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

Final Report
October 2010

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16. Abstract

Most bituminous adhesives or 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 biorenewable resources. However, until now, no research has studied the applicability of utilizing bio-oils as a bitumen replacement (100% replacement) in the pavement industry.

The main objective of this research was to test various properties of bio-oils in order to determine the applicability of using bio-oils as binders in the pavement industry.

The overall conclusions about the applicability of using bio-oils as bio-binders in the pavement industry can be summarized as follows:

1. Bio-oils cannot be used as bio-binders/pavement materials without any heat pre-treatment/upgrading procedure.
2. Current testing standards and specifications, especially Superpave procedures, should be modified to comply with the properties of bio-binders.
3. The temperature range of the viscous behavior for bio-oils may be lower than that of bitumen binders by about 30°–40° C.
4. The rheological properties of the unmodified bio-binders vary in comparison to bitumen binders, but the rheological properties of these modified bio-binders change significantly upon adding polymer modifiers.
5. The high-temperature performance grade for the developed bio-binders may not vary significantly from that of the bitumen binders, but the low-temperature performance grade may vary significantly.

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

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October 2010

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EXECUTIVE SUMMARY

Most bituminous adhesives or binders that are used for pavement materials are derived primarily from fossil fuels. Nevertheless, with petroleum oil reserves becoming depleted and the subsequent promotion to establish a bio-based economy, there is a drive to develop and produce binders from alternative sources, particularly from biorenewable resources. Recently, through the application of scientific research and development, a range of different vegetable oils have been investigated to determine their physical and chemical properties to study their applicability to be used as bio-binders in the pavement industry. Bio-binders can be utilized in three different ways to decrease the demand for fossil fuel based bituminous binders summarized as follows: (1) as a bitumen modifier (<10% bitumen replacement), (2) as a bitumen extender (25% to 75% bitumen replacement), and (3) as a direct alternative binder (100% replacement). On the other hand, there has been no research conducted until now that studies the applicability of the utilization of bio-oils as a bitumen replacement (100% replacement) to be used in the pavement industry.

The main objectives of this dissertation can be summarized as follows. First, the rheological properties of fast pyrolysis liquid co-products (bio-oils) were investigated to determine the heat pre-treatment/upgrading procedure required for developing bio-binders from bio-oils. The second objective included the modification of Superpave test procedure to comply with the properties of the developed bio-binders. Third, the chemical characterization of the developed bio-binders was studied in addition to the physical characterization. Fourth, the utilization of bio-oils as bio-binders in the pavement industry was explored through determining the temperature and shear susceptibilities of the developed bio-binders and comparing them with commonly used bitumen binders. Fifth, the temperature performance grades for the developed bio-binders were measured in addition to the determination of the mixing and the compaction temperatures. Sixth, the master curves for the developed bio-binders were studied and compared to commonly used bitumen binders.

The overall conclusions about the applicability of using bio-oils as bio-binders in the pavement industry can be summarized as follows. First, the bio-oils cannot be used as bio-binders/pavement materials without any heat pre-treatment/upgrading procedure due to the presence of water and volatile contents in considerable amounts. The heat treatment/upgrading procedure for deriving bio-binders from bio-oils should be determined for each type of bio-oil separately due to the significant difference between the different types of bio-oils, e.g. the chemical composition, the process by which the bio-oils were derived, and the type of the biorenewable resource from which the bio-oils were derived. Second, the current testing standards and specifications, especially Superpave procedures, should be modified to comply with the properties of the bio-binders derived from bio-oils because of difference in temperature susceptibility and aging. Third, the temperature range of the viscous behavior for bio-oils may be lower than that of bitumen binders by about 30-40°C. Fourth, the rheological properties, i.e. temperature and shear susceptibilities, of the unmodified bio-binders derived from bio-oils vary in comparison to bitumen binders, but upon adding polymer modifiers, the rheological properties of these modified bio-binders change significantly. Fifth, the high temperature performance grade for the developed bio-binders may not vary significantly from the bitumen binders; however, the low temperature performance grade may vary significantly due to the high oxygen content in the bio-binders and subsequent aging compared to the bitumen binders.

CHAPTER 1. INTRODUCTION

Background

Most bituminous adhesives or binders that are used for pavement materials are derived primarily from fossil fuels (Airey *et al.* 2008). Nevertheless, with petroleum oil reserves becoming depleted and the subsequent urge to reduce fossil fuel usage, there is a drive to develop and produce binders from alternative sources, particularly from biorenewable resources. Over the years, biorenewable natural resources including sugars, triglyceride oils and proteins have been tested as alternative sources for producing adhesives and binders (Airey *et al.* 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 *et al.* 2008 and Shields 1976). Due to the availability of large quantities of biorenewable 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 *et al.* 2008). Recently, through the application of scientific research and development, a range of different vegetable oils have been investigated to determine their physical and chemical properties to study their applicability to be used as bio-binders in the pavement industry (Airey *et al.* 2008, Tan *et al.* 2002 and Kaplan 1998).

Bio-binders (synthetic binders) can be utilized in three different ways to decrease the demand for fossil fuel based bituminous binders summarized as follows: (1) as a direct alternative binder (100% replacement), (2) as a bitumen extender (25% to 75% bitumen replacement), and (3) as a bitumen modifier (<10% bitumen replacement) (Williams *et al.* 2009 and Airey *et al.* 2008).

Report Objectives

The main objectives of this report are sevenfold. First, the rheological properties (viscosity versus time) of fast pyrolysis liquid co-products (bio-oils) will be investigated. The first objective will be concerned about the determination of the heat pre-treatment/upgrading procedure required for developing bio-binders from bio-oils. In other words, the first objective will concentrate on identifying the temperature and the duration for heating the bio-oils before usage. The second objective will include the modifications of Superpave standards and test procedures to comply with the properties of the developed bio-binders. Third, the chemical characterization of the developed unmodified bio-binders (pre-treated/upgraded bio-oils) will be investigated using Gas Chromatography-Mass Spectrometry (GC/MS) and Fourier Transform Infrared Spectroscopy (FTIR). Fourth, the utilization of bio-oils as bio-binders in the pavement industry will be explored through understanding the rheological characteristics of the bio-oils/bio-binders. In addition, a comparison between the rheological properties of bio-oils/bio-binders and petroleum based bitumens will be investigated. Moreover, the effect of polymers on the rheological properties of bio-oils/bio-binders will be explored. Fifth, the performance testing for the developed bio-binders will be conducted including the determination of the mixing and the compaction temperatures. Sixth, developing the master curves for the developed bio-binders will be studied and compared to commonly used bitumen binders. Seventh, an outline or a protocol to optimize bio-oil products to be used as bio-binders will be developed.

Current State of the Practice for Bio-oils

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 the dark color of lignin, it has not been exploited as an antioxidant; however, the dark color of lignin is not of concern in certain applications, such as its use in asphalt pavement (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 1992 and Sundstrom *et al.* 1983).

Currently, the state of the art for the utilization of bio-oils is concentrated on its uses as biorenewable fuels to replace fossil fuels. However, there has been a limited amount of research conducted to investigate the applicability of using bio-oils as a bitumen modifier or extender. Based on the conclusion of these investigations, the utilization of bio-oils as a bitumen modifier is very promising. On the other hand, there has been no research conducted until now that studies the applicability of the utilization of bio-oils as a bitumen replacement (100% replacement) to be used in the pavement industry. As a result, there is scarcity of data that illustrate the procedure to develop bio-binders from bio-oils.

Overall Report Experimental Plan

The experimental plan is outlined here. The plan considers different types of bio-oils, derived from different biomass sources, i.e. oakwood, switchgrass, and cornstover, but by the same technique, which is fast pyrolysis. The plan includes three integrated plans: one for the physical properties, one for the chemical properties, and one for the rheological properties. For the physical plan, the physical characteristics of the developed bio-binders are determined through measuring the separation potential and the specific gravity. The chemical plan is considered mainly about chemical characterization of the developed unmodified bio-binders (pre-treated/upgraded bio-oils) through testing them by Gas Chromatography-Mass Spectrometry (GC/MS) and Fourier Transform Infrared Spectroscopy (FTIR). These tests are capable of quantifying the amount of oxidative aging occurred and identifying the possible types of chemical bonds (functional groups) presented in the developed unmodified bio-binders. For the rheological plan, it has many steps that can be summarized as follows: (1) measuring the viscosity over time of the untreated bio-oils (original/virgin bio-oils) using the rotational viscometer through which the temperature and the duration for the development of bio-binders from bio-oils to be determined, (2) determining the effect of adding different types of polymer modifiers with different percentages, i.e. polyethylene 9 and 617, and oxidized polyethylene 680, on the viscosity of the pre-treated/upgraded bio-oils/bio-binders, (3) measuring the viscosity of the pre-treated/upgraded bio-oils/bio-binders using a rotational viscometer to determine the mixing and compaction temperatures for bio-oils, (4) using a dynamic shear rheometer (DSR) to determine the modified temperature for the rolling thin film oven (RTFO) that mimic the effect of short-term aging during construction, (5) using a DSR to measure the high and intermediate temperatures performance grade of the pre-treated/upgraded bio-oils/bio-binders, and (6) after

the pressure aging vessel (PAV) treatment of the RTFO pre-treated/upgraded bio-oils/bio-binders, the low temperature performance grade of the PAV-aged pre-treated/upgraded bio-oils/bio-binders is determined using a bending beam rheometer (BBR). Figure 1.1 shows the overall experimental plan for the physical, chemical and rheological testing.

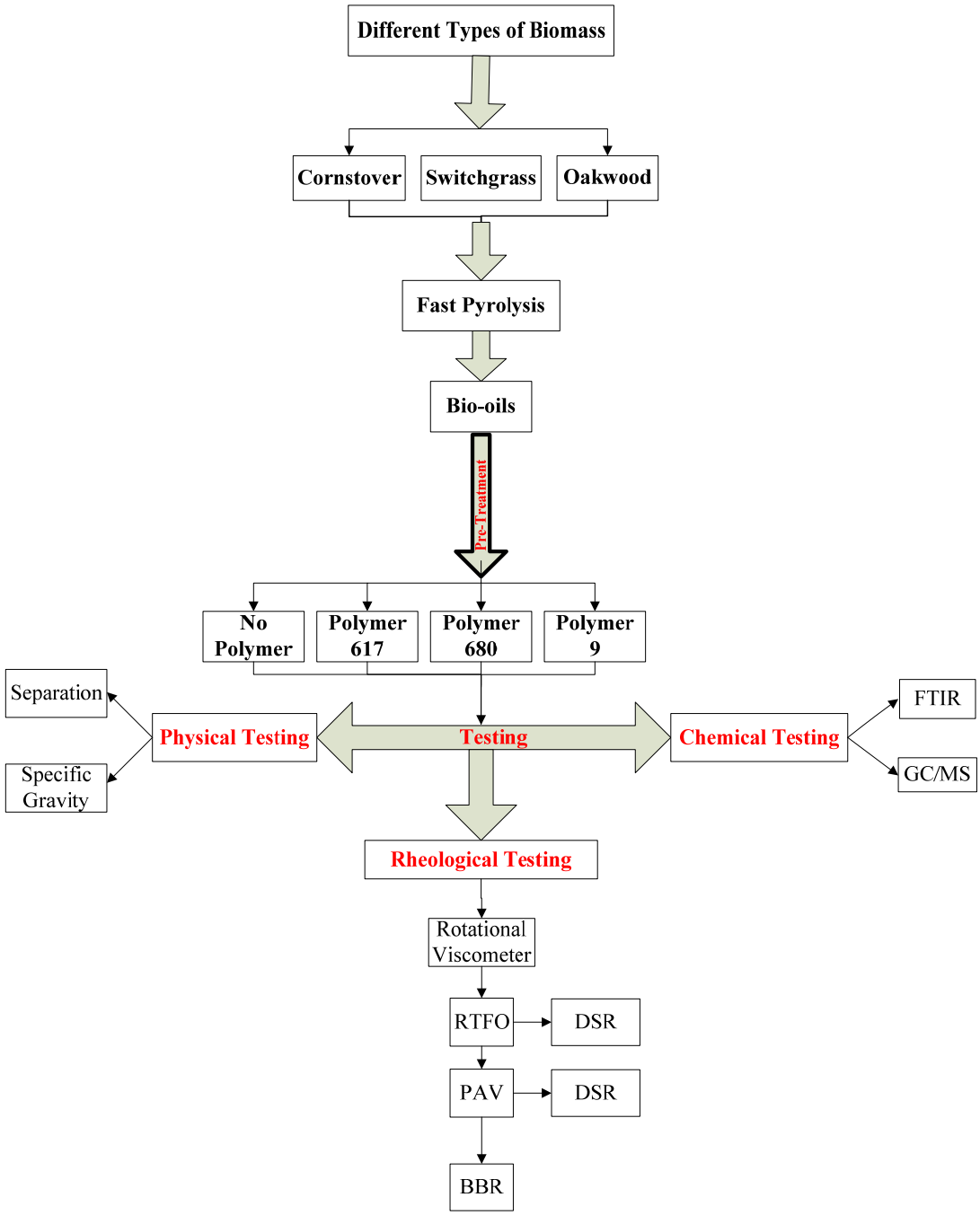


Figure 1.1. Overall Experimental Plan for Physical, Chemical and Rheological Testing

Hypotheses for Testing Results

Hypotheses were formulated regarding the different factors considered in the experimental plan based upon the testing required to determine the chemical, physical, and rheological characteristics of the developed bio-binders. The following hypotheses were analyzed:

- What are the pre-treatment temperatures and durations required to develop bio-binders from bio-oils?
- What is the amount of oxidation occurred in the untreated bio-oils and the pre-treated/upgraded bio-binders before and after the heat treatment?
- What are the temperatures and the durations of the rolling thin film oven (RTFO) test to mimic the short-term aging due to in-site construction for the different types of the developed bio-binders?
- What are the physical properties of the developed bio-binders?
- What are the possible types of chemical bonds (functional groups) presented in the pre-treated/upgraded unmodified bio-binders?
- What are the rheological properties of the different types of the pre-treated/upgraded bio-oils/bio-binders?
- What is the effect of the addition of different types of polymer modifiers with different percentages on the rheological properties of the different types of developed bio-binders?
- What is the resemblance between the rheological properties of the developed bio-binders and bitumen?
- What type of behavior is exhibited by the developed bio-binder?
- What are the mixing and compaction temperatures of the developed bio-binders?
- What are the performance grades of the developed bio-binders?

Content of this Report

Chapter 1 presents on overall view of the objectives of this report and the current state of practice for bio-oils. Chapter 2 discusses past research and investigations conducted that is related to utilizing the bio-oils as asphalt extenders or modifiers. Chapter 3 rationalizes and outlines the experimental plan and the procedures used to sample, prepare, and test the different types of bio-oils for this report. The determination of the temperature and the duration required for developing bio-binders from bio-oils are explored and investigated in Chapter 4. Chapter 5 represents the modifications of the Superpave standards and test criterion to comply with the properties of the developed bio-binders. The physical and chemical characterization of the developed bio-binders is summarized in Chapter 6. Chapter 7 includes the rheological characteristics of the developed bio-binders. The performance testing and the determination of the mixing and the compaction temperatures are listed and summarized in Chapter 8. Chapter 9 is concerned with the development of master curves for the developed bio-binders and comparing them with commonly used bitumen binders. Chapter 10 summarizes the overall conclusions of the experiments and tests along with the recommendations for future work that can be performed to better understand the development and characterization of bio-binders from bio-oils. Importantly, Chapter 10 includes an outline/protocol to optimize bio-oils product to be used as bio-binders in the pavement industry.

CHAPTER 2. LITERATURE REVIEW

Bio-Based Economy

The United States, nowadays, is prompting to establish a bio-based economy which generates energy from renewable organic matter rather than fossil fuels (Demirbas and Balat 2006). Biofuels have many advantages over fossil fuels as they are renewable, environmentally friendly, provide energy security, and present a great economic opportunity for the United States (Demirbas and Balat 2006). Bio-fuels can be classified as liquid or gaseous fuels. They are produced from plant matter and residues, such as agricultural crops, municipal wastes and agricultural and forestry by products (Demirbas and Balat 2006 and Mohan *et al.* 2006).

Background of Biomass

Biomass, which are agricultural and forestry residues, contains a significant amount of carbohydrates, e.g. cellulose and hemicelluloses. Bio-fuels are produced from biomass through biochemical or thermochemical processes. In general, carbohydrates are potential sources for production of bio-fuels and chemicals (Demirbas 2008). By hydrolysis processes, carbohydrates can be converted to sugars and then subsequently through fermentation, such as an anaerobic biological process; sugars are converted to bio-fuels by the action of microorganisms, usually yeast (Demirbas 2008).

Biomass is anything living matter on earth in which solar energy is stored. By the process of photosynthesis, plants produce biomass continuously. There are a large variety of agricultural products, which include but are not limited to straw, grasses, wood shavings, sawdust, roots, branches, leaves, and bark, that can be utilized to produce energy (Demirbas and Balat 2006). According to Goyal *et al.* (2006), biomass resources can be divided into two broad categories, e.g. natural and derived materials and then subdivided into three categories that can be listed as follows: (1) wastes that include but are not limited to agricultural production wastes, agricultural processing wastes, crop residues, mill wood wastes, urban wood-wastes, and urban organic wastes, (2) forest products that include but are not limited to wood, logging residues, trees, shrubs and wood residues, sawdust, bark, and (3) energy crops that include but are not limited to short rotation woody crops, herbaceous woody crops, grasses, starch crops (corn, wheat and barley), sugar crops (cane and beet),and oilseed crops (soybean, sunflower, safflower).

History of Bio-fuels

In the ancient times, the Egyptians used the biomass as a combustion fuel for cooking and providing warmth in houses. Nowadays, due to the promotion towards a bio-based economy, biomass, which is available in abundance and has low cost, has been converted to energy rich products using suitable processes (Boateng *et al.* 2007 and Goyal *et al.* 2006). Biomass is the single-largest renewable energy resource; it compromises about 47% of the total renewable energy consumption (Mohan *et al.* 2006).

Since the turn of the century, ethanol derived from agricultural crops, which is the main contributor in the current bio-economy, has been utilized as a fuel source (Demirbas and Balat 2006). Henry Ford was the pioneer who initiated the notion of designing an affordable vehicle that can be powered by a fuel derived from agricultural crops, e.g. corn (Demirbas and Balat 2006). Ethanol derived from corn has been used since 1930s. However, post World War II, due to the abundant and cheap supply of fuel, the interest of using derived fuels had been declining. In the 1970s, there were many reasons that led to the rising interest of using fuels derived from agricultural crops (McCready 2007). First, the interruptions of oil supply for the United States caused by the political strife in the Middle East and the Organization of Petroleum Exporting Countries (OPEC). Second, Federal and State tax incentives resulted in the renewal of the ethanol industry from production volumes of $10x10^6$ gallons in 1979 to $2.81x10^9$ gallons in 2003 (Bothast and Schlicher 2005). Third, ethanol derived from agricultural crops reduces the dependence of the United States on foreign oil (over 62% imported). Fourth, ethanol derived from agricultural crops had the opportunity to spur rural development by creating new jobs in economically depressed rural areas and small communities. Fifth, in 1990, the Clean Air Act Amendment was passed by the Congress which mandates the usage of oxygen source within the gasoline to reduce emissions (McCready 2007 and Gulati *et al.* 1997). Sixth, ethanol has a higher oxygen level than Methyl Tert-Butyl Ether (MTBE), which caused contamination of thirty percent of urban water supplies (Renewable Fuels Association 2004). Therefore, the utilization of renewable energy or fuel helps to displace toxic components of gasoline, and to reduce emissions of volatile organic compounds, carbon monoxide, nitrogen oxides, and other toxics (Bothast and Schlicher 2005 and Renewable Fuels Association 2004).

Because bio-fuels are CO_2/GHG neutral, they have many environmental advantages over fossil fuels (Mohan *et al.* 2006). Explicitly, bio-fuels have no SO_x emissions and 50% less NO_x than diesel oil. Thus, bio-fuels are cleaner and cause less pollution (Mohan *et al.* 2006). In the United States, transportation energy consumes about 63% of all fossil fuels used. About 97 % of this transportation energy is derived from nonrenewable petroleum resources (Mohan *et al.* 2006). The burning of these fossil fuels, which is the main contributor of carbon dioxide (about two-thirds of the global emissions), leads to serious environmental problems (Mohan *et al.* 2006). Due to the Kyoto agreement, the United States is obliged to reduce the carbon dioxide emissions to a level 7% below the 1990 emissions to reduce the greenhouse gas (GHG) (Mohan *et al.* 2006). According to a recent report from the U.S. Department of Energy's through Energy Information Administration (EIA), GHG emissions, in the United States, have grown at an average annual rate of 1.0 percent since 1990 (DOE/EIA-0573, 2008).

Current State of Bio-fuels

Recently, due to the necessity of finding another source of energy rather than fossil fuels, the economic availability and the environmental advantages, and the well developed technology of the production of bioethanol from crop-based substrates such as sugar cane juice and cornstarch, bioethanol is considered one of the important renewable fuels (Demirbas 2008).

