubber than by car tire rubber (Artamendi and Khalid 2006). In this context, natural rubber is more effective than synthetic rubber, but the latter is much more prevalent. The two are likely to be mixed in any commercially prepared product and be predominantly synthetic (Glover et al. 2002).

During the interaction process, rubber particles absorb light fractions of asphalt and swell to different extents. The measured swelling ratio can vary from 200 to 400% and is mainly related to the rubber content and the asphalt composition. The rubber gradation has a limited effect on that swelling ratio (Ould-Henia and Dumont 2006).

A key element to understanding the interaction process is the effect of temperature on the swelling activity. Green and Tolonen (1977) considered a concept for the change in free energy and concluded that temperature has two effects on the interaction process. The first effect is on the rate of swelling of rubber particles. As the temperature increases, from 160 to 200 °C, the rate of swelling increases. The second effect is on the extent of swelling. As the temperature increases, the extent of swelling decreases as the rubber network becomes stiffer to achieve an equivalent change in entropy. They explained that experimental data showed an increase in swelling with temperature, indicating that some other reaction is taking place, which they called detachment (Jensen and Abdelrahman 2006).

The increase on the specific surface and, consequently, on the contact area between rubber particles and asphalt contribute to the process of absorption of the light fractions of the binders by the rubber particles (Neto et al. 2006). Surface area and particle sized of the rubbers

contribute significantly to the increase of the critical high temperature grade of rubber-modified binders (Willis et al. 2013). Moreover, very small particle size crumb rubber will tend to more quickly reduce viscosity during storage due to its quicker and more thorough swelling and subsequent depolymerization (Fontes et al. 2006a).

Particle size controls the swelling mechanism over time and affects the binder matrix. The time required for swelling increases with the particle radius is squared. Larger particle sizes require much greater times to swell. Finer particle sizes may require almost no time to react. An #80 mesh particle size requires about one minute to react with an AC-30 grade asphalt at 163 °C (Jensen and Abdelrahman 2006).

The increase in rubber mass through the absorption of the light molecular weight fractions of the binders is independent of the rubber-asphalt ratio provided that there is sufficient asphalt (light fractions) to allow absorption to occur (Airey et al. 2003).

The equilibrium swelling mass uptake depends upon the asphalt origin and grade; hence, on its chemical composition. In general, asphalts with high asphaltene content are less prone to swell the rubbers (Artamendi and Khalid 2006). The absorption of the light fractions of asphalt not only increases the effective volume of rubber particles, but also changes the nature of the asphalt liquid phase (Jensen and Abdelrahman 2006).

Asphalt composition is a major factor affecting the interactions between asphalt and rubber. It is accepted that light fractions of asphalt swell the rubber particles and some authors introduced the concept of compatibility between rubber and asphalt and recommended the use of base asphalt containing highly aromatic oily fractions (Ould Henia and Dumont 2006).

The aromatic content is considered to be a factor that affects the asphalt-rubber interaction. Bouldin et al. (1990) indicated that softer asphalts would be more compatible with rubber and crumb rubber modification would be more effective than with stiffer asphalts. Green and Tolonen (1977) listed asphalt viscosity as a factor that affects the time required for rubber particles to swell (Jensen and Abdelrahman 2006).

When crumb rubber is added to an asphalt binder, the crumb rubber absorbs the maltenes fraction (saturates, aromatics and resins) leaving the asphalt rubber binder with a higher content of asphaltenes (Martinez et al. 2006). The amount of swelling mostly depends on the temperature, particle size, test duration, viscosity and complex chemical nature of the solvent (Rahman 2004).

The maximum increase in rubber mass (asphalt absorption) after 48 hours at 160 ºC appears to be independent of crude source and only marginally related to the penetration grade of the asphalt. With softer-high penetration grade asphalts, there is generally a greater amount of absorption compared to the harder-low penetration grade asphalts (Rahman 2004).

Equilibrium swelling and diffusion coefficient increase when the grade of the binder used is increased. For the same penetration grade, binders with high asphaltene content swell the rubbers markedly less and at a lower rate than those with lower asphaltene content (Artamendi and Khalid 2006). The initial rate of asphalt absorption is directly related to the viscosity (penetration grade) as well as the chemical composition (crude source) of the binders with the softer (less viscous) and lower asphaltene content binders having the highest rates of absorption (Rahman 2004).

Gawel et al. (2006) concluded that the rate of swell increases as the viscosity of the liquid decreases. The extent of swelling is greater when the rubber content in an asphalt is lower. This finding suggests that it is not the whole asphalt material but only some components contribute to the swelling of rubber; primarily lighter fractions are involved, occurring in rather small amounts. The lighter asphalt-vacuum residue blend components penetrate more readily in the internal matrix of the polymer. Thus, when rubber is removed, the asphalt-rubber binder is richer in higher molecular weight components.

Gawel et al. (2006) also found that, of the nonpolar components, the n-alkenes and n-alkylbenzenes possessed the highest propensity to penetrate into rubber particles. Preferential absorption of the compounds with linear aliphatic chains into the rubber suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

Green and Tolonen (1977) emphasize the importance of controlling the swelling process by controlling the interaction time and temperature. They concluded that rubber particles absorb the lighter fractions of the "maltenes phase" of the asphalt, and the viscosity of the "continuous phase" of the binder increases. They also concluded that the swelling process may continue at a reduced rate even at ambient temperature (Jensen and Abdelrahman 2006).

According to Holleran and Reed (2000), the asphaltenes and the light fractions (maltenes and resins) of conventional asphalts interact with the rubber particles forming a gel film on these particles' surface, causing the fixation of light fractions which cease to be influenced by the climatic agents, thus avoiding its evaporation with time.

Rubber Devulcanization and Depolymerization During AR Production: Two main types of processes that affect asphalt rubber binder properties have been reported in the literature: particle swelling and detachment or depolymerization. These processes occur as the binder is subjected to different combinations of time and temperature (Jensen and Abdelrahman 2006).

The substantial decrease in the fatty acid content of the rubber (the component of the curing system of the polymer) after immersion in hot asphalt-vacuum residue blend gives evidence supporting the movement of these components from the rubber into the asphalt. They are most probably concentrated in the naphthene-aromatic fraction, as it may be inferred from the increased content of this fraction in the residual asphalt (Gawel et al. 2006).

Lower molecular weight, highly aromatic asphalts are more able to devulcanize the rubber during interaction. On the other hand, higher molecular weight asphalt cements, with high content of polar compounds and asphaltenes, are able to depolymerize the rubber during the curing process (Leite and Soares 1999).

The viscosity of asphalt rubber binders also depend on the asphalt. The lower the saturates and asphaltenes content in an asphalt, the better it dissolves rubber. High shear, high temperature curing conditions and very low particle size, reduce the effect of saturates and asphaltenes content in the rubber dissolution (Leite and Soares 1999).

Different particle sizes can be in different interaction stages at any time, mainly because finer particles achieve their maximum swelling faster than coarser particles and begin to depolymerize earlier. Modification of the liquid phase is also affected by the size of the particles. Because of their high surface area, fine particles absorb more light asphalt components in a shorter period of time, leaving the liquid phase of the binder stiffer. When rubber particles significantly depolymerize after time at high interaction temperature, the liquid phase of a binder made with fine material will be stiffer than the liquid phase of a binder made with a coarse material Figure 8. Using a high shear rate (or high frequency) mixer reduces the particle size of coarse crumb rubber and allows the interaction process to progress with greater speed (Jensen and Abdelrahman 2006).
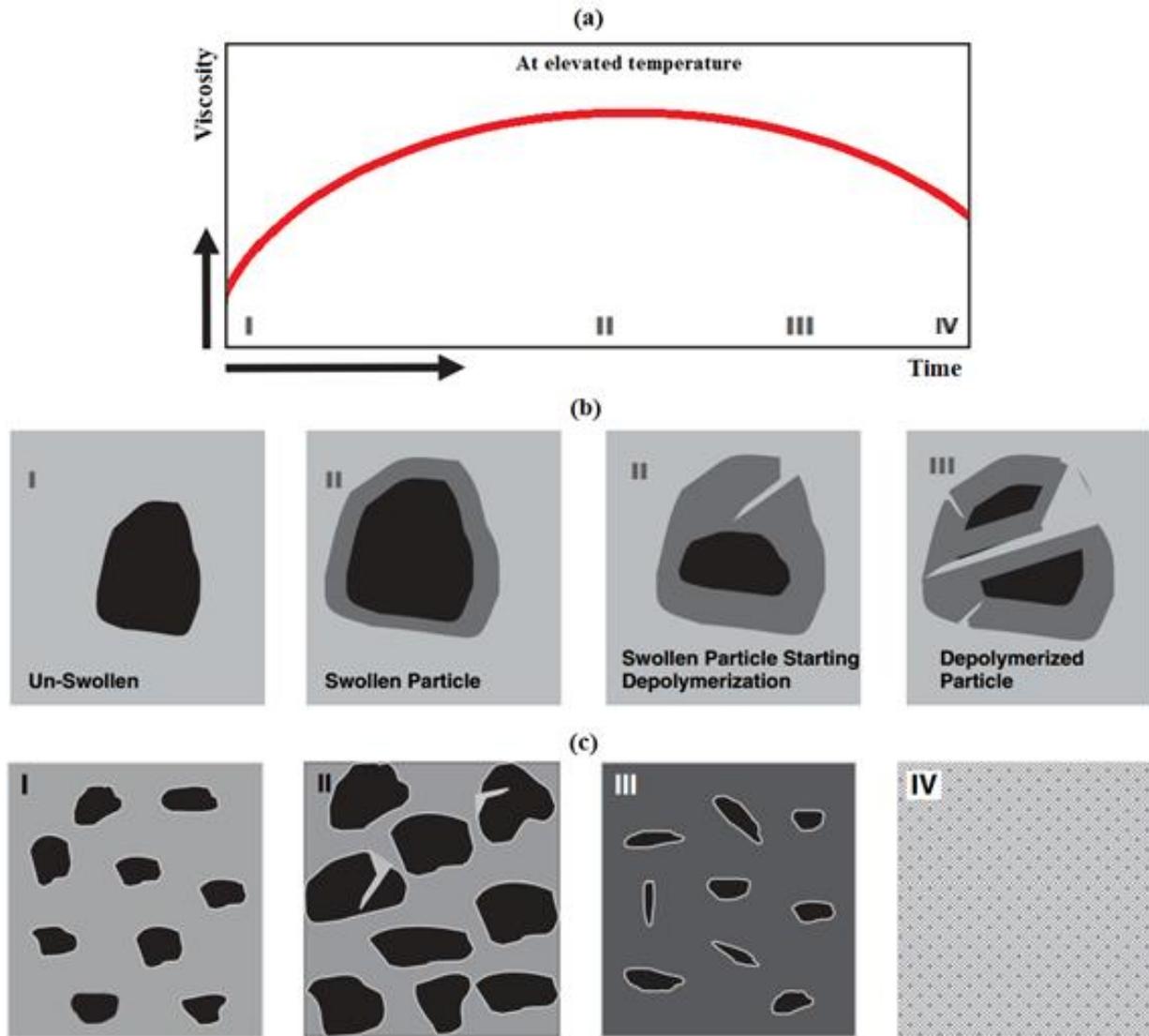
Abdelrahman 2006

Figure 8. Progression of asphalt–rubber interaction at elevated temperature: (a) change in binder viscosity over time at elevated temperature, (b) change in particle size over time at elevated temperature, and (c) change in binder matrix over time at elevated temperature

The extension of curing time and increase of curing temperature and rate of mixing can reduce the high temperature viscosity due to the devulcanization and depolymerization of the rubber during the curing process. This allows the asphalt to digest rubber producing a more homogeneous product with better compaction properties and fewer tendencies to settle (Leite and Soares 1999).

The asphalt rubber binder should be homogeneous with the rubber after being devulcanized, but not depolymerized. However, it is possibly reasonable that rubber depolymerization to a great extent can worsen the aging characteristics of the binder (Leite and Soares 1999).

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Takallou and Sainton (1992) concluded that after a very long interaction time, there is a change in the viscosity of the asphalt-rubber. This change, evaluated at the high temperatures at which the material is heated, is caused by devulcanization or depolymerization, as shown in Figure 9 (Fontes 2009).
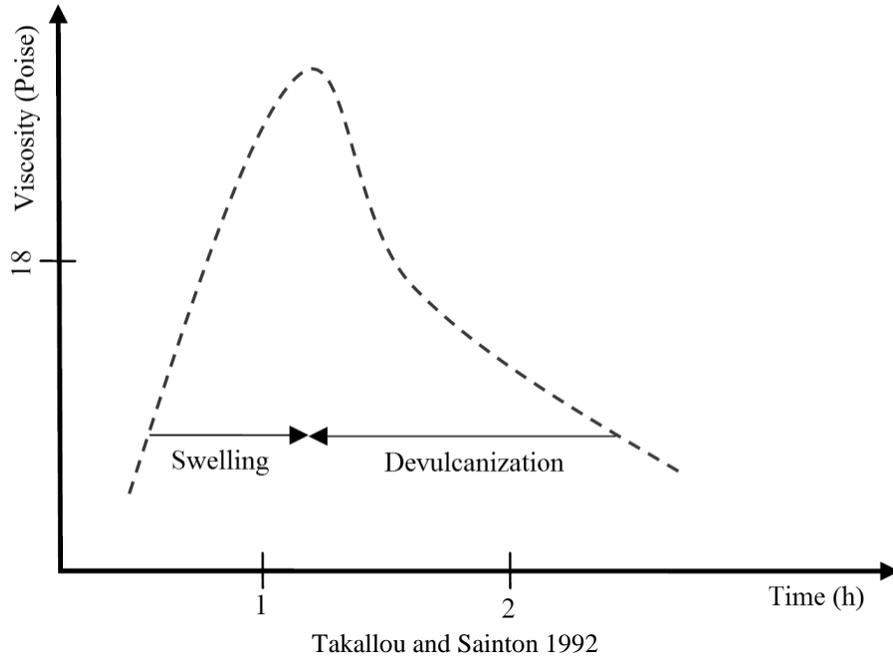
Figure 9. Effect of digestion time in the viscosity of the asphalt-rubber

Moreover, post-vulcanization (Green and Tolonen 1977) is an interesting phenomenon that sometimes occurs when mixing an asphalt binder with rubber. During rubber processing there are sulfur and other agents that have not been entirely chemically bonded during vulcanization of the rubber. When mixing rubber with hot asphalt, the vulcanization process can be reactivated and continue for some time, depending on the interaction temperature. This extra time is longer for lower interaction temperatures than for higher interaction temperatures. This extra time was reported as thirty minutes at 150 °C (Green and Tolonen 1977). Vulcanization delays the development of modified binder properties. This phenomenon should be considered when GTR interacts with asphalt for short interaction periods and targeted properties are not achieved (Jensen and Abdelrahman 2006).

Other authors state that some breakings in crosslinks (devulcanization) due to heating during the curing process can occur (Billiter et al. 1997b). This phenomenon induces a progressive decrease in viscosity, which is considered in some papers as the initial degradation of the polymer chains. Both swelling and devulcanization are present during the asphalt rubber curing, even for the so-called dry process. The predominance of one of the phenomena relies on the processing parameters and essentially on the blending temperature and duration (Ould-Henia and Dumont 2006).

Effects of Ground Tire Rubber Addition on the Binder Properties

When crumb rubber is mixed and heated with asphalt, the produced modified binder has significantly different properties than the original asphalt. Property modification is due to physical and compositional changes during the interaction process (Jensen and Abdelrahman 2006).

Adding rubber particles to asphalt binder changes the performance of HMA for paving applications by modifying binder properties. Property modification depends on both material variables and interaction variables. Material variables include asphalt properties and crumb rubber properties. Asphalt properties include stiffness and chemical composition, while crumb rubber properties include source and method of processing. Another material factor affecting the binder properties is crumb rubber concentration. Interaction process variables include time and temperature. The compatibility between asphalt and crumb rubber is another material variable that must be considered (Jensen and Abdelrahman 2006).

Hanson and Duncan (1995) concluded that asphalt sources had little or no effect on the way the rubber reacted with asphalt. Western Research Institute (WRI) found that asphalt source controlled the asphalt rubber binder properties and had significant effect on the way asphalt-rubber interacted at different temperatures (Jensen and Abdelrahman 2006).

The properties of asphalt-rubber binders produced by the wet process depend basically on the characteristics of both crumb rubber and asphalt used in the process (Neto et al. 2006). The changes in binder properties reflect changes in the gel-like structure developed during the interaction process. Particle swelling stiffens the binder by reducing the inter-particle distance and by decreasing the liquid phase of the binder (Jensen and Abdelrahman 2006).

The use of two different base asphalts of the same "commercial" asphalt grade in asphalt rubber production results in two final products with different properties. Thus, the base asphalt should be selected carefully to ensure that the content of light fractions of asphalt is large enough at the end of the curing process (Ould-Henia and Dumont 2006). Since the interaction that occurs with asphalt rubber binders is dependent on the presence of aromatic oils in the asphalt, the source of the base asphalt binder has a significant effect on the performance of asphalt rubber binders (Putman and Amirkhanian 2006).

In fact, asphalt grades were shown to have more effect on the performance related properties of asphalt rubber binders than the crumb rubber source. Another major factor affecting the final product was found to be the rubber content. Moreover, the interaction conditions of time and temperature were shown to affect the developed properties of asphalt rubber binders. The effect of time is greatly dependent on the temperature (Jensen and Abdelrahman 2006).

According to ASTM D 6114 (1997), the asphalt-rubber binders are obtained from a combination of asphalt, crumb rubber recycled from used ground tires and other additives, as necessary. These additives are normally extender oils used to improve the workability of asphalt-rubber or

the compatibility between the asphalt and the crumb rubber used (Neto et al. 2006), and to reduce the viscosity of the asphalt rubber binder, thus reducing the manufacturing temperature (Rodriguez-Alloza et al. 2013).

In general, crumb rubbers can be used within a wide range of contents and sizes to reduce the low-temperature stiffness of asphalt binders. However, the optimum crumb rubber content must be determined for each crumb rubber size and asphalt binder (Gopal et al. 2002), because rubber concentration was found to have the largest effect on the final properties of the binder (Jensen and Abdelrahman 2006).

In 1995, Bahia and Davies concluded that the impact of crumb rubber content (2% to 20%) on the reduction of stiffness at low temperatures (-20 ℃ to 0 ℃) is a linear function of the rubber content and was independent of the rubber source, and that the lower the stiffness of the asphalt the less significant the effect of the rubber (Gopal et al. 2002). Compared to the other factors, rubber source is not found to have an important effect on the change in properties (Bahia and Davies 1995).

The addition of rubber results in improving high-temperature performance grade of the binder, although rubber type, content, particle size and reaction time are factors affecting the level of improvement. Increasing stiffness brings up an effect of improving high-temperature performance of asphalt-rubber binder (Amirkhanian and Kim 2004). Experiments on binders made with finely ground rubber indicate faster property modification than coarser ground rubber (Jensen and Abdelrahman 2006).

The small particle size of elastomer (GTR) was a very important factor to achieve good properties in the asphalt-rubber blends. It contributed to reduce time and temperature curing, and consequently reduced depolymerization and improved aging resistance (Leite and Soares 1999).

The effect of the interaction conditions on the development of the high temperature properties can be summarized as follows (Jensen and Abdelrahman 2006):

- The interaction temperature controls the activity of the interaction process. There are two main activities within the interaction process: swelling and depolymerization. Interaction temperature affects the process by controlling the time when swelling is replaced with depolymerization.
- Shearing energy can be very effective in controlling crumb rubber particle sizes during the interaction process. Higher shear turns coarser particles into fine particles and help stabilize asphalt-rubber binder properties.

According to Fontes (2009), the characteristics of the asphalt-rubber produced with the wet system and its relationship with the asphalt and rubber are summarized in Table 1.

Table 1. Summary of asphalt-rubber characteristics

Characteristics	Test	Influential factors	Benefits
Consistency	Viscosity (ASTM D 2196) Penetration (ASTM D 5)	- Type of rubber - Percent of rubber - Interaction time	- Higher resistance to permanent deformation - Slower crack propagation - Less raveling - Better thermal susceptibility - Higher durability
Stiffness	Softening Point (ASTM D 36)	- Conventional asphalt consistency - Type of rubber - Interaction time	- Higher resistance to permanent deformation - Higher flexibility - Higher cracking resistance
Elasticity	Resilience (ASTM D 5329)	- Type of rubber - Percent of rubber - Interaction time	- Higher resistance to fatigue cracking

Adapted from Fontes 2009

Rheological Representation of Binders for Flexible Pavements

The physical, mechanical, and rheological behavior of asphalt in road and building construction is governed by its structure and chemical composition (Petersen et al. 1994, Rahman 2004). For this reason, considerable effort goes toward widening the knowledge of this composition and relating it to performance (Raki et al. 2000). The principal value of composition studies is to develop an understanding of what compositional features are needed to produce a material with the desired properties. Then, this information can be used to select, mix, or modify asphalts to obtain binders that will perform in a cost-effective manner (Robertson 1991).

Since asphalt is a viscoelastic material, its response to an applied stress consists of both viscous and elastic responses. The relative amounts of each are determined by the temperature and duration of load application and by the rheological characteristics of the asphalt. The behavior of asphalts over wide ranges of frequencies can be represented in a single master curve (Simpson et al. 1961), of which an example is plotted in Figure 10, explaining the significance of certain features (Oliver 2001).
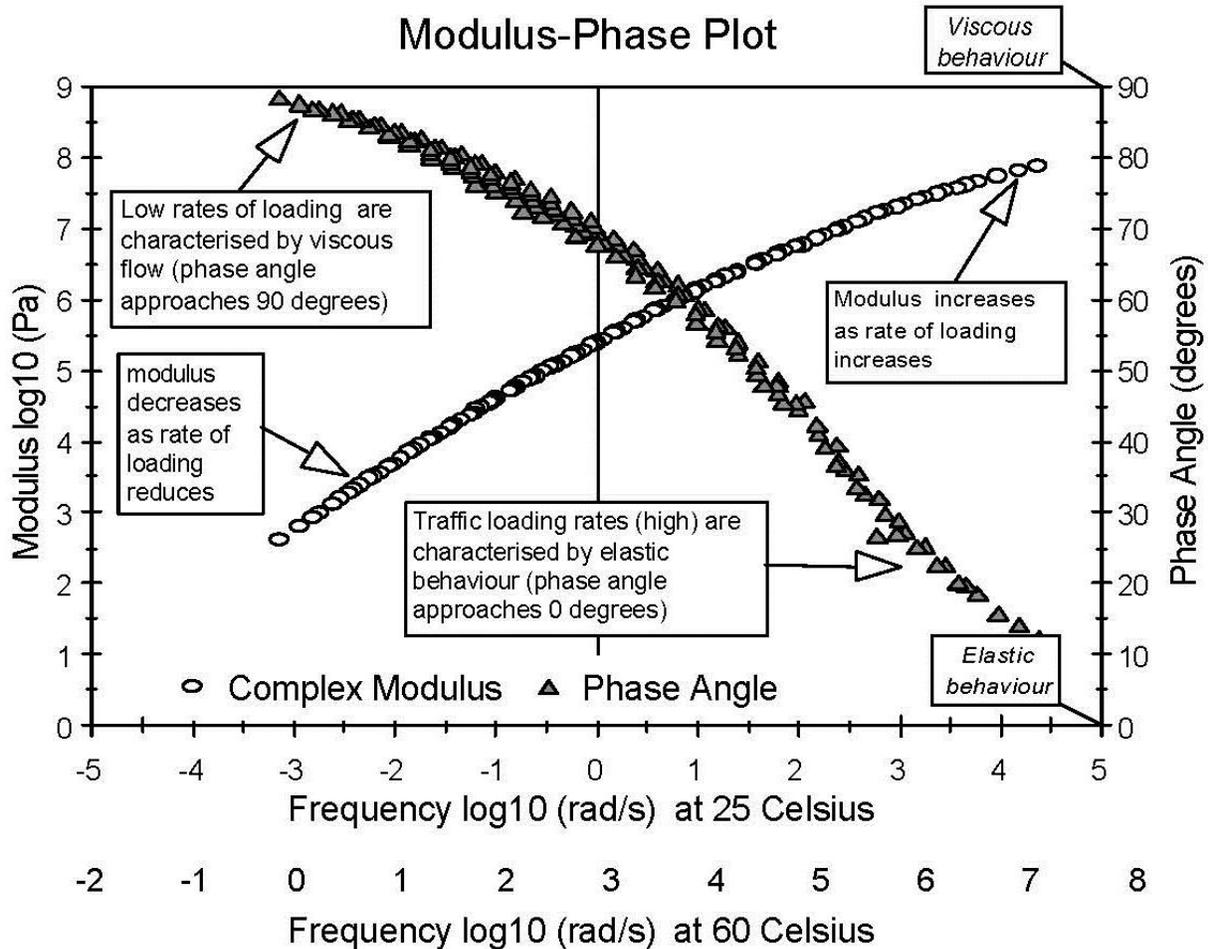
ARRB Transport Research 1997

Figure 10. Example of stiffness modulus and phase angle master-curves plot for an asphalt binder

The Christensen-Anderson-Marasteanu (CAM) model is used to develop master curves for asphalt binders with the main purpose of provide a simple model that can be used for routine engineering problems (Marasteanu and Anderson 1996). The first step is to perform the testing in the asphalt material:

- Three or four temperatures at three or four different rotational rates in the rotational viscometer (RV) for original binder
- Frequency sweeps between 0.1 and 100 rad/s, at three temperatures 12 °C apart, using 25 mm plates, in the dynamic shear rheometer (DSR), for original binder
- Frequency sweeps between 0.1 and 100 rad/s, using the 8 mm plates, at three temperatures 12 °C apart in the DSR, for RTFO aged binder
- Bending beam rheometer (BBR) testing carried out at three temperatures and 6 °C apart for both RTFO and PAV aged binder

An isothermal plot or isotherm is an equation, or a curve on a graph, representing the behavior of a system at a constant temperature. In this type of plot, data at a given temperature is plotted over a range of frequencies. The curve can be used to compare different viscoelastic functions at different frequencies at a constant temperature (see Figure 10). In addition, this type of plot can be used to study the time dependency of the material. As DSR, BBR and RV testing are only performed over a limited frequency range, it is impossible to represent a wide range of rheological properties in an isothermal plot. Therefore, master curves are used to extend the data over a wider range of frequencies using the time temperature superposition principle.