As reported by Demirbas and Balat (2006), Brazil, the United States and the European Union have the largest three programs supporting the utilization of bio-fuels in the world. For instance, the corn based ethanol production in the United States is booming significantly; the ethanol

production totaled almost 2.8 billion gallons in 2003 and increased to around 7.2 billion gallons in 2008 with an additional 6.2 billion gallons of capacity under construction (Ethanol Fuel History 2008 and Demirbas and Balat 2006). Furthermore, as reported by Urbanchuk (2006), the ethanol production is expected to be approximately 9.8 billion gallons in 2015.

In Europe and the United States, bio-diesel, that is a bio-oil derived from vegetables oils, is gaining support, acceptance and market share (Demirbas and Balat 2006). For example, the production of bio-diesel has been increased considerably from zero in 1995 to more than 1.5 billion liters in 2003 in Europe (Demirbas and Balat 2006). Figure 2.1 shows the rapid increase of the world ethanol and biodiesel production as reported by Demirbas and Balat (2006). The main reason, which leads to this increase in the utilization of the bio-diesel, is the reduction of the emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons and particulate matter (Demirbas and Balat 2006).

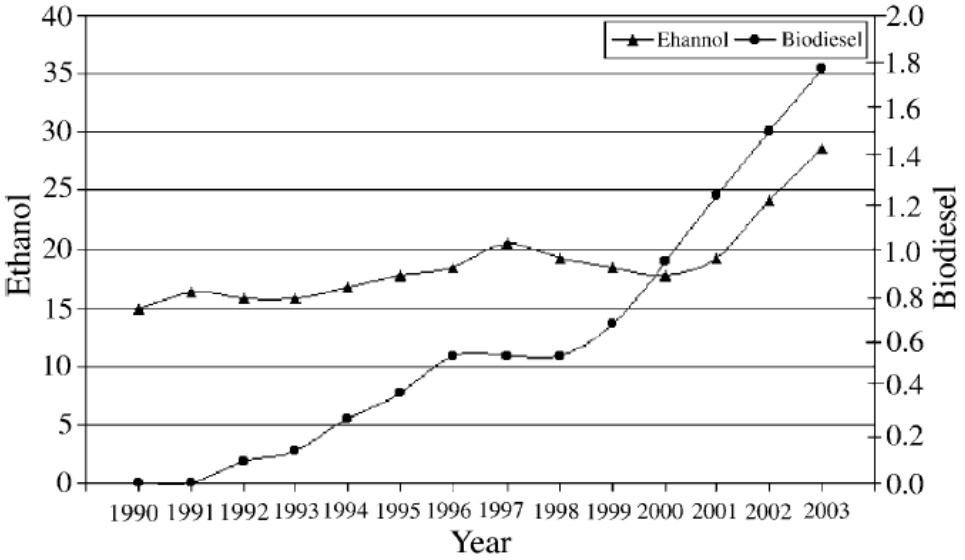


Figure 2.1. World Production of Ethanol and Bio-Diesel (Billion Liters), 1990-2003 (Adopted from Demirbas and Balat 2006)

During the last decade, the use of bio-fuels has increased to a total volume of approximately 30 billion in 2003 (Demirbas and Balat 2006). For example, ethanol production nowadays replaces gasoline that would require the use of 600,000 barrels of oil a day (Driving Ethanol 2009). Significantly, ethanol raises the demand for corn which benefits many economically depressed rural areas. Nowadays, there are more than 139 ethanol plants across the United States that produce 7.8 billion gallons of ethanol per year, with more than 60 plants under construction or expansion. Thus, U.S. ethanol production replaced about 228 million barrels of imported gasoline or crude oil (Driving Ethanol 2009). The ethanol industry contributes to the saving of approximately $45 million per day, generating a surplus of $1.2 billion to the Federal tax treasury, creating more than 238,000 jobs in all sectors of the economy and boosting U.S. household income by $12.3 billion (Driving Ethanol 2009).

Different Types of Ethanol Production

According to Bothast and Schlicher (2005), ethanol production produces many different co-products depending on the method of production. In the United States, there are two different methods employed to produce ethanol; dry mill (67%) and wet mill (33%) (Bothast and Schlicher 2005). Figure 2.2 shows a schematic diagram of the two different ethanol production methods. Most of the production plants in the United States are dry mill as they focus on the production of ethanol which in return maximizes the capital return (Bothast and Schlicher 2005). For example, approximately 2.8 gallons of ethanol and 17 lbs of dried distillers grains (DDG) are produced from every one bushel of corn (56 lbs) (Bothast and Schlicher 2005, and Iowa Corn 2006). Furthermore, dried distillers grains which are the main co-product of dry milling are usually used as livestock feed. Dry milling has many processes which can be summarized as follows; milling the corn kernel, liquefying the corn kernel to produce a mash, adding enzymes and yeast to produce ethanol and then distilling ethanol from the produced mixture (Bothast and Schlicher 2005).

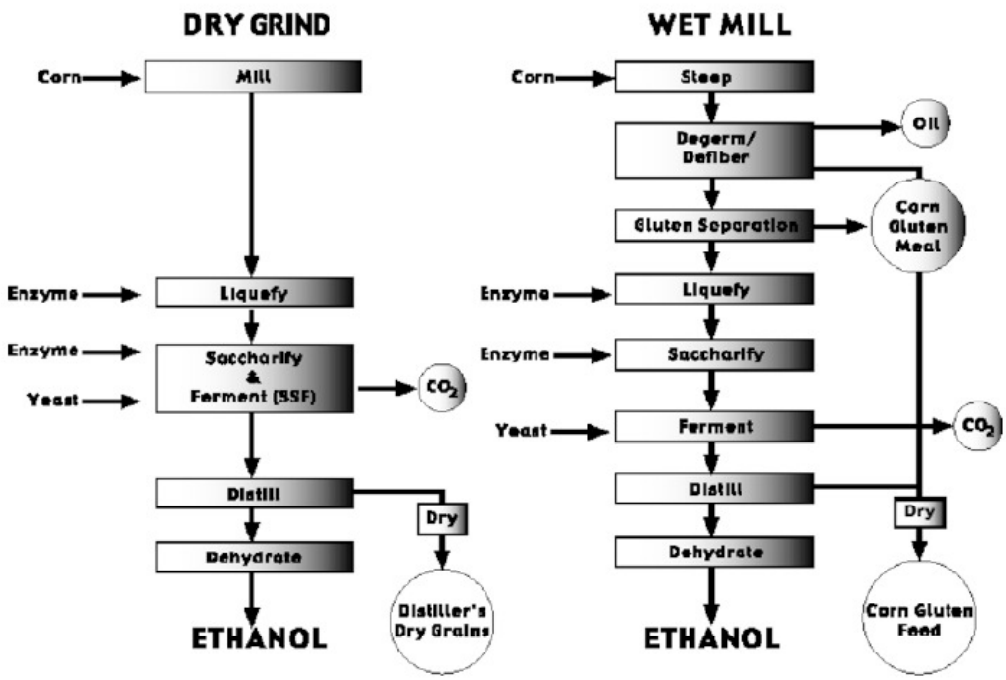


Figure 2.2. Schematic Diagram of Dry and Wet Mill Ethanol Production (Adopted from Bothast and Schlicher 2005)

Wet mill plants have different processes from dry mill; wet mill plants are considered biorefinary as they tend to separate the corn kernel into different components before the ethanol production (Bothast and Schlicher 2005, and Gulati *et al.* 1997). Every one bushel of corn kernel, that has approximately 70 percent of starch, produces approximately 2.5 gallons of ethanol, 1.6 lbs of corn oil, 2.6 lbs of gluten meal, and 13.5 lbs of gluten feed (Bothast and Schlicher 2005). Figure 2.3 shows the amount and the co-products produced by using the dry and wet mill processes. Different co-products are produced depending on the wet mills plants. Some of these co-products are not utilized in any other industry; therefore, more effort should be placed to discover new

uses and applications for these co-products. Utilizing the co-products is crucial for the success and profitability of the whole ethanol production industry (Bothast and Schlicher 2005 and Van Dam and DeKlerk-Engles 2005).

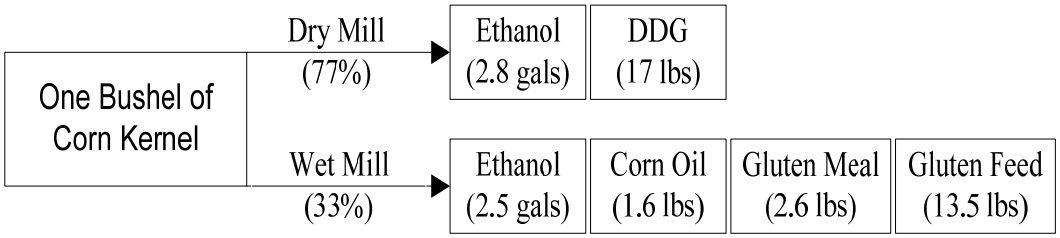


Figure 2.3. Conversion of Corn to Ethanol by Dry and Wet Mill

Most of the fibers which are contained in the outer hull of the corn kernel are composed of cellulose, hemicellulose, and lignin (Gulati *et al.* 1997). Nowadays, these fibers are used to produce corn gluten meal that is used as an animal feed source. Therefore, the price of the produced corn gluten varies with the supply and demand of the animal feed market (Bothast and Schlicher 2005). Subsequently, the ethanol production plants are not making a remarkable profit from the lignin-containing co-products. As a result, new uses for the co-products should be discovered to increase the margin of profits to the ethanol production plants (Cooper 2005). Employing the lignin-containing co-products as a chemical antioxidant or a bio-binder in the asphalt pavements could predominantly have mutual benefits on both industries.

Background of Bio-oils

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 and Oasmaa *et al.* 1999). In other words, it is the liquid produced from the rapid heating of biomass in vacuum condition (Oasmaa *et al.* 2005). Bio-oils have many synonyms that can be listed as follows: pyrolysis oil, pyrolysis liquid, bio-crude oil (BCO), wood liquid, wood oil, liquid smoke, wood distillates, and pyroligneous acid (Mohan *et al.* 2006 and Oasmaa *et al.* 2005). 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 (Mohan *et al.* 2006). 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 temperature (Mohan *et al.* 2006).

According to the literature review conducted by Mohan *et al.* (2006), there are many unusual attributes for the bio-oils because of the complexity and the redundancy of the chemical structure of the bio-oils. Even though the recovery of pure compounds from the complex bio-oils is technically and chemically feasible, it is uneconomic due to costs for recovery of the chemical and its low concentration in the oil as claimed by Demirbas and Balat (2006).

Bio-oils are derived from biomass contains oligomeric species that are derived mainly not only from lignin, but also from cellulose and hemicellulose. As decomposition rapidly occurs, oligomeric species may never be vaporized but simply "blown apart" into aerosols. Thus, these oligomeric species form as part of the aerosols and have various molecular weights (Mohan *et al.* 2006).

Extraction of Bio-oils by Pyrolysis

Since the oil crisis in the mid 1970s, considerable effort has been directed toward the development of processes for producing liquid fuels from biomass. According to Oasmaa *et al.* (1999), one of the most efficient methods for such conversion is pyrolysis. Historically, pyrolysis was used during the ancient Egyptians times as tar was produced for caulking boats and certain embalming agents (Mohan *et al.* 2006). By definition, pyrolysis of biomass is the thermal decomposition of the organic matter in the absence of oxygen to obtain solid, liquid, and gas products. Through pyrolysis of different sources of biomass, a wide range of fuels, solvents, chemicals, and other products can be produced (Demirbas 2008, Yaman 2004, and Demirbas 2000). There are different methods to convert different sources of biomass to bio-fuels or hydrogen as reported by Demirbas and Balat (2006). Table 2.1 shows the merits and demerits of each method.

Table 2.1. Merits and Demerits of Different Types of Pyrolysis*

Conversion process	Merits	Demerits
Steam gasification	Maximum product can be obtained	Significant gas conditioning is required
Fast pyrolysis	Bio-oil and chemicals are produced	Changes of catalyst deactivation
Solar gasification	High hydrogen yield can be obtained	Requires effective collectors
Supercritical fluid extraction	Products can be obtained without gasification	Selection of supercritical medium
Microbial fermentation	Wastewater can also be treated simultaneously	Selection of suitable microorganisms

*Adopted from Nath and Das 2003

As stated by Goyal *et al.* (2006), the pyrolysis process can be categorized as follows:

- Slow pyrolysis: Biomass is pyrolysied at slow heating rates (around 260°C/min). This leads to less liquid and gaseous product and more of char production.
- Flash pyrolysis: Flash pyrolysis is the process in which the reaction time is for only several seconds or even less time as the heating rate is very high. This requires special reactor configurations in which biomass residence times are only of few seconds. Two of appropriate designs are entrained flow reactor and the fluidized bed reactor. There are many types of flash pyrolysis designs which can be summarized as follows:
  a) Flash hydro-pyrolysis: it is flash pyrolysis conducted in hydrogen atmosphere at a pressure up to 20 MPa.
  b) Rapid thermal process: it is a particular heat transfer process with very short heat residence times (between 30 ms and 1.5 s). It is conducted at temperatures between 400

and 950°C where rapid de-polymerization and cracking of feed stocks takes place. Rapid heating eliminates the side reactions yielding products with comparable viscosity to diesel oil.

c) Solar flash pyrolysis: concentrated solar radiation can be used to perform flash pyrolysis.
d) Vacuum flash pyrolysis: in this process, pyrolysis is conducted under vacuum. It limits the secondary decomposition reactions, which in turn gives high oil yield and low gas yield.

- Catalytic biomass pyrolysis: Bio-oils obtained from biomass by slow, flash or fast pyrolysis processes cannot be directly used as transportation fuel due to the high oxygen and water content. Also, these bio-oils are found to be less stable and less miscible in conventional fuels. Thus, catalytic biomass pyrolysis is introduced to improve the quality of the oil produced. Various catalysts such as zeolites and basic materials were introduced with the biomass feed stock. The oil obtained by catalytic biomass pyrolysis does not require costly pre-upgrading techniques involving condensation and re-evaporation.
- Fast pyrolysis: 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). In other words, 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 and Mullen *et al.* 2008). Another detailed definition of fast pyrolysis is given by Mohan *et al.* (2006) which describes fast pyrolysis 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 and after cooling and condensation of these vapors and aerosols, a dark brown mobile liquid (bio-oils) is formed.

When the organic matter is biomass, the produced oils are named bio-oils. Generally, fast pyrolysis is used to obtain high-grade bio-oil. Organic biomass consists of biopolymers, e.g. cellulose, hemicelluloses, and lignin. Therefore, fast pyrolysis of lignocellulosic biomass leads to extensive depolymerization and fragmentation of these biopolymers (Mullen *et al.* 2008). Due to the different sources of biomass, the amount of production of the liquid bio-oils, solid char and noncondensable gases vary. For example, fast pyrolysis processes produce about 60-75 wt % of liquid bio-oil, 15-25 wt % of solid char, and 10-20 wt % of noncondensable gases (Mohan *et al.* 2006).

Some researchers reported that bio-oils produced from fast pyrolysis have some potential problems. Mullen *et al.* (2008) reported that bio-oils produced from bio-oils have high oxygen and water content which leads to poor volatility, high viscosity, and corrosiveness. In addition, bio-oils have hundreds of various oxygenated organic compounds that are highly reactive leading to instability problems and an increase in viscosity over time (Mullen *et al.* 2008).

Mohan *et al.* (2006) reported that almost 200 intermediate products formed during the pyrolysis of biomass and cellulose is the major constituent. Despite that wide variety of products, most of these products, such as bio-oil, solid char, and gases can be re-used in different ways. The amount and distribution of the solid, liquid and gas formed during the pyrolysis depends on the process variables, such as type of biomass and catalytic process and temperature (Mohan *et al.* 2006).

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 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 palletizing and briquetting of combustible organic waste materials, or an adhesive material. In addition, the char can be utilized in many industrial usages including use as a solid fuel in boilers, as brickets that are mixed with biomass to be used as high efficiency fuel in boilers, as a raw material to produce activated carbon or carbon-nano-tubes, or in the gasification process to obtain hydrogen rich gas by thermal cracking (Goyal *et al.* 2006). 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).

Fast pyrolysis has four main processes that can be summarized as follows: (1) very high heating and heat transfer rates, (2) a carefully controlled pyrolysis reaction temperature (in the range of 425-500°C), (3) short vapor residence times (typically < 2s), and (4) rapid cooling of pyrolysis vapors and aerosols to produce bio-oils (Mohan *et al.* 2006).

It initially starts with slow heating rates, and then involves a rapid heating rate of biomass, that can reach up to 300°C/min, but not as fast as flash pyrolysis. According to Goyal *et al.* (2006) and Luo Z. *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: feed drying, 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 as reported by Mohan *et al.* (2006).

In this research, the bio-oils were extracted from different biomass materials using an existing 25kWt fast pyrolysis system developed at Iowa State University by CSET, shown in Figure 2.4. The different biomass feedstocks were oakwood, switchgrass, and cornstover. The pilot unit consists of a 16.2 cm diameter fluidized bed reactor, a burner to externally heat the reactor, a two-stage auger to feed the solid, two cyclones to remove particulate matter, and a vapor-condensing system consisting of four condensers and an electrostatic precipitator. The system can process 6-10 kg/h of solid feed.

The separation of bio-oils into multiple fractions was conducted using a fractionation condenser system which facilitated the selection of bio-oil fractions that would be optimal for being used as a pavement binder. As an example,

Table 2.2 shows the properties of bio-oil fractions collected from fast pyrolysis of cornstover. It can be seen that those bio-oil fractions have significantly different properties, especially in water and lignin contents. Bio-oil fractions collected from condensers #1 and #2 and ESP have high lignin content and low water content, which make them most suitable for using as pavement binders.

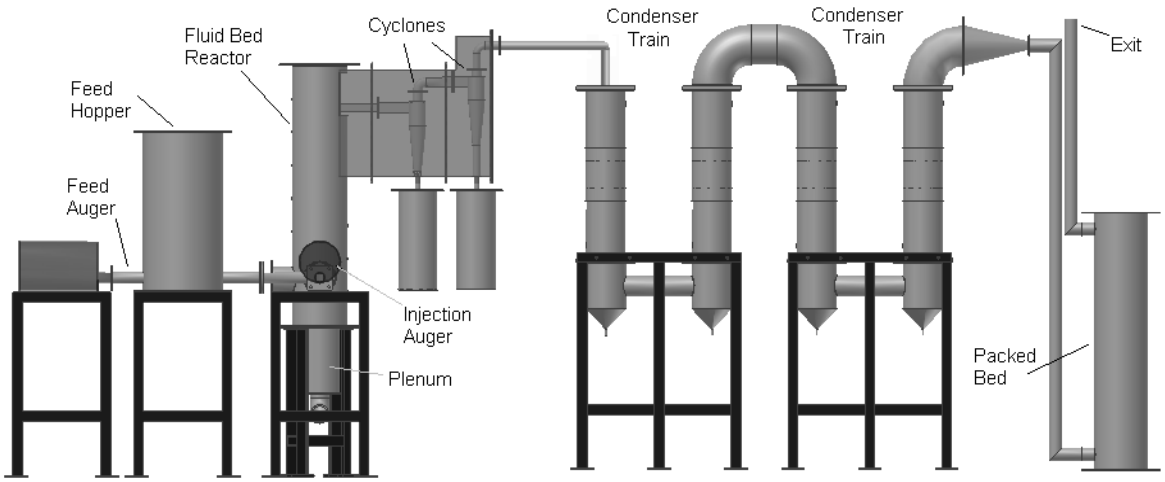


Figure 2.4. Schematic Diagram of the 25kWt Fast Pyrolysis Reactor with Staged Condensation Unit at CSET

Table 2.2. Properties of Bio-oils Fractions Collected from Fast Pyrolysis of Cornstover

Property	**Cond. 1**	**Cond. 2**	Cond. 3	Cond. 4	**ESP**
Fraction of total oil (wt%)	**6**	**22**	37	15	**20**
pH	**-**	**3.5**	2.7	2.5	**3.3**
Viscosity @40°C (cSt)	**Solid**	**149**	2.2	2.6	**543**
Lignin Content (wt%)	**High**	**32**	5.0	2.6	**50**
Water Content (wt%)	**Low**	**9.3**	46	46	**3.3**
C/H/O Molar Ratio	**1/1.2/ 0.5**	**1/ 1.6/ 0.6**	1/ 2.5 / 2	1/ 2.5 /1.5	**1/1.5/ 0.5**

Different Types of Bio-oils

In this research, three different types of bio-oils were used to study the applicability of developing bio-binders for usage as pavement materials. The different bio-oils were extracted from three different types of biomass, e.g. oakwood, switchgrass, and cornstover. Demirbas (2008) defined stover as the above-ground portion of the corn plant which consists of stalk (including tassel), leaves, cob, husk (and silks). As reported by Demirbas (2008), because of the abundance and proximity to existing grain-to-ethanol conversion facilities of cornstover, it can be considered as a strategic feedstock for bio-fuel products. In addition, cornstover has a special interest due to the large quantities and inexpensive costs. Approximately 19–26 billion liters of ethanol per year can be produced from about 60–80 million tons/yr of dry cornstover (Kadam and McMillan 2003). An increase in the utilization of cornstover as an energy crop has been increased due to the recent developments in converting cellulose and hemicellulose to glucose and xylose through acid hydrolysis and subsequently to ethanol through fermentation (Demirbas 2008, Spindler *et al.* 1989, and Barrier *et al.* 1986). However, the capability of ethanol production from wood and other lignocellulosics is much higher than that from corn as reported by Demirbas and Balat (2006). In addition, switchgrass, which is a perennial crop, is considered a great potential energy crop. As reported by Mullen *et al.* (2008), switchgrass plants do not requires annual reseeding; therefore, they require lower agricultural inputs (e.g. fertilizer and pesticides).

Bio-oils derived from wood have specific oxygenated compounds that are present in relatively large amounts (Demirbas and Balat 2006). A large fraction of the bio-oils is the phenolic fraction which consists of relatively small amounts of phenol, eugenol, cresols and xylenols and much larger quantities of alkylated (poly-) phenols (water insoluble pyrolytic lignin). This phenolic fraction has showed good performance as an adhesive for waterproof plywood as stated by Demirbas and Balat (2006). The yield products of bio-oils derived from woody biomass can be typically summarized as follows: organic liquid (61-68%), gaseous materials (8-12%), char (6-9%), and water (10-14%) (Demirbas and Balat 2006). The elemental analysis for the wood derived bio-oils can be typically summarized as follows as weight percentage of moisture free: carbon (56.8-65.9), hydrogen (5.8-7.9), oxygen (28.7-38.3), nitrogen (0.07-0.41), sulfur (0.00-0.03), and ash (0.02-0.24) (Demirbas and Balat 2006).

As a result of the high oxygen content, the energy content of the bio-oils is about half of that crude oil. It is also plagued by poor volatility, high viscosity, and corrosiveness. Raw bio-oil can contain between 10 and 30% by weight of water and hundreds of various oxygenated organic compounds. Some of these components are highly reactive and can cause pyrolysis oil to be unstable, resulting in higher water content and an increase in viscosity over time as declared by Mullen *et al.* (2008).

Chemical Composition of Bio-oils

The chemical composition, and hence the physical properties, of bio-oils depends on the feedstock, pyrolysis condition, and product collection methods (Mullen *et al.* 2008 and Garcia-Perez *et al.* 2005). The chemical composition of bio-oils is a crucial factor as it gives insights into quality and stability issues as emphasized by Mullen *et al.* 2008. Bio-oils have five different compounds that can be summarized as follows: (1) hydroxyaldehydes, (2) hydroxyketones, (3) sugars and dehydrosugars, (4) carboxylic acids, and (5) phenolic compounds (Piskorz *et al.* 1988). Based on the analysis conducted by many researchers, Table 2.3 displays the chemical composition of the different bio-oils. In addition, the elemental analysis of the bio-oils is a significant factor to be studied to properly determine and predict the characteristics of bio-oils. Table 2.4 lists the elemental analysis of the different bio-oils based on the available data on the literature review.

Table 2.3. Chemical Composition of Bio-oils*

Wt (%)	Cornstover	Oakwood/Oak Flour	Switchgrass
Cellulose	40	40	41
Hemicellulose	30	26	36
Lignin	14	16	20

*Adopted from Mohan *et al.* 2008 and Mullen *et al.* 2008

Table 2.4. Elemental Analysis of Bio-oils*

Wt (%)	Cornstover	Oakwood/Oak Flour	Switchgrass
C	46.50	60.50	47.47
H	5.90	6.50	6.96
O	46.20	34.60	45.19

*Adopted from Mohan *et al.* 2008 and Mullen *et al.* 2008

The three major structural chemical components of biomass which have high molar masses are carbohydrate polymers and oligomers (65%-75%) and lignin (18%-35%) (Mohan *et al.* 2006). These chemical components consist of cellulose (which is called polymer glucosan), hemicelluloses (which are also called polyose), lignin, organic extractives, and inorganic minerals (as shown in Figure 2.5). The weight percent of cellulose, hemicelluloses, and lignin products varies depending on the biomass (Mohan *et al.* 2006). Generally, in biomass, cellulose is the largest fraction followed by hemi-cellulose, lignin, ash, etc. as stated by Goyal *et al.* (2006).

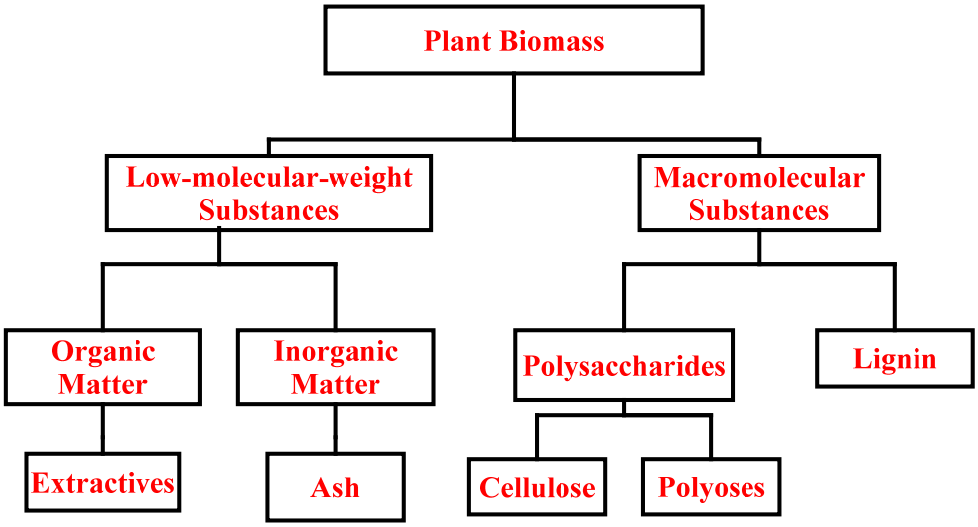


Figure 2.5. Chemical Structure of Bio-oils (Adopted from Mohan *et al.* 2006)

Cellulose

Cellulose, which is a high molecular weight linear polymer, compromises about 40-50% of biomass. Cellulose forms long chains that are bonded to each other by a long network of hydrogen bonds (Figure 2.6). Thus, cellulose is the main contributor to strength. Upon removal of water, glucose anhydride is formed and polymerized into long cellulose chains that contain 5000-10000 glucose units with an average molecular weight of around 100,000. The basic repeating unit of the cellulose polymer is called a cellobiose unit that consists of two glucose anhydride units as shown in Figure 2.6 (Mohan *et al.* 2006). Degradation of cellulose occurs at 240-350°C to produce anhydrocellulose and levoglucosan as reported by Mohan *et al.* (2006).

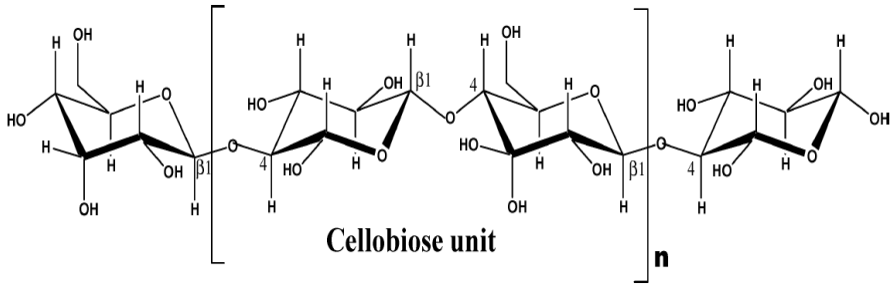


Figure 2.6. Chemical Structure of Cellulose
(Adopted from Mohan *et al.* 2006)

Cellulose is tending to form crystals using extensive intramolecular and intermolecular hydrogen bonding which makes it completely insoluble in normal aqueous solutions (as shown in Figure 2.7). In addition, these crystalline are the main factor that helps to resist thermal decomposition better than hemicelluloses. According to Mohan *et al.* (2006), when the water of hydration in amorphous regions and the free water in the biomass get heated rapidly, the structure of cellulose gets disrupted leading to a steam explosion-like process prior to chemical dehydration of the cellulose molecules.

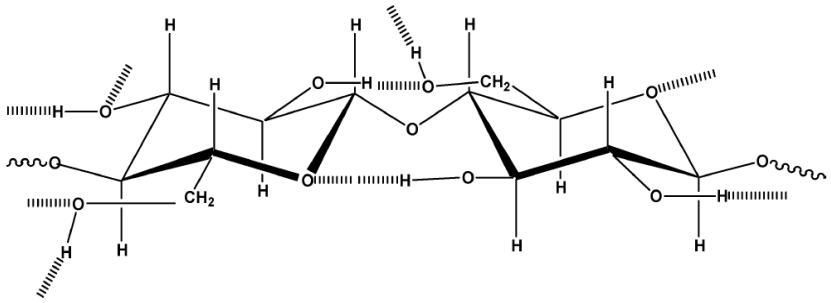


Figure 2.7. Interachain and Interchain Hydrogen-Bonded Bridging
(Adopted from Mohan *et al.* 2006)

Hemicellulose

Hemicellulose is the second major chemical constituent and it is known as polyose. By definition, hemicellulose is a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid and galacturonic acid residues as shown in Figure 2.8 (Mohan *et al.* 2006). Compared to cellulose, the average molecular weight of hemicellulose is around 30,000, so it exhibits lower molecular weights. For example, the number of repeating saccharide monomers is only 150, compared to the number in cellulose (5000-10000). In addition, the decomposition of hemicelluloses occurs at temperatures of 200-260°C, and gives rise to more volatiles, less tars, and less chars than cellulose. Also, cellulose has only glucose in its structure, while hemicellouse has a heteropolysaccharide makeup and some contain short side-chain "branches" pendent along the main polymeric chain as stated by Mohan *et al.* (2006). In other words, hemicelluloses that are derived mainly from chains of pentose sugars occur in much shorter molecule chains than cellulose (Demirbas 2008).

Importantly, hemicelluloses act as the cement material holding together the cellulose micelles and fiber as reported by Demirbas (2008).

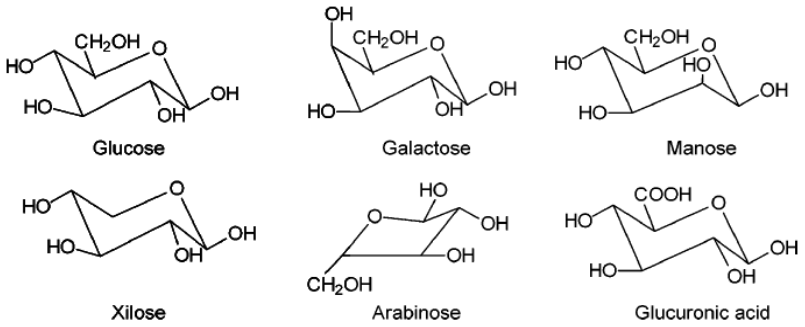


Figure 2.8. Main Components of Hemicellulose
(Adopted from Mohan *et al.* 2006)

Lignin

The third chemical component is lignin, which is an amorphous cross-linked resin with no exact structure. According to the definition given by Brauns (1952), lignin is not a constitutionally defined compound, but rather a collective term for groups of high molecular amorphous compounds that are chemically closely related. Most fibrous plants contain large amounts of lignin. Worldwide, lignin is the second most abundant biological polymer next to cellulose (Dizhbite *et al.* 2004). Trees, grasses, and many agricultural plants contain large amounts of lignin in the plants' cell walls.

Lignin is an extremely complex polymer that originates from the plant kingdom (Glasser and Sarkanen 1989 and Brauns 1952). Due to its complexity, it can be defined or described in many ways that can be summarized as follows: (1) it is a macromolecule, which consists of alkyl phenols and has a complex three-dimensional structure (Demirbas 2008), (2) it is an amorphous compound with no set chemical formula, but its general structure can be illustrated as shown in Figure 2.9, (3) it is a hydrocarbon that consists mainly of carbon, hydrogen, and oxygen (Brauns 1952), and (4) it can technically be defined as the "incrusting material of a plant built mainly from phelypropane building stones, which are unhydrolyzable by acids, readily oxidizable, soluble in hot alkali and bisulfate, and readily condenses with phenols and thio compounds" (Brauns 1952).

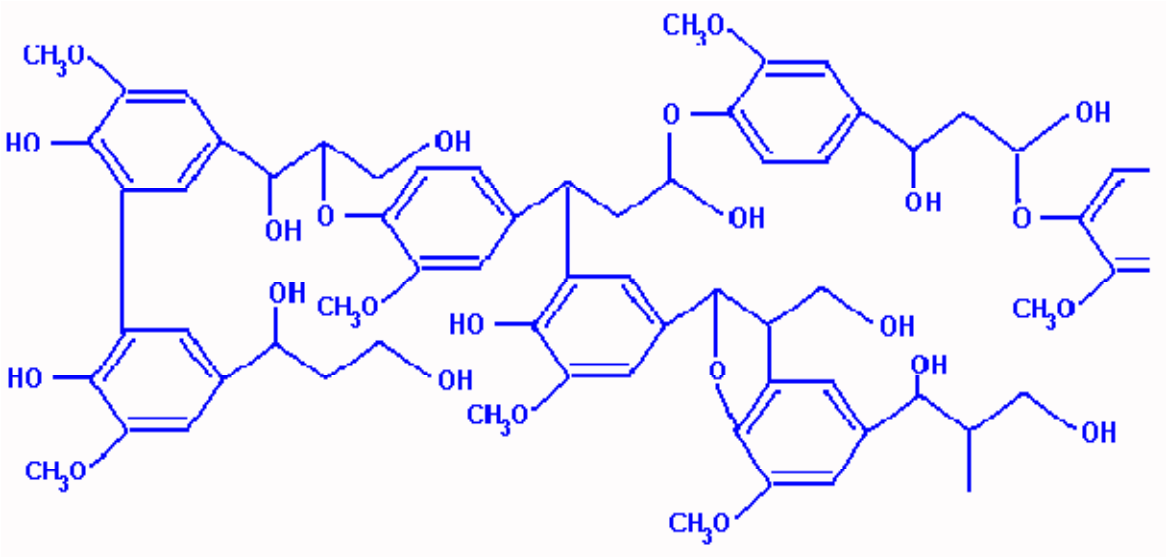


Figure 2.9. Chemical Structure of Lignin
(Adopted from McCready 2007)

The three-dimensional structure can be further described as highly branched, polyphenolic substance that consists of an irregular array of variously bonded "hydroxy-" and "methoxy-"substituted phenylpropane units as shown in Figure 2.10 (Mohan *et al.* 2006). These three general monomeric phenylpropane units exhibit the *p*-coumaryl, coniferyl, and sinapyl structures.

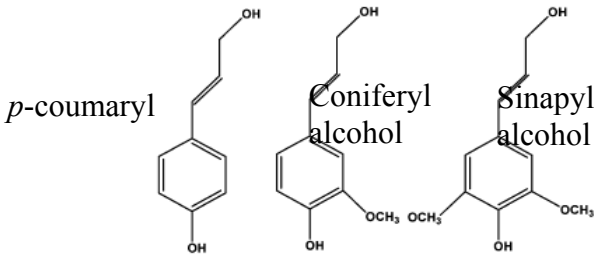


Figure 2.10. Main Structure of Lignin
(Adopted from Mohan *et al.* 2006)

The chemical structure of lignin is highly aromatic in nature with many randomly attached methoxyle and hydroxyl groups. Lignin can also contain aromatic hydrogen atoms, carbonyl groups, and aliphatic double bonds. This illustrates the complex chemical structure of lignin. Through thermal decomposition of lignin above 252°C, free phenoxyl radicals are formed then subsequently form a solid residue through condensation or repolymerization (Demirbas 2008). Lignin also has complex physical and chemical properties that vary with plant source, growth conditions, and extraction mechanism as reported by Dizhbite *et al.* (2004).

Lignin has significant roles in biomass which are binding for the agglomeration of fibrous cellulosic components and providing a shield against the rapid microbial or fungal destruction of the cellulosic fibers (Mohan *et al.* 2006). One key chemical property that is evident from all

lignins is its ability to act as an antioxidant. The antioxidant effects of lignins are derived from the scavenging action of their phenolic structures on oxygen containing free radicals (Dizhbite *et al.* 2004). In other words, lignins contain a large amount of phenolic groups, making them an effective antioxidant as emphasized by Boeriu *et al.* (2004) and Dizhbite *et al.* (2004). Phenolic structures are benzene rings with one or more attached hydroxyl groups. Benzene rings are six carbon structures with each carbon sharing a single and double covalent bond to another carbon. The ability of phenolic compounds to be antioxidants is the functional groups ability to neutralize free radicals (Boeriu *et al.* 2004, Dizhbite *et al.* 2004, Glasser and Sarkanen 1989). Free radicals are known to actively break down substances by breaking apart the substance's chemical structure. Phenols can neutralize a free radical by either donating a proton or an electron as reported by Dizhbite *et al.* (2004). Because of its structure, phenols are able to do both while remaining relatively stable. There are many factors that can affect the antioxidant ability of lignin. The source of biological origin is the most important factor in determining the lignin structure as reported by Dizhbite *et al.* (2004).

McCready and Williams (2008) utilized different lignin fractions collected from fast pyrolysis of cornstovers as an antioxidant agent. They blended different types of lignin fractions with different asphalt binders to determine the effect of lignin in asphalt binders. They concluded that the addition of lignin fractions led to a stiffening effect that vary upon the type and amount of co-products and the temperature of blending (McCready and Williams 2008). In addition, they reported that the high temperature properties have been positively affected, but the intermediate and low temperature properties have been negatively affected. However, they concluded that the performance grade of the asphalt binders with lignin co-products has been increased and widened because the intermediate and low temperature properties were slightly affected (McCready and Williams 2008).

Each plant is biologically and chemically different; therefore, the lignin obtained after extraction will be different. The extraction method is also very important in determining the lignin's antioxidant ability. Lignins can be extracted from the plant material by chemicals such as ethanol, acetone, acetic acid, methanol and propanol (Dizhbite *et al.* 2004). Each extraction method will produce a slightly different lignin, with each lignin having slightly different antioxidant ability. Depending on the extraction or isolation technology used to isolate them, the chemical of lignins vary and thus physical properties as reported by Mohan *et al.* (2006). Lignin decomposes when heated at 280-500°C; therefore, lignin is more difficult to dehydrate than cellulose or hemicelluloses. Unlike pyrolysis of cellulose, lignin pyrolysis produces more residual char as stated by Mohan *et al.* (2006).

Inorganic Minerals

After pyrolysis, biomass has a small inorganic/mineral content that ends up in the pyrolysis ash (Mohan *et al.* 2006). For example, these mineral components are potassium "K", sodium "Na", phosphorus "P", calcium "Ca" and magnesium "Mg". Nowadays, there is no standardized method or procedure to accurately determine the particle size distribution of solids in pyrolysis liquid as reported by Oasmaa *et al.* (2005).

Chemical Properties of Bio-oils

Mohan *et al.* (2006) reported that the chemistry of bio-oils is complex; thus, a complete chemical characterization is difficult or almost impossible. The complexity of chemical characterization or analysis resulted from the presence of high molecular weight of phenolic species from lignin decomposition (Mohan *et al.* 2006). In addition, the fragmented oligomeric products exist with different numbers of phenolic and carboxylic acids, and hydroxyl groups as well as aldehyde, alcohol, and ether functions. Thus, phenolic species exist as different hydrogen-bonded aggregates, micelles, droplets and gels. Due to the complexity of the chemical structure and the broadness of chemical properties of bio-oils, only few chemical properties are studied hereafter.

Corrosiveness

Bio-oils have pH values ranges between 2-3 and an acid number of 50-100 mg KOH/g due to the existence of substantial amounts of organic acids, mostly acetic and formic acid. Due to that, the bio-oils are corrosive to common construction materials such as carbon steel and aluminum, but not stainless steel as reported by Oasmaa *et al.* (1999). The elevated temperature and the high content of water lead to the increase of the corrosiveness effect (Oasmaa *et al.* 1999).

Distillation

Bio-oils contain substantial amount of nonvolatile materials such as sugars and oligomeric phenolics, besides water and volatile organic components. Also, during distillation, the slow heating of the bio-oils results in polymerization of some reactive components as stated by Oasmaa *et al.* (1999). Consequently, the oils start boiling below 100°C but the distillation stops at 250-280°C leaving 35-50% of the starting material as residue. Thus, it is apparent that bio-oils could not be used for applications requiring complete evaporation before combustion. Since the temperature associated on the pavement industry is between 100°C and 165°C, the bio-oils can be studied to be utilized as a bio-binder as an alternative to pavement materials.

Homogeneity

Most biomass oils seem to be homogeneous, though some, especially those produced from feedstocks rich in extractives, can have a frothy top layer, which usually represents less than 10% of the oil as reported by Oasmaa *et al.* (1999). In addition, microscopic observation of oil samples reveals black solid particles suspended in the liquid. These particles are mostly pyrolysis char, but fine sand or other heat transfer medium entrained from the reactor may also be present. Presence of char also seems to catalyze reactions leading to the increase of viscosity of the bio-oils and, eventually, formation of gummy tars (Oasmaa *et al.* 1999).