The procedure of superposing curves at different times (frequencies) and temperatures is known as the time-temperature superposition (TTS) and the resulting master curves cover large time or frequency domains well beyond the frequency range experimentally accessed by a rheometer. An important criterion to use the method of reduced variables is that the shapes of the original curves at different temperatures must match over a substantial range of frequencies or times. An equally important criterion to evaluate the applicability of the method of reduced variables is the requirement that the same values of the horizontal shifting factor must superpose all viscoelastic functions. After the tests, a treatment of the experimental results is needed to obtain the complete master curves of complex modulus ($|G^*|$) versus frequency (Freq).

The DSR provides isotherm curves of $|G^*|$ versus Freq, but the results provided from the RV and BBR tests need further calculations to obtain $|G^*|$ versus Freq isotherms.

When asphalt is tested in an RV it behaves as a fluid in steady state. So, it is possible to relate the steady state with the complex viscosity (Equation 1).

$$\eta^* = |G^*|/\omega \tag{1}$$

where:
ω – Angular frequency (rad/s)
G^* – Complex modulus (Pa)
η^* – Complex viscosity

The ω value can be obtained by changing the rotational rate from rpm to rad/s. Then, for each frequency, using the respective viscosity it is possible to obtain the $|G^*|$ value and finally draw the $|G^*|$ versus Freq isotherms.

The BBR provides three parameters (a, b, and c) to be used the polynomial equation that describes the variation of stiffness with frequency, respectively presented in Equations 2 and 3.

$$logS(t)= a+b.log(t)+c.log2(t) \tag{2}$$

$$G^* = S(t)/3 \tag{3}$$

Then, it is possible to build the |G*| isotherms at each of the tested temperatures, since the frequency (rad/s) is the reciprocal of the frequency (seconds).

Some mathematical functions were identified to describe the master curves (|G*| versus Freq, and phase angle versus Freq – CAM model) of asphalts reasonably well. Thus, Equations 4 and 5 can be used to describe the complex modulus |G*|.

$$|G^*|(\omega) = G_g \left[1 + \left(\frac{\omega_0}{\omega} \right)^{\frac{log(2)}{R}} \right]^{\frac{-W \times R}{log(2)}} \qquad (4)$$

$$R = log[G^*(\omega_o)/G_g] \qquad (5)$$

where:
$G^*(\omega)$ – complex dynamic modulus (Pa) at frequency ω (rad/s)
G_g – glassy modulus (typically 1 GPa)
ω_o – crossover frequency (rad/s)
R – rheological index

The phase angle (δ), in degrees, at a frequency ω (rad/s), can be described with the related Equation 6.

$$\delta(\omega) = \frac{90^0}{\left[1 + \left(\frac{\omega}{\omega_0} \right)^{\frac{log(2)}{R}} \right]} \qquad (6)$$

Equations 5 and 6 can be combined and algebraically evolved to express the rheological index (R) as shown in Equation 7.

$$R = \frac{log(2).log \left| \frac{G^*(\omega)}{G_g} \right|}{log \left| 1 - \frac{\omega}{90^o} \right|} \qquad (7)$$

The angular frequency in Equations 5 and 7 is not an absolute frequency, but a reduced frequency (Equation 8) that allows the construction of the master curves.

$$\omega_r = \omega \times a_T \qquad (8)$$

The time dependency is reflected in the location and shape of the master curve. The temperature dependency is indicated by the plot of log a_T versus temperature. So, a_T is the shift factor that will allow the construction of the master curves and is obtained from the Arrhenius or WLF

equations. The use of Arrhenius or WLF equations is done in specific ranges of temperatures, as follows:

- For temperatures between T_g and $T_g + 100$ °C the WLF equation is used
- For temperatures lower than T_g a modified WLF equation is used, which includes a parameter that depends both on test temperature and in conditioning time
- For temperatures greater than $T_g + 100$ °C the Arrhenius equation is used

The shift factor is a positive value greater than 1 for temperatures below the chosen reference temperature, equal to 1 at the reference temperature, and less than 1 for temperatures above the reference one.

Combining the previous equations, and the Arrhenius or WLF equations at the defined conditions, it is possible to obtain the master curve of the tested material. Figure 11 shows the graphic mechanism of constructing a master curve.
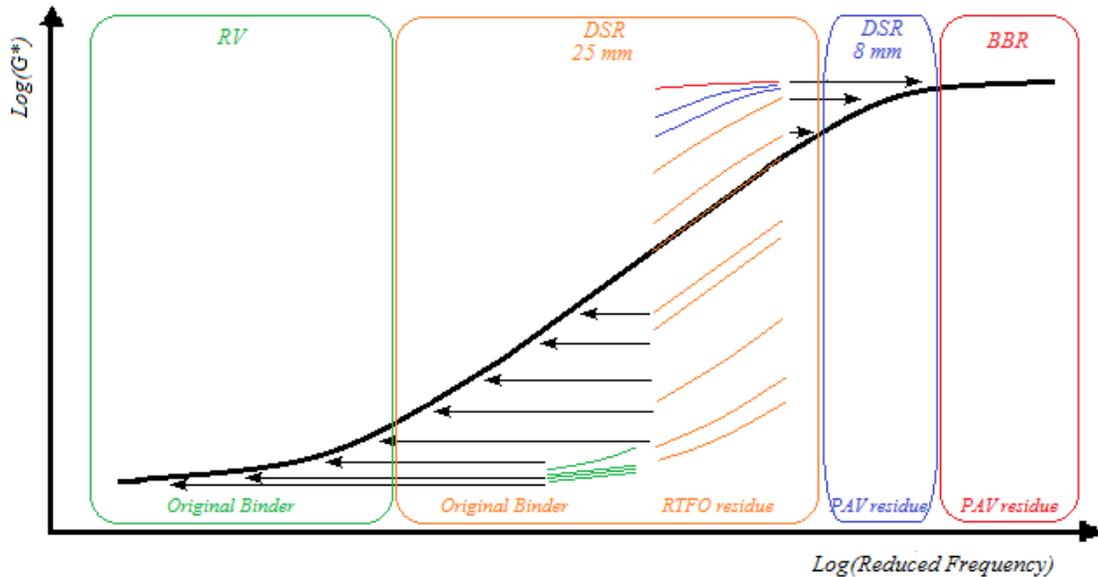
Arrows represent the different shifting factors (aT) at the different temperatures

Figure 11. Schematic of the use of CAM model

After all the isotherms are determined, the CAM equation with the Arrhenius or WLF equations will fit the several small curves in a unique curve (master curve). This is carried out by choosing a reference isotherm (reference temperature in the calculations) and by applying a horizontal translation of each small curve, superposing the initial part of one curve to the final part of the other curve. In order to do this procedure, the isotherms obtained for temperatures lower than the reference one will move to the right, and the higher temperature isochrones will move to the left.

Binder Interactions and Pavement Applications

Asphalt

Relationship between the Chemical Properties of the Asphalt and the Pavement Performance

The significant failure modes in asphalt pavements that may be related to materials are generally agreed to be permanent deformation, rutting, fatigue cracking, low-temperature cracking, moisture damage, and total loss of adhesion (Robertson 1991).

The results of laboratory tests together with observations of performance in practice have identified key links between physical properties and the constitution of the asphalt. Thus, it has been indicated that if the molecular weight distribution and chemical constitution of the asphalt is unbalanced, it can exhibit heterogeneity which may adversely affect both the cohesive and adhesive properties of the asphalt (Read and Whiteoak 2003).

Cracking can be related to binder composition. If the molecular network (agglomerate, micelle, colloid, or whichever term is preferred) becomes too rigid, the ability of asphalt to deform elastically will be lost. Instead, the asphalt fractures and likely will be separated to a point that healing cannot occur. The constant working of a very rigid matrix will eventually suffer fatigue and cracking (Robertson 1991).

Asphalt chemistry may have a significant influence on the low-temperature behavior of asphalt pavements (Isacsson and Zeng 1997). Cracking at low temperatures is expected to be most closely related to the compositional feature of aliphatic/aromatic ratio (Robertson 1991).

Effects of Aging in the Pavement Performance

Asphalt aging occurs during the mixing and construction process as well as during long-term in-situ service in the road. The circumstances at different aging stages vary considerably. The factors affecting asphalt aging include characteristics of the asphalt and its content in the mix, nature of aggregates and particle size distribution, void content of the mix, production related factors, temperature and time. All these factors operate at the same time, making the process of asphalt aging very complex (Johansson 1998).

The simulation of field aging entails increasing the temperature, decreasing asphalt film thickness, increasing oxygen pressure, or using combinations of these factors. Kinetics of asphalt aging may vary with test conditions (Lu and Isacsson 2002). By comparison with changes induced by field aging, it has been established that binder aging is characterized by (FEHRL 2006):

- Changes in the generic composition
  - Appearance of oxidized functions (development of ester, acid and sulfoxide functions) and transformation of the cyclic compounds into resins and then into asphaltenes
  - With preferential formation and accumulation of resins during field aging
  - With preferential formation of asphaltenes during the "in construction" aging
- Modifications of the properties
  - Increase of ring and ball (R&B) softening point
  - Decrease of penetration
  - Variations in rheological properties
  - Increase of viscosity and complex modulus
  - Decrease of phase angle

Asphalt aging is one of the principal factors that cause the deterioration of asphalt pavements. Important aging related modes of failure are traffic and thermally induced cracking, and raveling (Lu and Isacsson 2002). Furthermore, asphalt-aggregate debonding (adhesion failure) and asphalt phase separation (cohesion failure) are also a result of oxidative hardening (Glover 2007).

The aging dependency of rheological properties of asphalt is similar to the temperature dependency of asphalt, but is reversed in nature. An increase in the aging level corresponds to a decrease in temperature (Huang and Zeng 2007).

Gel-type asphalts tend to lose complex flow (a measure of non-Newtonian behavior) upon heating. The phenomenon of isothermal, reversible age hardening, termed steric hardening, is strong evidence of the formation of secondary structures in the asphalt unstable to heat and mechanical agitation (Petersen et al. 1994).

For asphalt-rubber binders, the increase on the crumb rubber content decreases the aging index of viscosity and $G^*/\sin \delta$, and increases $\tan \delta$, thus indicating a reduction of the aging effect on physical and rheological properties of asphalt rubber binders (Ali et al. 2013).

Bio-Binders

Most asphalt binders that are used for pavement materials are derived primarily from fossil fuels. With petroleum oil reserves becoming depleted and the drive to establish a bio-based economy, there is a push to produce binders from alternative sources, particularly from bio-renewable resources.

Thus, bio-binder is an asphalt binder alternative made from non-petroleum-based renewable resources, polymer modified or not, which should not rival any food material, and have environmental and economic benefits. Presently, bio-binders are produced by upgrading bio-oils produced from the rapid heating of biomass in a vacuum condition (Peralta et al. 2012a).

Natural Resources used to Produce Bio-Binders

Simply stated, bio-based materials include industrial products, not food or feed, made from renewable agricultural and forestry feed stocks, including wood, wood wastes and residues, grasses, crops, and co-products of crops (Mohanty et al. 2002).

Over the years, bio-renewable natural resources including sugars, triglyceride oils and proteins have been tested as alternative sources for producing adhesives and binders (Airey and Mohammed 2008). For example, adhesives derived from soy protein, starch, cellulose and other polysaccharides have been extensively used for adherents such as wood, paper, plastic, metal, leather and glass (Airey and Mohammed 2008, Shields 1976). Due to the availability of large quantities of bio-renewable sources such as triglyceride oils, proteins, starch and other carbohydrates from different botanical sources, there are virtuous technical and economic prospects in utilizing them to produce bio-binders (Airey and Mohammed 2008). Recently, a range of different vegetable oils have been investigated to determine their physical and chemical properties and their applicability as bio-binders in the pavement industry (Airey and Mohammed. 2008, Tan and Man 2002, Kaplan 1998).

Application of Bio-Binders

The main field of application of bio-binders is in the paving industry. However, market opportunities exist in housing products via roofing shingles and sealants. Bio-binders can be utilized in three different ways to decrease the demand for fossil fuel based asphalt binders: a direct alternative binder (100% replacement), an asphalt extender (25% to 75% asphalt replacement), or an asphalt modifier (<10% asphalt replacement).

Williams et al. (2009) conducted research on the use of bio-oils fractions as an extender in original and polymer modified asphalt binders. They reported that the bio-oils can considerably increase the performance grade of polymer modified asphalt binders by nearly six degrees Celsius. Moreover, it was concluded that the effect of bio-oils was dependent upon many factors including the base asphalt, source of the biomass from which the bio-oils were derived, and the amount of bio-oils blended with asphalt binders. Williams et al. (2009) also reported that up to 9 percent of a bio-oil could be blended with asphalt binders with significant improvement in performance grade of the bio-oil modified asphalt binder.

Combined Binders

In asphalt or flexible pavements, all types of failure or distress can be classified by whether they are structural or functional failures or load associated or non-load associated distresses. Surface course aging is considered a non-load associated distress caused by climatic/environmental effects. Many environmental factors can cause surface course aging damage, such as ozone, ultraviolet rays, oxygen, and thermal radiation. Oxidative aging causes the asphalt binder to become harder and more brittle and thus more susceptible to thermal cracking (Ruan et al. 2003).

The common asphalt additives, such as polymer, rubber, and plastic do not prevent oxidative aging of the binder. The polymer additives can react with the free radicals and degrade. The SBS polymer and other rubbers cannot prevent the propagation of the free radical or peroxyl radicals, because the polymer degradation can form new free radicals and the cycle repeats (Ouyang et al. 2006). However there is several asphalt additives that prevent oxidative aging of the binder (polyphosphoric acid, ground tire rubber, limestone among others).

The bio-oil generated from waste bio-mass at low cost is an environmentally friendly material containing the natural antioxidant lignin. In fact, the bio-oil shows the potential to be successfully applied as an antioxidant additive in asphalt pavements (Peralta et al. 2012b).

Lignin contains several functional chemical groups, such as phenolic, methoxyl, carbonyl and carboxyl. Most antioxidant effects of lignin are provided by the phenolic group capturing and reacting with the free radicals, which contain oxygen. Free radicals are known to "attack" stable molecule structures of a substance by "stealing" an electron. Once the "attacked" molecule loses its electron, the chemical structure of the substance is then changed. When the chemical reaction occurs, new bonds are formed and the asphalt starts aging with asphaltenes being generated. Instead of letting the free radicals, which contain the oxygen, oxidize the aromatics and convert aromatic molecules to asphaltenes, the lignin first reacts with those free radicals as a reducing agent. This radical scavenging property of lignin makes it possible to recognize it as an efficient antioxidant additive (Peralta et al. 2012b).

Mix Behavior and Performance in Flexible Pavements

The asphalt mixes constitute some of the pavement layers and, depending on the layer to be built, good mechanical characteristics or the ability to perform functions related to the safety and comfort of road users may be required (Branco et al. 2005).

In general, the asphalt mixtures are constituted by a set of granular material dosed by weight or by volume that are mixed in an asphalt plant with a predetermined amount of binder. The mechanical behavior of asphalt mixtures used in pavement structures depends on the properties of the mixture constituents (aggregates, asphalt binder, and additives) and on the respective proportions (Antunes 2005).

In a pavement layer system, the asphalt mixtures should have the following characteristics to achieve a satisfactory structural performance (Epps et al. 2003):

- Ability to distribute stresses
- Stability to resist permanent deformation
- Resistance to cracking
- Resistance to freezing and thawing cycles

The main properties required for asphalt mixtures are stability, durability, flexibility, fatigue resistance, resistance to permanent deformation, skid resistance, impermeability, and workability (Branco et al. 2005).

Asphalt Mixes

Asphalt mixtures are developed by the combination of mineral aggregates, filler, and asphalt. To understand the behavior of asphalt mixtures, it is necessary to characterize the individual components. Thus, a standard procedure is required to define the dosage of each of the mentioned components and conduct performance tests that may indicate if the mixture will have a proper behavior on the field before the action of traffic and weather (Fontes 2010). These procedures were used in this study and are introduced and described in Chapter 3 and Chapter 7.

Asphalt Rubber Mixes: History, Application and Mix Design

History of Asphalt Rubber Mixes

The first patent for the combination of tar with natural rubber to manufacture a waterproofing material for wooden ships was granted in 1823 to T. Hancock. Then, the first patent to combine asphalt material with natural rubber for road construction was awarded in 1844 to E. E. Cassell.

The practical applications of modified asphalts began in France, in 1901, when the Société du Pavage en Asphalt Caoutchoute was established, and the construction of the first road using rubber-modified asphalt occurred in 1902 in Cannes. All asphalt modifications before World War II were carried out with natural rubber, the only suitable material available at that time. Reports on road performance were positive and, with the development of synthetic macromolecular materials after World War II, an entire line of new materials with the potential of being used for asphalt modification was available to the asphalt mix design engineer. The initial experiments with scrap rubber started in the 1920s (Zanzotto and Kennepohl 1996).

Then, the history of adding recycled tire rubber to hot -mix asphalt (HMA) materials can be traced back to the 1940s, when the U.S. Rubber Reclaiming Company of Vicksburg, Mississippi, began marketing a devulcanized, recycled rubber product as a dry particle additive to asphalt mixtures (Baker et al. 2003).

In the early 1950s, Lewis and Welborn, of the Bureau of Public Roads, conducted an extensive laboratory study to evaluate the effect of rubbers on the properties of asphalts. In 1960, the Asphalt Institute held the first Symposium on Rubber in Asphalt in Chicago, Illinois, which consisted of five paper presentations (Caltrans 2007).

Charles H. McDonald, from the City of Phoenix, Arizona, worked extensively with asphalt and rubber materials in the 1960s and 1970s, and his work was essential in the development of the "wet process" of producing asphalt rubber (also called the McDonald process). He was the first to routinely use asphalt rubber in hot-mix patching and surface treatments for repair and

maintenance of pavements. Since then, many road agencies in the US have developed experiments using asphalt rubber in pavement mixtures. Arizona, California, Florida, and Texas have led the way in evaluating asphalt rubber pavements (Baker et al. 2003).

In 1975, Caltrans tested asphalt rubber chip seals in the laboratory and in small test patches. The first Caltrans rubberized asphalt concrete pavements were constructed in 1980, being made with early versions of the wet process for asphalt-rubber (AR) binder production and dense-graded mix gradations. After that, several studies and projects were developed, and Caltrans concluded that AR materials can perform very well when properly designed and constructed (Fontes et al. 2006b).

The Arizona Department of Transportation (ADOT) became involved with the material in the mid-1960s, working with McDonald and the City of Phoenix, trying different applications of asphalt rubber materials. The ADOT work through the years has led to successful routine usage of the process in seal coats, interlayer, membranes, gap graded asphalt-rubber concrete and open-graded asphalt rubber concrete surface courses (Carlson 2003).

From the mid-1970s through the early 1980s, ADOT sponsored comprehensive research projects to develop a fundamental understanding of the asphalt rubber binders. The research indicated that the properties of AR mixtures vary depending on rubber type, rubber gradation, rubber concentration, asphalt type, asphalt concentration, type and concentration of extender oil, and reaction time and temperature (Hicks 2002).

In the 1970s, Caltrans began evaluating asphalt rubber uses in spray applications, and in the 1980s they studied its uses on hot mixes. This early work resulted in the development of their current thickness design guide for mixes with asphalt rubber, with a reduction up to 2:1 in thickness when compared with conventional hot mixes (Van Kirk 1992 and 1997). Other agencies, including Arizona and Texas, continued their use of asphalt rubber for both spray applications and hot mixes during this period (Hicks 2002).

In 1992, a federal mandate on the use of asphalt rubber was instituted. This resulted in several studies carried out by the Federal Highway Administration to help the States Highway Administrations in implementing the mandate (Hicks 2002). However, before all the studies were completed, the mandate was repealed and the patents on the asphalt rubber binder had expired. This resulted, particularly in Arizona and California, in a number of new producers of asphalt rubber binders.

It came at a time when California was expanding their use of asphalt rubber because of good early performance. As a result, many projects constructed during this period experienced early distress, either because they were used in the wrong place, were not constructed properly, or the binder did not meet specifications (Hildebrand and Van Kirk 1996).

The early distresses exhibited in the asphalt rubber projects prompted Caltrans to begin research on a performance related specification (PRS) to minimize the observed distresses (Reese 1994

and 1995). This also prompted Caltrans to partner with industry to develop an improved recipe specification to minimize the impact of the other construction problems (Hicks 2002).

Application of Asphalt Rubber Mixes in Flexible Pavements

Various types of asphalt rubber mixtures, including gap graded and open graded friction course mixes, are used in the state of California. These thinner types of pavement preservation and rehabilitation mixtures are used to reduce noise and improve resistance to reflective cracking over distressed flexible and rigid pavements (Carlson 2003, Caltrans 2007).

Paving with asphalt rubber mixtures can offer several advantages, including the following (Hicks 2002):

- Durability - Asphalt rubber pavements have excellent durability in terms of cracking and aging resistance.
- Constructability - Asphalt rubber pavements are machine placed and can be opened to traffic almost immediately, and almost no delay is required to allow the pavement to cure and be used.
- Economics - Asphalt rubber pavements are cost effective. Their construction costs, as well as long life (when properly designed and constructed), are important attributes.
- Recyclability - A major attribute of asphalt rubber pavements is its ability to be completely recycled. Not only can the aggregates be reused, but the asphalt rubber binder retains much of its cementing properties and can also be reused in a mix. However, there are still concerns regarding whether air quality standards can be met when recycling AR mixes.
- Safety - Asphalt rubber pavements provide safe surfaces with good surface friction for all users. Open-graded or gap-graded mixes offer additional advantages for roads such as reduced splash and spray under wet conditions.
- Reduced maintenance - Asphalt rubber pavements result in reduced maintenance when properly designed and constructed.
- Reduction in noise - Lower tire noise has been demonstrated when using asphalt rubber mixtures in pavements, with reductions of 3 to 5 dB reported in the literature.

However, asphalt rubber mixtures and pavements can also present some drawbacks (Hicks 2002):

- Raveling and Flushing - Problems such as early raveling or flushing have been reported. These are often related to lack of construction quality control sometimes observed in these mixtures.
- Cracking - Despite AR mixes resistance to cracking being very good when used in the correct application or thickness, problems of early cracking have been reported, mainly associated with the use of asphalt rubber as a last resort to correct badly distressed pavements.
- Tackiness of product - Asphalt rubber mixes are more prone to track exiting pavement surfaces.

Design of Asphalt Rubber Mixes

Gap graded mixtures specified in Caltrans as ARHM-GG can be produced with asphalt rubber binders. The gap (missing fraction) is used to accommodate the asphalt rubber binder. The purpose of gap grading is to provide improved stone-to-stone contact by reducing the fine aggregate content so as to provide a strong aggregate skeleton that creates space for more engineered binder than a dense graded mix can hold. Furthermore, the crumb rubber increases the viscosity of the binder increasing the binder contents without bleeding (Fontes et al. 2006a).

The stone to stone contact of the gap graded asphalt rubber mixtures can improve the permanent deformation resistance and the extra binder has been found to aid in fatigue and cracking propagation resistance. Gap grading is also a good way to increase the Voids in Mineral Aggregate (VMA) of a mixture. The increase in voids allows the mix to accommodate the larger particles of rubber present in asphalt rubber binders. The binder content may be 7 to 9% (Caltrans 2005b).

The design of gap graded mixtures with asphalt rubber can also reduce the thickness in pavement rehabilitation. Caltrans conducted research between 1980 and 1992, which compared asphalt rubber concrete to conventional asphalt concrete in field evaluations. At the end of the research, it was determined through these field evaluations that the pavements with gap graded asphalt rubber mixtures could be significantly reduced in thickness, providing the same service life as thicker conventional asphalt concrete pavements (Van Kirk et al. 2000).

Application of Bio-Oil in Asphalt Mixes

So far, the development of this new type of binder has been tested mostly at the binder level. Besides the bike path at Des Moines, Iowa, built in 2010 (ISU 2010), there is no documentation about any other pavement where bio-oil material has been applied as a bio-binder.

In this project at Des Moines, 3% of petroleum asphalt was replaced with bio binder. After three years in service no signs of damage have been found in the pavement of the bike path. Therefore, and as a natural sequence of this work, another demonstration project is being planned for the near future, where 20% of asphalt will be replaced with bio-binder in a road pavement with real traffic. It is expected that the success of this new project will lead to higher asphalt replacement by bio-binders in the future, until a 100% bio-binder pavement can be built.

Environmental and Economic Impact

The economic impact of the replacement of asphalt with bio-oil is very significant, taking into account that a replacement of 25% of asphalt with bio-binder, at the current prices for paving asphalt and bio-oil, would result in direct economic savings of about 5%. If the reduction in mixing and compaction temperatures is also accounted, the economic opportunity in the use of this technology is even higher.