Water Content

Water in bio-oils is present due to the original moisture in the feedstock and the dehydration reactions occurring during pyrolysis. Thus, the water content varies between a range of 15 and 30%, depending on the feedstock and process conditions. At this concentration, water is

generally miscible with the oligomeric lignin-derived components because of the solubility effect of other polar hydrophilic compounds, i.e. low-molecular-weight acids, alcohols, hydroxyaldehydes, and ketones, which are originating from the decomposition of carbohydrates (Oasmaa *et al.* 1999). In addition, bio-oils are derived from biomass with 25% by weight water, which cannot readily be separated, and a large content of oxygen (almost 45-50%), which is the primary reason for the difference in the properties and behavior between hydrocarbon fuels and biomass bio-oils (Mohan *et al.* 2006). Although the pyrolysis liquid is called "bio-oil", it is actually different from liquid hydrocarbons, because of its high polarity and hydrophilic nature as claimed by Mohan *et al.* (2006).

The bio-oils' properties, which are related to its utilization as a bio-fuel, are affected positively and negatively due to the presence of water (Oasmaa *et al.* 1999). Negatively, it contributes to the increase of ignition delay and the decrease of combustion rate. Positively, it improves bio-oil flow characteristics (reduces the oil viscosity), which is beneficial for combustion (pumping and atomization).

Molecular Weight

Bio-oils consist of different size molecules, ranging from water to oligomeric phenolic compounds. Thus, their average molecular weight varies depending on many factors which includes but are not limited to, biomass used, reactor type, heating rate, residence time, particle size, pyrolysis temperature, vapor post-treatment, and the age and storage conditions of the bio-oils (Mohan *et al.* 2006 and Oasmaa *et al.* 1999). Precisely, weight-average molecular weight ranges from 370 to 1000 g/mol. Molecular weight is strongly related to important physical properties such as volatility and viscosity of the bio-oils. The continuous liquid phase stabilizes a discontinuous phase that is largely composed of pyrolytic lignin macromolecules (Mohan *et al.* 2006). Due to the presence of hydrogen bonding and the formation of nanomicelle and micromicelle, microemulsion stabilization is attained as reported by Mohan *et al.* (2006).

Oxidation and Aging

Bio-oils compounds, e.g. cellulose, hemicellulose, and lignin, can react with each other to form larger molecules. The main chemical reactions observed can be summarized as follows: (1) polymerization of double-bonded compounds (Oasmaa *et al.* 1999), and (2) etherification and esterification occurring between hydroxyl, carbonyl, and carboxyl group components which produce water as a by-product (Oasmaa *et al.* 1999 and Czernik *et al.* 1994). Due to these reactions, physical properties of bio-oils are changing slowly with time; therefore, these slow reactions are called "aging". Aging can lead to the increase of viscosity with a corresponding decrease of volatility. Generally with the increase of water content, the viscosity of the bio-oils decreases. However, the observed water release due to aging is rather small and its effect is overcompensated by the increase in average molecular weight of the bio-oil. Therefore, the rate of viscosity increase, which is directly related to the average molecular weight, may be a measure of the aging rate as emphasized by Oasmaa *et al.* (1999).

The growth of molecular weight can be also recognized as an increase in the amount of water-insoluble fraction, i.e. lignin derived material. The aging rate depends on many factors that can

be listed as follows: the oil composition (the type of feedstock), on pyrolysis conditions, and on the efficiency of solid removal and product collection. However, the most important factor is the temperature, which affects the rate of aging exponentially as reported by Oasmaa *et al.* (1999).

Phase Stability

Bio-oils can be considered as mixtures of water, water-soluble organic compounds and water-insoluble materials (oligomeric). As aforementioned, the ratio of these fractions varies for the different types of bio-oils, depending on the feedstock and the process condition. Generally, the lignin derived oligomers account for 30-40% of the bio-oil while water concentration ranges from 15 to 30%. In addition, due to the presence of polar carboxyl and hydroxyl compounds, bio-oils are usually single-phase liquids (Oasmaa *et al.* 1999). A high-quality bio-oil can be defined as the one which will remain as a homogeneous single-phase liquid for a minimum of sixth month's storage at room temperature; while, the poor-quality bio-oil is the one which separates into two or more phases during six months of storage at room temperature as defined by Oasmaa *et al.* (2005). The stability of the bio-oils is measured as an absolute increase in its viscosity. In the viscosity test, the bio-oil is kept at 80°C for 24 hours and the increase in viscosity (measured at 40°C) is determined (Oasmaa *et al.* 1997, 2001, and 2005).

However, phase separation can take place for several reasons that can be summarized as follows: (1) higher water and/or lignin-derived material concentrations, (2) a long-term storage of the bio-oils, and (3) high temperature through the pyrolysis process (i.e. above 600°C). For instance, at elevated temperatures, significant amounts of cellulose-derived compounds (hydrophilic) decompose, while lignin-derived compounds (aromatic) survive (Oasmaa *et al.* 1999). Thus, the main causes for the instability and bad odor of pyrolysis liquids are the presence of water, which is the main cause for phase-separation, and some light compounds (Oasmaa *et al.* 2005). Therefore, the removal of water and organics from the bio-oils lead to an increase in viscosity and flash point and an improvement in stability of the bio-oils. This can be done by simultaneous removal of reactive volatile aldehydes and ketones which contribute in the aging reactions as reported by Oasmaa *et al.* (2005). It has been observed that the stability of the pyrolysis liquid is improved when the light compounds, which participate in the aging reactions, are removed (Oasmaa *et al.* 2005).

Physical/Rheological Properties of Bio-oils

Due to the complexity of the chemical structure of bio-oils as aforementioned, it is extremely difficult to use chemical analyses to characterize performance. Thus, physical property measurements can be considered as the primary means of studying the applicability and the reliability of the utilization of bio-oils as bio-binders.

As reported by Garcia-Perez *et al.* (2008), the physical state of bio-oils can be described as follows: "The multiphase complex structure of bio-oils can be attributed to the presence of char particles, waxy materials, aqueous droplets with different natures, and micelles formed of heavy compounds in a matrix of hollocellulose-derived compounds and water." In addition, bio-oils comprise aldehydes, ketones, and other compounds that may react via condensations to form larger molecules during storage, handling, or transportation (Mohan *et al.* 2006). Therefore,

these reactions lead to the undesirable changes in physical properties. For example, viscosity and water content can increase, whereas the volatility will decrease (Mohan *et al.* 2006). As reported by Czernik *et al.* (2004), this is analogous to the behavior of asphaltenes contained in petroleum by some means.

The physical characteristics of bio-oils can be summarized as follows: (1) the density of the bio-oil is about 1200 kg/m^3 which is higher than the original biomass, (2) the viscosity of the bio-oil varies from 25 cPoise up to 1000 cPoise depending on the water content, the amount of light compounds and the aging (Demirbas and Balat 2006), and (3) the water content in bio-oils ranges typically between 14–33% by weight; this water cannot be removed by conventional methods like distillation as phase separation may occur above certain water contents (Demirbas and Balat 2006).

Airey *et al.* (2008) stated that the characterization of the rheological properties of the materials is given primary emphasis in the measurement of physical properties of pavement binders, i.e. bitumen. Likely, rheological properties play a significant role in describing the behavior of bio-oils as reported by W.S. Wan Nik *et al.* (2006). Measuring the rheological properties is useful to determine behavioral and predictive information for bio-oils as well as knowledge of the effect of processing, formulation changes and aging phenomena (W.S. Wan Nik *et al.* 2006). As a result, it is important to have theoretical knowledge as related to rheological aspects.

Definition of Rheology

As stated by Ferry (1980), the word "rheology" is derived from the Greek words "ρεω" and "λογοσ" which translate literally as "to flow" and "science"; therefore, rheology literally means "the study or the science of the flow". In other words, rheology is the study of the deformation or flow properties of materials, whether in liquid, melted or solid form, in terms of the materials' elasticity and viscosity (Airey *et al.* 2008 and Barnes *et al.* 1989).

Pavement Performance Related to Rheological Properties

There are some pavement distresses which are related to the rheological properties of a pavement binder (Roberts *et al.* 1996). Therefore, investigating the rheological properties of a pavement binder is very important in order to determine the pavement distresses and hence to predict and evaluate the pavement performance. The pavement distresses include but are not limited to raveling, cracking, rutting and stripping (Roberts *et al.* 1996). These pavement distresses are occurring due to many factors, therefore, only the factors that are related to the pavement binder are discussed in this section.

Raveling

Raveling, by definition, is the progressive separation of aggregate particles in a pavement from the surface downward or from the edges inward (Wolters 2003). In other words, raveling or weathering is the wearing away of the pavement surface due to the dislodging of aggregate particles as a result of the loss of binder due to hardening as shown in Figure 2.11 (Huang 2004).

Age hardening or oxidation of the binder in pavements leads to the increase in viscosity, which is a rheological property; therefore, a progressive increase in the brittleness of the binder and lack of binding characteristics of the binder with the aggregates will take place resulting in raveling of the pavement surface. As a result, assessing the age hardening or oxidation of the binder is a crucial factor to evaluate and estimate the probability of the occurrence of raveling.

Figure 2.11. A Pictorial View of Raveling

Cracking

Cracking can be categorized into two main groups: load associated and non-load associated. Load associated cracking is known as fatigue cracking or alligator cracking as shown in Figure 2.12. The main reason that is related to binder characteristics for load associated cracking is binder consistency (Huang 2004). According to Roberts *et al.* 1996, the stiffness or the viscosity of the pavement binder should be specified carefully according to the thickness of the pavement. For example, low stiffness or low viscosity binder should be used in thin pavement sections, while high stiffness or high viscosity binder should be used in thick pavement sections.

Figure 2.12. A Pictorial View of Load Associated Cracking (Fatigue or Alligator Cracking)

Non-load associated cracking is known as low-temperature cracking as shown in Figure 2.13. According to Roberts *et al.* (1996), high asphalt stiffness at low temperatures is the principal cause of this kind of cracking. Some researchers reported that the asphalt binder consistency and temperature susceptibility are the major asphalt cement characteristics influencing this type of cracking (Roberts *et al.* 1996). Therefore, care should be taken if pavement binders having high temperature susceptibility are used. According to some researchers, it is recommended that the viscosity of the binder to range from 250 and 390 centistokes and the penetration of the binder to range from and 60 to 75 at 60°C (Roberts *et al.* 1996). In summary, binders having low stiffness at low temperatures should be used in cold climates.

Figure 2.13. A Pictorial View of non-Load Associated Cracking (Low-Temperature Cracking)

Rutting

Rutting, by definition, is the progressive movement of materials under repeated loads (Roberts *et al.* 1996) or it is the surface depression in the wheel path (Huang 2004). The viscosity of the binder has a minor role in the rutting resistance of the binder because the shape and texture of the aggregate are the main contributors to the rutting resistance (Roberts *et al.* 1996). However, using a binder having a high viscosity or a high stiffness could minimize the degree of rutting.

Figure 2.14. A Pictorial View of Rutting

Stripping

Stripping can be defined as the weakening or the loss of adhesion between the binder and the aggregate (Huang 2004). This loss of adhesion may be due to the moisture damage or moisture incursion. Some researchers reported that binders having high viscosity should be used, but care should be exercised because the high viscosity of the binder may lead to low-temperature cracking (Roberts *et al.* 1996).

Viscosity as a Rheological Property

It has been well established that the rheological properties of any new binder should be studied extensively in order to decide whether this binder is applicable to be utilized or not. Traditionally, the most common rheological characterization of a binder has been reported using viscosity (Airey *et al.* 2008). Viscosity is the physical material characteristics or property that can be employed and utilized to describe the resistance of liquids to flow (Asphalt Institute 2003). According to Roberts *et al.* (1996), viscosity is defined as the ratio of shear stress to shear strain rate at any given temperature and shear rate. Figure 2.15 displays the mechanism of how the adjacent layers of molecules in a liquid, i.e. asphalt cement or bio-oils, are sliding over each other.

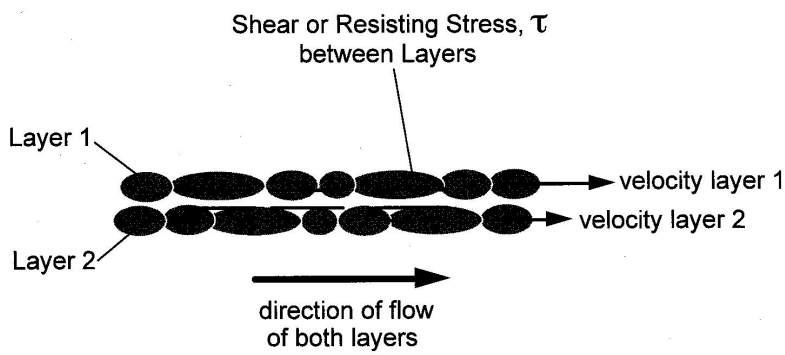


Figure 2.15. Microscopic View of Liquid Flow Characteristics (Adopted from Asphalt Institute 2003)

The resisting or the friction force between these layers is related to the relative velocity at which these layers are sliding to each other (Asphalt Institute 2003). The relationship or the difference between the resisting force and the relative velocity can be different for different liquids. Viscosity is one property or characteristic which can be employed to illustrate this difference or this relationship. Equation 2.1 shows how the coefficient of viscosity/viscosity "μ" explain the differences in flow characteristics of different liquids:

$$\tau = \mu * \textit{rate of shear strain} \qquad \text{Equation 2.1}$$

where:
τ = the shearing resistance between layers, and
Rate of shear strain = the relative speed at which layer 1 slides over layer 2.

Significance of Measuring Viscosity

It is very crucial to determine the viscosity of any binder to determine whether it is a Newtonian or non-Newtonian liquid. For the Newtonian liquids, the ratio of shear stress to rate of shear strain is constant. On the other hand, the non-Newtonian liquids, the ratio of shear stress to rate of shear strain is not constant. For instance, asphalt cements behaves like a Newtonian liquid at high temperatures while behaves like non-Newtonian at low temperatures.

Asphalt cements typically show either Newtonian or non-Newtonian behavior as shear rate is changing. Newtonian fluids have a linear relationship between resisting force and relative velocity between sliding layers. For example, a Newtonian fluid will move twice as fast if the force applied is doubled. Common Newtonian fluids include but are not limited to air, water and asphalt (at temperatures above 60°C). Figure 2.16 displays the linear relationship between shear stress and rate of shear strain which explicitly shows that the viscosity is constant regardless of the shear rate.

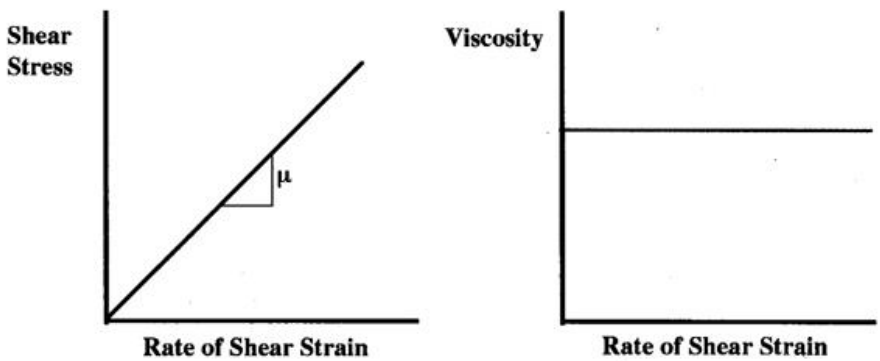


Figure 2.16. Newtonian Flow Behavior
(Adopted from The Asphalt Institute 2003)

Paving binders, i.e. asphalt binders, may show non-Newtonian flow behavior in two different ways; pseudoplastic (shear thinning) or dilatants (shear thickening). Figure 2.17 show the pseudoplastic flow behavior of non-Newtonian fluid, i.e. asphalt binder. This type of behavior, that is more common at moderate temperatures, is characterized by a decrease in viscosity as shear rate increases. In other words, the faster the shear rate is increased the more fluid (thinner) it gets.

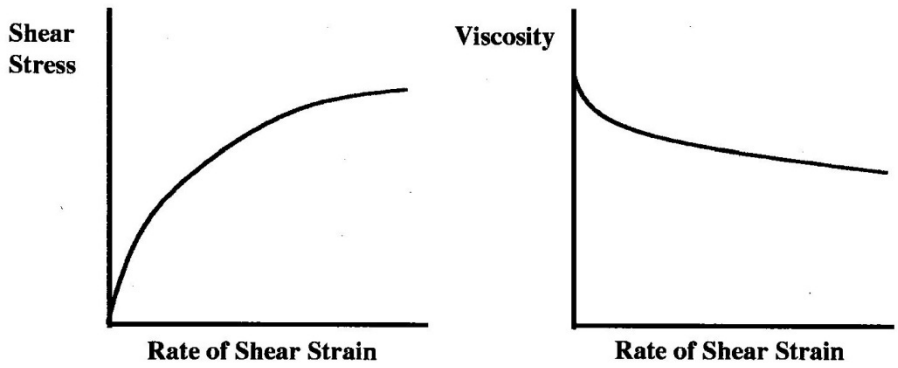


Figure 2.17. Pseudoplastic Flow Behavior "Shear Thinning"
(Adopted from The Asphalt Institute 2003)

The other type of non-Newtonian flow behavior is the dilatant or shear thickening which is less common in asphalt cements. This behavior is characterized by an increase in viscosity as shear rate increases (as shown in Figure 2.18). In other words, the faster the shear rate in increased the less fluid (thicker) it gets.

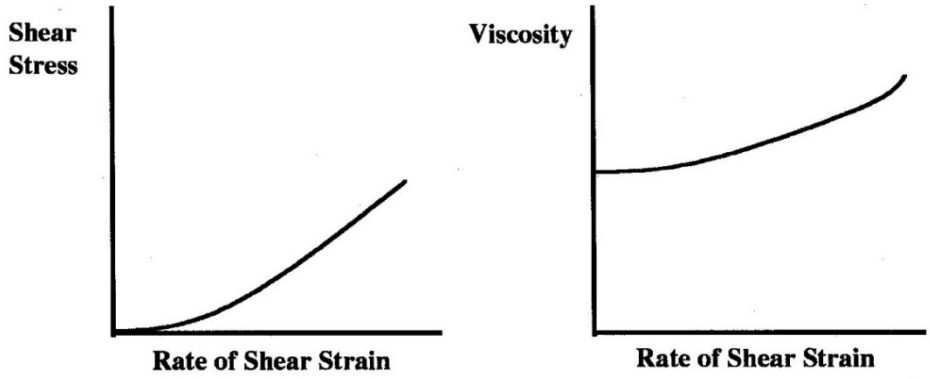


Figure 2.18. Dilatant Flow Behavior "Shear Thickening"
(Adopted from The Asphalt Institute 2003)

Factors Affecting Viscosity of Bio-oils

Ingram *et al.* (2008) reported the difficulty of determining accurately the viscosity and the rheological properties due to the complex multiphase nature of the bio-oils. Many researchers stated that temperature is the main contributor in affecting the viscosity and, hence the rheological properties, as temperature changed the phase behavior of the bio-oils (Ingram *et al.* 2008). Figure 2.19 shows the different phases present in the bio-oils at 25°C; the left and right pictures captured at 40x and 200x, respectively.

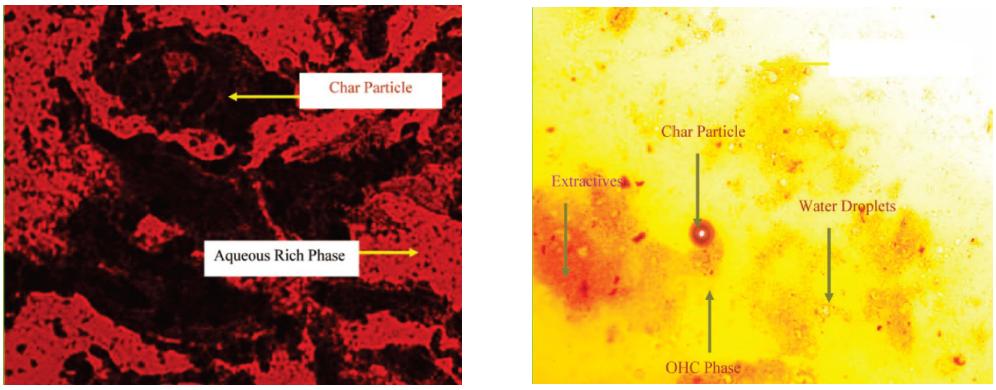


Figure 2.19. View of Phases in Bio-oils at 25°C at 40x (left) and 200X (right) (Adopted from Ingram *et al.* 2008)

W.S. Wan Nik *et al.* (2006) investigated the shear rate dependence and temperature dependence on the viscosity of the bio-oils. The shear rate dependence of the bio-oils was studied using the modified power law (Equation 2.2) of rheological model in order to investigate the temperature effect on the flow behavior index "*n*". On the other hand, the temperature dependence of the bio-oils was studied using the Arrhenius-type-relationship (Equation 2.3) in order to determine the activation energies "E_a" at different shear rates.

$$\boldsymbol{\eta - (\eta_{hrpm} - \eta_{ref}) = K\gamma^{n-1}} \qquad \text{Equation 2.2}$$

$$\boldsymbol{\eta = \eta_{\infty T} e^{\frac{E_a}{RT}}} \qquad \text{Equation 2.3}$$

Where η, η_{hrpm}, η_{ref}, and $\eta_{\infty T}$ are viscosity at the tested temperature (Pa·s), viscosity at the highest revolution per minute (Pa·s), viscosity focus point of all curve lines at 0.010 (Pa·s), and viscosity at infinite-temperature (Pa·s), respectively. "*n*" is the flow behavior index, γ is the shear rate (s^{-1}), R is the universal gas constant ($N.mmol^{-1}$) and T is the temperature (K).

Generally, the effect of shear rate on viscosity of the bio-oils was studied. As shown in Figure 2.20, at low shear rates, the viscosity of the bio-oil changed due to the change in the shear rate, while at high shear rates, the viscosity did not change due to the increase in the shear rates. This behavior indicates that the shear thinning of the bio-oils is significant; thus, it should be studied extensively before application of the bio-oils in any industry (W.S. Wan Nik *et al.* 2006).

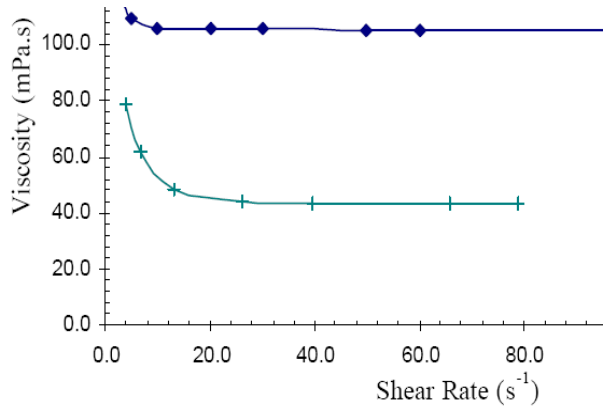


Figure 2.20. The Effect of Shear Rate on Viscosity for Bio-oil (Adopted from W.S. Wan Nik *et al.* 2006)

The result achieved by W.S. Wan Nik *et al.* (2006) is in compliance with another investigation conducted on the effect of different shear rates at different temperatures on the viscosity of the bio-oils by Ingram *et al.* (2008). Figure 2.21 shows the effect of different shear rates on the viscosity of bio-oils at different temperatures, e.g. 25, 50 and 80°C. As shown in Figure 2.21, the bio-oils exhibits Newtonian behavior at 25°C, but at 50 and 80°C, a shear thinning behavior is observed (Ingram *et al.* 2008).

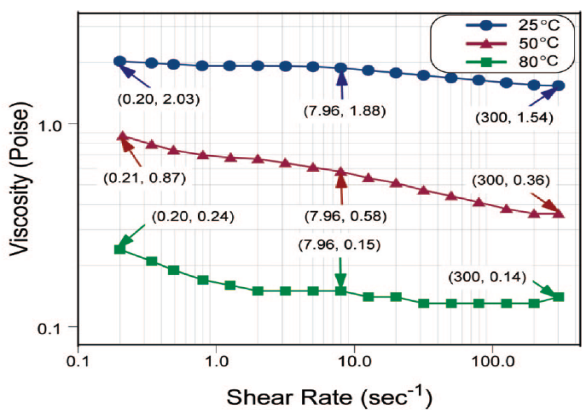


Figure 2.21. The effect of Shear Rates on the Viscosity of Bio-oils at 25, 50 and 80°C (Adopted from Ingram *et al.* 2008)

The effect of shear rate on viscosity of the bio-oils at different temperatures was studied using the modified power law of rheological model as shown in Equation 2.2 (W.S. Wan Nik *et al.* 2006). This model was employed to determine the flow behavior index *n* to evaluate the Newtonian level of the bio-oils. In other words, the flow behavior index *n* indicates the degree of Newtonian or non-Newtonian. Precisely, low flow behavior index *n* (less than unity) represents non-Newtonian behavior (pseudo-plastic), high flow behavior index *n* (more than unity) represents non-Newtonian behavior (shear thickening), and flow behavior *n* equal to unity indicates Newtonian behavior. As the consistency index "K" increases, the bio-oils tend to be more viscous. Therefore, heating the bio-oil would lead to a better Newtonian behavior.

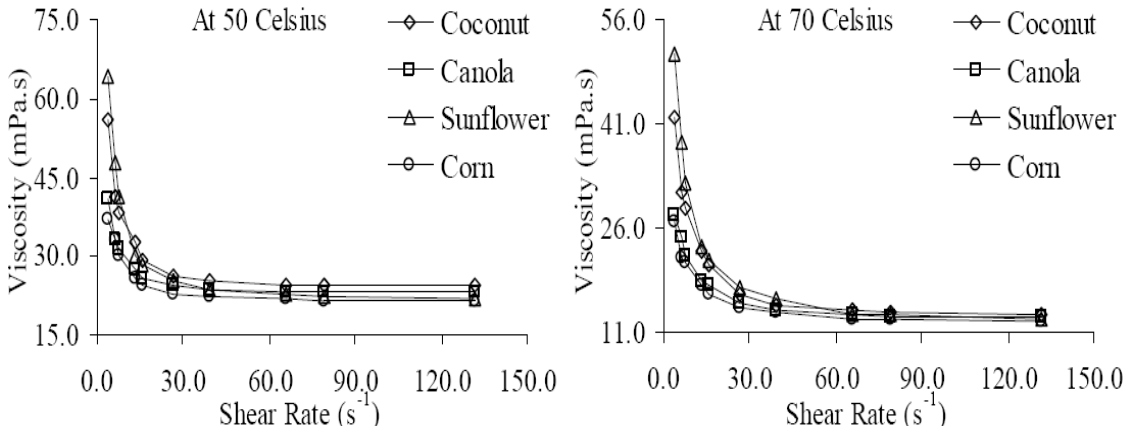


Figure 2.22. The Effect of Shear Rate on Viscosity at Different Temperatures (Adopted from W.S. Wan Nik *et al.* 2006)

Figure 2.22 displays the effect of shear rate on the viscosity of the bio-oils at different temperatures. Although the increase in the shear rate is not significant on changing the viscosity of the bio-oils, its contribution should not be ignored especially in the case of high shear rates as reported by W.S. Wan Nik *et al.* (2006). The authors concluded that the flow behavior index *n* values were calculated to be less than unity, which indicates that the bio-oils follow pseudo-plastic behavior. In addition, the authors concluded that heating the bio-oils leads to a better Newtonian behavior.

Temperature plays a major role in changing the viscosity of bio-oils. In addition, the reduction in viscosity's measurement due to temperature is more significant as compared to shear rate. Explicitly, the viscosity of a bio-oil is reduced rapidly as the temperature increases, and then, the bio-oil's viscosity started to display temperature independence effect.

The temperature dependence of the bio-oils was studied using the Arrhenius-type-relationship (Equation 2.3) as investigated by W.S. Wan Nik *et al.* (2006). Activation energy E_a and infinite-temperature viscosity at different shear rates were determined as they are important parameters to reflect bio-oils characteristics. In other words, low activation energy represents strong temperature independence effect, while high activation energy shows a strong temperature dependence effect (W.S. Wan Nik *et al.* 2006). Generally, this viscosity temperature profile shows that the viscosity of the bio-oil is exponentially decreasing while increasing temperature, so this relationship can be described as Arrhenius-type-relationship (see Figure 2.23). According to W.S. Wan Nik *et al.* (2006), the activation energy E_a of the bio-oils indicated the strong temperature dependence of the viscosity of the bio-oils.

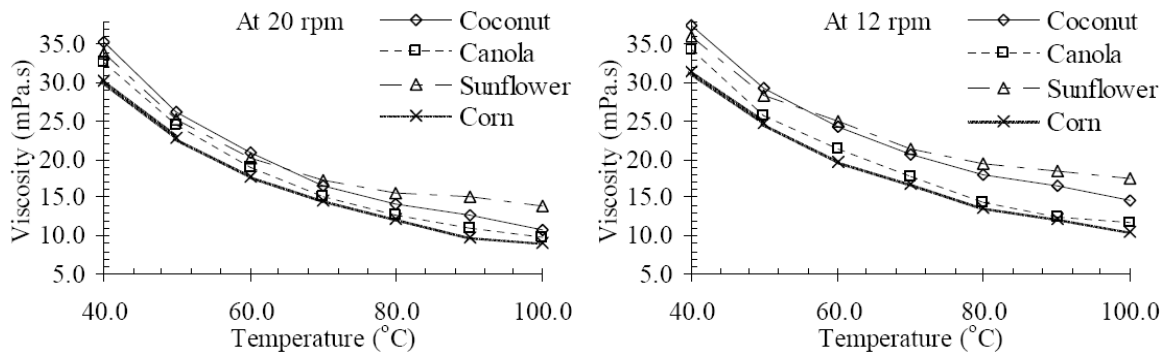


Figure 2.23. The Effect of Temperature on Viscosity at Different Shear Rates (Adopted from W.S. Wan Nik *et al.* 2006)

As reported by W.S. Wan Nik *et al.* (2006), the applied temperature not only provides sufficient energy to rapidly break down the internal structure within the bio-oils by reducing attraction forces between molecules, however, it promotes molecular interchange. On the other hand, the shear rate did not provide the sufficient energy to break down the internal structure and to promote molecular interchange. As a result, this could justify the reason behind the significance of temperature on the viscosity of the bio-oils compared to the shear rates as deduced by W.S. Wan Nik *et al.* (2006).

In summary, W.S. Wan Nik *et al.* (2006) concluded that the viscosities of the bio-oils (corn, coconut, canola and sunflower) are influenced by the change of temperature and shear rate. Precisely, the effect of temperature on the viscosity of the bio-oils is more significant that the effect of shear rate. Using the modified power law model, it is proven that these bio-oils behave as the pseudo-plastic liquids where viscosity decreased as the shear rate increased. Moreover, corn bio-oils, as reported by the authors, have the closest Newtonian behavior (more significant as temperature increased).

Rheological Characteristics of a Paving Binder

According to Roberts *et al.* (1996), there are many rheological characteristics that are crucial in determining the behavior and performance of the binder. These rheological characteristics are viscoelasticity, temperature susceptibility, shear susceptibility, and age hardening or oxidation.

Viscoelastic Behavior

Viscoelastic behavior means that the binder/material concurrently shows viscous and elastic characteristics. Asphalt as an example of viscoelastic binder, at high temperatures, asphalt cement behaves like viscous material, showing the consistency of a lubricant, while at very low temperatures, asphalt cement behaves like an elastic solid, returning back to its original shape when loaded or unloaded (Asphalt Institute 2003).

For this kind of mixed behavior, the liquid or binder is called viscoelastic, which can be described using the “spring-dashpot” model as shown in Figure 2.24. Any force exerted on the

model causes a parallel reaction in both the spring and the dashpot. In hot climates, the spring represents the immediate elastic response while the dashpot represents the viscous reaction in cold climates (Asphalt Institute 2003). Most of the response is elastic or viscoelastic, which means that it is recoverable with time, while some of the responses are plastic, which means that it is non-recoverable. Because of its viscoelastic properties, the binder behavior depends on both temperature and rate of loading (Asphalt Institute 2003).

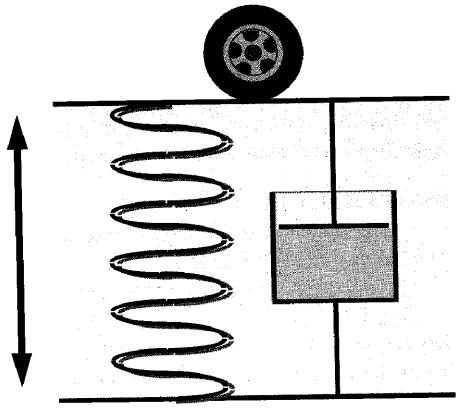


Figure 2.24. Spring-Dashpot Model of Viscoelastic Behavior (Adopted from The Asphalt Institute 2003)

As an example of paving materials, bitumen can be classified as a thermoplastic, viscoelastic liquid that behaves as a glass-like elastic solid at low temperatures and/or during rapid loading (short loading times − high loading frequencies) and as a viscous (Newtonian) fluid at high temperatures and/or during slow loading (long loading times − low loading frequencies). As a viscoelastic material, bitumen exhibits both elastic and viscous components of response and displays both a temperature- and time-dependent relationship between applied stresses and resultant strains. The rheology of bitumen is consequently defined by its stress−strain−time−temperature response. However, within the linear viscoelastic (LVE) region of response, the interrelation between stress and strain is influenced by temperature and time alone and not by the magnitude of the stress (i.e. deformation at any time and temperature is directly proportional to the applied load).

Bituminous materials are viscoelastic/thermo-rheological materials and the time-temperature superposition principle is applicable in the linear viscoelastic region. Hence, the complex modulus "G^*" of viscoelastic materials can be shifted along the frequency axis to form single characteristic master curves at a desired reference temperature or frequency. In other words, the master curve extends the modulus values to a wider temperature or frequency domain.

Since there is scarcity of data to study the bio-binders derived from bio-oils as a pavement material (100% replacement), there is no data until now to construct master curves based upon shear modulus (G^*) data. For viscoelastic materials, the master curve can be constructed using any non-linear curve-fitting technique. Microsoft Excel Solver can be used to fit the master curve

for each set of data. This method uses the Generalized Reduced Gradient nonlinear optimization approach to find the parameters that give the "best fit" between the equation and the data. The nonlinear regression algorithm seeks the values of the parameters that minimize the sum of the squared differences between the values of the observed and predicted values of the complex modulus.

Rheology of bituminous or viscoelastic materials in general is dependent on the loading time and temperature. The interrelationship between frequency and temperature for these types of materials makes it possible to obtain the same mathematical behavior in different experimental conditions (Chailleux *et al.* 2006). As reported by Marateanu and Anderson (1996), a quantitative mathematical model to describe the time-temperature dependency of viscoelastic materials is required for many reasons that can be listed as follows; (1) to calculate the modulus for a wide range of loading times and temperatures from measurements made at limited loading times and temperatures, and (2) to determine parameters that describe the time and temperature dependency of the rheological properties to relate physical behavior to binder chemistry. In other words, mechanical properties, such as "G^*", determined at high loading time (or low frequency) and at low temperature, can be determined at low loading time and at high temperature. As reported by Chailleux *et al.* (2006), for thermo-rheologically simple bituminous or viscoelastic materials, the relationship or equivalence between time and temperature can be used to construct master curves from linear viscoelastic data by shifting measurement at different temperature to obtain a continuous curve at a reference temperature. As stated by Ferry (1980), this method is commonly applied for polymers is also suitable for bituminous or viscoelastic materials. When the time-temperature principle is applied, master curve construction for shear modulus G^* allows one to obtain material behavior on a time and temperature scale larger than the one which is measurable.

Temperature Susceptibility

Temperature susceptibility, as defined by Roberts *et al.* (1996), is the rate at which the consistency of a binder changes with a change in temperature. The temperature susceptibility of a binder is a very crucial property as binders having high susceptibility to temperature are not desired or required for two reasons. First, at high temperatures, their viscosity can be very low resulting in mixing problems during compaction. Second, at low temperatures, their viscosities can be very high resulting in low temperature shrinkage cracking. Due to the change in the behavior as a result of changing temperature, the behavior of a paving binder should be studied at three different temperatures, e.g. high, intermediate and low.

Asphalt binder or bitumen, as an example, has three different behaviors due to the change in temperature. At high temperatures or under sustained loads (slow moving or parked trucks), an asphalt binder behaves like a viscous liquid (Asphalt Institute 2003). At intermediate temperatures, an asphalt binder displays the characteristics of both viscous and elastic solids. At low temperatures or under rapidly-applied loads (e.g. fast moving trucks), an asphalt binder behaves like an elastic solid. Elastic solids can be described as rubber bands which deform when loaded and return to their original shape when unloaded. Due to this range of behavior, asphalt binder is an excellent adhesive material to be used as a paving material. For example, asphalt binder when heated acts like a lubricant so it facilitates the process of mixing, coating and

compaction of binder with aggregates to form a smooth and dense surface. On the other hand, asphalt binder when cooled acts like a glue to hold the aggregate together in a solid matrix.

For a number of years, asphalt technicians have employed the viscosity-temperature susceptibility VTS method of binder temperature susceptibility classification (Rasmussen *et al.* 2002 and Roberts *et al.* 1996). Even though it has not been a common index value used for evaluating temperature susceptibility of binders, it does inherently possess a simple formulation (as shown in Equation 2.4).

$$\boldsymbol{VTS} = \frac{\log[\log(\eta_{T2})] - \log[\log(\eta_{T1})]}{\log(T_2) - \log(T_1)} \qquad \text{Equation 2.4}$$

where:
T_1 and T_2 = temperatures of binders at known points (R = degrees Rankine)
η_{T1} and η_{T2} = viscosities of the binder at the same known points (cp).

The temperature susceptibility of the binder can be characterized using two parameters; viscosity temperature susceptibility (VTS) and an intercept (A). Based on the literature review conducted, Rasmussen *et al.* (2002) reported a simple method to predict the parameters for a binder based on conventional test results. A least-squares fit is employed between log-log viscosity and log temperature to determine the ‘‘best’’ VTS and A values to be used to classify the binder (Rasmussen *et al.* 2002 and Roberts *et al.* 1996). More importantly, it is recommended that the viscosity data to be measured at temperatures that encompass the range of temperatures of interest to the engineer.

The larger the magnitude of the VTS value is calculated to be, the more susceptible the binder is to changes in viscosity with temperature. As a reference, Puzinauskas (1967) calculated the VTS values for over 50 binders commonly used in the U.S. at that time, and concluded that the VTS values were ranging from 3.36 to 3.98, based on the aforementioned equation (Rasmussen *et al.* 2002 and Puzinauskas 1967).

Age Hardening or Oxidation

It is well agreed that the rheological properties of any binder affect its pavement performance. The rheological properties change during the binder production and subsequently in service. Since the bio-oils are chemically organic, they react with oxygen from the environment and this kind of reaction is called “oxidation”, which can change the structure and the composition of the bio-oil. Oxidation can cause the material to become more brittle (stiffer), which leads to the term oxidative or age hardening. The rate of oxidation increases rapidly at high temperatures. On the other hand, oxidative hardening or aging occurs at a slower rate in a pavement, but this rate increases in warmer climates. Age hardening is considered to be one of the most important factors that leads to the change in the rheological properties.

There are many factors that contribute to age hardening of binders, such as oxidation, volatilization, and polymerization as reported by Roberts *et al.* (1996). First, oxidation, by definition, is the reaction of oxygen with the binder and the oxidation rate depends on the binder's chemical composition and the temperature. Second, volatilization is the evaporation of the lighter constituents from the binder and is usually a function of temperature and it is not usually contribute to long-term aging. Third, polymerization is the combination of like molecules to form chains of larger molecules, which subsequently increase the rate of hardening.

As reported by Mohan *et al.* (2006), the viscosity of bio-oils increases due to the aging effect. Temperature is the most driving variable that leads to the aging effect, and hence the viscosity of the bio-oils. In addition, some phase separation may also happen. As a result, instability problems may arise that are believed to result from a breakdown in the stabilized microemulsion and to chemical reactions, which continue to proceed in the bio-oils (Mohan *et al.* 2006).

The amount of aging that occurred in binder during production and in service can be quantified in terms of viscosity as the Aging Index "AI" as shown in Equation 2.5 (Roberts *et al.* 1996). This aging index has been employed to evaluate relative aging of asphalt cements of different grades and/or from different sources.

$$\textbf{Aging Index} = \frac{\textbf{Viscosity of Aged Binder}}{\textbf{Viscosity of original Binder}} \qquad \text{Equation 2.5}$$

Shear Susceptibility

Roberts *et al.* (1996) defines the shear susceptibility as the rate of change of viscosity with the rate of shear. In other words, for Newtonian fluids, since the viscosity is independent of shear rate, the fluid will not have shear susceptibility. On the other hand, for non-Newtonian fluids, the fluid will have shear susceptibility as the viscosity increases with increasing the shear rate. The shear susceptibility or shear index is the tangent of the angle of log shear rate versus log viscosity plot. Specifically, the shear susceptibility can be calculated by plotting the log shear rate in the X-axis versus log viscosity in the Y-axis, so the slope of this plot is the shear susceptibility as stated by Roberts *et al.* (1996).

Due to the different rates of aging for different paving materials, the shear susceptibility changes at different rates. In addition, shear susceptibility is affected by the chemical composition of the paving materials. Importantly, shear susceptibility does not depend significantly on the viscosity of the aging material, but it depends on the rate of gain in shear susceptibility with respect to the increase in viscosity (Roberts *et al.* 1996). It is well established that relatively lower gain in shear susceptibility relative to the increase in viscosity is associated with better pavement performance (Roberts *et al.* 1996).