However, the biggest gain in the application of this technology is environmental. The feedstocks for the production of bio-oil are agriculture and forestry residues; thus, no additional energy is spent to collect these materials. The fast pyrolysis plants are less complex than a crude petroleum refinery and often smaller, therefore they can be placed near to the feedstock production, and in consequence, also near places where the binder will be used. The fast pyrolysis units are energy auto-sufficient, and as previously stated, there is no residue produced in the system. The reduction in mixing and compacting temperatures when bio-oil is used, instead of asphalt, results in smaller carbon emissions. In sum, this technology can improve the pavement performance with important savings, both economic and environmental.

CHAPTER 3. EXPERIMENTAL METHODS

Chemical Characterization of Bio-Oil for Utilization as an Asphalt Binder

The experimental plan for the chemical characterization of bio-oil as an asphalt binder consists of a description of the materials, including the production of the bio-binders, and the chemical and rheological testing. The specific components of the experimental plan are discussed in the following subsections.

Materials

The main material used for the chemical characterization was the bio-oil derived from the fast pyrolysis of red oak wood residues in the Iowa State University pyrolysis unit (Figure 12) and two sources of crumb rubber from used tires from different suppliers that were procured using two different processing methods: mechanical shredding – ambient rubber and cryogenic milled rubber.
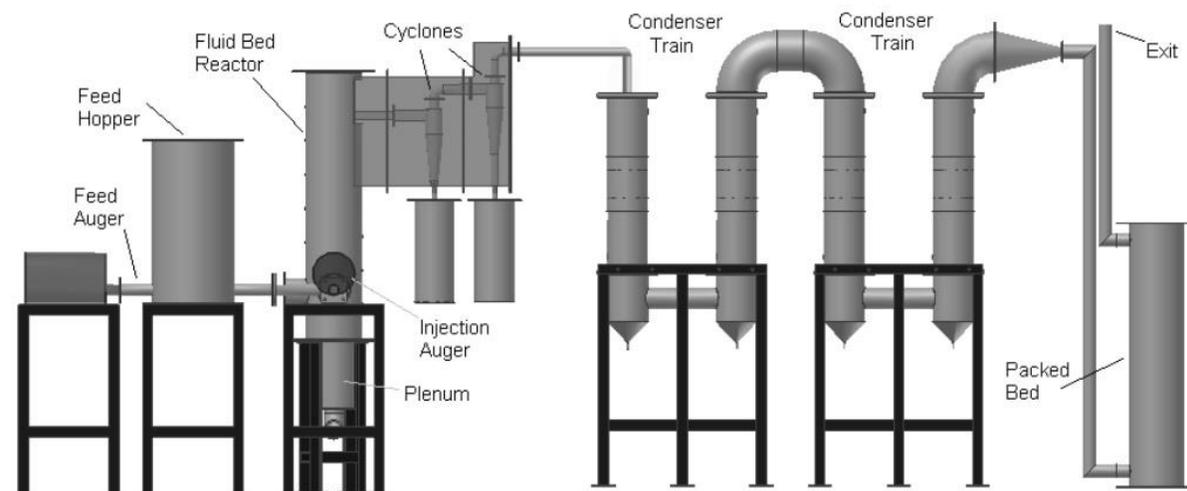
Raouf 2010

Figure 12. Bio-oil fast-pyrolysis pilot plant

For comparison purposes with the developed bio-binders, the asphalt binder chosen as the control for this study is AAM-1 from the Federal Highway Administration (FHWA) Materials Reference Library. AAM-1 is a performance grade (PG) 64-16 and from a West Texas crude source.

Bio-Binder Production

To obtain a bio-binder with suitable characteristics for use as a comparable replacement for conventional, petroleum-derived asphalt, the bio-oil produced from fast pyrolysis needs to be

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upgraded. According to previous studies, the bio-oil by itself possesses very good characteristics, similar to asphalt, at high and medium temperatures (Raouf and Williams 2010b). However, the performance at low temperatures was not acceptable for use in the majority of the US, as they were too stiff at low temperatures and susceptible to low-temperature cracking. The approach used to solve this issue was to react rubber with the bio-oil.

Rubber swells in contact with some solvents and is time-temperature dependent. Additionally, the characteristics of the final binder also depend on the concentration and properties of the rubber. Therefore, the first approach to this concept was to determine whether the rubber swells when in contact with bio-oil. Since the swelling rate depends directly on the interaction temperature, the temperature used for the bio-binder production was the maximum temperature possible to minimize the degradation of the bio-oil, e.g., 125 °C. The selected concentration of rubber for the first test was 15 percent. The rubber was allowed to interact with the bio-binder in a Silverson L4RT shear mixer at 1,000 rpm and small samples of the material were collected every 30 minutes (interaction times: 30 minutes and 1, 1.5, 2, 2.5, and 3 hours) for visual and physical inspection. As a result, an interaction time of 1.5 hours was initially considered adequate.

In order to determine the parameters that would produce a bio-binder with the adequate characteristics, the two sources of rubber were used in two different percentages, 10 and 15 percent, for blending with the bio-oil. Applying these parameters, four bio-binders were produced:

- A – 90% bio-oil plus 10% cryo rubber
- B – 85% bio-oil plus 15% cryo rubber
- D – 90% bio-oil plus 10% amb rubber
- E – 85% bio-oil plus 15% amb rubber

In addition, to assess the changes that occur in the bio-oil that were independent from the interaction with the rubber particles, the bio-oil was heated with agitation for 1.5 hours at 125 °C to obtain the comparatively aged bio-oil.

After the bio-binder production, a sample was taken for subsequent analysis and testing. The remaining bio-binder was separated using a centrifuge consisting of a cylindrical cage with a fine meshed wire and a cloth filter (Figure 13). The binder accelerated separation method was developed to separate the two phases of the bio-binder: the residual bio-oil (Res) and the swelled rubber.
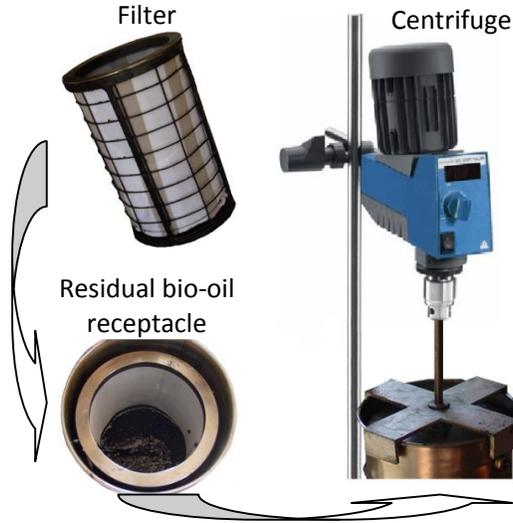
Figure 13. Binder accelerated separation method – BAS

The main constituents of the separation equipment are the aforementioned filter and the centrifuge. The method consists in introducing the bio-binder in the filter, place the filter in the heated residual bio-oil receptacle and centrifuge at a velocity about 2,000 rpm for 3 minutes. The centrifuged material (Res) could then be rheologically tested as well as chemically analyzed, and the retained material weighed to determine the amount of rubber swelling.

Chemical Analysis and Performance Grading of the Bio-Binders

The residual bio-oil (Res) was subjected to two aging methods in order to evaluate its grade. First, the residual bio-oil was aged by the aforementioned modified rolling thin film oven test (RTFOT) that was performed at 120 °C for 20 minutes. After taking a sample for analysis, the remaining material was aged using the pressurized aging vessel (PAV) at 100 °C for 2.5 hours. The degassing was performed at 120°C for 30 minutes.

The chemical analysis of the materials was made using the FTIR method and the resulting spectra were compared. Thus, the characterized materials were (1) the base bio-oil, (2) the aged bio-oil, (3) the ambient and cryogenic rubbers, (4) the four bio-binders, and (5) the four residual bio-oils that resulted from the BAS method.

The evaluation of the critical temperatures (T_c) of the materials was performed using a dynamic shear rheometer (DSR) for high and intermediate temperatures and a bending beam rheometer (BBR) for low temperatures.

The materials characterized in the DSR were the base bio-oil, the aged bio-oil, the four residual bio-oils (two each for each type of rubber at the two different percentages), the four RTFOT residual bio-oils (RTFOT res) and the four PAV residual bio-oils (PAV res). The BBR testing was performed only on the four bio-binders.

Development of Bio-Oil Blends

Materials

The main materials used in the development of the bio-oil blends were a bio-oil produced from the fast pyrolysis of red oak (Quercus rubra) (Wood Residual Solutions, LLC of Montello, Wisconsin) in the Iowa State University pyrolysis unit, and two sources of crumb rubber from used tires (GTR) from different suppliers. These were obtained using two different processing methods: mechanical shredding – ambient rubber (ambGTR), supplied by Seneca Petroleum (# 30 mesh) and frozen and milled – cryogenic rubber (cryoGTR), supplied by Lehigh Technologies (# 80 - #200 mesh).

Two asphalts were also chosen as controls, for comparison to the developed bio-binders, a 160/220 [Performance grade (PG) 58-28] and a 50/70 [PG64-22] asphalts.

Methods

Initially, the asphalt and bio-oil properties were evaluated using conventional CEN standard tests: (1) Penetration at 25 ℃ (Pen) – NP82/1964, (2) viscosity (RV) – ASTM D 4402-06, and (3) ring and ball softening point (R&B) – E34/1955. After this preliminary characterization, the asphalt and bio-oil were blended with 10 and 15 percent of crumb rubber using a Silverson L4RT shear mill at 125 °C and 1,000 rpm for one hour.

After blending, the binder accelerated separation – BAS method (Figure 14) was used to separate the constituents of the asphalt rubber (AR) and modified bio-oil (MBO) into residual and swelled rubber. The changes in the AR and MBO and in the residual binders (residual asphalt and residual MBO) were evaluated by replicating the same tests used for initial binder characterization.

Some of the ARs and the MBOs, as well as the respective residual materials, were aged by the Rolling Thin-Film Oven test (RTFO) – EN 12607-1, followed by the pressurized aging vessel (PAV) – ASTM D 6521-08.

The rheological characteristics of the produced materials were assessed using a dymanic shear rheometer (DSR) – ASTM D 7175-08 and a bending beam rheometer (BBR) – ASTM D 6648-08.

Additionally, the chemical analysis of the materials was made using Fourier transform infrared (FTIR) spectroscopy, a Thermo Scientific Nicolet iS10 (Thermo Scientific, Hanover Park, Illinois) equipped with a Smart iTR accessory, utilizing OMNIC Software (Thermo Scientific, Hanover Park, IL) operating system.
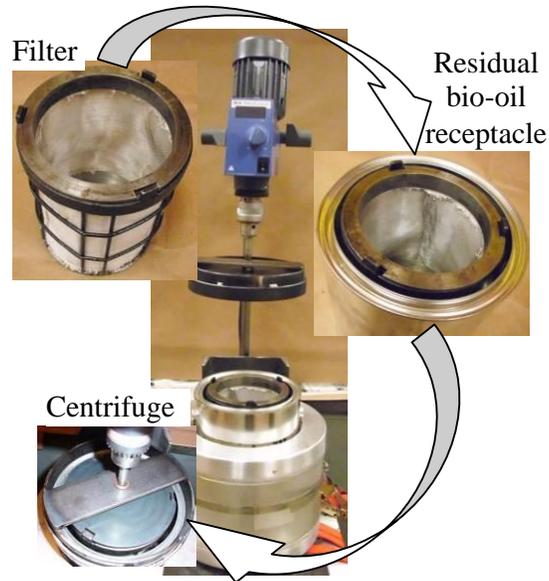
Figure 14. Binder accelerated separation method

Background was collected before every sample and attenuated total reflectance (ATR) correction was used with 4 wavenumber resolution. Spectra were obtained by averaging 32 scans in the range of 4,000-650 cm^{-1}. The solid samples were placed on a diamond crystal plate and prepared for analysis with an equipped constant pressure press.

TQ Analyst software was used to obtain the similarity matches used in the chemical comparison. The regions used for the similarity matches included 3,500-3,100 cm^{-1}, 3,000-2,800 cm^{-1}, 1,500-1,200 cm^{-1}, and 1,150-800 cm^{-1}. The materials and test matrix is presented in Table 2.

Development of Bio-Oil Mix Designs and Performance Testing

The development of bio-oil mix designs and performance testing consisted in the production, study and selection of a new binder constituted by 80 percent of a conventional binder and 20 percent of a rubber-modified bio-oil, which was then applied in the production of two asphalt mixes. These mixtures were than compacted and characterized with performance related tests to verify that they would have adequate performance when used in pavements.

Table 2. Materials and tests used in this work

Materials					FTIR	RV	Pen	R&B	DSR	BBR
CryoGTR					X					
AmbGTR					X					
Bio-oil					X	X	X	X	X	
	Aged bio-oil				X	X				
	CryoGTR	10%			X	X	X	X		X
				RTFO	X					
				PAV	X					
			Residual		X	X	X	X	X	
				RTFO	X				X	
				PAV	X				X	
		15%			X	X	X	X		X
				RTFO	X					
				PAV	X					
			Residual		X	X	X	X	X	
				RTFO	X				X	
				PAV	X				X	
	AmbGTR	10%			X	X	X	X		X
				RTFO	X					
				PAV	X					
			Residual		X	X	X	X	X	
				RTFO	X				X	
				PAV	X				X	
		15%			X	X	X	X		X
				RTFO	X					
				PAV	X					
			Residual		X	X	X	X	X	
				RTFO	X				X	
				PAV	X				X	
160/220 (PG58-28)						X	X	X		
	CryoGTR	10%							X	
			Residual			X	X	X		
		15%								X
			Residual			X	X	X		X
				RTFO					X	
				PAV					X	
	AmbGTR	10%	Residual			X	X	X		
		15%				X	X	X	X	
50/70 (PG64-22)						X	X	X	X	
	CryoGTR	10%	Residual			X	X	X		
		15%				X	X	X		
	AmbGTR	10%	Residual			X	X	X		
		15%				X	X	X		

* Rheological testing (RV, DSR, and BBR) done in triplicate

Materials

The materials used in the production and study of the new binders were, bio-oil from the fast pyrolysis of red oak wood wastes supplied by Ensyn (bio-oil), and two types of rubber. Ground tire rubber from cryogenic milling supplied by Lehigh Technologies under the designation of MicroDyne MD 184 TR – 180 µm to 75 µm (80 - 200 mesh) (cryoGTR) and ground tire rubber from ambient shredding supplied by Seneca Petroleum (30 mesh) (ambGTR), as well as, two conventional asphalt binders, a PG58-28, and a PG64-22, also supplied by Seneca Petroleum.

Several different aggregate fractions from Iowa quarries were used to obtain a final aggregate gradation with 9.5 mm nominal maximum aggregate size (NMAS) (Figure 15). The aggregates used were as follows:

- 12.5 mm crushed limestone with a NMAS of 9.5 mm
- 9.5 mm crushed limestone with a NMAS of 4.75 mm
- Natural Sand with a NMAS of 4.75 mm
- Agricultural Lime with a NMAS of 2.36 mm
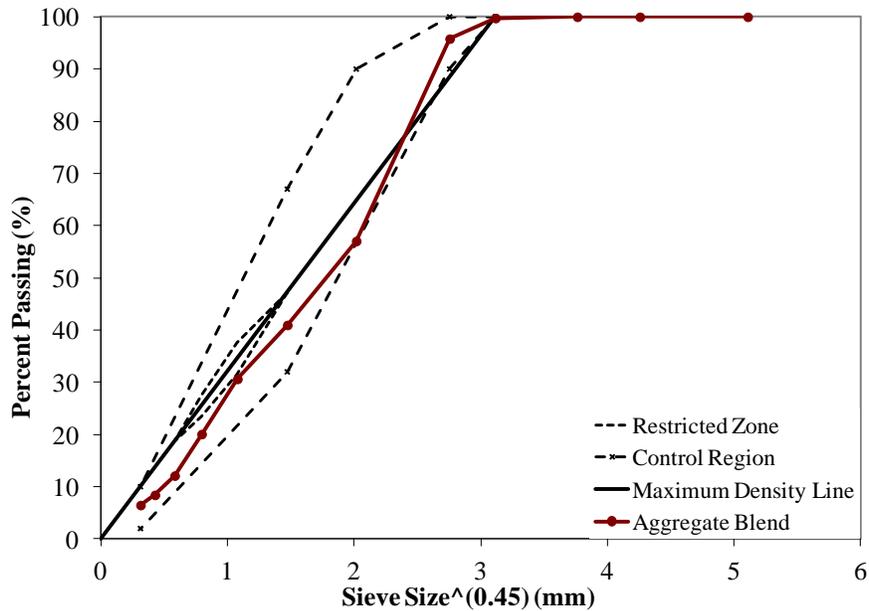
Figure 15. Final aggregate blend of the mixture, restricted zones, and control points for an aggregate gradation with a NMAS of 9.5 mm in the 0.45 power chart

Experimental Procedure

The experimental work starts with the production and testing of several binders. Later, the binder selected in this first phase of this work is used in the production of asphalt mixtures. These mixtures were finally tested to estimate their field performance in the pavement.

Production and Testing of Binders

Initially, the changes in the viscosity of the bio-oil upon heating were monitored over time to evaluate the effect of using this material at high production temperatures. The changes in the bio-oil viscosity were assessed using a Brookfield viscometer. The samples were heated at 95 °C and placed in the testing chamber. The spindle used was the S21 and the velocity was 20 rpm. The sample was tested for 8 hours and 30 minutes, and readings were recorded every 15 minutes.

The next phase of the work was the production of a bio-oil without additives and with a suitable viscosity. The bio-oil was placed in a Silverson L4RT shear mixer at a velocity of 3,000 rpm for about one hour. The initial temperature of 90 °C was steadily incremented to 110 °C, in order to maintain the bio-oil steaming (with low boiling). When the bio-oil reached 110 °C, the temperature was maintained until it stopped boiling, for a total time of treatment of 1 hour. The final product obtained at the end of this phase was called Heat-Treated Bio-Oil (HTBO) (Figure 16).
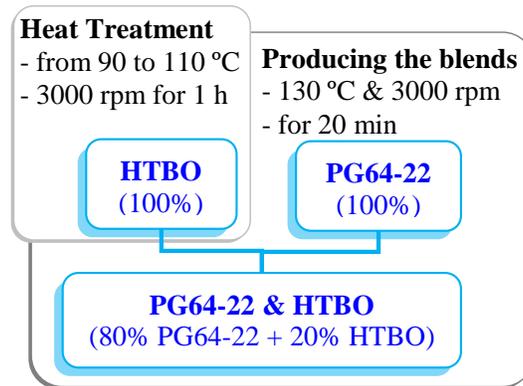
Figure 16. Production of the PG64-22 and HTBO

Another batch of bio-oil was modified with the two ground tire rubbers selected for this study, cryoGTR and ambGTR. The bio-oil was placed in a Silverson L4RT Shear Mill at 95 °C with an agitation of about 1,000 rpm, until the bio-oil stopped boiling (about 15 minutes). During this stage, most of the water is removed from the bio-oil, with a mass loss of about 15%. Then, 15wt% of rubber was added and blended with the bio-oil, and the velocity was raised to 3,000 rpm, while the temperature was steadily increased to 120 °C. These conditions were maintained for some time to facilitate the interaction between bio-oil and rubber. Samples were collected after 30 minutes and 1 hour of interaction. Only the material that interacted for 1 hour was subsequently used for testing because the interaction for 30 minutes was insufficient to obtain a consistency similar to that of conventional paving asphalt (PG58-28 or PG64-22) at room temperature. Therefore, the modified bio-oils (MBO) produced in this part of the work were the following:

- The material obtained after 1 hour of interaction of the cryogenic rubber (cryoGTR) with the bio-oil was a "cryogenic modified bio-oil" (cryoMBO)

- After 1 hour of interaction of the ambient rubber (ambGTR) with the bio-oil, the obtained material was a "ambient modified bio-oil" (ambMBO)

The next phase was the production of asphalt binders modified with the previously modified bio-oils (cryoMBO and ambMBO). Previous studies showed that a replacement of asphalt by 5 and 10% of bio-oil produce good results in laboratory pavement performance tests (Yang et al. 2014). Moreover, at the present prices of asphalt and bio-oil, it is estimated that a higher rate of replacement of asphalt (20%) would represent an economical advantage for the paving industry and owners. Thus, the two conventional asphalt binders (PG58-28 and PG64-22) were blended with 20 wt% of the modified bio-oil based materials formerly produced, cryoMBO and ambMBO (Figure 17) and with HTBO (Figure 16), in a Silverson L4RT Shear Mill, at a velocity of 3,000 rpm, for 20 minutes and at 130 °C. This temperature was selected because at higher temperatures the bio-oil based materials will quickly change their properties. The four asphalt binders produced in this phase were as follows:

- Asphalt PG58-28 blended with 20% cryoMBO
- Asphalt PG64-22 blended with 20% HTBO
- Asphalt PG64-22 blended with 20% cryoMBO
- Asphalt PG64-22 blended with 20% ambMBO
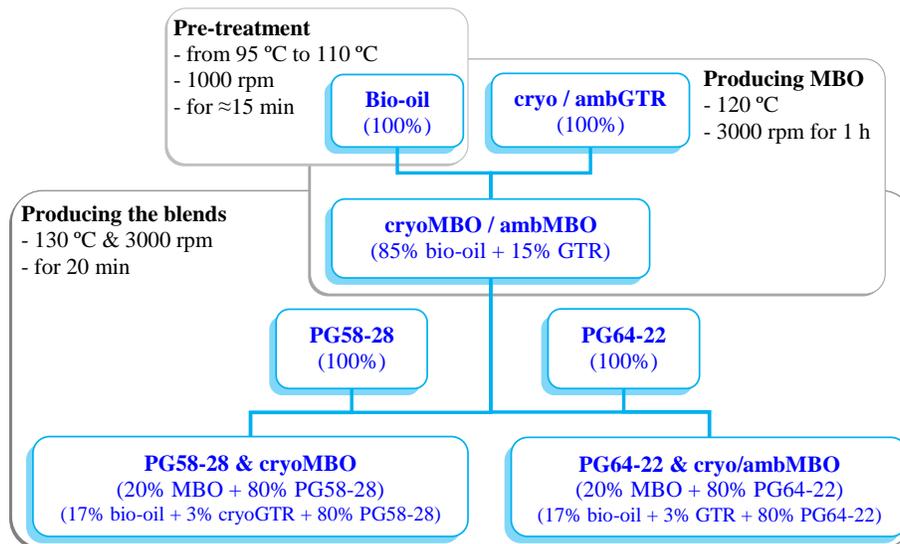
Figure 17. Production of the PG64-22 and cryoMBO, PG64-22 and ambMBO, and PG58-28 and cryoMBO

Finally, all binders previously produced were aged to better simulate their characteristics and performance in the pavement. The binders were aged with the rolling thin film oven test (RTFO), according to ASTM D 2872-04 standard, although the aging temperature was changed to 140 °C (this lower temperature, in comparison with that presented in the standard, was used to better simulate the compaction temperature of the asphalt mixtures applied in the next phase of the work). The four aged binders obtained after the RTFO tests were labeled as follows:

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- RTFO (Asphalt PG58-28 blended with 20% cryoMBO)
- RTFO (Asphalt PG64-22 blended with 20% HTBO)
- RTFO (Asphalt PG64-22 blended with 20% cryoMBO)
- RTFO (Asphalt PG64-22 blended with 20% ambMBO)

Additionally, another aging process was applied to assess the mass loss without oxidation of the binders. The method consisted in filling eight ounces metal cans with the binders, cover the cans and place them in an oven at 140 °C for 24 hours. To assess the interaction and differences between the materials used to produce the binders, they were tested by FTIR. Then, a dynamic shear rheometer (DSR) was used to obtain the master curves and high temperature performance grades of the binders. Finally, some properties required to do the formulation of the mixes were assessed: mixing and compaction temperatures using a Brookfield viscometer, binder density, and storage stability.

Production and Testing of Asphalt Mixtures

After analyzing the results of the binders testing, the blend of PG64-22 asphalt with 20% cryoMBO was selected to produce the mixtures. The optimum binder content was determined as being 5.5 percent using the SuperPave mix design methodology (Asphalt Institute 2001). The mixtures were designed for a traffic level between 3 and 30 million equivalent single-axle loads (ESALs).

The mixing temperature was 150 °C and the specimens produced with the mixture were compacted at 140 °C. With the aforementioned materials, two air void (AV) levels were prepared for the performance tests, 4 and 7 percent air voids. The compacted specimens were tested, according to the procedures described below, to evaluate their field performance in the pavement.

The moisture sensibility of the mixtures was determined according to AASHTO T283-07 standard. The result obtained in this test (tensile strength ratio, or TSR) must be in compliance with the criteria accepted by road administrations, otherwise the mixture studied will not be considered suitable for pavements, and thus no further tests will be needed.

The fatigue cracking resistance of the mixtures was evaluated according to AASHTO T321-07. This test simulates the repetitive load application in the pavement, and the results of this test can indicate the level of traffic that the mixture could bear in the pavement without cracking.

The dynamic modulus of the mixtures was accessed in accordance with the AASHTO TP 79-10 and AASHTO T 342-11 standards. This non-destructive test is performed to determine the temperature and rate temperature dependent behavior of asphalt mixtures applied in pavement layers, being the main input in the MEPDG pavement design method. It can also be used to evaluate the pavement ability to resist permanent deformation.

The triaxial repeated load permanent deformation (AASHTO TP 79-10) test or flow number (F_N) test can also be used to determine the pavement susceptibility to permanent deformation, which is one of the most important pavement distresses to avoid. This is a destructive test performed on the samples previously used on the dynamic modulus test. The flow number is one of the outputs of this test, which gives an indicative number of how soon permanent deformation or rutting can appear in the pavement.