Bio-oils Binders as a Bitumen Modifier

Williams *et al.* (2009) conducted some research concerned about the usage 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 (Williams *et al.* 2009). In addition, 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 percentage of bio-oils blended with asphalt binders (Williams *et al.* 2009). Moreover, Williams *et al.* (2009) reported that up to 9 percent of bio-oils could be blended with asphalt binders with significant improvement in performance grade of the bio-oil modified asphalt binder.

Bio-oils Binders as a Bitumen Replacement

Some researchers compared the rheological properties of conventional and polymer modified bitumens with binders derived from renewable resources (synthetic binders), i.e. triglyceride oils and carbohydrates. Their study was focused on the applicability of the utilization of binders derived from renewable resources as a viable bitumen replacement (Airey *et al.* 2008).

Their investigations concluded that the synthetic binders were not showing the same rheological properties. For instance, one synthetic binder behaved as a "soft" 100/150 penetration grade while the other behaved as a "hard" 10/20 penetration grade. In addition, one of the binders showed very soft behavior, so they concluded that it cannot be used as an asphalt replacement but it can be used as a modifier for hard bitumen binders. Generally, synthetic binders displayed partly the same rheological properties compared to the conventional bitumen binders even though there were some differences in their temperature susceptibility. In addition, synthetic binders showed almost the same rheological properties compared to polymer modified bitumens in terms of their ability to switch between viscous and elastic dominated behavior as concluded by Airey *et al.* (2008).

Although the rheological properties of the binders derived from renewable resources were promising, Airey *et al.* (2008) emphasized that other physical and mechanical properties, such as high temperature viscosity, thermal stability, adhesion, and durability considerations in terms of aging and moisture incursion should be studied extensively before the utilization of the synthetic binders as a bitumen replacement.

CHAPTER 3. EXPERIMENTAL METHODS

General

The experimental program of this research was designed to characterize the different bio-oils and to study the applicability of developing bio-binders from them to be used in the pavement industry. In this chapter, the experimental materials used, the experimental plans designed, and the experimental procedures followed during testing are discussed.

Experimental Materials

In this study, only two types of materials, i.e. bio-oils derived from biomass and polymer modifiers, were used.

Bio-oils

In this research, three different kinds of bio-oils were selected. As aforementioned, these bio-oils were extracted from different biomass materials using an existing 25kWt fast pyrolysis system developed at Iowa State University by CSET. The different biomass feedstocks were oakwood, switchgrass, and cornstover. These bio-oils were collected from specific condensers, i.e. #1, #2, and ESP, as they had high lignin content and low water content, which make them most suitable to be studied for developing bio-binders to be used as pavement binders.

The testing on bio-oils were divided into two many categories, which were virgin (untreated) or heat pre-treated bio-oils. Further, the heat pre-treated bio-oils was subdivided into two main subcategories, which were unmodified and polymer modified. Then, the heat pre-treated bio-oils were aged in two phases in order to mimic the different oxidation phases that take place during the life cycle of a pavement material. These phases can be summarized as follows: (1) rolling thin film oven- to simulate the short term aging due to mixing and compaction temperatures, and (2) pressure aging vessel- to simulate the long term aging during the in-situ life cycle of the pavement materials.

Polymer Modifiers

Definition of Polymer

The word *polymer* is derived from the classical Greek words *poly* and *meres* which literally means “many” and “parts’ (Fried 2003). A polymer is a long-chain molecule that is composed of a large number of repeating units of identical structure. There are many ways to classify polymers; the simplest method is to classify them according to their origin whether they are natural or synthetic (man-made). Natural polymers are polymers that are found in nature, such as cellulose, hemicellulose, and lignin; while, the synthetic polymers are man-made polymers that are formed through synthetic routes, such as polystyrene, polyethylene and nylon. Another method of classifying them is based on thermal properties whether they are thermoplastics or

thermosets (Fried 2003). First, thermoplastics are polymers that can be heat-softened in order to process into a desired form. In addition, thermoplastics can be recovered and refabricated by application of heat and pressure. Famous examples of thermoplastics include polystyrene, polyethylene and polypropylene. Second, thermosets are polymers whose individual chains have been linked by covalent bonds during polymerization or by subsequent chemical or thermal treatment during fabrication. Thermoset polymers once formed will resist heat softening, creep, and solvent attack and will not be thermally processed. Due to these properties, thermosets are suitable and appropriate materials for composites, coating, and adhesive applications (Fried 2003). Principal examples of thermosets are epoxy and phenol-formaldehyde resins.

Significance of Polymer Modifiers

Since the early 1970s, the utilization of petroleum derived polymers has been well developed to be blended with conventional bituminous binders to modify the performance and rheological properties by decreasing temperature susceptibility and increasing cohesion as reported by Airey *et al.* (2008). In other words, the practical experience has showed that the blending of bitumen binders with polymer modifiers (e.g. polyethylenes) has many advantages that include but are not limited to enhanced fatigue resistance, improved thermal stress cracking, decrease in temperature susceptibility and reduction of rutting (Gonzalez *et al.* 2006). Generally, the modified polymers, which are used in pavement industry, can be classified as elastomeric (75%), plastomeric (15%), and rubber or miscellaneously modified (10%) as stated by Airey *et al.* (2008).

Elastomers modify the characteristic of bituminous binders by having high elastic response and subsequently resist permanent deformation by stretching and recovering their initial shape when stress is removed (Roberts *et al.* 1996). This kind of polymer does not increase the strength of the asphalt binder significantly until they are elongated as the tensile strength of these polymers increases with elongation (Roberts *et al.* 1996). Styrnic block copolymers, as an example of elastomeric polymers, have the most significant effect when blended with bitumen. According to Nien *et al.* (2008), elastomeric copolymers enhance the rutting resistance of polymer modified asphalt at high temperature and improve the ductility, elasticity, and cyclic loading properties of the mixture at low temperatures. Sengoz and Isikyakar (2007) reported that elastomers (e.g. SBS copolymers) derive their strength and elasticity from physical and cross linking of the molecules into a three dimensional network. Other examples of elastomeric polymers include natural rubber, polybutadiene, polyisoprene, isobutene isoprene copolymer, polychloroprene and styrene butadiene rubber.

On the other hand, plastomers modify the characteristics of bituminous binders by forming tough, rigid and three dimensional networks to resist deformation and by modifying the workability of asphalt during construction (Airey *et al.* 2008 and Roberts *et al.* 1996). Additionally, plastomers have early strength upon loading but may fracture under high strain (Roberts *et al.* 1996). Plastomers include but are not limited to polyethylene, polypropylene, polyvinyl chloride (PVC), and ethylene propylene (EPDM). For instance, semi-crystalline copolymer (e.g. ethylene vinyl acetate "EVA") is one of the principal plastomers used in the pavement industry over the past 25 years.

Properties of Polymer Modifiers

In this bio-asphalt study, four types of polyethylene (homopolymers) were used and their properties can be summarized in Table 3.1. By definition, polyethylene "PS" is a polymer consisting of long chains hydrocarbon molecules of the monomer ethylene and it is a grade from polyolefins. In addition, Polyethylene is a thermoplastic commodity heavily used in consumer products. The ethylene molecule consists of C_2H_4, which are linked together by a double bond as reported by Jew *et al.* (1986). Over 60 million tons of polystyrene, approximately, are produced worldwide every year (Fried 2003).

The four polymer modifiers used can be classified as thermoplastics according to the classification method aforementioned. These polymers were provided by Honeywell International, Inc.

Table 3.1. Properties of Polymer Modifiers Used

Property	Polyethylene 617	Oxidized Polyethylene 680	Polyethylene 9
Drop Point, Mettler (°C)	101	108	115
Density (g/cc)	0.91	0.93	0.93
Viscosity @140°C (cps)	180	250	450
Bulk Density (kg/m^3)	563	536	508

Experimental Plan

The experimental plan was designed in order to determine the overall characteristics of the bio-binders developed from different kinds of bio-oils. The experimental plan was not concerned only about the rheological properties, which are the main factor in predicting the behavior of the developed bio-binders as pavement materials, but the experimental plan emphasized the overall physical and chemical characteristics in order to have a better understanding of the applicability of developing bio-binders from bio-oils. The experimental plan included three different plans, i.e. physical plan, chemical plan, and rheological plan, that are discussed in details hereafter.

Physical Testing Plan

The physical testing plan consists of two different tests as shown in

Figure 3.1. First, the original/developed bio-binders were tested for separation effects according to ASTM D 7173 (2005). The significance of this test was to examine the consistency and

susceptibility of the developed bio-binders against separations. Physical separation may occur due to the blending of the polymer modifiers.

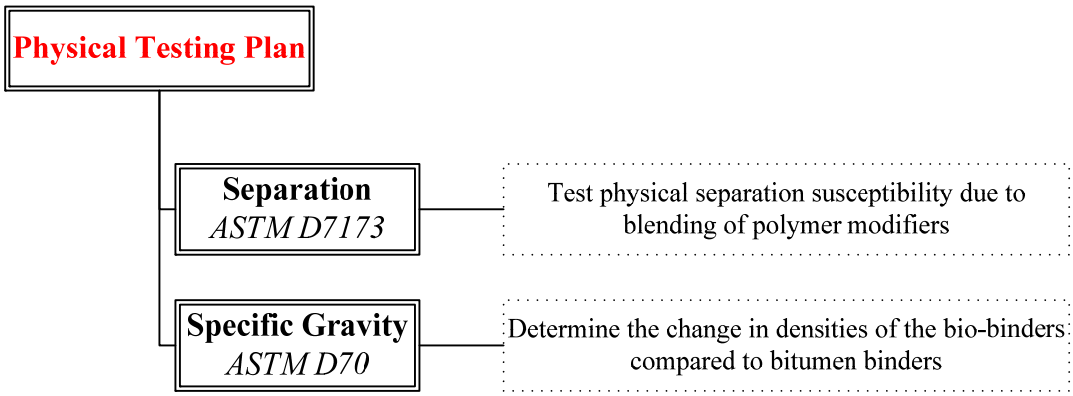
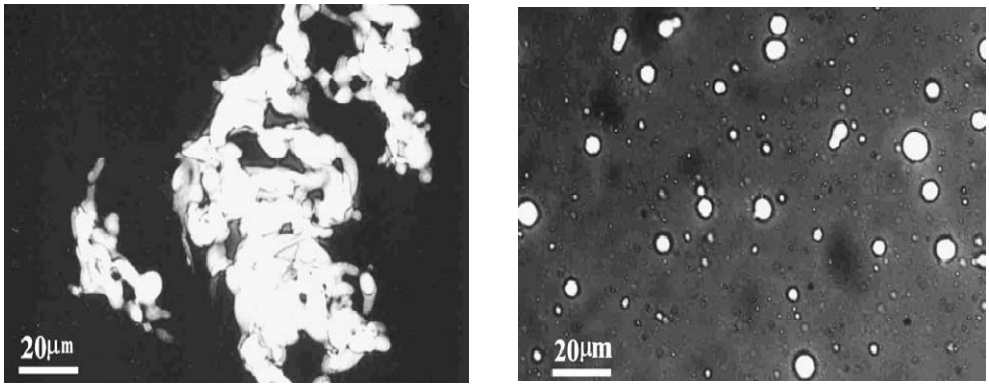


Figure 3.1. Physical Testing Plan

According to Gonzalez *et al.* (2006), physical separation is a very crucial factor to be studied as instability via drop diffusion is a serious disadvantage as coalescence favors the tendency of polymer modifiers to float on the surface of the bitumen which leads to creaming (as shown in Figure 3.2). This condition of separation is called Brownian coalescence, which is followed by gravitational flocculation and then creaming as stated by Gonzalez *et al.* (2006).



(a) Creaming Effect **(b) Fully Dispersed**

Figure 3.2. Creamy Effect versus Fully Dispersed Polymer Modifier (Adopted from Gonzalez *et al.* 2006)

The separation test was conducted in partially compliance with the procedure as there were some deviations in temperature and duration for heating. The basic or standard procedure states that the temperature should be 155°C and for at most 2 hours. Since the original/developed bio-binders cannot be heated at this temperature for this long duration as the chemical structure of the bio-oils may be substantially changed. The cellulose, hemicellulose and the lignin may decompose at this high temperature and for this duration. Hence, the procedure was modified to accompany the chemical structure of bio-binders. The temperature was set to be 110°C and for at most 30 minutes during blending. Then, the blended samples were poured into aluminum cigar tubes and set vertically into an oven at 110°C for at most 4 hours. After heating, the tubes were

removed and immediately frozen. The tubes were then cut into three equal-sized portions. According to ASTM D 4402 (2006), the top and bottom portions were tested in a dynamic shear rheometer to determine G*/sin(delta) differences at a constant temperature of 40°C. If the difference between G*/sin(delta) values was large, then the original/developed bio-binder must be chemically or physically separating out. The concept of separation testing of polymer modifiers from the developed bio-binders was crucial as any separation effect could cause potential problems during binder handling and construction.

Second, specific gravity was also determined according to ASTM D 70 (2003). Specific gravity testing would determine the change in densities between the developed bio-binders and bitumen binders. This test is important as it will be needed during the design of the pavement material.

Chemical Testing Plan

The chemical testing plan included two tests, i.e. Fourier transform infrared spectroscopy (FTIR) and Gas Chromatography-Mass Spectrometry (GC/MS), as shown in Figure 3.3. These tests were performed to quantify the amount of oxidative aging that occurred with the developed bio-binders, and to identify the different types of chemical bonds (functional groups) presented in the developed/original bio-binders. Due to the oxidation, the chemical structure of the bio-binders changed. Functional groups, such as CH_3-CH_2 and CH_2, are formed from oxidation. It was expected that the more oxidation took place, a greater concentration of CH_3-CH_2 and CH_2 groups in the bio-binders would develop. A FTIR test, generally, produces a spectrum with peaks that illustrates wave number versus absorbance or transmittance. At a given wave number, a large peak means that this functional group is present in the developed bio-binders in a large concentration. For instance, CH_3-CH_2 and CH_2 groups are at approximately 2990 cm^{-1} and 1475 cm^{-1}, respectively. A decreased amount of either groups would indicate less oxidative aging.

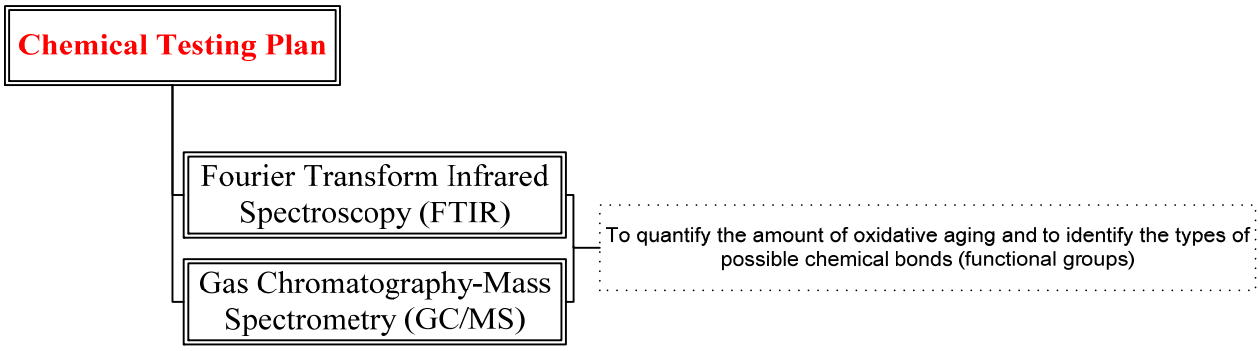


Figure 3.3. Chemical Testing Plan

Rheological Testing Plan

General

The rheological testing plan was designed to measure the different rheological properties of the bio-oils, to investigate the applicability of utilizing them as a pavement binder and to compare the performance of the developed bio-binders with respect to bitumen binders, which are the most widely used as pavement materials. In addition, the plan included measuring the rheological properties of the bio-oils after the blending of different polymer modifiers and studying the corresponding effect due to their addition. Hence the bitumen binders are the most extensively used material in the pavement industry, the rheological properties of the developed bio-binders were compared to the rheological properties of the bitumen binders. Moreover, all the testing procedure for measuring and studying the rheological properties of the developed bio-binders were conducted in accordance with the standard procedure AASHTO M 320 (2002) and ASTM D 6373 (1999) used for measuring the rheological properties of the bitumen binders, but with some deviations due to the different chemical, physical and rheological properties of the bio-oils compared to bitumen binders. In the past, the bitumen binders were evaluated based mainly on the laboratory tests and analysis without emphasizing the field performance. Recently, the significance of testing and evaluating the bitumen binders based on field performance besides the laboratory testing and analysis has gained interest. Based on this, the Superpave specifications were established. Figure 3.4 shows the overall rheological testing plan, which is discussed in details hereafter, and the accompanying testing equipment.

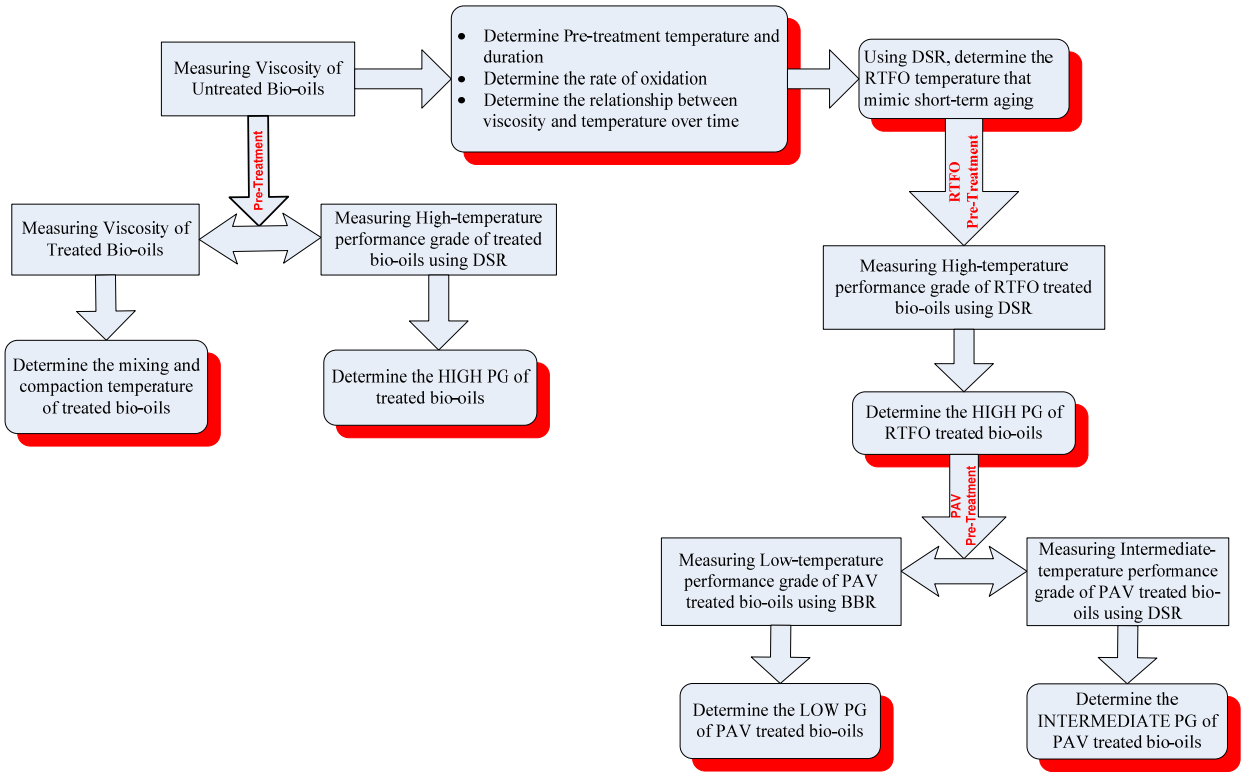


Figure 3.4. Rheological Plan for Testing Bio-oils

Testing Blends and Codes

The experimental matrix was designed to test all types of bio-oils with all four polymers modifiers at varying percentages. Each bio-oil was blended with each polymer modifier at two and four percent by weight. Table 3.2 shows the different bio-oils and polymer modifiers at different percentages.

Table 3.2. Experimental Matrix of Bio-oils with Polymer Modifiers

Polymer Modifiers	Bio-oils		
	Oakwood	**Switchgrass**	**Cornstover**
Polyethylene 617	0, 2,4	0, 2,4	0, 2,4
Oxidized Polyethylene 680	0, 2,4	0, 2,4	0, 2,4
Polyethylene 9	0, 2,4	0, 2,4	0, 2,4

Table 3.3 shows the experimental variables and the corresponding testing codes while Figure 3.5 represents the sample identification code that was used to differentiate between different blends and samples. The experimental matrix of the different blends tested is displayed in Table 3.4. Twenty seven different blends were tested to investigate the applicability of developing bio-binders from them.

Table 3.3. Experimental Variables and Testing Codes

Experimental Variables	Variables	Testing Code
Bio-oils	Oakwood	OW
	Switchgrass	SG
	Cornstover	CS
Polymer Modifiers	No Modifier	P0
	Polyethylene 617	P1
	Oxidized Polyethylene 680	P2
	Polyethylene 9	P3
Blending Ratios	100% bio-oil	B0
	98% bio-oil + 2% polymer	B2
	96% bio-oil + 4% polymer	B4
Pre-Treatment Temperature	100°C - 110°C	T
Pre-Treatment Duration	2 hours	H

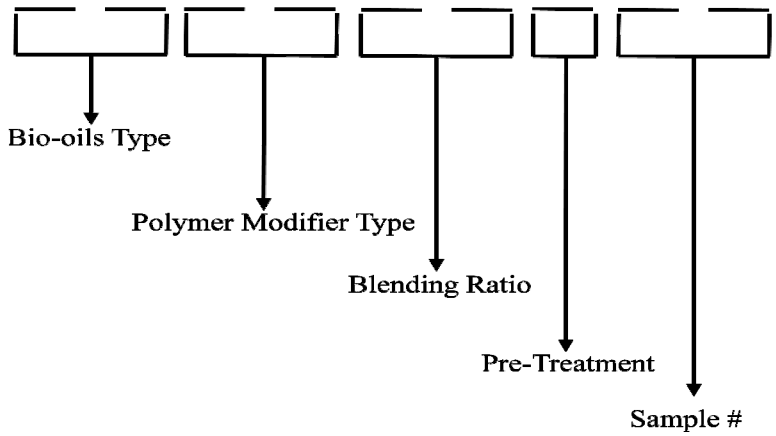


Figure 3.5. Sample Identification Code

Table 3.4. Bio-Binder Experimental Matrix

Blend #	Proportions by Mass (%)									
	Preheating Temperature	Bio-oils			Polymer					
		Oak wood	Switch grass	Corn Stover	617		680		9	
					2	4	2	4	2	4
Blend 1	X	X			Control					
Blend 2	X	X			X					
Blend 3	X	X				X				
Blend 4	X	X					X			
Blend 5	X	X						X		
Blend 6	X	X							X	
Blend 7	X	X								X
Blend 8	X		X		Control					
Blend 9	X		X		X					
Blend 10	X		X			X				
Blend 11	X		X				X			
Blend 12	X		X					X		
Blend 13	X		X						X	
Blend 14	X		X							X
Blend 15	X			X	Control					
Blend 16	X			X	X					
Blend 17	X			X		X				
Blend 18	X			X			X			
Blend 19	X			X				X		
Blend 20	X			X					X	
Blend 21	X			X						X

Introduction to Superpave Specifications and Procedures

Superpave (Superior Performing Asphalt Pavements) is a product of SHRP asphalt research. The SHRP was established by Congress in 1987 as a five year with a $150 million research program to improve the performance and durability of United States roads and to make roads safer for both motorists and highway workers. $50 million of the SHRP research funds were used for the development of performance based asphalt specifications to directly relate laboratory analysis with field performance. The Superpave system incorporates performance based asphalt materials characterization with the design environmental conditions to improve performance by limiting the potential for the asphalt binder to contribute toward permanent deformation, low temperature cracking, and fatigue cracking in asphalt pavements.

One important distinction between typical asphalt specifications and the Superpave specifications is the overall format of the requirements. The required physical properties remain constant for all of the performance grades (PG). However, the temperatures at which these properties must be reached vary depending on the climate in which the binder is expected to be used. The Superpave tests measure physical properties that can be related directly to field performance by engineering principles. The Superpave binder tests are also conducted at temperatures that are encountered by in-service pavements. Table 3.5 lists the binder test equipment and a brief description of how each test is used in the Superpave specifications.

Table 3.6 describes how each test provides some indication of binder performance; however, the pavement structure and mixture proportions will have additional bearing on this performance.

Table 3.5. Superpave Binder Test Equipment

Equipment	**Purpose**
Rolling Thin Film Oven (RTFO) Pressure Aging Vessel (PAV)	Simulate binder aging (hardening) characteristics due to production and construction processes (RTFO) and in-situ conditions (PAV)
Dynamic Shear Rheometer (DSR)	Measure binder stiffness and elasticity properties at high and intermediate temperatures (G* and δ)
Rotational Viscometer (RV)	Measure binder viscosity at high temperatures for selection of mixing and compaction temperatures
Bending Beam Rheometer (BBR) Direct Tension Tester (DTT)	Measure low temperatures stiffness and failure properties

Table 3.6. Superpave Laboratory Tests and Relation to Performance

Test Equipment	**Performance Property**	
Rotational Viscometer→	Handling Pumping→	Flow
Dynamic Shear Rheometer→	Permanent Deformation→	Rutting
	Fatigue Cracking→	Structural Cracking
Bending Beam Rheometer→ Direct Tension Tester→	Thermal Cracking→	Low Temperature Cracking

The main theme of the Superpave binder specifications is its reliance and dependence on testing asphalt binders in conditions that mimic the three critical stages during the binder's life. First, tests conducted on the original binder represent the first stage of transport, storage, and handling of the binder. Second, tests performed on the RTFO residue binder represent the second stage that the binder undergoes during mix production and construction. The second stage of tests is simulated for the specification by aging the binder in a rolling thin film oven (RTFO). Third, tests conducted on the pressure aging vessel (PAV) residue binder displays the third stage that the binder ages over a long period of time in-situ as part of the hot mix asphalt pavement layer; this stage is simulated by aging the RTFO residue binder in the PAV.

Testing Procedures and Concepts

In this section of the study, the different testing procedures and the concepts underneath them are described. These testing procedures can be listed as follow: rotational viscometer (RV"), blending and mixing of polymer modifiers, rolling thin film oven (RTFO), pressure aging vessel (PAV), dynamic shear rheometer (DSR), and bending beam rheometer (BBR).

Rotational Viscometer (RV)

This test was used to determine the flow characteristics of the virgin bio-oils (untreated) and the developed bio-binders (heat pre-treated bio-oils). The data acquired by rotational viscometer were used to determine the temperature and duration required for pre-treatment, to evaluate and quantify the amount of oxidation and aging that occurs, to measure the mixing and compaction temperatures at the hot mixing facility, and to determine the viscoelastic behavior of the developed bio-binders. The rotational viscometer was conducted by measuring the torque required to maintain a constant rotational speed of a cylindrical spindle at a specific temperature or measuring the torque at different rotational speeds at different temperatures. The torque applied is directly related to the binder viscosity. Figure 3.6 shows the pictorial view of a rotational viscometer along with the working principle of the test.

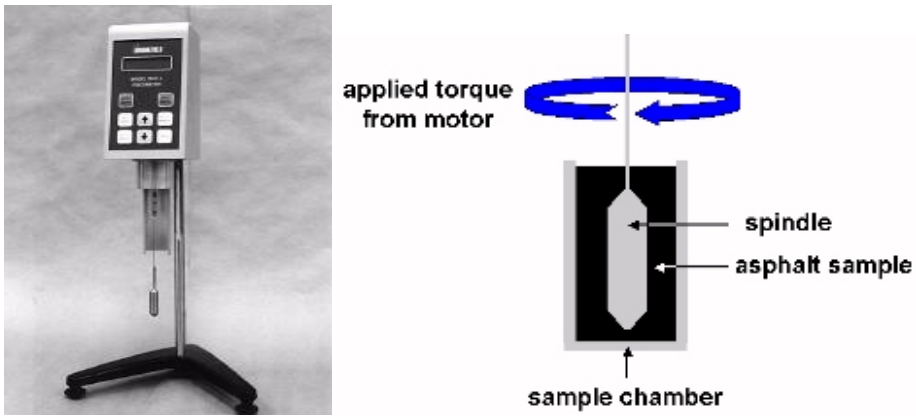


Figure 3.6. A Pictorial View of the Rotational Viscometer with the Working Principle

The rotational viscometer procedure was varied based on the required data or measurement that was needed. In order to determine the pre-treatment temperature and duration and to evaluate

and quantify the amount of oxidation and aging occurred; the following test was conducted in accordance to ASTM D 4402 (2006) with some deviations that can be summarized as follows:

- 30 grams of bio-oil were heated in an oven until sufficiently fluid to pour.
- The sample was stirred during heating to remove entrapped air.
- 8 or 11 grams were used typically according to the size of spindle.
- The temperature was kept constant.
- The motor was set to operate at 100 rpm.
- The viscosity reading and the percent torque should be between 2 and 98%. If the percent torque was out of the range, the size of the spindle should be changed.
- The five readings required for the report were: viscosity, test temperature, spindle number, speed and percent torque.
- Three viscosity readings were recorded at 1-minute intervals and the reported value was the average of them.
- The viscosity readings were recorded at 0, 30, 60, 120, 240, and 480 minutes at two different temperatures of 125° and 135°C.

In order to determine the mixing and compaction temperature of the developed bio-binders, the same aforementioned procedure were followed except that the viscosity readings of the developed bio-binder (pre-treated bio-oils) were recorded just after 15 minutes (from turning on the rotational viscometer) and at four different temperatures ranging from 70°C to 145ºC.

In order to determine the viscoelastic behavior of the bio-oils or the developed bio-binders; the following test was conducted in accordance to ASTM D 4402 (2006) with some deviations that can be summarized as follows:

- The motor was set to operate at different speeds; 5, 10, 20, 40, 80, and 100 rpm.
- The temperature was kept constant during measuring viscosity of the developed bio-binder at different motor speeds.
- The viscosity readings were recorded at 0, 30, 60, and 120 minutes.
- The entire procedure was repeated for other temperatures ranging between 70°C and 160°C to study the effect of temperature on the viscoelastic properties of the developed bio-binders.

<u>Rolling Thin Film Oven (RTFO)</u>

The RTFO procedure served two purposes. The first was to provide an aged binder that can be used for further testing of physical properties. The second was to determine the mass quantity of volatiles lost from the developed bio-binder during the process. Volatile mass loss was an indication of the aging that may occur in the binder during mixing and construction operations. Therefore, the main objective of RTFO was to measure the effect of temperature and moving current of air on the properties of the semi-solid developed bio-binders. Figure 3.7 shows the RTFO chamber and the sample cylinders used in the test.

Figure 3.7. The RTFO Chamber and the Sample Cylinders

The test was conducted in accordance to ASTM D 2872 (2004) with some deviations that can be summarized as follows:

- According to Superpave specifications and procedures, the aging temperature, originally, should be 163°C and the aging duration should be 85 minutes. As the chemical structure of the original bio-binder may change due to this high temperature, these temperature and duration were modified. The temperature was adjusted and kept constant at 110°C but the duration was changed accordingly. The G*/sin(delta) of the original binder calculated by the DSR should be at least 1.00 kPa and the G*/sin(delta) of the RTFO residue of the developed bio-binder calculated by the DSR should be at least 2.2 kPa. This means that the G*/sin(delta) had increased by about 120%. Therefore, the temperature of the RTFO was adjusted and kept constant at 110°C and the durations were changed ranging between 60, 80, 100 and 120 minutes and the G*/sin(delta) were determined until the G*/sin(delta) values were increased by 120%. The duration at which the DSR value increased by 120% was considered the RTFO duration.
- The RTFO oven must be preheated to the aging temperature, 110ºC, for a minimum of 16 hours prior to use.
- The binder sample was heated until fluid, not exceeding 120ºC.
- Eight sample bottles were required for Superpave binder testing. Two samples (bottles) were required for the mass loss determination. The other six were used for further testing.
- RTFO bottles were loaded with 50-60 grams of developed bio-binders.
- The bottles were turned on their side to a horizontal position and placed in a cooling rack for 10, 20, and 30 minutes. Then, sample bottles were placed in the carriage and rotated at a rate of 15 revolutions per minute.
- The air flow was set at a rate of 4000 ml/min for the calculated duration aforementioned. Then the weights of the bottles were measured to the nearest 0.001 gram.
- Calculation of mass loss was determined according to the following equation:

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

Pressure Aging Vessel (PAV)

The PAV exposed the developed bio-binder to high pressure and temperature for 20 hours to simulate the effects of long-term in-situ aging. According to Bahia and Anderson (1994), the PAV procedure simulates 5-10 years of in-service aging. Generally, the PAV aged bio-binders were used to test the intermediate critical temperature with the DSR. Since pavement binders exposed to long-term aging have also been through the mixing and construction process, the PAV procedure requires that the samples used should have been aged in the RTFO. In other words, PAV procedure was performed on RTFO residue developed bio-binder samples. Figure 3.8 shows the pressure aging vessel and the sample rack.

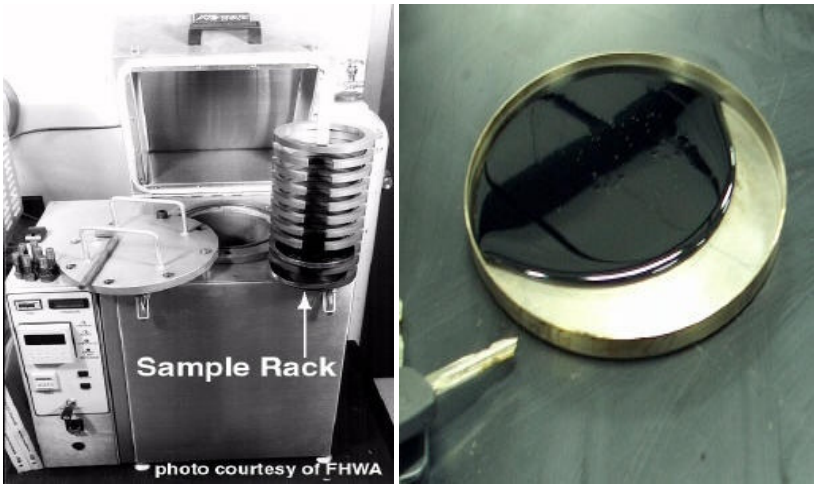


Figure 3.8. The Pressure Ageing Vessel Equipment and Sample Rack

The test was conducted in accordance to ASTM D 6521 (2004) with some deviations that can be summarized as follows:

- The PAV procedure used developed bio-binder aged in the RTFO. The pressure vessel was designed to operate under the pressure and temperature conditions of the test (2070 kPa and either 90º, 100º, or 110ºC). The vessel must accommodate at least 10 sample pans. The oven should be able to control the internal temperature of the PAV to within ±0.5ºC during the aging period. In this procedure, the temperature was set to 100°C.
- The RTFO-aged bio-binder was heated until fluid and stirred to ensure homogeneity.
- Three PAV sample pans of 50 grams each were prepared and placed in the sample rack.
- The sample rack with the samples was placed in the hot vessel and the lid was quickly secured to avoid excessive heat loss.
- The aging process was conducted at different temperatures depending on the design climate.
- When the vessel temperature entered the range from 20ºC to 2ºC of the required temperature, the pressure was applied and the timing for the aging periods begun.

- After 2.5 hours, the pressure was gradually released- 8 to 10 minutes were usually required (if the pressure was released too quickly, foaming may occur).
- The sample rack was then removed from the rack and placed in the oven at 100°C (instead of 163ºC for bitumen binders) for 15 minutes. The temperature was set to 100°C instead of 163°C as the chemical structure of the bio-oils may change considerably at this high temperature.
- The sample was then transferred to a storage container and degassed in a 100°C (instead of 170ºC for bitumen binder) vacuum oven for 30 minutes at a pressure of 15 kPa absolute. The temperature was set to 120°C instead of 170°C due to the aforementioned reason.
- PAV report included many readings that can be listed as follows: sample identification, aging test temperature to the nearest 0.5ºC, maximum and minimum aging temperature recorded to the nearest 0.1ºC, total time during aging that temperature was outside the specified range to the nearest 0.1 minute and total aging time in hours and minutes.

Dynamic Shear Rheometer (DSR)

Since pavement binder behavior depends on both temperature and loading time, the ideal test for binders should include both factors. Rheometers are adaptable for use in testing, so both time and temperature effects can be evaluated. The main objective of dynamic shear rheometer testing was to measure the rheological properties (shear modulus and phase angle) at intermediate to high temperatures using parallel plate geometry and was typically applicable to unaged and RTFO aged samples. Figure 3.9 shows the pictorial view of the dynamic shear rheometer and a sample.

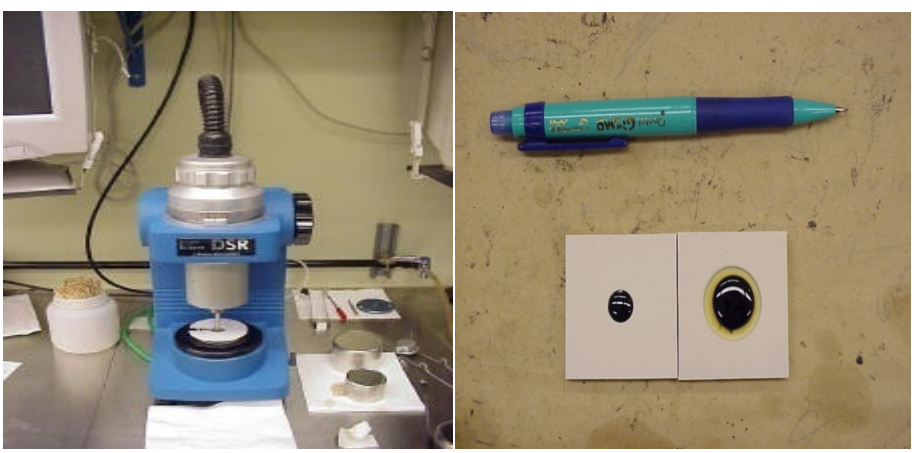


Figure 3.9. Dynamic Shear Rheometer Machine and the Sample

The test was conducted in accordance to ASTM D 7175 (2005) with some deviations that can be summarized as follows:

- The developed bio-binder binder was heated until fluid with stirring to remove air bubbles and achieve a homogeneous sample.
- The bio-binder was poured into silicon mold with the appropriate diameter and thickness for testing (because lighter constituents of the binder may be absorbed by

the silicone, care should be taken not to let the sample sit in the mold for any more than two hours before loading it in the DSR).

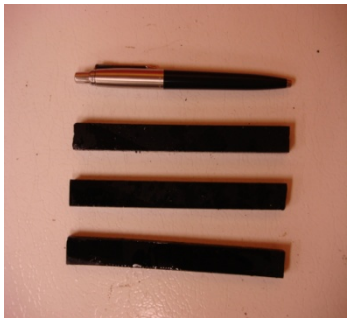
- The bio-binder specimen should be attached to the plates of the DSR. Then, the DSR plate was lowered down automatically.
- The specimen was trimmed flush with the parallel plates, and the extra 50 microns was "dialed out" so that the gap is exactly at the desired value.
- The water was circulated through a temperature controller that precisely adjusted and maintained the desired sample temperature.
- A computer controlled the DSR test parameters and recorded test results (testing consisted of setting the DSR to apply a constant oscillating stress and recording the resulting strain and time lag, δ). The Superpave test procedures required that the oscillation speed to be 10 radians/second. The rheometer software automatically computed and reported G* and δ, using the relationship between the applied stress and the resulting shear strain.
- The operator set the approximate value of shear strain "strain amplitude". Original (unaged) binder and RTFO aged binders were tested at strain values of approximately ten to twelve percent. PAV-aged bio-binders were tested at strain values of about one percent. In all cases, strain values must be small enough that the response of the binder (G*) remains in the linear viscoelastic range.

Bending Beam Rheometer (BBR)

The bending beam rheometer (BBR) was used to determine the low temperature performance grade of a pavement binder. Figure 3.10 shows pictorial view of a BBR and a sample. A BBR tested the developed bio-binder at low service temperatures to determine its susceptibility to thermal cracking as pavement binder is very susceptible to thermal cracking at low temperatures due to the fact that bio-binders becomes less viscous as they are cooled and contracts. In other words, the BBR was used to measure how much a bio-binder deflected under a constant load at a constant temperature. The BBR tested pavement binders that had been aged in both a rolling thin film oven and the pressure aging vessel. Therefore, the test measured the performance characteristics of bio-binders as they had been exposed to hot mixing in a mixing facility and some in-service aging.

BBR Machine (Outer view)

BBR Machine (Inner view)



(c) BBR Sample

Figure 3.10. Bending Beam Rheometer pictorial view

The test was conducted in accordance to ASTM D 6648 (2001) with some deviations that can be summarized as follows:

- Test specimens were prepared using a rectangular aluminum mold. The inside surfaces of the two side plates and base plate were lightly greased with petroleum-based jelly. The mold was then assembled and held together with two rubber O-rings.
- The developed bio-binder was heated until fluid (usually about 110°C, but not to exceed 120°C) and poured into small, rectangular aluminum beams.
- After a cooling period of about 45 to 60 minutes, excess binder was trimmed from the upper surface using a hot spatula. Then, the specimen remained in the mold at room temperature, but no longer than two hours.
- The specimen was stored below -0.5°C to allow for proper handling. The beams were placed in a fluid bath that maintained low temperatures.
- After being in the fluid bath for one hour, the beams were individually placed on a loading frame and subjected to a load for 240 seconds.
- The deflection was measured versus time, which was used to calculate the two key properties of stiffness and change in stiffness (m-value). A sample of bio-binder can fail at a given temperature by either having a stiffness value "S" of greater than 300 MPa or an m-value less than 0.300 (Asphalt Institute 2003).