The semicircular bend geometry test (AASHTO TP 105-13) was used to evaluate the low-temperature cracking performance of the mixture in the pavement, after confirming that all test results obtained at intermediate and high temperatures are acceptable according to road administration specifications and expectations. This test evaluated the cracking resistance of the studied mixtures at temperatures of 0, -12 and -24 ºC, because the initial asphalt binder used has a low-temperature PG of -22.

CHAPTER 4. CHEMICAL CHARACTERIZATION OF BIO-OIL

Physical Characteristics of Rubber

The first important result obtained from the application of the BAS method was the amount of rubber swelling. Despite of the accepted knowledge that rubber only swells at high temperature and in the presence of solvents derived from petroleum, both crumb rubbers samples swelled significantly (Table 3).

Table 3. Amount of rubber swelling

Samples	Crumb rubber	Rubber (%)	Swelling (% of the initial crumb rubber weight)
A	cryogenic	10	351
B		15	270
D	ambient	10	325
E		15	228

At the selected interaction temperature (125 °C) for a reduced time of interaction (1.5h), the rubber swelled an average of nearly 300 percent of its initial weight. The rubber swelling in the bio-oil is similar to that observed in the conventional asphalt (Airey et al. 2003, Peralta et al. 2010a), been higher for the lower concentration of crumb rubber. Despite the small differences between the two types of rubber, the cryogenic rubber swelled more than the ambient one.

As previously described, the bio-binder production process consists of a blending and heating process, during which two phenomena occur simultaneously: the diffusion of parts of the bio-oil causing the rubber to swell and the volatilization of some molecules of the bio-oil that increases its stiffness.

Chemical Analysis of the Bio-Binders

To understand the relative effects of the chemistry, Fourier Transform Infrared Spectroscopy (FTIR) of the base bio-oil was compared with that of the bio-oil aged at 125 °C with agitation, mimicking the bio-binder production, but without the addition of rubber (Figure 18).
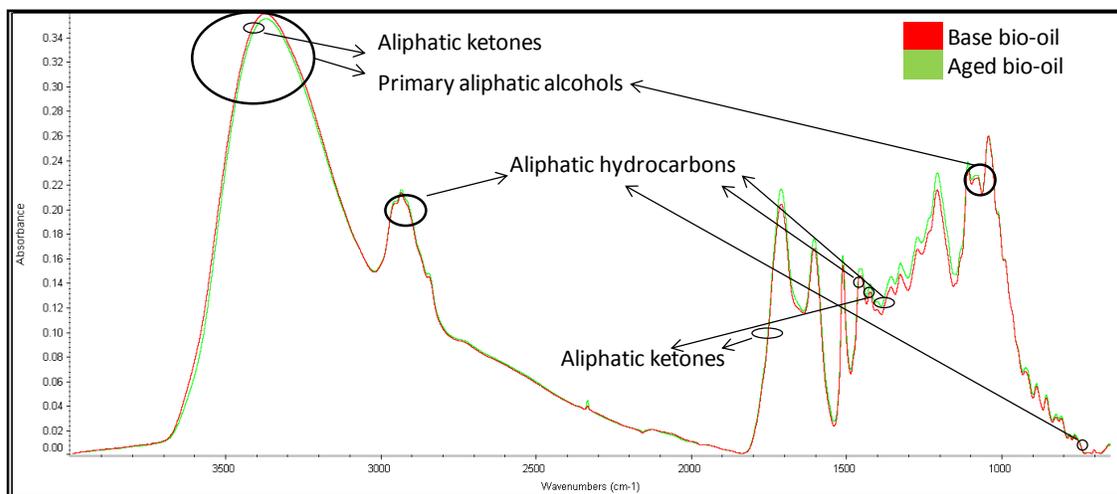
Figure 18. Comparative FTIR spectra of the base and aged bio-oils

The bio-oil chemical composition can be determined from a qualitative point of view by assessing Figure 18. Observing the comparative spectra, the bio-oil did not have significant changes due to aging during bio-binder production. To confirm these observations, a similarity match was done, computing and comparing match values from the base bio-oil with the aged bio-oil.

The similarity match is a spectral classification technique that indicates how closely an unknown material matches a known material. The similarity match method compares the spectral information in the specified region or regions of an unknown sample spectrum with that of a known set of standard spectra to determine how closely the sample matches the standards. The result of this comparison is called a match value. The match value represents the unexplained variation in the spectrum of the unknown sample. The maximum similarity is indicated by a match value equal to 0, and a complete dissimilarity is indicated by a match value equal to 100.

The match value of the base bio-oil compared with the aged bio-oil was about 0.30, which shows that there were almost no changes in the chemical composition of the bio-oil during the bio-oil to bio-binder production.

Additionally, since the cryogenic and ambient rubber were provided by two different companies (one in the Chicago metropolitan area and the second in the Atlanta metropolitan area), the spectra of the two crumb rubbers were also compared (Figure 19).
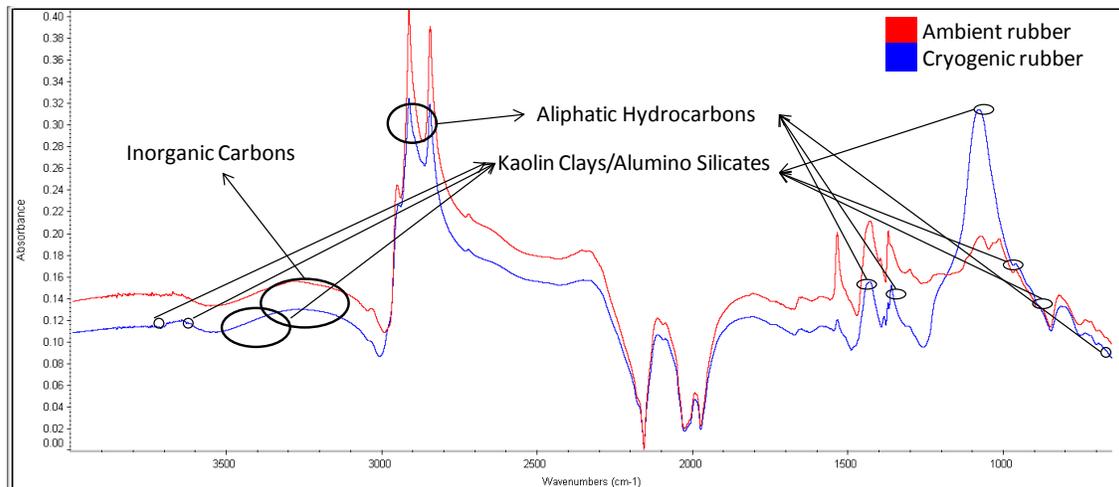
Figure 19. Comparative FTIR spectra of the cryogenic and ambient crumb rubbers

As expected, the FTIR spectra of the two crumb rubbers (Figure 19) present the peaks in the same wave numbers, showing very similar constitutions. The higher difference is observed at a wave number at about 1,000 cm^{-1}, which can be identified as aliphatic hydrocarbons. The match number computed for the comparison between cryogenic and ambient crumb rubbers is about 1.0 reflecting the small differences between the two materials.

Several materials were obtained after the bio-binder production and the application of the BAS method, including the bio-binder, the swelled rubber, and the residual bio-binder that results from the separation of the bio-binder. The analysis of these materials can provide very important information about the way that the bio-oil and the different crumb rubber samples interact. Thus, the FTIR spectra of the referred materials were also compared (Figure 20 and Figure 21).
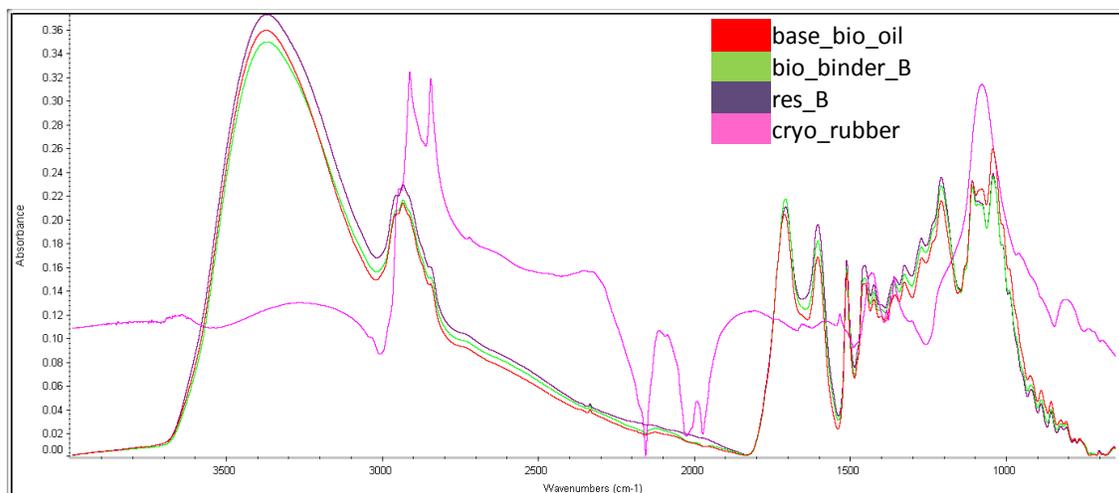
Figure 20. Comparative FTIR spectra of the base bio-oil, cryogenic crumb rubber, bio-binder B (15% of cryogenic rubber), and the residual bio-oil B

In Figure 20 the spectra of the base bio-oil and the cryogenic crumb rubber were compared with the bio-binder B (15% of cryogenic rubber) and the residual bio-oil B.

From the analysis of the spectra presented in Figure 20, it is noticeable the transferences of parts of rubber to the bio-oil and from the bio-oil to the rubber.

Between wave numbers 800 and 1,150 cm-1 it is clear that some molecules disappear from the bio-oil (this is not due to volatilization, as previously observed in Figure 18) meaning that these molecules are most probably diffusing into the rubber particles making them to swell. This region of the spectra can be correlated to the aliphatic hydrocarbons from the rubber, but can also be related to primary aliphatic alcohols from the bio-oil. Since these molecules decreased from the base bio-oil to the bio-binder and the residual bio-oil, they are probably the molecules that facilitate the swelling process in the rubber.

These observations are consistent with results previously reported by Gawel et al. (2006), that refers to a preferential absorption of the compounds with linear aliphatic chains into the rubber and suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

Besides the movement of material from the bio-oil to the rubber, many different molecules migrate from the rubber to the bio-oil, including the ones between wave numbers 2,800 and 3,000 cm^{-1}, which correspond to the aliphatic hydrocarbons resulting from the de-polymerization of the un-vulcanized rubber. In the regions between 1,200 and 1,500 cm^{-1} and 3,100 and 3,500 cm^{-1}, the transfer of some kaolin clays/alumino silicates and inorganic carbon (carbon black) from the rubber to the bio-oil is obvious. This is an expected result because these materials represent about 30% of the tire rubber.

The same approach was adopted to assess the changes in the base bio-oil and the ambient crumb rubber reflected in the bio-binder E (15% of ambient rubber) and the residual bio-oil E (Figure 21).
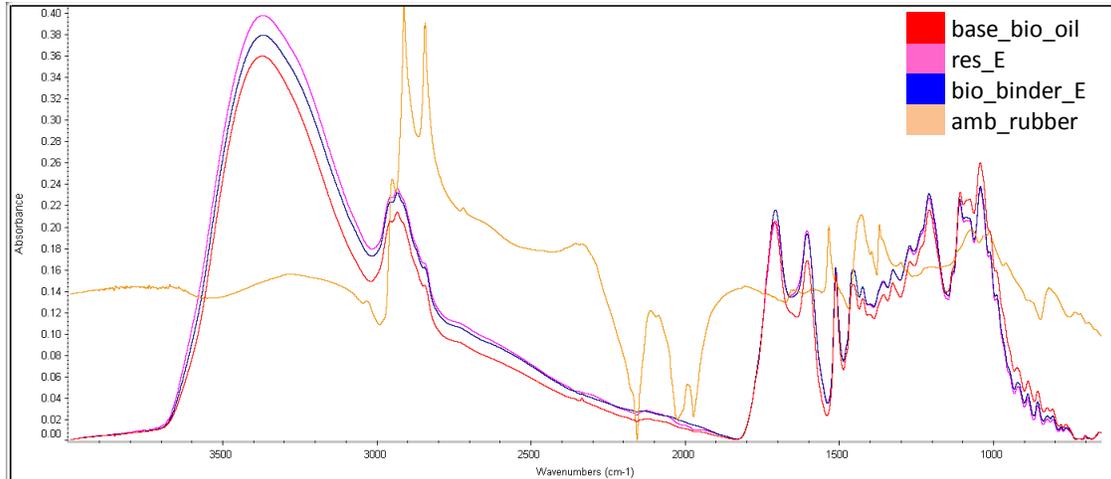
Figure 21. Comparative FTIR spectra of the base bio-oil, ambient crumb rubber, bio-binder E (15% of ambient rubber), and the residual bio-oil E

Comparing Figure 20 and Figure 21, it is clear that the interaction between both types of rubber with the bio-oil is similar in all the study regions. Nevertheless, the extension of the transference between the rubber and the bio-oil is more effective when the cryogenic rubber is used.

The comparison between the FTIR spectra is a preliminary approach to the chemical transformations that occur during the bio-binder production, and a more profound study is needed. However, the FTIR results are a very useful tool to show that chemical interactions are occurring and contribute to explain the results from the performance grading of the materials presented in the subsequent subsection.

The difference between the materials occurred during the bio-binder production, that can be observed in their spectra, was also quantified using the similarity match method. The resulting match values, evaluated as being the variation in the spectrum of the materials compared to the bio-oil, are presented in Figure 22.
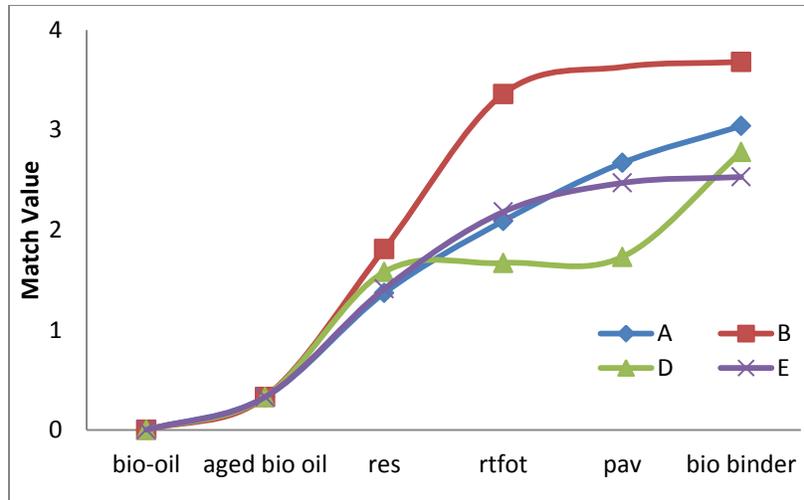
Figure 22. Comparative evolution of the match value between the bio-oil and the different materials assessed

The match values in Figure 22 show a noticeable difference between the aged bio-oil and the residual bio-oil, demonstrating the chemical changes related to its interaction with the two types of rubber. Other noticeable changes are caused by the RTFO aging test and the PAV test. The greatest dissimilarity is measured in relation to the bio-binder, since the rubber is still present in this material.

The match values also show that, as observed in the spectra, the similarity is lower when cryogenic rubber is used and thus indicates a higher interaction between this material and the bio-oil than that observed with the ambient rubber. In addition, the similarity is also related with the rubber concentration in the bio-binder, since the materials produced with a lower content of rubber are more similar. These results confirm those of the rubber swelling.

Performance Grade of Bio-Binders

Since one of the objectives of this work is to develop a bio-binder capable of replacing traditional asphalt derived from crude oil, it is necessary to assess the bio-binder performance grade and compare it with a known paving asphalt. As mentioned previously, the asphalt binder chosen as a control for this study was AAM-1 from the FHWA Materials Reference Library (MRL). AAM-1 is a PG64-16 and is obtained from a West Texas crude source.

The DSR critical temperatures of the AAM-1 and the bio-binders at the various stages of aging used for grading paving asphalt are presented in Table 4.

Table 4. Critical temperatures - T_c (°C) for asphalt AAM-1 and the bio-binders

	Control	Bio-Binder			
	AAM-1	A	B	D	E
base	67.77	47.87	47.87	47.87	47.87
aged	---	49.20	49.20	49.20	49.20
res	---	60.51	67.50	62.58	68.12
RTFOTres	66.68	67.76	70.66	68.06	71.57
PAVres	20.26	22.43	30.35	26.71	32.60

The performance grade of the bio-binder was determined indirectly by the analysis of the bio-oil given that the material that effectively behaves as the binder in the bio-binder is the residual bio-oil (the swelled rubber particles provide elasticity and toughness at low temperatures but do not have binding characteristics). Furthermore, the difficulties and errors associated with the rheological analysis of heterogeneous materials are known, such as the bio-binder or asphalt rubber binders with high volumetric fractions of rubber particles. In fact, the T_c determination is made using parallel plate geometry consisting of a 1 and 2 mm gap, and the particles in those binders would interfere with the movement of the plates due to the rubber size and swelling, thus producing scattered more variable results. Therefore, the materials presented in Table 4 are the base and aged bio-oils before the bio-binder production and the residual bio-oil separated from the bio-binder by the BAS method, which was sequentially aged by the RTFOT and PAV methods.

From the results presented in Table 4, it is possible to infer that the bio-oil presents very similar results to the control asphalt after interacting with rubber, particularly at high and medium test temperatures. Additionally, the asphalt used as control is also commonly used to produce asphalt rubber. Therefore, these results suggest that the developed material is adequate for use as a binder in the construction of flexible pavements.

Previous studies pointed out that the principal difficulty to use bio-oils as binders is their behavior at low temperatures (Raouf and Williams 2010b, 2010c). Figure 23 and Figure 24 present the results from the Bending Beam Rheometer - BBR testing of the four studied bio-binders.
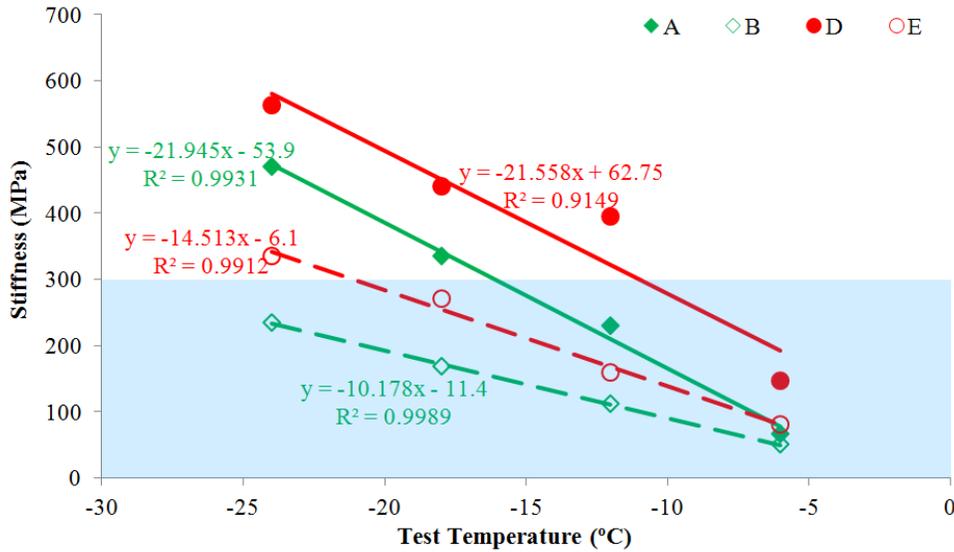
Figure 23. Evolution of the stiffness in the BBR test of the four bio-binders with the test temperature

The different bio-binders were tested in the BBR between -6°C and -24°C or at a performance criteria ranging from -16°C to -34°C. The stiffness values obtained were plotted against the test temperatures for the different binders, as shown in Figure 23. The best performance results at low temperatures were surprisingly obtained for the bio-binders produced with the lower percent of rubber (10%), and the binder produced with the cryogenic rubber was better than that obtained with the ambient rubber. The performance of all binders was very good, always below a test temperature of -10°C, which corresponds to a field temperature of -20°C. The bio-binder consisting of 10 percent cryogenic rubber has a low-temperature grade below -34°C.
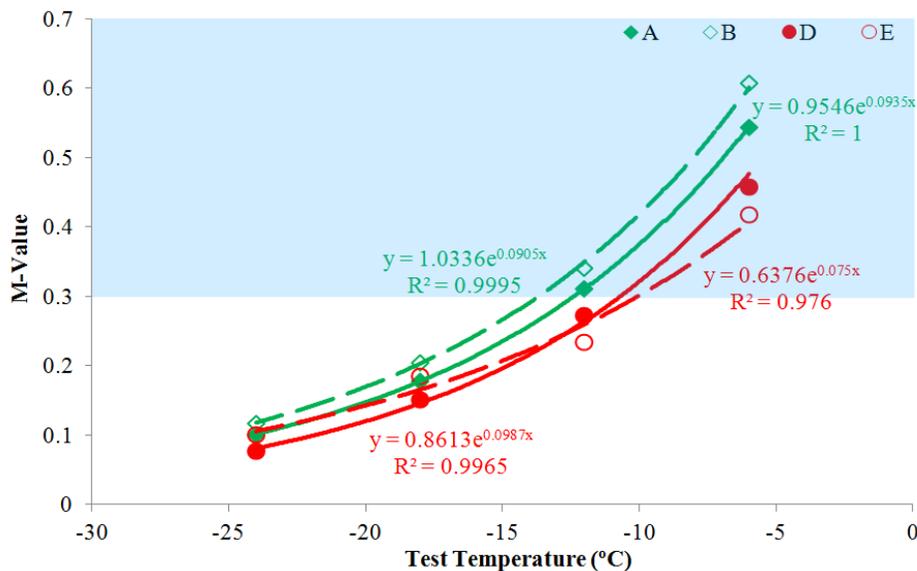
Figure 24. The BBR m-values of the four bio-binders with the test temperature

Assessing the m-values (Figure 24), the very good behavior of the bio-binders at low temperatures maintains below the test temperature of -10°C. However, by using the m-value as a parameter, the specifications for the bio-binder B are achieved at a maximum test temperature of about -15°C (specification temperature of below -22°C). The materials with the best performance in relation to this parameter were the two bio-binders produced with the cryogenic rubber. Overall, the m-value clearly dominates the low-temperature grade of the bio binders

Summarizing the behavior of the bio-binders at low temperatures, it can be stated that all the materials fulfill the specifications for temperatures equal or superior to a field temperature of -22°C or less. Considering the high temperature results for the residual bio-oils, it can be inferred that the overall binder grades of at least PG 58-22 and PG 64-22 were obtained for the bio-binders containing 10 and 15 percent cryogenic rubber, respectively; whereas, the bio-binders containing 10 and 15 percent ambient rubber produced binder grades of at least PG 58-16 and 64-16, respectively.

CHAPTER 5. DEVELOPMENT AND CHEMICAL CHARACTERIZATION OF BIO-OIL BLENDS

The feedstock materials, initial bio-oils and rubbers, and those after the bio-binder production and the application of the BAS method (and particularly the MBO and the residual MBO that resulted from the separation of the bio-binder for this part of the work) were analyzed. The analysis of these materials provides very important information about interactions between the bio-oil and the crumb rubber. Therefore, the FTIR spectra of the reference materials, as an example, are compared in Figure 25.
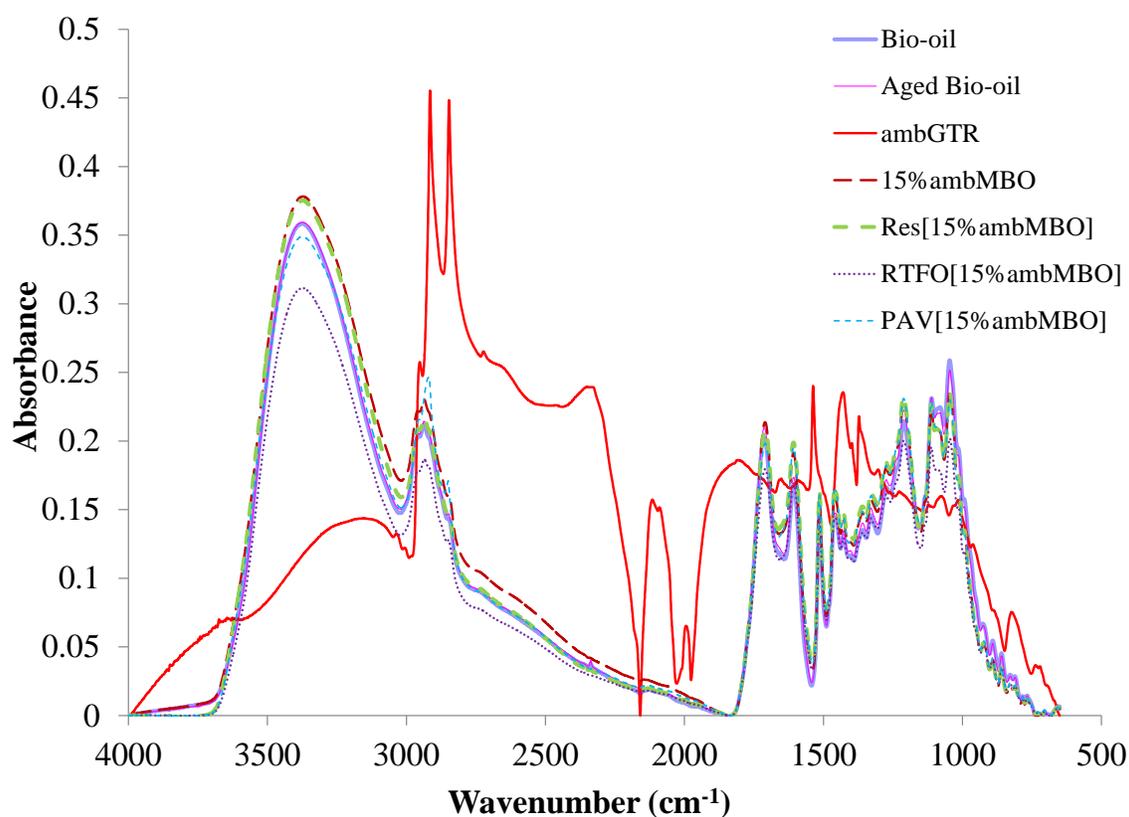
Figure 25. Spectrogram from FTIR of the materials related with the use of 15% ambMBO

The spectra comparison showed that the bio-oil did not have significant changes due to aging during bio-binder production. To confirm these observations, a similarity match was done, computing and comparing match values from the base bio-oil with the aged bio-oil. (The definition of similarity match was provided in the chemical characterization of bio-oil section in Chapter 4.)

From the analysis of the spectra presented in Figure 25, it is noticeable the transference of parts of rubber to the bio-oil and from the bio-oil to the rubber. Between wavenumbers 800 and 1,150 cm-1 it is clear that some molecules disappear from the bio-oil (this is not due to volatilization, as previously observed in aged bio-oil). It is probable that these molecules diffused into the

rubber particles causing them to swell. This region of the spectra can be correlated to the aliphatic hydrocarbon region from the rubber, but it can also be related to primary aliphatic alcohols from the bio-oil. Because these molecules decreased from the base bio-oil to the bio-binder and the residual bio-oil, it is most likely that these molecules facilitate the swelling process in the rubber. These observations are consistent with results previously reported by Gowel et al. (2006) that mention a preferential absorption of the compounds with linear aliphatic chains into the rubber and suggest that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

The comparison between the FTIR spectra is a preliminary approach to the chemical changes that occur during the bio-binder production, but a more in-depth study is necessary. However, the FTIR results are a very useful tool to show that chemical interactions are occurring and these interactions contribute to changes in the materials' consistency.

The spectral differences between the materials that occurred during bio-binder production were also quantified using the similarity match method. (The similarity match method was explained in Chapter 4.) The comparative spectra do not indicate significant changes due to aging during bio-binder production. The similarity matched values from the base bio-oil and the aged bio-oil were computed and compared to confirm the observations on the comparative spectra. The resulting match values, evaluated as the variation in the spectrum of the materials compared to the bio-oil, are presented in Figure 26. The match value of the base bio-oil in comparison to the aged bio-oil was about 0.28 percent, which indicates minimal changes in the chemical composition of the bio-oil during the bio-oil to bio-binder production.

Additionally, since the cryogenic and ambient rubber were provided by two different companies (one in the Chicago metropolitan area – ambGTR, and the second in the Atlanta metropolitan area - cryoGTR), the spectra of the two crumb rubbers were also compared. The match number computed for the comparison between cryogenic and ambient crumb rubbers is 1.15 percent reflecting minor differences between the two rubbers.

The different bio-oil base materials were compared among them generating a series of match values. Figure 26 displays how the different materials differ. The match values presented in Figure 26 show obvious differences between the bio-oil and the MBOs, demonstrating chemical changes related to interaction with the two types of rubber. Other noticeable changes are caused by the RTFO aging test and the PAV test. The greatest dissimilarity is measured in relation to the PAV material, since it is the most aged material and the rubber is still present.
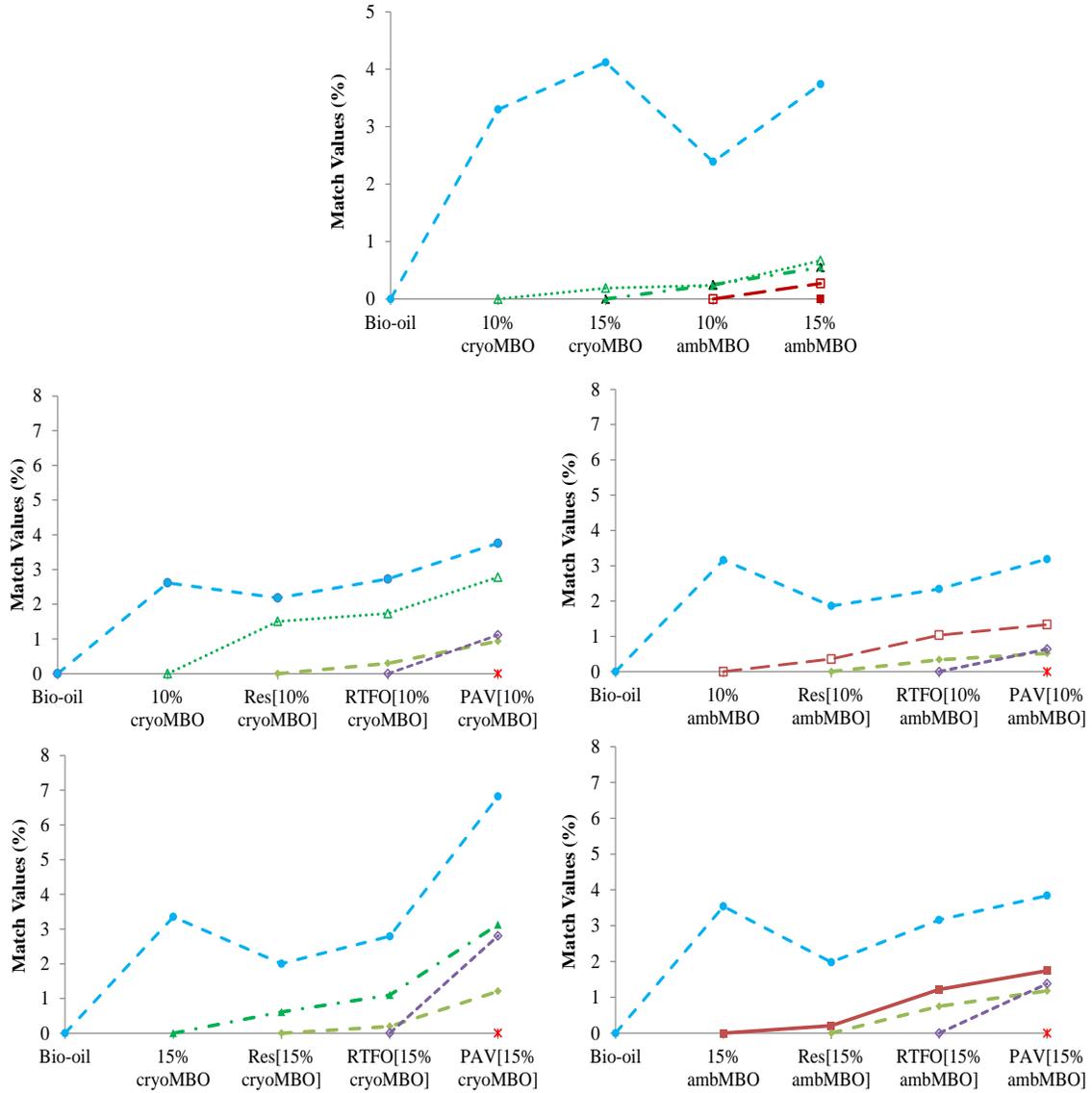
Figure 26. Comparison among the match values for four types of bio-oil based materials

The most important observation is the difference between the bio-oil and the ResMBO, which reflects the changes caused by the interaction with the rubber, without the influence of the rubber particles. The smallest match number was 1.86 percent, observed for the Res[10% ambMBO], which subtracting the 0.28 percent difference, due to aging, results in a difference of about 1.58 percent that can be attributed solely to the rubber interaction. The match values also show, as seen in the spectra, that the similarity is lower when cryogenic rubber is used, and thus indicates a higher interaction between this material and the bio-oil than that observed with the ambient rubber. In addition, the similarity is also related to the rubber concentration in the bio-binder, since the materials produced with a lower content of rubber are more similar.

CHAPTER 6. RHEOLOGY TESTING OF BIO-OIL BLENDS

The results of physical characterization of the bio-oil based materials using conventional European standards are presented in Figure 27 to Figure 32. The viscosity of the cryo and amb MBOs, and correspondent residual materials was measured at 100 ºC for both percentages of rubber used. Figure 27 depicts the comparative results.
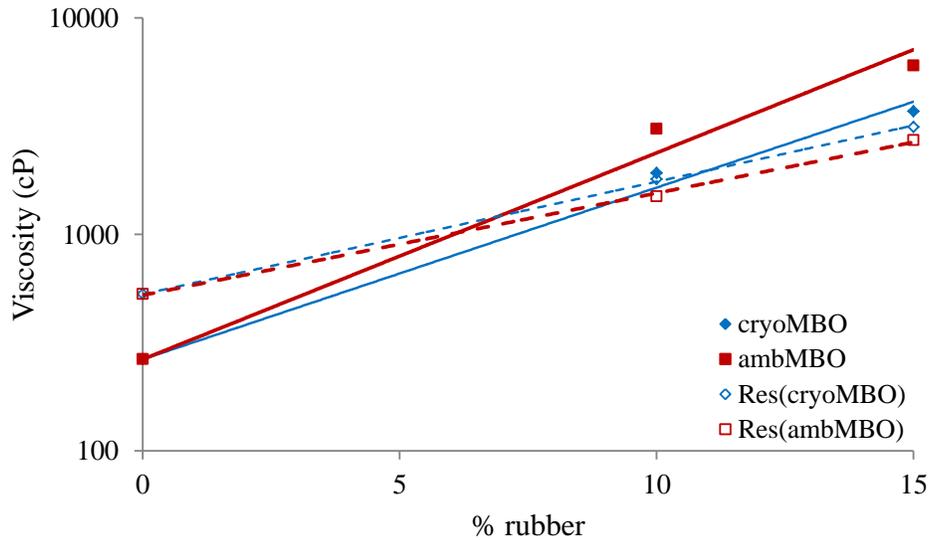
Figure 27. Changes in the viscosity of the MBOs and in the residual MBO at 100 ºC

The results presented in Figure 27 show significant changes in the viscosity of the biobinder after interaction with rubber, demonstrating the good interaction between these materials. The lines describing the changes in the viscosity of the MBO start at the viscosity of the un-aged bio-oil. According to the presented results, the ambGTR has more effect on the viscosity of the MBO than the cryoMBO. This is mainly caused by the roughness and bigger dimension of the particles of this type of rubber, when compared to the cryoGTR particles.

The data point for zero percent rubber of the resMBOs corresponds to the viscosity of the aged bio-oil. These lines show the difference in the viscosity of the residual materials caused by the interaction with the different GTR.

The most relevant information that can be derived from the viscosity results is that despite the higher particle effect of the ambGTR in the MBO, it seems that some chemical constituents of the GTR are migrating to the liquid bio-oil, and this phenomenon is more evident when using the cryogenic rubber to produce the cryoMBO.

When mixtures for flexible pavements are produced, the most important information needed are the mixing and compaction temperatures. This information can usually be obtained from the analysis of the binder viscosity. To understand how the bio-oil derived binders behave in

comparison to the AR binders (produced with bituminous binder), the viscosities of those materials at different temperatures were compared (Figure 28).
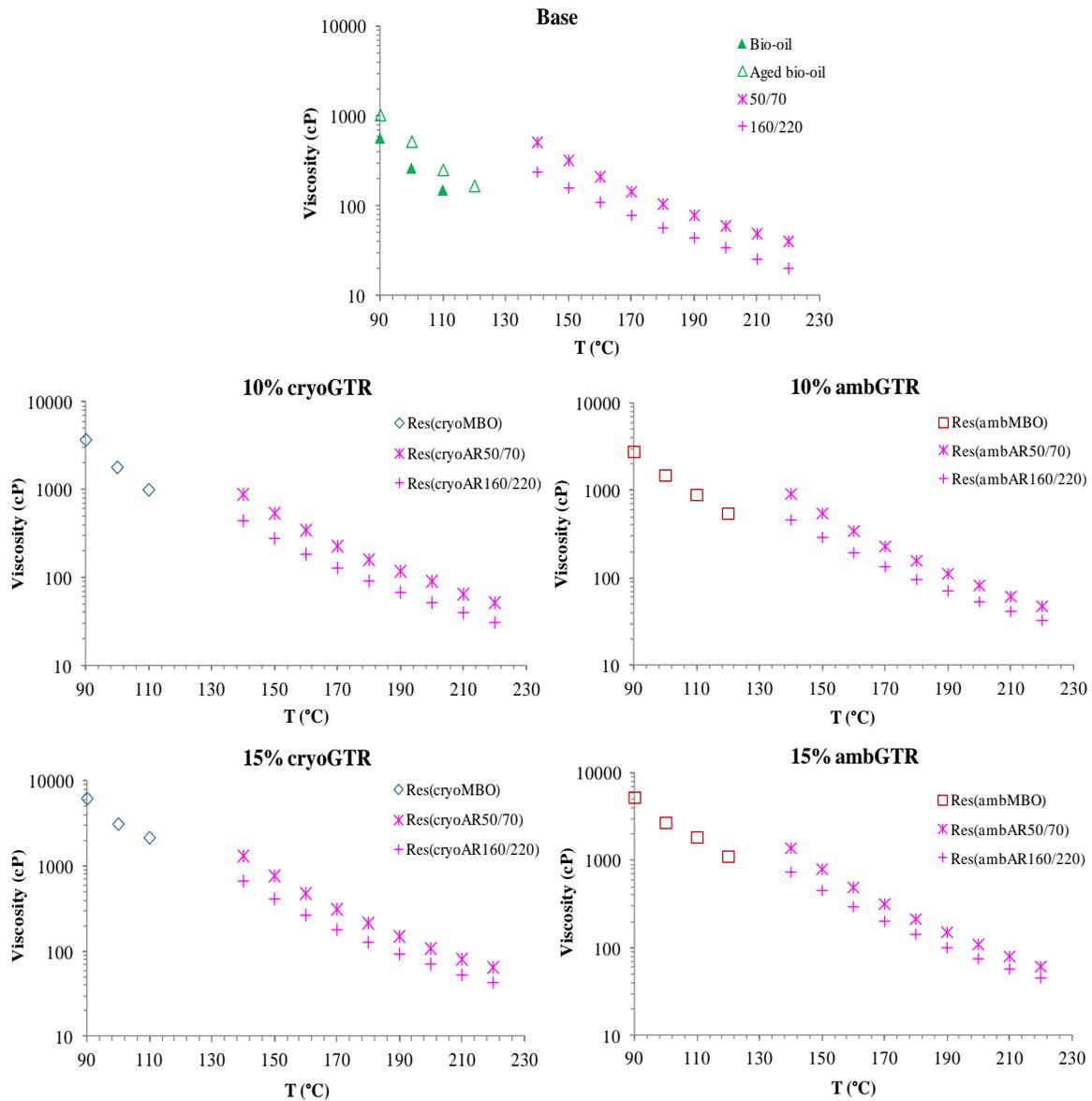
Figure 28. Comparison between the viscosities of the bio-oil and the asphalt base materials modified with ambient and cryogenic crumb rubber

Figure 28 presents the changes in the viscosity with the test temperature. When bio-oil and aged bio-oil are compared with the 50/70 and 160/220 asphalts, the aged and un-aged bio-oil at temperatures ranging from 90 to 120°C behave similarly to the 50/70 and 160/220 asphalts at temperatures ranging from 140 to 170°C.

The addition of GTR, and posterior centrifugation of the rubber binders (AR and MBO) show an increase of viscosity that is more noticeable when bio-oil was used. Thus, to obtain residual

materials with a viscosity of about 1,000 cP, it is necessary to apply nearly less 11 and 3 °C to the 10 and 15 percent cryoMBO than to the 10 and 15 percent cryoAR160/220, and for the 10 and 15 percent ambMBO, the reduction in the required temperature, when compared with the 10 and 15percent ambAR160/220, would be about 14 and 10 °C.

Most importantly, as the 50/70 asphalt is the most common asphalt used in the production of AR binders, the reduction in the temperature necessary to obtain residual binders with the same viscosity is about 26 and 19 °C when 10 and 15 percent cryoGTR is used with bio-oil, and 29 and 23 °C for the 10 and 15 percent Res(ambMBO). Disregarding the type and amount of GTR, this technology requires on average 24 °C less to obtain the same viscosity in the resMBO than in the resAR50/70 asphalt, and a reduction, on average, of 10 °C in comparison to the resAR160/220 asphalt. Thus, the reduced temperatures for the bioasphalt as compared to equiviscous asphalt (from crude petroleum) would result in reduced production temperatures and therefore savings in plant fuel consumption and reduced emissions.

The needle penetration test is one of the most important characterization used to evaluate the consistency of asphalt binders, and is broadly used to grade these materials. Therefore, the penetration values of the MBOs and AR materials are presented in Figure 29 and Figure 30.
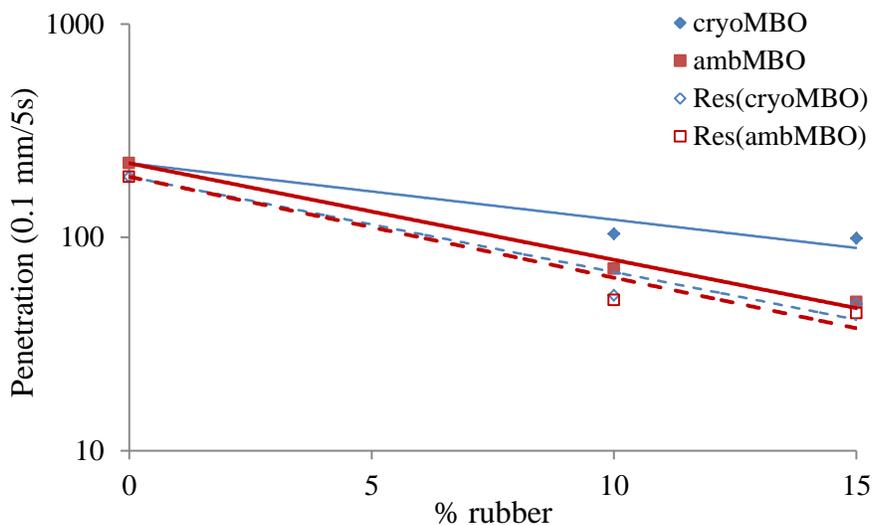
Figure 29. Changes in the penetration of the MBOs and in the residual MBO

Analyzing the variation of the penetration of the MBOs and their respective residuals, it is clear that there is a decrease in the penetration value when the content of rubber increases. The residual binders of both the cryoMBOs and ambMBOs present a very similar variation of the penetration. Interestingly, the line defining the changes in the penetration of the ambMBO is almost parallel to the respective residual. In contrast, the changes in the penetration of the cryoMBO are less affected by the content of cryoGTR than its residual.
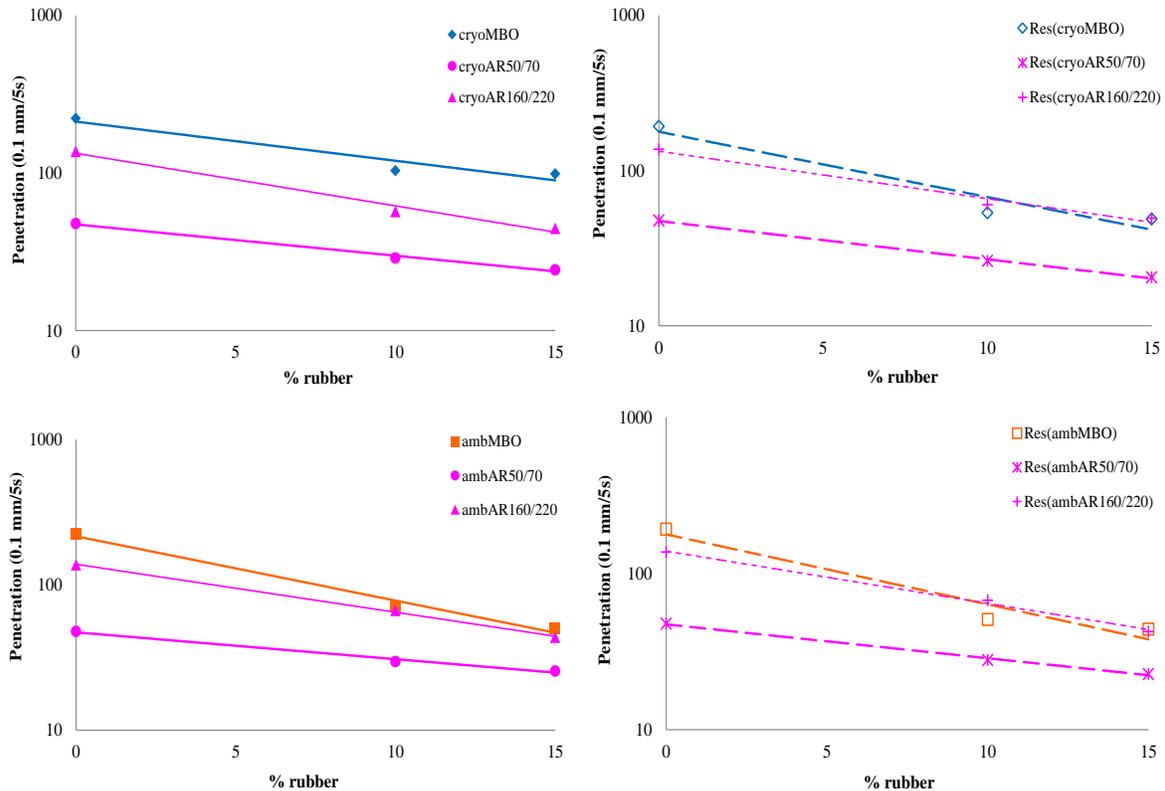
Figure 30. Comparison between the penetrations of the bio-oil and the asphalt base materials modified with ambient and cryogenic crumb rubber

The comparison between rubberized bio-oils and asphalt rubber show that even though bio-oil is softer than most of the asphalts currently used in paving mixtures, after being modified with about 15 percent rubber, the latter is able to present penetrations equivalent to those of asphalt rubberized materials with the same rubber content. The exception is the bio-oil modified with cryoGTR, that follows the same trend as cryoARs, which is a very good tendency, as it is softer as a base material, but the effective binder (res cryoMBO) has a lower penetration, indicating a good performance regarding both stiffness and fatigue cracking resistance.

The ring and ball softening temperatures provide some important information about the workability and rutting resistance of the mixture where the binder will be used. This characteristic was evaluated and compared among the different tested materials (Figure 31 and Figure 32).

Although the two residual MBOs show very similar trends for the variation of the softening temperatures with the content of both types of rubber, the ambMBO has higher softening point temperatures. On the other hand, the softening temperatures of the cryoMBOs have a very small response to the increase of the rubber content, with quite low softening temperatures. The softening point results also show very similar residual binders obtained with both types of rubber, although the cryoMBO residual binder is more workable than that of the ambMBO binder.
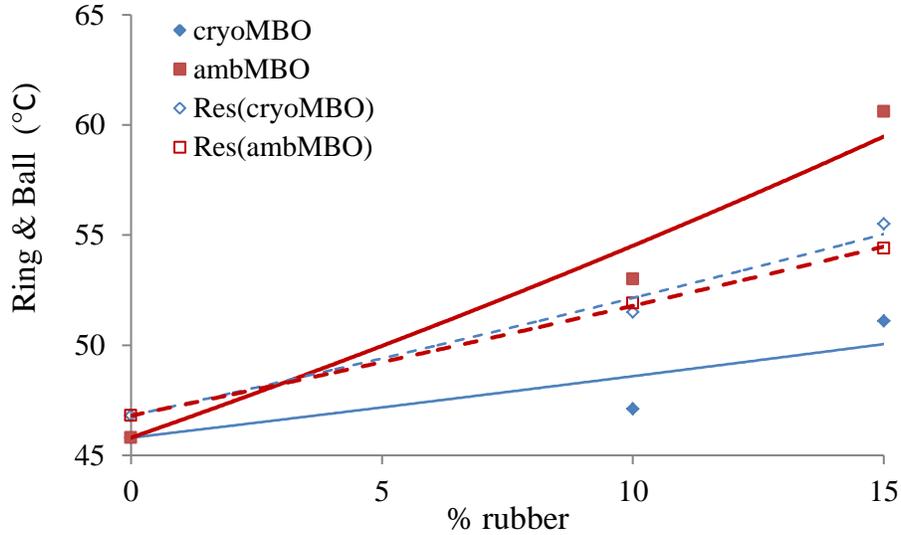
Figure 31. Changes in the ring and ball softening temperatures of the MBOs and their residual binders
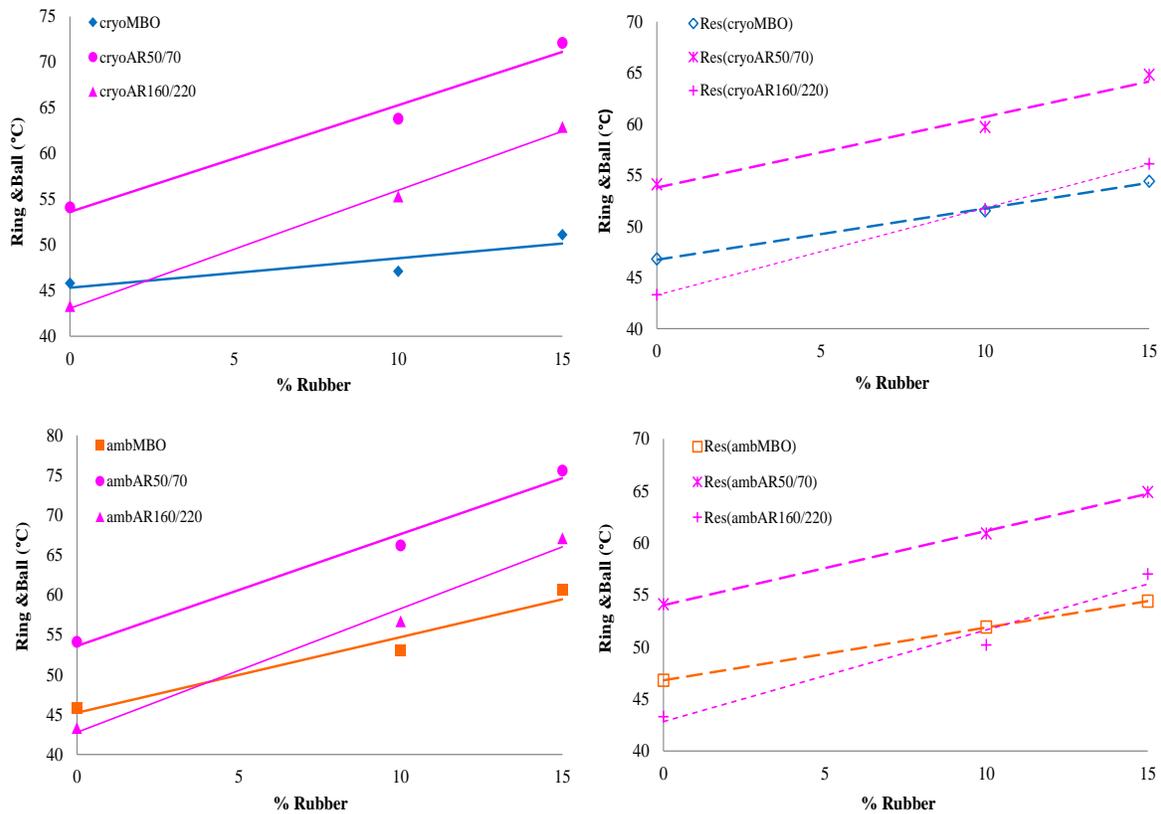
Figure 32. Comparison between the ring and ball softening temperatures of the bio-oil and the asphalt base materials modified with ambient and cryogenic crumb rubber

Concerning the residual materials, and when compared with conventional ARs, the MBO presents similar R&B temperatures for rubber contents of about 10 percent. Nevertheless, the

residual materials of the MBO seem to be more workable than those of conventional ARs, because the MBOs are less susceptible to performance changes when the GTR content varies, thus maintaining low R&B temperatures for different rubber contents.

The master curves and the PG of the binders (MBOs and AR) were determined indirectly by the analysis of the residual materials, because the residual materials are the ones that effectively behave as binder. Although the swelled rubber particles provide elasticity and toughness at low temperatures, they do not have binding characteristics.

Furthermore, there are significant errors associated with the rheological analysis of heterogeneous materials, such as the MBO or AR binders that contain high volumetric fractions of rubber particles with particle sizes higher than 300 μm (after swelling). In fact, most of the rheological determinations were made using parallel plate geometry consisting of a 1 mm gap, therefore the probability of the rubber particles in those binders interfering with the movement of the plates is very high, producing variability in the results. Therefore, the materials presented in Figure 33 and Table 5 are the base and aged bio-oils before the bio-binder production and the residual bio-oil separated from the bio-binder by the BAS method, which was sequentially aged by the RTFO and PAV methods.
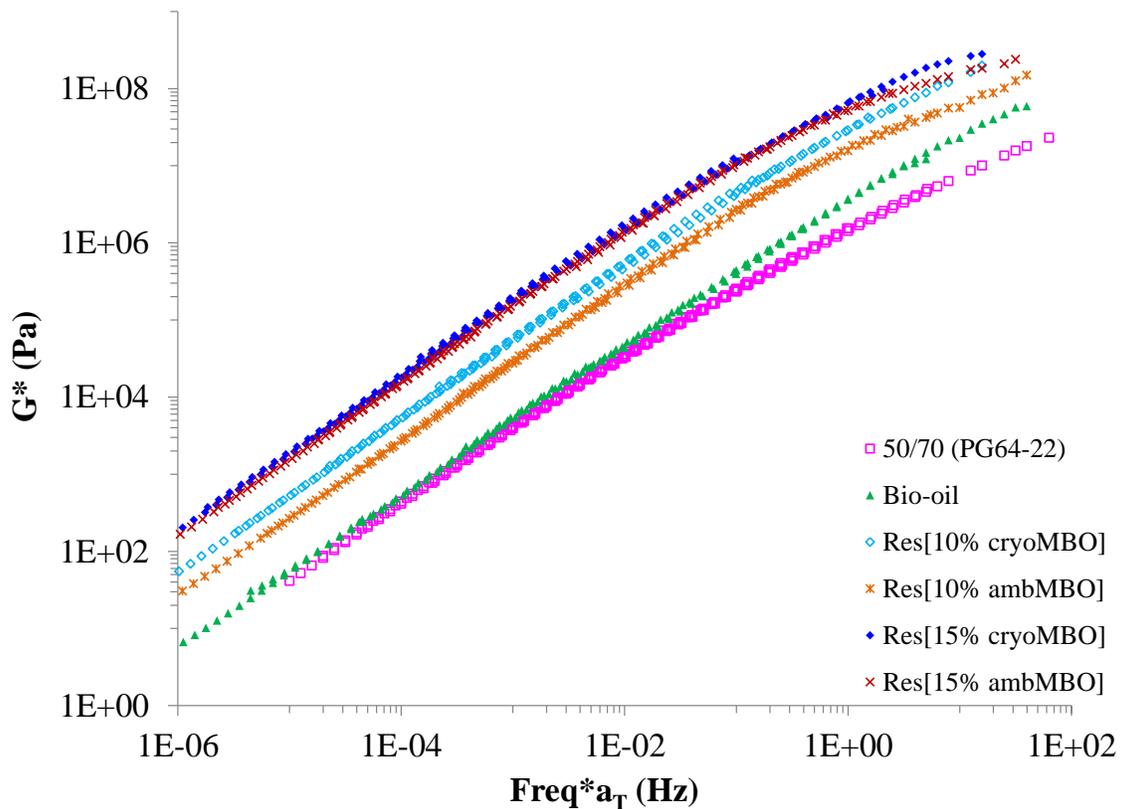
Figure 33. Comparison between the master curves (T$_{ref.}$ = 20 ºC) of the un-aged bio-oil and residual MBOs with a (Pen)50/70 (PG64-22) asphalt

Assessing the master curves of the unmodified and unaged materials (asphalt and bio-oil), they illustrate different behaviors, as the bio-oil is stiffer than the asphalt at low temperatures (high frequencies). At high temperatures (low frequencies), asphalt and bio-oil show similar rheological behavior. The change on the shape of the curves of residual MBOs is evident: although the shape of the master curve of the bio-oil differs from that of the asphalt, that difference reduces with the increase in the content of GTR, as the master curves of residual MBOs assume the same shape as that of the asphalt after interacting with 15 percent of GTR.

In terms of modulus, the difference between the MBOs and asphalt is that the increase in the rubber content shifts the MBOs master curves towards higher modulus values. Another interesting observation is that for a content of 15 percent of both types of rubbers, the residuals of the MBO are very similar in terms of rheological behavior at in-service temperatures (the cryoMBO and ambMBO master curves are almost totally overlapping).

The DSR critical temperatures of the ResAR160/220 and the ResMBOs binders at the various stages of aging used for grading paving asphalt are presented in Table 5.

Table 5. High and intermediate continuous PG from the DSR test

		CryoGTR		AmbGTR	
		10%	15%	10%	15%
res	Bio-oil	60.51	67.50	62.58	68.12
	160/220 (PG58-28)	-	-	-	72.69
RTFOT(Res)	Bio-oil	67.76	70.66	68.06	71.57
	160/220 (PG58-28)	-	-	-	69.74
PAV(Res)	Bio-oil	22.43	30.35	26.71	32.60
	160/220 (PG58-28)	-	-	-	21.43

Based on the results presented in Table 5, it is possible to infer that the bio-oil presents very similar values in comparison to the control asphalt after interacting with rubber, particularly at high and medium test temperatures.

Considering the high temperature results for the residual bio-oils, it can be assumed that the high temperature binder grades are of at least PG 58 and PG 64 for the bio-binders containing 10 and 15 percent cryogenic rubber, respectively. Similarly, the bio-binders containing 10 and 15 percent ambient rubber have high temperature binder grades of at least PG 58 and 64, respectively. These results suggest that the developed materials are adequate for use as binders in the construction of flexible pavements.

Previous studies pointed out that the principal difficulty in using bio-oils as binders was their behavior at low temperatures (Raouf and Williams 2010a, Raouf 2010). Table 6 presents the results from the Bending Beam Rheometer (BBR) testing of the four studied bio-binders and a 15% ambAR160/220 binder.

Table 6. Parameters from the BBR test at low temperatures

	Test temperature (°C)	Stiffness (MPa)	m-value
15% ambAR160/220	-18	117	0.317
10% cryoMBO	-12	230	0.311
15% cryoMBO	-12	112	0.341
10% ambMBO	-12	395	0.274
15% ambMBO	-12	160	0.235

The different bio-binders were tested in the BBR at -12 °C and -18 °C, corresponding to performance criteria of -22 °C to -28 °C, respectively. Assessing the m-values of the several binders, a very good behavior of the bio-binders can be observed at low temperatures.

The best performance in respect to this parameter was one of the two bio-binders produced with the cryogenic rubber. Overall, the m-value clearly dominates the low-temperature grade of the bio binders. The performance of all binders was very good, with just one performance grade below for the binder 15% ambAR160/220 binder.

Contrarily to the previous tests, the presence of the rubber particles do not impair the accuracy of the results in this test, as the test consists in loading a beam under flexural tension, and in this case the rubber particles do not interfere with the equipment. Thus, this test is able to successfully assess the effect of the rubber in the binder performance at low temperatures without the need of using separation methods to test the residuals. At low temperatures, the bio-oil by itself is too brittle, thus justifying the use of GTR given that this material has a very low freezing temperature (T_g = -80 ºC). This fact is evident in the results obtained, as an increase in the GTR content reduces significantly the stiffness of the binder, which reflects the softness of the rubber at this temperature.

Summarizing the behavior of the bio-binders at low temperatures, it can be stated that all the materials fulfill the specifications for temperatures equal or superior to a field temperature of -20 ºC. The continuous grades for the bio-binder produced with the ambient rubber are 62.6-20.7 and 68.1-20.1 for 10 and 15 percent, respectively. Similarly, 60.5-22.4 and 67.5-23.7 were the continuous grades obtained for the bio-binder produced with 10 and 15 percent of cryogenic rubber, respectively. Therefore, the overall binder grades of PG 58-22 and PG 64-22 were obtained for the bio-binders containing 10 and 15 percent cryogenic rubber, respectively. The bio-binders containing 10 and 15 percent ambient rubber produced binder grades of PG 58-16 and 64-16, respectively.

CHAPTER 7. DEVELOPMENT OF BIO-OIL MIX DESIGNS AND PERFORMANCE TESTING

Results of the Binder Testing

The results of the binder testing are presented sequentially, in the same order as they were described in Chapter 3 when the corresponding methods were presented.

Changes in the Bio-Oil Viscosity upon Heating over Time

The initial viscosity of the bio-oil was 42.5 cP and increased following an exponential trend to a final viscosity of 207.5 cP after 8 hours and 30 minutes in the Brookfield viscometer at 95 °C (Figure 34).

The changes in the viscosity of the bio-oil were expected and are mainly due to polymerization of the phenols combined with the furfural within the bio-oil *(Williams et al. 2009)*, and volatilization of some free water.

The plot shows data points with fitted curve: $y = 37.629e^{0.0032x}$, $R^2 = 0.9889$. X-axis: Time, min (0 to 500+). Y-axis: Viscosity, cP (0 to 250).
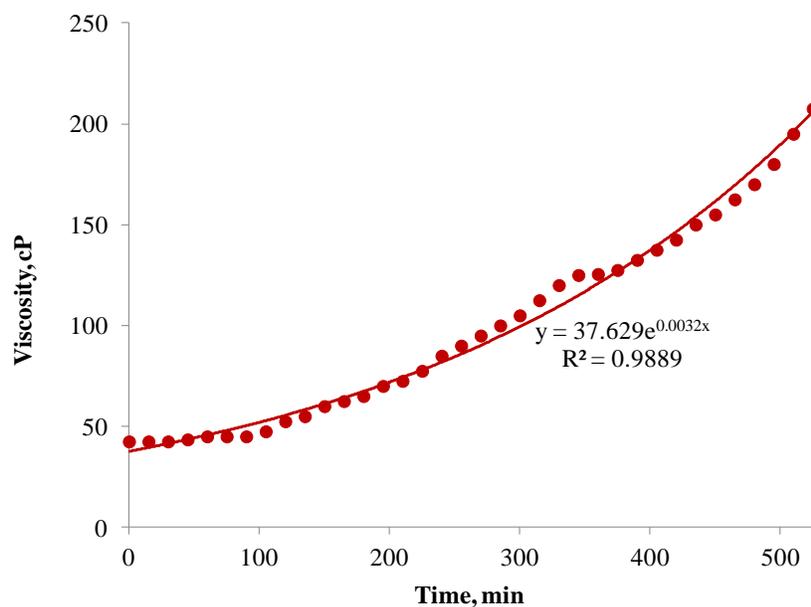
Figure 34. Changes in the viscosity of the bio-oil over time at 95 ºC

Fourier Transform Infrared Spectroscopy (FTIR) of the Binder Materials

The binder materials were analyzed by FTIR and the comparison between spectra show the results of a preliminary approach to the chemical changes that occur during the bio-binder production, and a more in-depth study should be carried out in the future to confirm these results. However, the results are very useful to show chemical interactions that are occurring and

contributing to change the materials' consistency and therefore the performance of the binder materials.

In Figure 35 the spectra of the base materials (bio-oil, asphalt, cryoGTR), the bio-binders (cryoMBO), and the bio-blends (PG64-22 and cryoMBO) before and after RTFO aging are compared. The interactions observed are very similar to the ones observed in the production and aging of the other bio-binders studied.
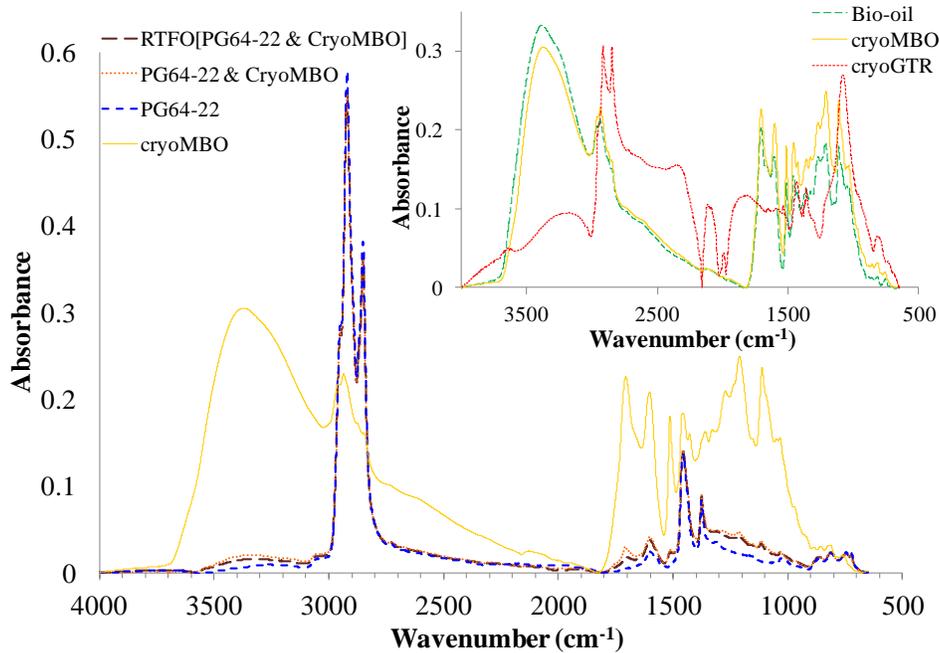
Figure 35. FTIR spectra of the un-aged and RTFO aged asphalt binder materials

The transferences of parts of rubber to the bio-oil and from the bio-oil to the rubber are visible from the analysis of the spectra presented in Figure 35. Between wavenumbers 800 and 1,150 cm-1 some molecules decreased from the base bio-oil to the cryoMBO. This region of the spectra can be correlated to the aliphatic hydrocarbon region from the rubber, but it can also be related to primary aliphatic alcohols from the bio-oil. These are most likely the molecules that facilitate the swelling process in the rubber (Peralta et al. 2012a). These observations suggest that these components are compatible with the linear polymeric skeleton of the rubber, and this is consistent with results that have been previously reported by Gawel et al. (2006), that mention a preferential absorption of the compounds with linear aliphatic chains into the rubber.

The bio-oil contains between 15 and 30 wt% of moisture (Bridgwater 2012, Meier et al. 2013, Yang et al. 2014) that can be seen in the band at about 3,300 cm-1, and this moisture content is smaller in the bio-binder (cryoMBO). The moisture can be present in the bio-oil in two different forms, dissolved or as emulsion, and some of this free moisture can evaporate during the production of the bio-binder (Oasmaa and Peacocke 2010). However, some more moisture is added with the rubber, thus justifying the final higher content of moisture in the cryoMBO.

Although the spectrum of the binder blend (PG64-22 and cryoMBO) is similar to that of asphalt, the addition of 20 percent of cryoMBO caused some changes. In the band, at about 3,300 cm^{-1}, there is an increase of moisture from the asphalt to the binder blend that decreases after the RTFO aging of the material, which is in agreement with the mass loss of 3.6 wt% obtained for this material. At about 1,300 cm^{-1}, there is a higher amount of aliphatic compounds in the bio-binder, which came from the bio-oil and rubber, than in asphalt. These elements present very small changes with the RTFO process, indicating that they are stable in the final binder blend. Additionally, new peaks in the spectra of the bio-binder are due to the incorporation of the cryoMBO in the asphalt.

Rheology of the Binder Materials

The rheology of the binder materials was assessed with a DSR, by carrying out frequency sweeps at different temperatures (ASTM D 7175-08). The results were then used to build the |G*|/sinδ master curves of the several materials (Figure 36), and to determine their high temperature continuous performance grade (Table 7) specified in the SuperPave methodology (Asphalt Institute 2003).
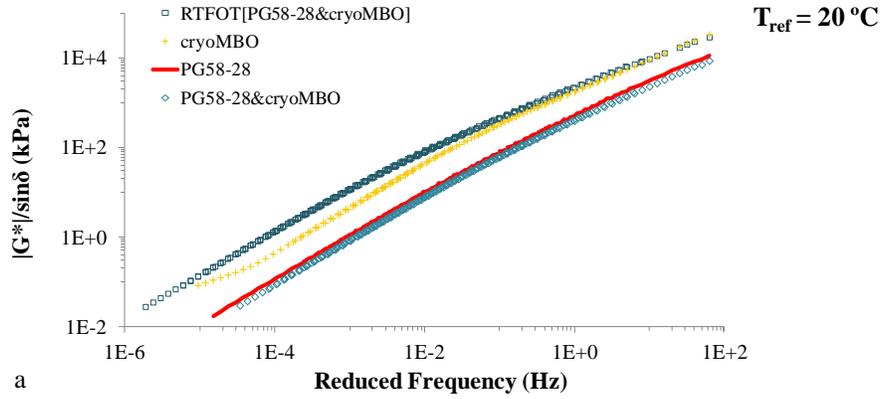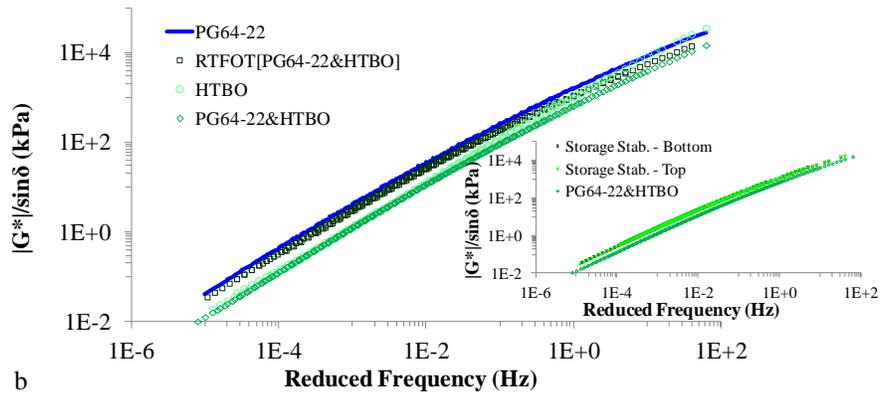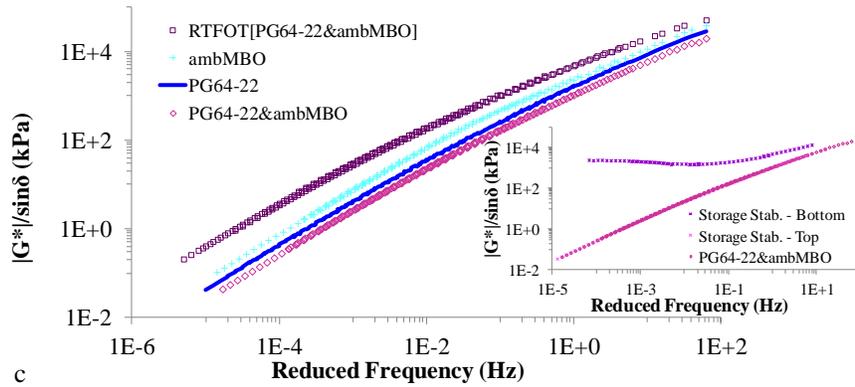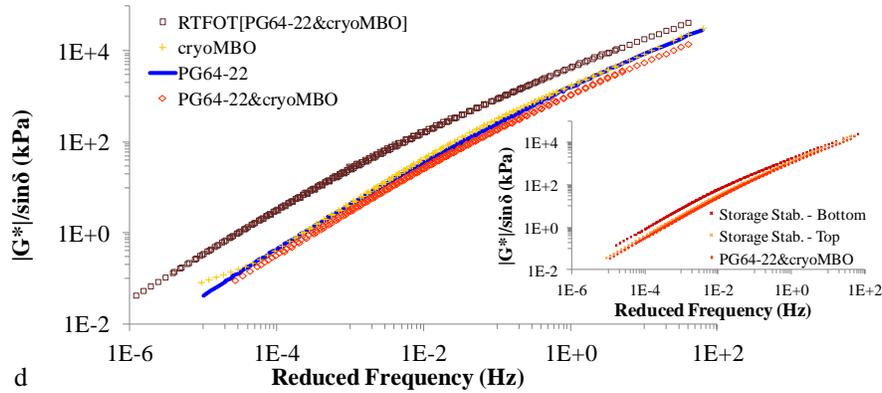
Figure 36. Master curves of the different binder materials (T_{ref} = 20 ºC)

Table 7. High temperature continuous performance grade of the unaged and RTFO aged binder materials

Materials	High Temperature Continuous Performance Grade (°C)*	
	Un-Aged	RTFO Aged
PG58-28	59.2	-
PG64-22	66.6	-
HTBO	54.8	-
cryoMBO	61.3	-
ambMBO	63.4	-
PG58-28 and cryoMBO	59.3	66.4
PG64-22 and HTBO	60.1	67.4
PG64-22 and cryoMBO	65.5	70.7
PG64-22 and ambMBO	65.2	72.1

*The indicated continuous grade for the RTFO residues does not refer to the standardized in AASHTO M 320. The RTFO aging temperature was modified from the standard to 140 °C.

A preliminary approach to the master curve of the bio-oil shows a material more sensitive to temperature and frequency than conventional asphalt. This scenario completely changes when the cryoMBO master curve is analyzed, as it presents a shape and consistency very similar to that of asphalt in a large range of temperatures and frequencies.

The master curves of all materials presented very similar shapes, and the master curves of the asphalts blended with 20 percent bio-oil based binders fitted between the master curves of the conventional asphalts (PG58-28 and PG64 22). The exception was the binder with PG58-28 asphalt blended with 20 percent cryoMBO, with a master curve below that of the conventional asphalt PG58-28 master curve. The master curves of the bio-binders (ambMBO and cryoMBO) are located above those of the other unaged binder materials. Nevertheless, it should be noted that the higher content of rubber particles in the MBO (15 wt%) can interfere with the DSR parallel plates, possibly affecting the rheological measurement of the MBO binders more than with the final binder blends containing only 3 wt% rubber particles.

After production, it is common to store the binder for some time before mixing, and during this period some changes can occur in the binder rheology. The master-curves of the top and bottom materials obtained from the separation tendency test of the binder blends showed that there was a small amount of hardening. By computing the percent differences of the values of the temperatures at which $G^*/\sin\delta$ equals 1.0 kPa, of the just blended and stored material, a difference of 7 percent was found for the PG64-22 and HTBO (Figure 36b), being this difference of 6 percent for the PG64-22 and cryoMBO (Figure 36d). The visible phase separation that occurred in the PG64-22 and ambGTR (Figure 36c) indicates that this material cannot be stored, and so it needs to be used immediately after production. Such process will imply using specific

equipment at the mixing plant to produce the blend, and/or the technology must evolve to solve this issue.

The binder ages during mixing and compaction in the pavement, and aging in asphalt is usually evaluated through the material hardening. Thus, the same calculations of the continuous PG for the RTFO-aged and just blended or unaged binders (Table 7) showed a difference of about 22.0 percent for the PG58-28 and cryoMBO and the PG64-22 and HTBO, and smaller differences of nearly 16.5 percent for the PG64-22 and cryo/ambMBOs. The hardening during the RTFO treatment is mainly due to water and volatiles loss, rubber swelling, and possible polymerization reactions.

The blending of conventional asphalts with 20 percent of bio-binders (ambMBO and cryoMBO) did not change the high temperature performance grade of the base asphalt. There are no clear differences in the performance grade when blending the asphalt PG64-22 with the ambMBO or cryoMBO, although the RTFO aging process caused minor differences in the performance grade of the blend PG64-22 with 20 percent cryoMBO (justifying the selection of this binder for production of mixtures).

In summary, these results indicate that the new blended binders are suitable for flexible pavement construction, with a few advantages justifying the selection of the blend PG64-22 with 20 percent cryoMBO to continue the study.

Viscosity of the Binder Materials

The viscosity of the binder materials was assessed by using a Brookfield viscometer according to ASTM D 4402-06 standard. The results obtained (Table 8) are indicative of the mixing and compaction temperatures for HMA production.

Table 8. Mixing and compaction temperatures for the blended asphalt binders

Materials	Mixing Temperature (°C)	Compaction Temperature (°C)
PG58-28 and cryoMBO	160	140
PG64-22 and HTBO	150	140
PG64-22 and cryoMBO	160	150
PG64-22 and ambMBO	170	*

* Could not be measured

The blends of asphalt with 20 percent cryoMBO and ambMBO have mixing and compaction temperatures higher than expected due to the particle effect of the GTR. In fact, the mixing and compaction temperatures of these blends could be slightly lower, as confirmed during the production of mixtures later in this work. From the results it would seem that the mixtures should

be produced at 160 ℃ and compacted at 150 ℃. However, it is known that the viscosity of a fluid with particles in suspension is higher than the fluid viscosity (Lefebvre and Maury 2005), being the fluid viscosity the parameter that is required for the definition of the mixing and compaction temperatures. Therefore, the binder is the liquid part, and the rubber particles are solely a different kind of aggregate (Peralta et al. 2013). Based on this, it was found that for this volume fraction of particles the suitable viscosity of the liquid for mixing and compaction temperatures would be achieved at 150 and 140 ℃ respectively.

Density of the Binder Materials

The density of the binders and their components is a very important characteristic of the materials, because it impacts the binder blends production and the volumetric formulation of the mixtures, as it is a volumetric design. The density of the binder materials was measured according to ASTM D 70-09 standard (Table 9).

Table 9. Density of the different bio-oil materials and asphalt binders

Materials	Density
Bio-oil	1218
HTBO	1281
cryoMBO	1246
ambMBO	1247
PG58-28 and cryoMBO	1063
PG64-22 and HTBO	1070
PG64-22 and cryoMBO	1066
PG64-22 and ambMBO	1067

The bio-oil has a high density when compared to asphalt, and the heat treatment increases the bio-oil density. Since rubber has a density of about 1,140 g/dm3, when added to the bio-oil, it slightly reduces the overall density of the cryoMBO or ambMBO. The final density of the blend between the asphalt and the HTBO or MBO materials reflect the lower density of asphalt (80 percent) and the different densities of the bio-oil based materials. The higher density of the binder blend (when compared to asphalt) implies it is necessary to add a higher weight percentage of the binder blend (5.5 wt%) than necessary with asphalt (5.0 wt%) in order to obtain the same volume of binder in the mixture.

Storage Stability or Separation Susceptibility of the Binder Materials

The different densities of the bio-oil and asphalt materials justify the evaluation of their separation susceptibility (ASTM D 7173-05 standard) after being blended in three chosen binders. Subsequently vertical column storage at high temperatures, the rheology of the top and bottom fractions of the tested materials was assessed by using a DSR and frequency sweep tests

at different temperatures. These results were used to assess their high temperature performance grade, which was then used to compute the differences between the performance grade of the top and bottom fractions of each material (Table 10).

Table 10. Difference between the top and bottom binders fractions in the separation test

Materials	High Temperature Continuous Performance Grade (°C)		Difference (%)
	Top	**Bottom**	
PG64-22 and HTBO	64.6	64.3	0.6
PG64-22 and cryoMBO	66.2	72.7	8.8
PG64-22 and ambMBO	66.3	*	*

* The value was too high and could not be measured; thus, the resulting difference was higher than 10%

The results show that the blends of PG64-22 asphalt with cryo and ambMBO were susceptible to separation. Nevertheless the blend of PG64-22 with cryoMBO was inside the specification criteria used by the Iowa Department of Transportation (DOT), but it was near the specification limit of 10 percent. The higher separation tendency of the blend of PG64-22 with ambMBO might be caused by ambGTR's bigger particle size when compared with cryoGTR's smaller particle size. Finally, although the HTBO presented the highest density, its blend with PG64-22 asphalt seems to be a more compatible system. Thus, the GTR is the main contributor for binder phase separation.

Mass Loss of the Binder Materials Due to Aging

The mass loss of the several binders using two aging tests procedures (with and without oxidation) was measured and the values are presented in Table 11.

Table 11. Mass loss due to asphalt binder aging with and without oxidation

Materials	RTFO (% mass loss)	Un-Oxidized (% mass loss)
PG58-28 and cryoMBO	3.9	3.3
PG64-22 and HTBO	3.7	3.0
PG64-22 and cryoMBO	3.6	3.1
PG64-22 and ambMBO	3.3	3.1

The results show higher percent mass loss than what would be expected for a conventional asphalt binder. However, most of this mass loss is caused by water loss (Meier et al. 2013). This is confirmed by the similarity between the modified RTFO and oven aged mass loss. Thus, the performance of these binders would not be as affected by oxidative aging as it could be concluded from these results.

Summing up the global evaluation of the binders, the material with best overall results in the binder characterization tests was the blend of PG64-22 asphalt with 20 percent cryoMBO, as this was the blend with the closest rheological behavior to the commercial asphalt PG64-22, lower mixing and compaction temperatures, and less tendency to separation than the PG64-22 and ambMBO blend. Therefore, this binder was selected to proceed with the production and characterization of asphalt mixtures in the remaining part of this work.

Results of the Mixture Testing

Mixtures designed and prepared according to the SuperPave mix design method (Asphalt Institute 2001) were compacted using the Superpave Gyratory Compactor (SGC) and the roller compactor to obtain specimens with 4 and 7 percent air voids. The specimens were tested to evaluate the suitability of these new mixtures for use in pavements.

Moisture Susceptibility of Asphalt Mixtures

The tensile strength ratio (TSR) value, that is the ratio between the indirect tensile strength (IDT) of unconditioned and water conditioned specimens, was used to measure the moisture susceptibility of the studied asphalt mixes (Table 12).

Table 12. Tensile strength ratio (TSR) of the asphalt mixes with an optimum asphalt content of 5.5% and a mean air voids content of 6.7%

	Unconditioned Strength (kPa)	Conditioned Strength (kPa)	TSR
Average	1756.4	1461.7	0.84
Standard Deviation	187.1	53.5	0.06
Coefficient of Variation	0.11	0.04	0.07

An adequate TSR result is fundamental to accept the new mixtures and to proceed further with their evaluation; otherwise, the mix design will not be appropriate and new binders or mixes should be designed and prepared.

A minimum TSR value of 0.70 is recommended (NCHRP 246), but many agencies specify a TSR value of 0.80 (Roberts et al. 1996, Williams and Breakah 2010). The average tensile strength ratio of the studied mixture (0.84) is greater than 0.8 and, thus, it can be considered that the mixes meet the Iowa DOT specifications for this parameter.

Harvey (2010) reported the relationship between the vales of the IDT of a mixture and its expected fatigue life. According to the criteria mentioned by Harvey (2010) and based on the presented IDT values, the studied mixtures will meet the design criteria (between 3 and 30 million ESALs), either conditioned or not, without cracking due to fatigue. Additionally, derived

from other criteria mentioned in the same work, it could be inferred that the studied mixes should not present rutting problems.

The following tests will provide additional and more accurate information about the performance of the studied mixtures related to the main pavement distresses that lead to premature failure, such as fatigue cracking, rutting, and low-temperature cracking, in order to validate the use of these new mixtures in pavements.

Fatigue Cracking Resistance of Asphalt Mixtures

The results of the four point beam fatigue tests carried out to evaluate the fatigue cracking resistance of the studied mixtures are summarized in Figure 37. The figure shows the variation in the number of load cycles (N_f) before fatigue failure as a function of the tensile micro strain (µε) applied in the test, both for mixes with 4 and 7 percent air void contents.
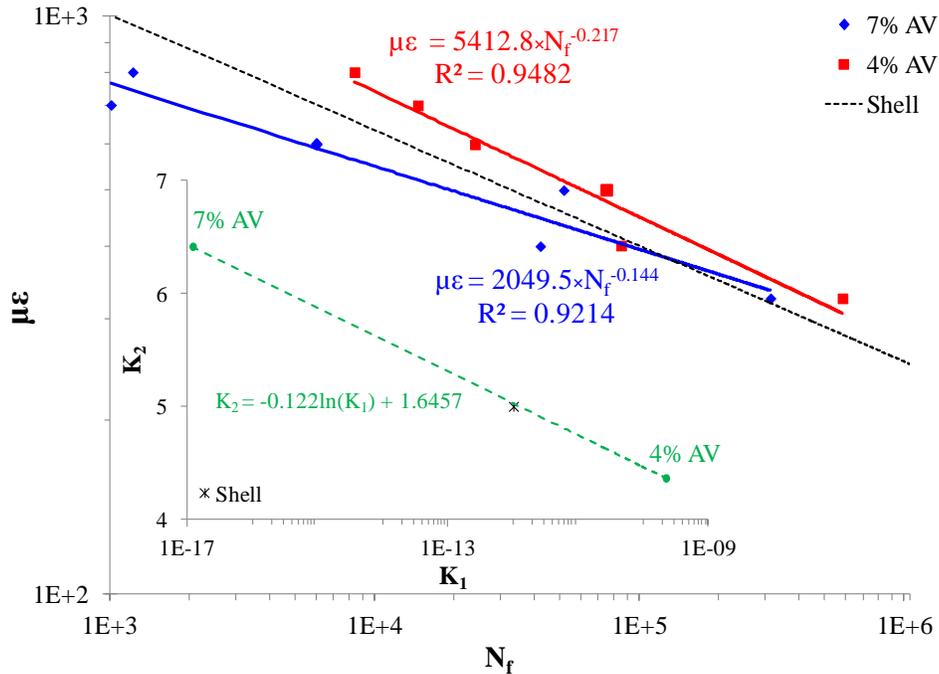
Figure 37. Variation of the fatigue life (N_f) with the tensile microstrain (µε) applied in mixtures with 5.5% asphalt content compacted to 4% and 7% air voids (AV)

The results of Figure 37 show that the mixture with 7 percent air voids is less resistant to fatigue cracking than the mixture with 4 percent air voids, at least in the range of the tensile microstrain values used in the fatigue test. This happens because the reduction of the air voids content corresponds to an increase of the asphalt and aggregates, resulting in a reduction of tensile sress on these samples, since air does not transfer stress. Moreover, smaller air voids content creates a more homogeneous structure with less stress concentration in critical solid-air interfaces in which the micro-cracks that begin to develop, under repetitive loading, grow slower and take

longer to interconnect because of the reduced number and smaller size of air voids (Harvery et al. 1995).

The fatigue laws for the mixtures with 4 and 7 percent air voids contents indicate a fatigue life similar to or slightly higher than the conventional mixtures. It is expected that these mixtures exceed the design number of ESALs (30 million) for a tensile strain level of 129 µε and 172 µε, respectively for the mixtures with 4 and 7 percent air voids. Moreover, considering that each ESAL would induce a tensile strain level of 100 µε when the studied mixtures are placed in the pavement, they will not show fatigue cracking distress before 65 million ESALs for the mixture with 4 percent air voids, and before 540 million ESALs for the mixture with 4 percent air voids.

Shell (1978) suggested a model to predict the fatigue life of a pavement, which related the tensile strain in the bottom of the asphalt concrete layers with the number of load cycles or ESALs. This model (Equation 9) was used in this work to compare the fatigue behavior of conventional mixtures (represented in a simple way by this model) with that of the new mixes produced in this work. This model is shown in Figure 37 for a conventional asphalt mix with 4,000 MPa and an asphalt volume content of 12 percent.

$$\varepsilon_t = (0.856 \times Va + 1.08) \times \left| E^* \right|^{0.36} \times N_f^{-0.2}$$

(9)

where:
ε_t – tensile strain
N_f – number of loading cycles (ESALs)
V_a – volume percentage of asphalt in the total volume of the mixture
$|E^*|$ – deformability or dynamic modulus of the asphalt mixture (Pa)

The Shell model, used in this work to represent conventional mixture, predicts that the new mixtures should be able to support 98 million ESALs for a tensile strain of 100 µε, and can support the design number of 30 million ESALs for a tensile strain level of 126.7 µε. Thus, these values show that the new mixtures developed in this work have an adequate fatigue cracking behavior.

The experimental fatigue coefficients K_1 and K_2 were determined to be respectively 2.2E-10 and 4.3675 for the mixture with 4 percent air voids. The mixture with 7 percent air voids had fatigue coefficients of K_1=1.2E-17 and K_2=6.4148. Thus, both mixtures show a fatigue performance similar to that of conventional asphalt mixtures, as reported in previous works:

- $2.907 < K_2 < 6.781$ and $2.497E-17 < K_1 < 1.398E-7$ (Cascione et al. 2011)
- $3.37 < K_2 < 6.43$ and $3.98E-15 < K_1 < 1.25E-7$ (Ghuzlan and Carpenter 2003)
- $3.31 < K_2 < 6.45$ and $3.04E-12 < K_1 < 3.81E-7$ (Pais et al. 2009)

The K_1 coefficient characterizes the flexural modulus, and the K_2 coefficient indicates the rate of damage accumulation in a sample. When using this relationship as failure criterion for pavement

design, a lower K_2 value is more conservative as it assumes faster accumulation of fatigue damage. The values suggested for K_2 are 4.477 by The Asphalt Institute, 4.0 by Shell, and 3.571 by the University of Nottingham (Huang 2004). Carpenter (2006) recommended the Illinois DOT to use a K_2 value in the range of 3.5 to 4.5 (Williams et al. 2011), as that obtained in the mix with 4 percent air voids.

The experimental K1 versus K2 values were plotted (insert of Figure 7) defining a line were the fatigue coefficients of the Shell model fit, which corroborates the suitability of the mixtures in terms of fatigue life.

Subsequently, Figure 38 shows the cumulative dissipated energy (computed according to AASHTO T 321-07 standard in the fatigue test in function of the number of load cycles for each studied mixture.
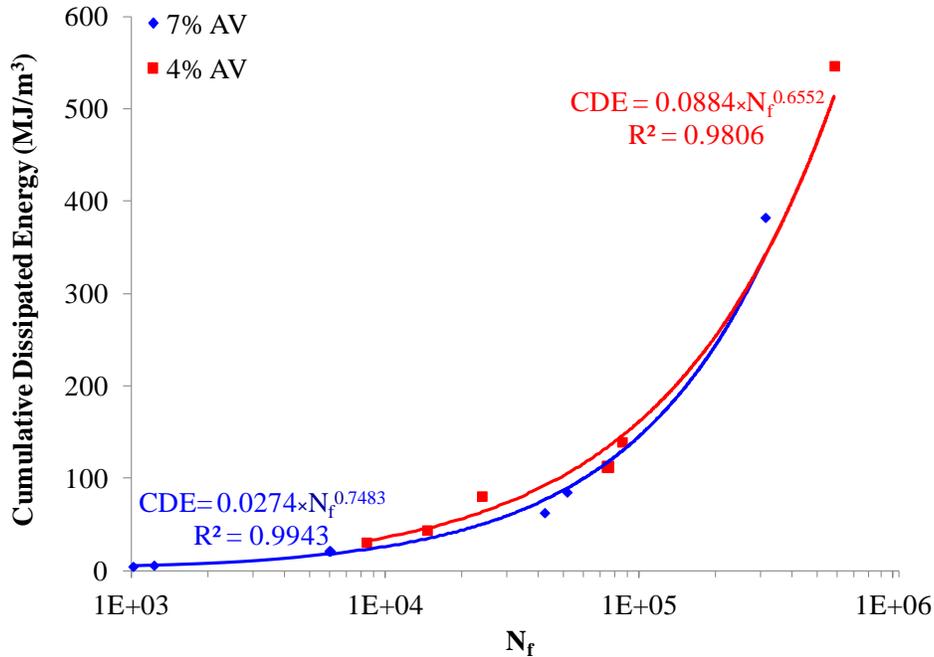
Figure 38. Variation of cumulative dissipated energy (CDE) with the number of load cycles (N_f) for mixes with 5.5% asphalt content compacted to 4% and 7% air voids (AV)

With higher air voids content, the mixture with 7 percent air voids has a lower area under its curve, which shows a lower cumulative dissipated energy than the mixture with 4 percent air voids (in the range of the tensile strain values used in the fatigue test). These results are in accordance with those currently obtained with traditional asphalt mixtures. The area below the stress/strain curve indicates the toughness of the asphalt mixtures with 7 and 4 percent air voids, which were 2.33 MPa and 2.14 MPa respectively.

The results obtained in the fatigue cracking test indicate that a pavement built with this mixture (with a range of 4 to 7 percent air voids content) should not present fatigue distresses within the design level of 30 million ESALs.

Dynamic Modulus of Asphalt Mixtures

Figure 39 shows the master curves of the dynamic modulus for the mixtures designed with 4 and 7 percent air voids, which were built by shifting the frequency sweeps (six frequencies) at three temperatures (4, 21, and 37 ℃) using the time-temperature superposition principle and the sigmoidal or Witczak prediction model (Garcia and Thompson 2007). The experimental data of the dynamic modulus at each temperature was shifted using a reference temperature of 21 ℃. The experimental master curve was then used to fit the prediction model.
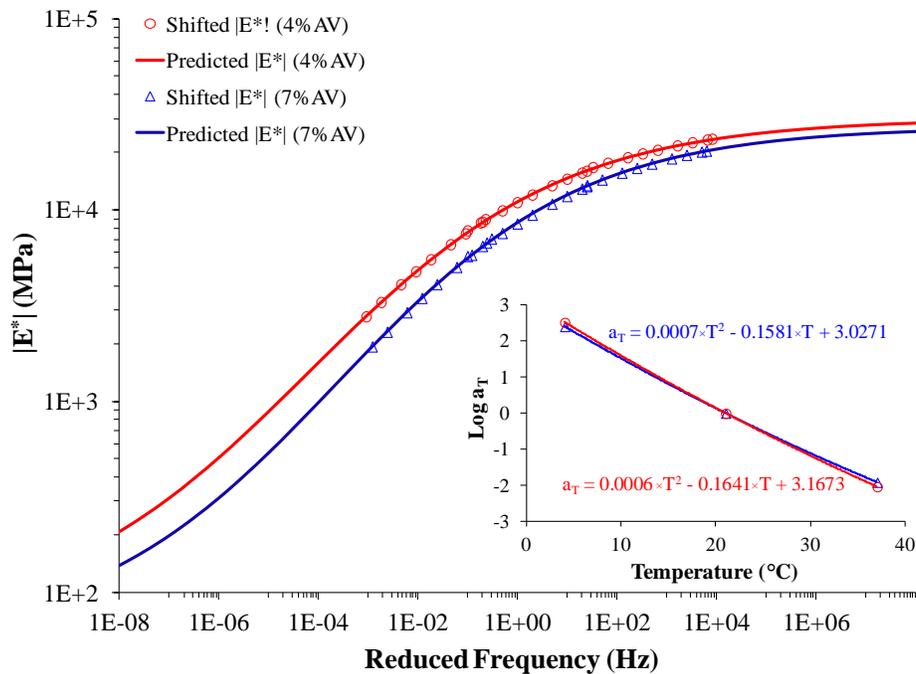
Figure 39. Master curve of the shifted and predicted dynamic modulus for the 4% AV and 7% AV samples (Tref = 21ºC), with an insert with the quadratic shifting

The fitted prediction model shows that the asphalt mixture with 4 percent air voids is stiffer than that with 7 percent air voids. Thus, it can be concluded that the mixture with 4 percent air voids should perform better at high temperatures, having a high rutting resistance (as a consequence of the high stiffness modulus at high temperature). Moreover, the values of the dynamic modulus at 37 °C for both mixtures with 4 and 7 percent air voids are higher than those of conventional asphalt mixtures (West et al. 2013, Williams et al. 2011). The viscoelastic behavior of the mixtures at both levels of compaction (4 and 7 percent air voids) converges at higher frequencies (or lower temperatures) as it approaches the glassy plateau, and diverges with the temperature increase (or reduction in frequency).

These results show that these new mixtures are very stiff materials after compaction, either for 4 or 7 percent air voids content, which are not prone to develop rutting. This result seems to be out-of-phase with the rheological evaluation of the binders, which indicated that the new binder blend is slightly softer than the conventional asphalt.

Rutting Resistance of Asphalt Mixtures

The triaxial repeated load permanent deformation test was used to evaluate the rutting resistance of an HMA specimen, with the permanent deformation of the specimen recorded as a function of the number of load cycles. Specimen loading is carried out for 0.1 sec followed by a 0.9 sec dwell (or unloading). There are three phases of flow that occur during this type of test: primary, secondary, and tertiary. Under primary flow, there is a decrease in the strain rate over the initial loading phase. With continuous repeated load application, the next phase of material response is referred to as secondary flow, which is characterized by a relatively constant strain rate. Finally, the material enters tertiary flow, where the strain rate begins to increase as the test progresses. Tertiary flow signifies that a specimen is beginning to deform significantly and individual aggregates composing the skeleton of the mix are moving past each other. The flow number is based upon the initiation of tertiary flow, or in the minimum strain rate recorded during the course of the test (Kvasnak et al. 2007).

The flow number of an asphalt mixture corresponds to the number of cycles needed to accumulate 5.5 percent strain in the sample tested. A higher flow number indicates a higher resistance to rutting. The test ends at 10,000 load cycles even if the sample has not accumulated 5.5 percent strain. A sample that reaches 10,000 load cycles is considered to be essentially rut resistant at the testing temperature. Since all the samples tested reached 10,000 load cycles at 37 ºC, the test was repeated at 54 ºC. The response measured in this test was the accumulated strain and is presented in Figure 40.
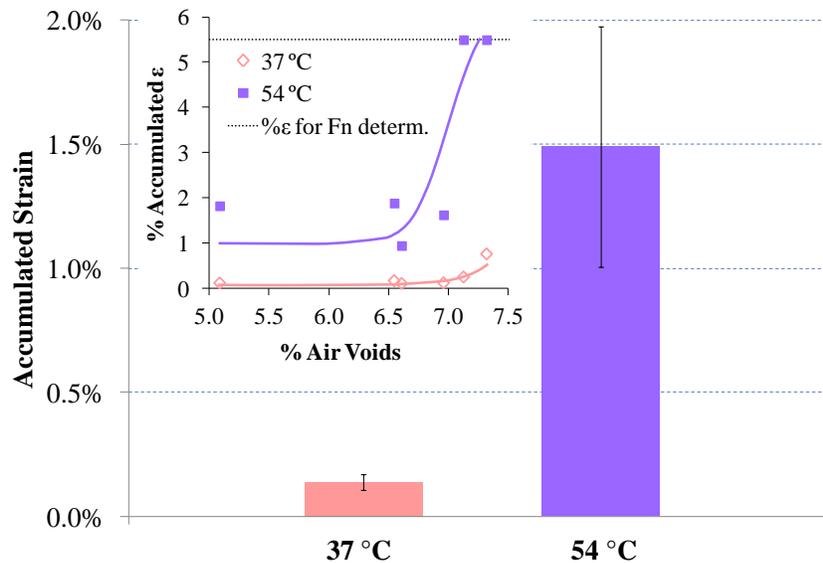
Figure 40. Accumulated strain at 10,000 cycles for the 7% air voids mixture

The values presented are the average strain levels of three samples in each batch and at each temperature. The lower accumulated strain level at the end of the test was interpreted as a mixture with higher resistance to rutting, which was necessarily obtained for tests carried out at 37ºC. The samples with air voids contents lower than 6.5 presented similar values of deformation at the end of the test, at each respective test temperature, 37 or 54ºC. However, the accumulated deformation at the end of the test started to increase for samples with higher air voids content, especially for samples tested at 54ºC.

Primarily, it was observed that the accumulated strain of the mixtures developed in this work is exceptionally low at both test temperatures in comparison with traditional mixtures. Thus, the rutting performance of these new mixtures in the field is expected to be very good even at high temperatures.

Low-Temperature Fracture Mechanics of Asphalt Mixtures

The previous results indicate that the mixes produced with the blend of PG64-22 asphalt with 20% cryoMBO are quite stiff. Thus, although the fatigue life is sufficient for the designed level of ESALs and the compacted mixes were not susceptible to moisture damage, it could be expected that the performance at low temperatures may not be adequate. Therefore, the semi-circular bending test (SCB) was performed to evaluate the low-temperature fracture mechanics of the studied mixtures. The results obtained with that test for several parameters are plotted in Figure 41.
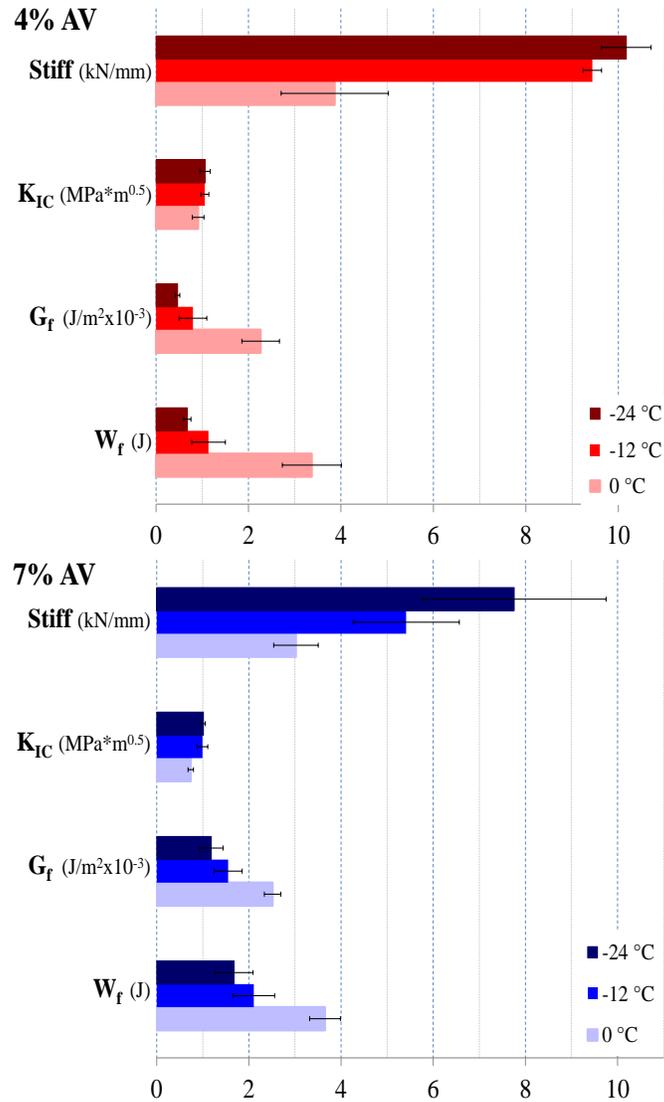
Figure 41. Low-temperature fracture mechanics of the studied mixtures in the SCB test

The results obtained for the newly developed mixes were compared with other results from the literature (West et al. 2013, Li and Marasteanu 2010, Velasquez et al. 2009), and it was found that, in all cases, the mixes studied in this work have higher values for the SCB parameters, especially the stiffness. This indicates, contrary to what was expected, that the designed mixes have a good resistance to fracture cracking at low temperatures, despite having presented a very high stiffness in the dynamic modulus test.

Bio-Oil Binder Compared to Typical Asphalt Rubber Binder

Binder Grading Comparison

The comparison of the continuous grading results for the newly develop bio-oil binder and a typical asphalt rubber binder is presented in Table 1.

Table 13. Continuous grading for high temperature performance

Binder type	Unaged	RTFOaged
PG64-22 and 20% cryoMBO	65.5	70.7
PG46-34 and 12% CryoRubber	66.1	66.7

As observed, both binders present very similar grading results, being both of them graded as a PG64 for the high temperature performance.

Mixture Performance Comparison

The performance of the newly developed bio-oil blend mixes was compared with a typical asphalt rubber mix utilizing the binder characterized in Table 1. The characteristics of the two mixes are presented in Table 2.

Table 14. Characteristics of mixes

Mix Type	Base Binder	Rubber Type	N.M.A.S. (mm)	% Binder
PG64-22 + 20%cryoMBO	PG64-22	cryogenic	9.5	5.5
PG46-34 + 12%CryoRubber	PG46-34	cryogenic	19.0	5.6

Moisture Susceptibility Comparison

The moisture susceptibility results for both types of mixes are presented in Table 3.

Table 15. Moisture susceptibility comparison

	PG64-22 + 20% cryoMBO			PG46-34 + 12% CryoRubber		
	Unconditioned Strength (kPa)	Conditioned Strength (kPa)	TSR	Unconditioned Strength (kPa)	Conditioned Strength	TSR
Average	1756.4	1461.7	0.84	545.3	712.8	1.31
Standard Deviation	187.1	53.5	0.06	26.1	45.9	0.13
Coefficient of Variation	0.11	0.04	0.07	0.05	0.06	0.10

The tensile strength ratio (TSR) result for a typical asphalt rubber binder shows that it should have superior anti-stripping performance. Whereas, the TSR value for the bio-oil mixes showed an acceptable performance for moisture susceptibility, according to the limit for many agencies (TSR≥0.80).

*Fatigue Cracking **Resistance** Comparison*

The fatigue life of the mixes is presented in Figure 1.
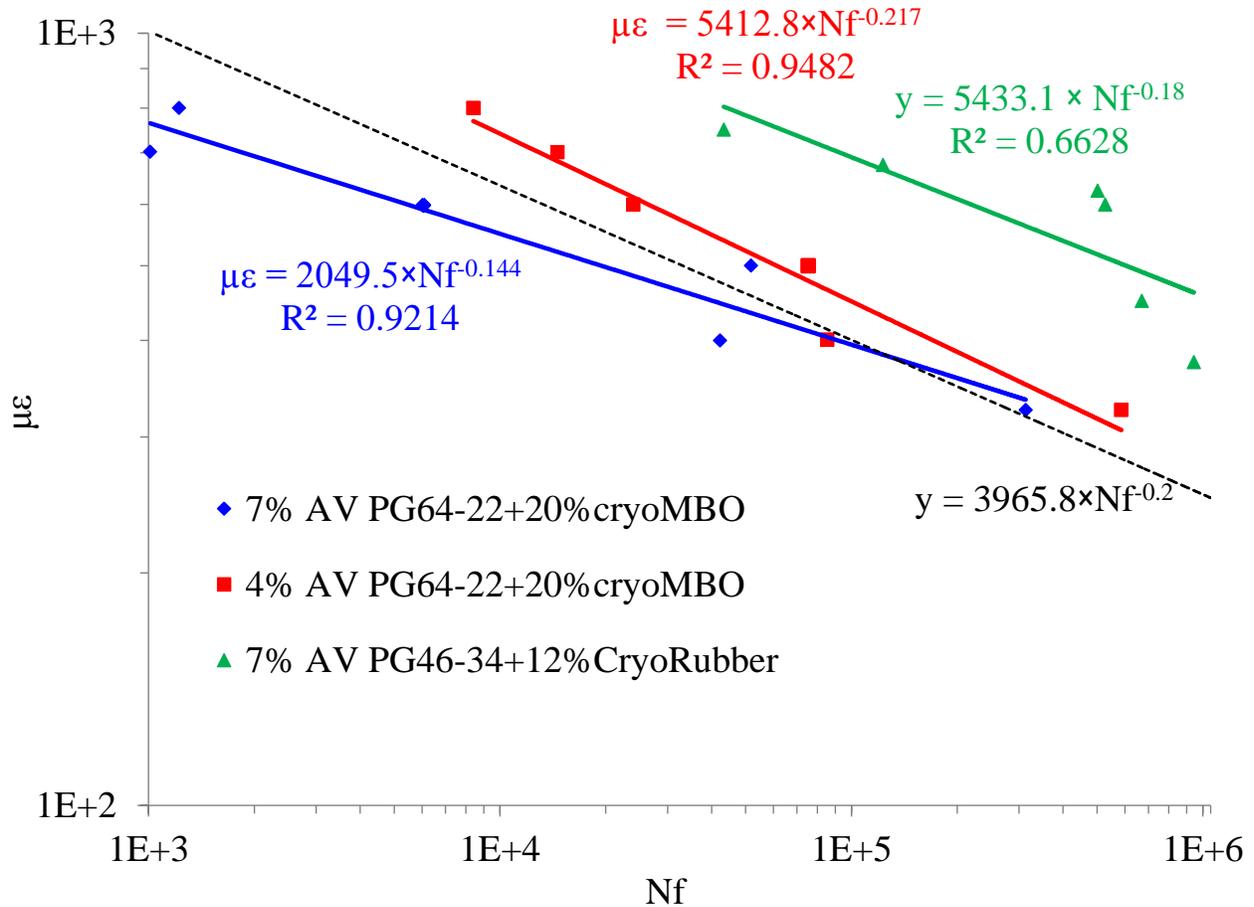
Figure 42. Variation of the fatigue life (Nf) with tensile microstrain (με) for a bio-oil mix and a typical asphalt rubber mix

As shown, the fatigue life of a typical asphalt rubber mix at the same tensile strain is better than the fatigue life observed for the bio-oil mix. However, it should be noted that the fatigue life of a typical asphalt rubber mix is usually far superior to the fatigue life of other types of modified asphalt mixes. When compared to the fatigue life of conventional asphalt mixtures, the bio-oil mix presents adequate fatigue performance.

The experimental fatigue coefficients K1 and K2 are plotted in Figure 2 and their values are summarized in Table 4.
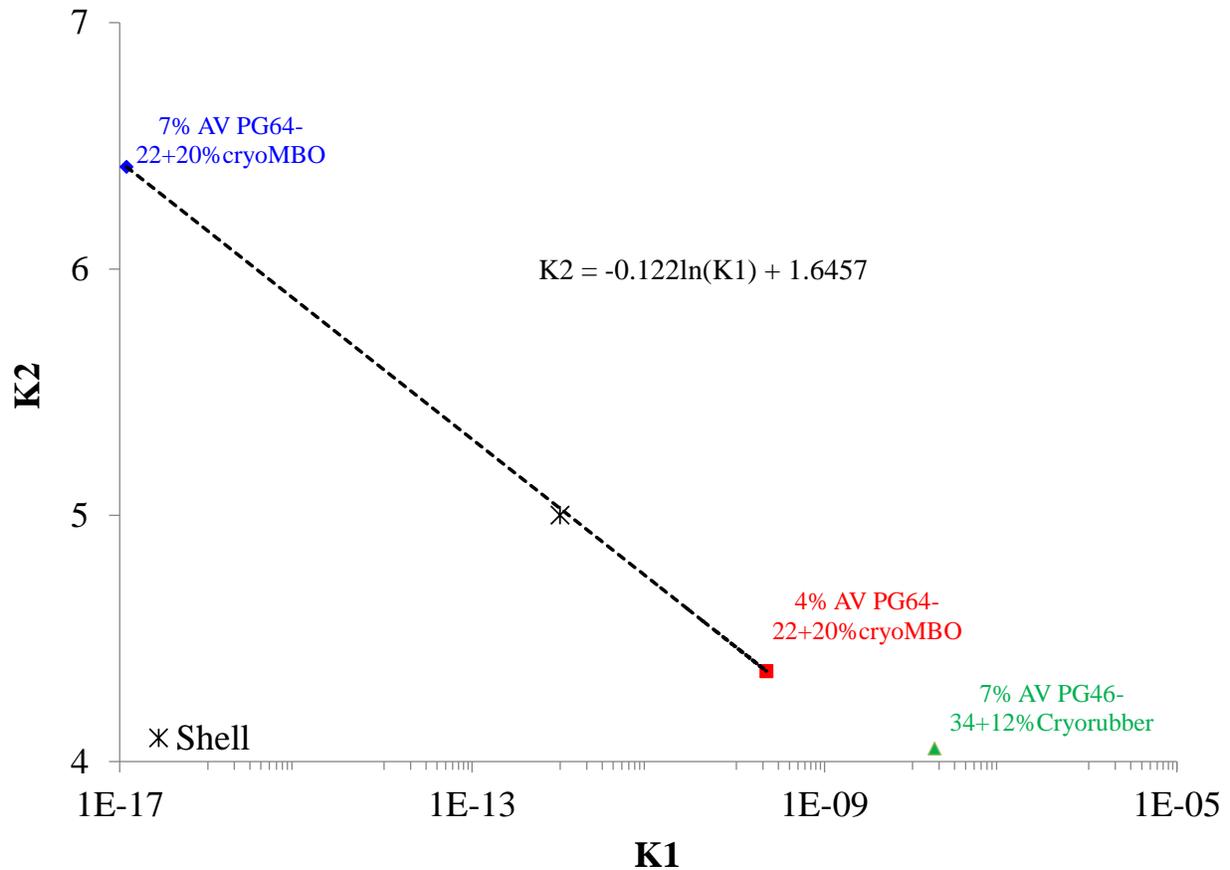
Figure 43. Experimental fatigue coefficients K1 and K2 for a bio-oil mix and a typical asphalt rubber mix

Table 16. Experimental coefficients K1 and K2 obtained for the mixes

Mix type	K1	K2
4% AV PG64-22+20%cryoMBO	2.2E-10	4.3675
7% AV PG64-22+20%cryoMBO	1.2E-17	6.4148
7% AV PG46-34+12%CryoRubber	1.8E-08	4.0528

The K_1 coefficient characterizes the flexural modulus, and the K_2 coefficient indicates the rate of damage accumulation in a sample. When using this relationship as failure criterion for pavement design, a lower K_2 value is more conservative as it assumes faster accumulation of fatigue damage. The values suggested for K_2 are 4.477 by The Asphalt Institute, 4.0 by Shell, and 3.571 by the University of Nottingham (Huang 2004). Carpenter (2006) recommended the Illinois DOT to use a K_2 value in the range of 3.5 to 4.5 (Williams et al. 2011) as that obtained in the mix with 4 percent air voids.

Comparing the results obtained, the mixtures show a fatigue performance similar to that of conventional asphalt mixtures, as reported in previous works:

- 2.907 < K_2 < 6.781 and 2.497E-17 < K_1 < 1.398E-7 (Cascione et al. 2011)
- 3.37 < K_2 < 6.43 and 3.98E-15 < K_1 < 1.25E-7 (Ghuzlan and Carpenter 2003)
- 3.31 < K_2 < 6.45 and 3.04E-12 < K_1 < 3.81E-7 (Pais et al. 2009)

Dynamic Modulus Comparison

The master curves of both mixes are compared in Figure 3.
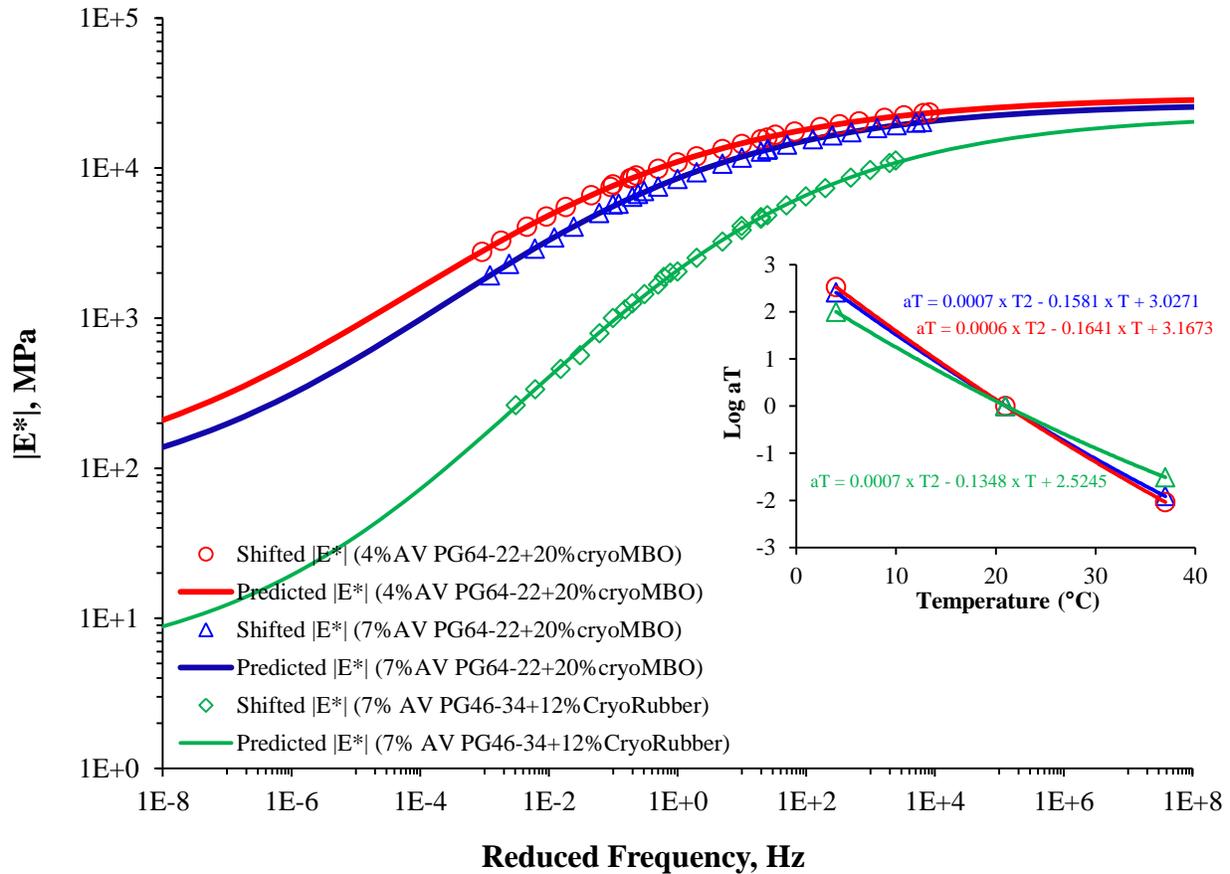
Figure 44. Master curves of the measured and predicted dynamic modulus |E*| of a bio-oil mix and a typical asphalt rubber mix (T_{ref} = 21 °C)

The bio-oil mixes have a higher dynamic modulus values than the typical asphalt rubber mix when comparing the results obtained at the same frequencies. Therefore, it can be said that the bio-oil mixes will have a better permanent deformation performance than the typical asphalt rubber mixes. These results were further validated when comparing the flow number test results for the mixes.

Rutting Resistance (Flow number test, F_N) Comparison

As expected from the dynamic modulus results, the rutting performance of the bio-oil mixes were far superior to the rutting performance of the typical asphalt rubber mix. The results are summarized in Table 5.

Table 17. Flow number (F_N) test results

Mix	Test Temperature 37 °C	
	Flow Number	**Accumulated Strain**
PG64-22+20%CryoMBO	>10,000	0.14%
PG46-34+12%CryoRubber	1805	5.5%

*Low-Temperature Fracture **Mechanics** Comparison*

The comparison of the low-temperature performance of the bio-oil mixes to a typical asphalt rubber mix is presented in Figure 4.
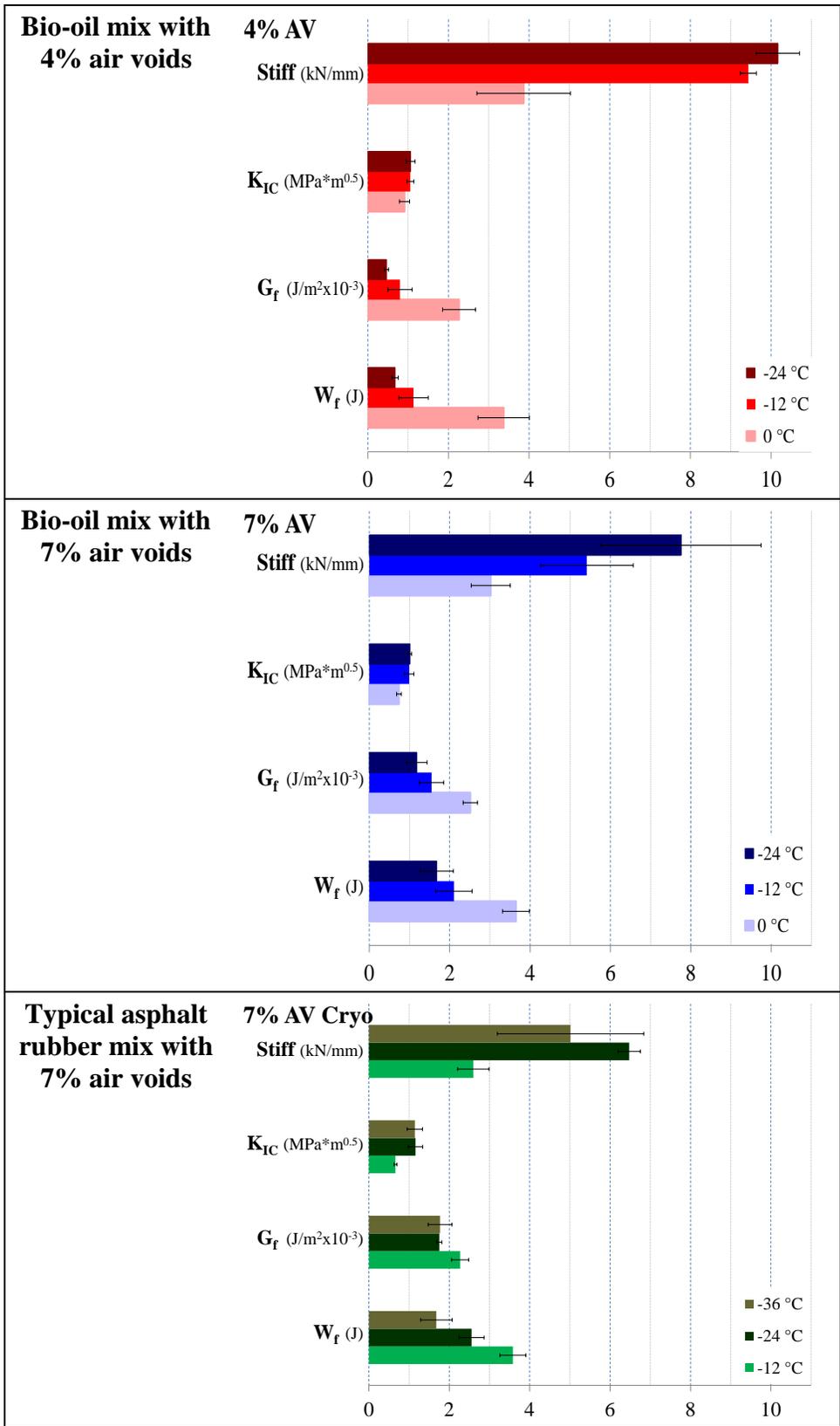
Figure 45. Low-temperature fracture mechanics of the mixes by means of the SCB test

The top graph shows the results of the bio-oil mix with 4% air voids. The middle graph shows the results of the bio-oil mix with 7% air voids. And, the bottom graph shows the results of the typical asphalt rubber mix with 7% air voids.

The stiffness (S) of the bio-oil mixes at -12 and -24 °C was higher than for a typical asphalt rubber mix. The fracture toughness (K_{IC}) in general was higher for the bio-oil mixes than for the typical asphalt rubber mix. The fracture energy (Gf) was higher for the typical asphalt rubber mix compared to the bio-oil mixes at the same testing temperatures (-12 and -24 °C); the same was observed for the work of fracture (W_f) at those same temperatures.

CHAPTER 8. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A bio-binder consisting of fractionated bio-oil reacted with crumb rubber can produce a binder that is comparable to asphalt binders derived from crude petroleum. The bio-oil can successfully react with crumb rubber at 125ºC, which is a substantially lower temperature than that used in normal asphalt binders (typically about 185ºC), and it was found that the rubber swells approximately three times its weight. Of the two types of ground tire rubber used in this study, the cryogenic rubber is more effective than the ambient ground rubber at producing lower temperature grades; the stiffness of the bio-binders containing the cryogenic rubber is lower than that of the ambient rubber at low temperatures. The FTIR results indicate that the styrene butadiene rubber from the tire rubber is likely migrating and chemically combining with the fractionated bio-oil.

In the second component of this study, the bio-oil was heat treated and further modified with cryogenic and ambient ground tire rubber. These three bio-oil binders were then blended with PG58-28 and PG64-22 asphalt. The bio-oil–based materials (bio-oil, HTBO, cryoMBO, and ambMBO), the asphalts (PG58-28 and PG64-22), and the final blends were then characterized. The developed bioasphalt/asphalt blends using ground tire rubber have been shown to perform as well or better than the traditional asphalt mixtures using ground tire rubber.

The tests performed included RTFO aging, FTIR, viscosity, rheology, density, and separation susceptibility. The results obtained in the characterization of these binders showed that the final blends have properties similar to those of conventional asphalts, except for the blend of the PG64-22 asphalt with ambMBO (which showed a higher susceptibility to separation during storage).

After the binder study, the blend of the PG64-22 asphalt with 20% cryoMBO was selected to produce asphalt mixes with a 9.5 mm NMAS, because this binder exhibited the best global performance across the multiple types of distress. Moisture susceptibility, flexural fatigue cracking, dynamic modulus, rutting resistance, and low-temperature fracture tests were performed to evaluate the global performance of the mixtures developed in this work. The mixtures with the chosen asphalt blend showed very good performance in all tests carried out. Thus, it is not expected that rutting or early fatigue cracking distresses will occur, and these mixtures should not be sensitive to moisture nor to low-temperature cracking.

Laboratory observations indicated that the bio-binders need to have agitation to avoid phase separation. Accommodations for special tanks with agitation systems should be made. Based on the laboratory results, it is not recommended to use particle sizes of GTR bigger than #80 mesh in bio-binders to avoid higher stability/phase separation issues. Besides the use of special tanks for its transportation, sufficient commercial production of fractionated bio-oil would also be necessary for this technology to be readily applicable. The researchers believe that there is a sufficient amount of agricultural and forestry residues for the commercial production of fractionated bio-oil.

To persuade transportation agencies to allow the use of higher quantities of bio-oil as an alternative binder material for pavements, the excellent laboratory performance of the new mixtures should be validated through pavement trials after asphalt plant production. The use of higher quantities of bio-oil in pavements would present technological, environmental, and economic advantages.

This report summarized the successful development of a bio-binder that is derived from a renewable source of material and represents a green technology. Additional work needs to be done using field trials, and this will assist in understanding the oxidative aging mechanisms of these new materials as well as their field performance.

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