Testing Sequence

The testing sequence of the rheological plan was conducted in subsequent stages. Figure 3.11 shows the different stages of the testing. The first stage was concerned about measuring the viscosity of the virgin bio-oils with the rotational viscometer to determine the pre-treatment temperature and duration required. After the pre-treatment procedure, the second stage contained two tests, e.g. DSR and rotational viscometer, on the original bio-binder (developed bio-binder). Then the third stage was testing the RTFO bio-binder in the DSR after placing the bio-binder in the RTFO oven to simulate the short-term aging due to mixing and compaction processes. Finally, the RTFO bio-binder residue was placed in the PAV oven to simulate the long-term aging due to pavement performance, and then the PAV bio-binder was tested using DSR and BBR.

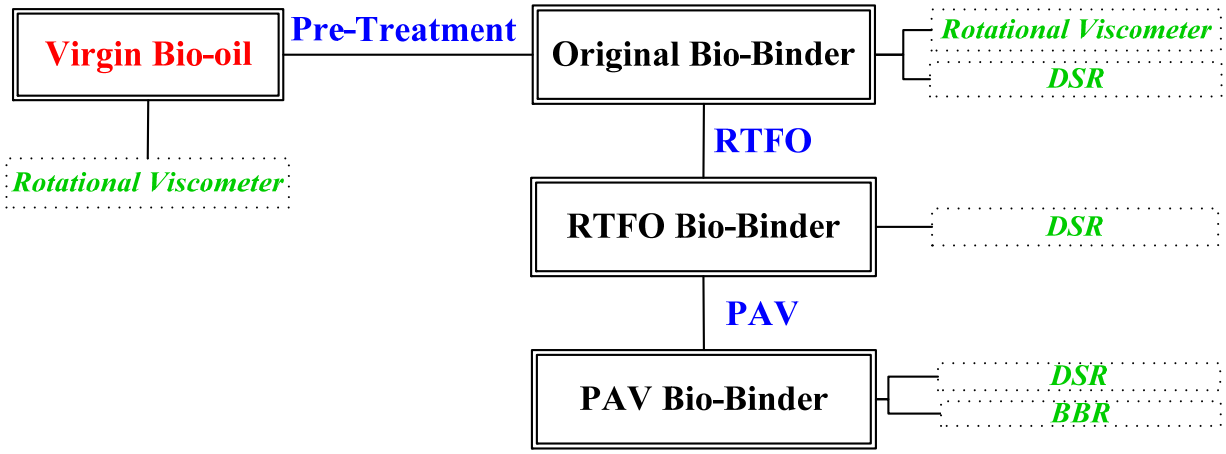


Figure 3.11. Testing Sequence of Rheological Testing Plan

Determination of Rheological Properties

Pretreatment Temperature and Duration

The pretreatment temperature and duration were determined after testing the virgin bio-oils (with and without polymers modifiers) using the rotational viscometer. The viscosity of the virgin bio-oils was measured during 8 hours at different temperatures, e.g. 125°C and 135°C. For instance, the virgin bio-oil was kept at 125°C in the rotational viscometer for 8 hours and the viscosity values was measured at 0, 30, 60, 120, 240 and 480 minutes. The viscosity of the virgin bio-oils throughout the whole period was compared to the viscosity specified in the Superpave specifications and requirements, which is to be less than 3.00 Pa·s. According to the relationship between viscosity and the duration, the pretreatment temperature and duration were specified for each virgin bio-oil and polymer modifier virgin bio-oil.

Mixing and Compaction Temperatures

The mixing and compaction temperatures were calculated in accordance to the Superpave specifications and requirements as shown in Figure 3.12. After the pretreatment procedure, the viscosity measurements of the original bio-binders at different temperatures, e.g. 70, 80, 90, 100, 110, and 120°C, were measured using the rotational viscometer. Then, determining the temperature range that corresponded to viscosity values of 0.17±0.02 Pa·s was the range of mixing temperature. Likely, determining the temperature range that corresponded to viscosity values of 0.28±0.03 Pa·s was the range of compaction temperature.

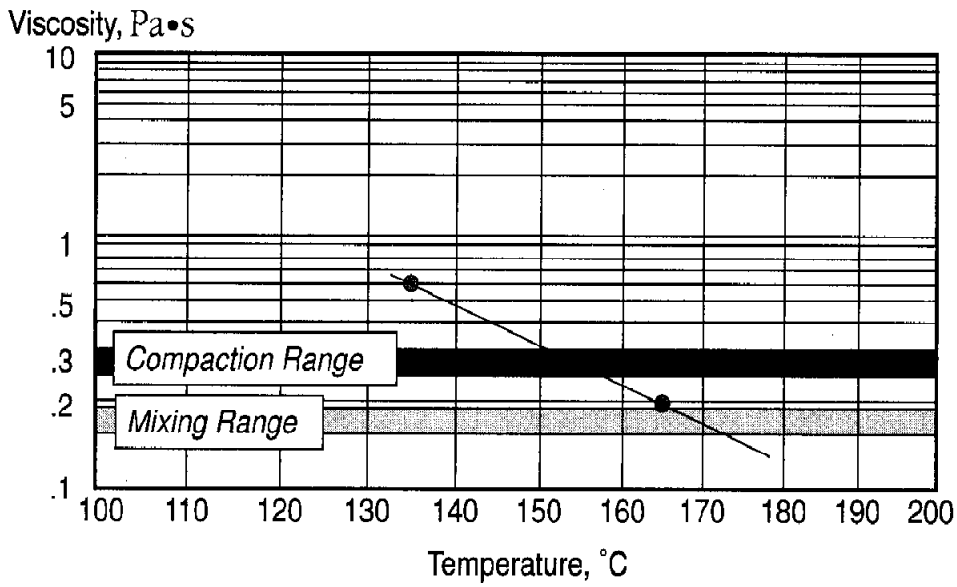


Figure 3.12. Temperature and Viscosity Relationship to Determine Mixing and Compaction Temperatures (Adopted from The Asphalt Institute 2003)

Aging Index

The amount of aging and oxidation was determined by measuring the aging index according to Equation 2.5. The aging index was calculated for the virgin bio-oils and the original bio-binders (after heat pre-treatment) by measuring the viscosity using the rotational viscometer for aged and unaged samples. For the virgin bio-oils, the aging index was determined by measuring the viscosity of the aged bio-oils at 2, 4 and 8 hours and comparing them to the viscosity of the unaged bio-oil (at 0 hours). Similarly, for the original bio-binders, the aging index was calculated by measuring the viscosity of the aged developed bio-binders at 1, 2 and 4 hours and comparing them to the viscosity of the unaged original bio-binder (at 0 hours).

Newtonian or Non-Newtonian Behavior

The Newtonian or non-Newtonian behavior of the original bio-binders was determined by measuring the shear rate and temperature dependences on the viscosity of the original bio-binders. The viscosity of the original bio-binders was measured at 80, 90, 100, 110, and 120°C at varying shear rates of 5, 10, 20, 40, 60, 80 and 100 rpm.

Using the modified power law (Equation 2.2), the flow behavior index and the consistency factor were calculated. As aforementioned in Chapter 2, the flow behavior index "*n*" indicates the degree of Newtonian or non-Newtonian. Precisely, low flow behavior index *n* (less than unity) represents non-Newtonian behavior (pseudo-plastic), high flow behavior index *n* (more than unity) represents non-Newtonian behavior (shear thickening), and flow behavior *n* equal to unity indicates Newtonian behavior. In addition, the consistency index "*K*" at different temperatures evaluates whether the original bio-binder was viscous or not. As the consistency index "*K*" increases, the original bio-binder tends to be more viscous.

Using the Arrhenius-type-relationship (Equation 2.3), the temperature dependence of the viscosity of the original bio-binders was measured. The activation energy "E_a" values of the original bio-binders at different temperatures were compared. High activation energy "E_a" value indicated high temperature dependence of the viscosity of the original bio-binder on the temperature.

Viscoelastic Behavior

The viscoelastic properties of the original bio-binders were determined by calculating the shear and temperature susceptibility. For the shear susceptibility, the fluid will not have shear susceptibility since the viscosity is independent of shear rate for Newtonian fluids. On the other hand, for non-Newtonian fluids, the fluid will have shear susceptibility as the viscosity increases with increasing the shear rate. The viscosity of the original bio-binder was measured at different shear rates at a constant temperature using the rotational viscometer. The shear rates used were 5, 10, 20, 40, 60, 80 and 100 rpm. The constant temperature was set constant at 110°C. Consequently, according to Roberts *et al.* (1996), the shear susceptibility can be calculated by plotting the log shear rate on the X-axis versus log viscosity on the Y-axis, so the slope of this plot is the shear susceptibility.

For determining the temperature susceptibility of a pavement binder, the viscosity-temperature susceptibility VTS method was employed (Rasmussen *et al.* 2002 and Roberts *et al.* 1996). The calculation was based upon the aforementioned Equation 2.4. The temperature susceptibility of the original bio-binder was characterized using two parameters; viscosity temperature susceptibility (VTS) and an intercept (A). According to Rasmussen *et al.* (2002) and Roberts *et al.* (1996), a least-squares fit is employed between log-log viscosity and log temperature to determine the ''best'' VTS and A values. The viscosity of the original bio-binder for all blends was measured at different temperatures ranging between 70 and 125°C. The VTS values calculated for the original bio-binders was compared to the VTS values of bitumen binders, which were reported by Rasmussen *et al.* (2002) and Puzinauskas (1967), ranging between 3.36 and 3.98.

Performance Grade

According to Superpave requirements and specifications, performance grading a pavement binder requires many steps and several separate testing procedures. Initially, each blend, abovementioned in Table 3.4, was tested using a dynamic shear rheometer (DSR) according to the procedure aforementioned. The viscoelastic properties of a pavement binder were characterized by determining the complex modulus (G*) and phase angle (δ) of the sample. By definition, the complex modulus is the overall resistance of the pavement material to deformation when repeatedly sheared (McCready 2007 and McGennis *et al.* 1994). The complex modulus consists of two parts, storage modulus (G') and elastic modulus (G") as shown in Figure 3.13.

At higher temperatures, pavement binders are required to behave like a viscous material and like an elastic material at low temperatures. However, at most intermediate temperatures, pavement binders are supposed to impose visco-elastic properties, exhibiting both viscous and elastic behavior. The phase angle characterizes how much the behavior of the complex modulus is viscous or elastic (McGennis *et al.* 1994).

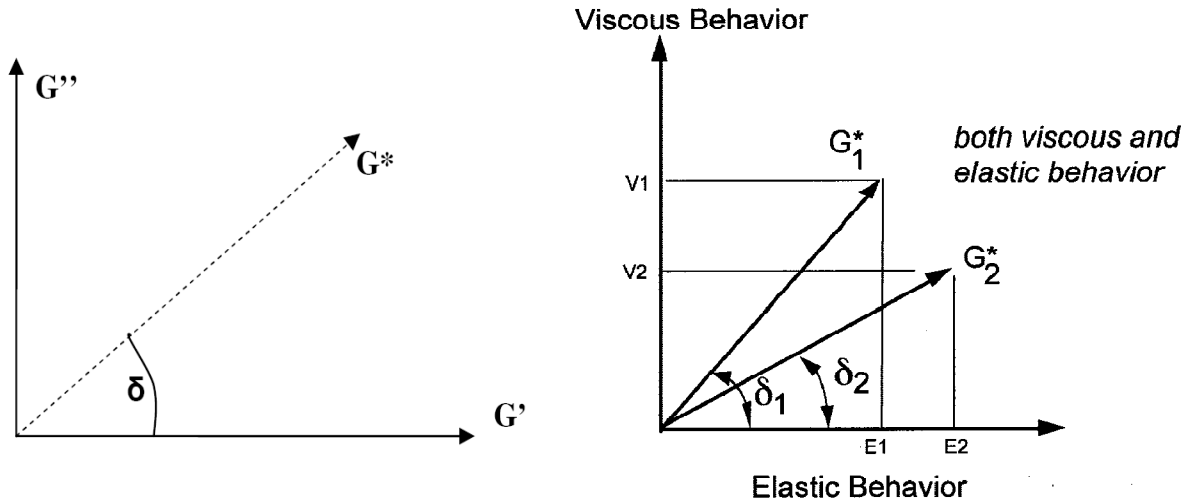


Figure 3.13. Elastic and Viscous Behavior of a Pavement Material

The high temperature performance grade was determined using the unaged blends immediately after heat pre-treatment using the DSR test. The DSR test was conducted at three different temperatures. A sample considered to be failed at a given temperature if the value of G*/sin(delta) was less than 1.00 kPa. In other words, if the G*/sin(delta) dropped below the cutoff value, the sample was assumed to be failed due to the increase in chance of rutting. Hence, according to The Asphalt Institute (2003) and Bahia and Anderson (1995), the high temperature performance grade is considered to be the major factor to control rutting. Typically, high temperature performance grades are determined in six degree increments. However, for this study, a continuous performance grade (PG) scale to the nearest 0.1°C was determined for each sample. The three test temperatures were used to provide sufficient data to produce a regression line that determined the predicted temperature when the G*/sin(delta) value was equal to 1.00 kPa. Each binder blend was tested in triplicate to provide a reliable estimation of the variation between the samples of the same treatment group. Next, each binder blend was short-term aged in a rolling thin film oven (RTFO) according to the aforementioned procedures. The rolling thin film oven procedure simulates the aging of a binder due to mixing and compaction in the field (The Asphalt Institute 2003 and Roberts *et al.* 1996). During RTFO procedure, the binder blend undergoes oxidative age hardening and hence had markedly stiffer properties. The high temperature properties were determined using DSR for each blend. The same three temperatures which were used during testing the unaged blend were used for testing each aged blend. However, the failure criterion of 1.0 kPa which was used for the unaged blends was replaced and increased to 2.2 kPa due to the stiffening of the aged blends (The Asphalt Institute 2003). The final high temperature performance grade was determined based upon the lower of the two high temperature performance grades determined for the unaged and RTFO aged blends.

At intermediate temperatures, G*sin δ was employed after RTFO and PAV aging as it better represents and predicts the fatigue cracking phenomenon that occurs in the pavement binder. In other words, due to the binder aging and oxidation, the pavement binder becomes more susceptible to fatigue cracking (Bahia and Anderson 1995). Although the intermediate temperature has no role in determining the performance grade of the pavement binder, the intermediate temperature is required to be reported to give an estimate of the susceptibility of the fatigue cracking. According to the Asphalt Institute 2003, a limit of 5000 kPa is employed for the

intermediate service temperature. Each blend was tested in triplicate at three temperatures; therefore, the intermediate temperature was determined.

The low temperature performance grade involved testing the pavement binder after RTFO and PAV aging using bending beam rheometer (BBR). According to the Asphalt Institute 2003 and Roberts *et al.* 1996, the BBR tested the pavement binder at low service temperatures to determine its susceptibility to thermal cracking. In other words, at low temperature, pavement binder is susceptible to thermal cracking due to the fact that it becomes less viscous as it is cooled. Rapid cooling and warming cause the binder to contract and expand, which lead to putting large thermal stresses on the material (Roberts *et al.* 1996). The experimental blends were tested according to the aforementioned procedures. The deflection was measured versus time, which was used to calculate the two key properties of stiffness and change in stiffness (m-value). According to Superpave requirements and specifications, a pavement binder can fail at a given temperature by either having a stiffness value "S" of greater than 300 MPa or an m-value less than 0.300 as shown in Figure 3.14 (The Asphalt Institute 2003 and Bahia and Anderson 1994). The low critical temperatures were calculated based upon regression analysis from the different test temperatures.

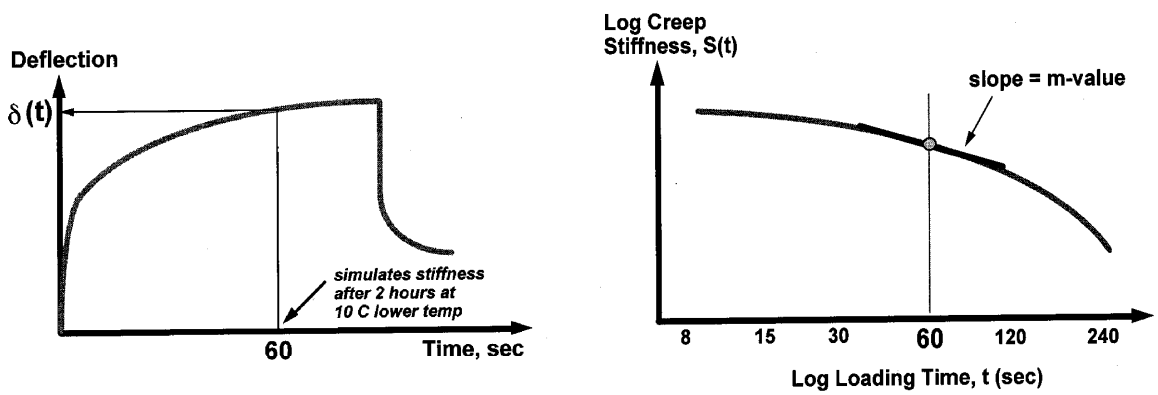


Figure 3.14. BBR Deflection and m-value
(Adopted from Asphalt Institute 2003)

Developing Master Curve for Complex Modulus G*

In this study, master curves were constructed by fitting a sigmoidal function to the measured shear modulus test data using non-linear least squares regression techniques. The shift can be done by solving the shift factors simultaneously with the coefficients of the sigmoidal function. The standard sigmoidal function or Richard's curve is defined by the following equation.

$$\log G^* = \delta + \frac{\alpha}{1+e^{(\beta+\gamma \log \omega)}}$$

Equation 3.1

where:

G* = shear modulus;
δ = lower asymptote;
δ+α = upper asymptote; and
β/γ = inflection point.

The creep response or modulus determined by the BBR can be converted to shear modulus using Equation 3.2 (Marateanu and Anderson 1996). Using the SHRP standard method for measuring the low temperature properties using the bending beam rheometer makes use of the flexural creep stiffness, S(t) = 1/D(t), so Equation 3.2 can be replaced by Equation 3.3. Moreover, the relationship between the complex modulus and stiffness can be expressed as shown in Equation 3.4. For values of m less than 0.5, the product of the trigonometric terms in Equation 3.5 falls between 0.95 and 1.05 and can consequently be reasonable approximated as unity. In addition, for the purpose of the master curve, the Poisson's ratio μ can be taken to be 0.5. Hence, the relationship between complex modulus and the stiffness can be expressed as shown in Equation 3.5.

$$J(t) = 2(1+\mu)D(t)$$

Equation 3.2

$$J(t) = 2(1+\mu)/S(t)$$

Equation 3.3

$$G^* = \frac{S(t)}{2(1+\mu)} \frac{\sin[(0.5b+0.5m)\pi]}{(0.5b)+(0.5m)\pi} \frac{1}{cas[arctg(\frac{m\pi}{2})]}$$

Equation 3.4

$$G^* = S(t)/3$$

Equation 3.5

where:

J(t): creep modulus in shear;
D(t): creep modulus in flexure;
S(t): stiffness modulus;
G*; complex modulus;
m: the slope of log S(t) versus log(t); and
μ: Poisson's ratio.

The most popular relationship between the dynamic and steady-state behavior of polymers is called Cox-Merz rule which can be expressed as shown in Equation 3.6. By definition, the complex viscosity and the steady-state are shown in Equation 3.7 and 3.8, respectively. Therefore, by replacing equation 3.7 and 3.8 in Equation 3.6, the relationship between τ and G* can be expressed as shown in Equation 3.9. Consequently, if the stress rate γ in reciprocal seconds is equal to ω in radians/second, Equation 3.9 can be replaced by Equation 3.10.

$$\eta(\gamma) = \eta^*(\omega)$$

Equation 3.6

$$\eta^* = G^*/\omega$$

Equation 3.7

$$\eta = \tau/\gamma$$

Equation 3.8

$$\tau/\gamma = G^*/\omega$$

Equation 3.9

$$\tau = G^*$$

Equation 3.10

Based on the above relationships, the G* for the tested bio-binders can be determined at high, intermediate and low temperatures through rotational viscometer, DSR and BBR test data, respectively. The following guidelines were followed to construct the master curves for the bio-binders tested in this research:

- Rotational viscometer: conducts test at four or five high temperatures.
- DSR: conduct tests using a 8mm plate for two or three intermediate temperatures with different frequency sweeps.
- BBR: conduct tests at two or three low temperatures.

CHAPTER 4. PRE-TREATMENT PROCEDURE FOR DEVELOPING BIO-BINDERS FROM BIO-OILS

Introduction

In this chapter, the pre-treatment procedure for developing bio-binders from bio-oils was determined for the three different bio-oils (oakwood, switchgrass and cornstover). The pre-treatment procedure can also be referred to as an upgrading procedure. The pre-treatment/upgrading procedure was determined through measuring the viscosity of the bio-oils at different temperatures (125 and 135°C) over 8 hours, then the aging indexes were calculated based on equation 2.5 that was previously discussed in Chapter 2. The viscosity measurements were recorded using a Brookfield viscometer based on the procedure described previously in Chapter 3.

Viscosity Measurements and Aging Index before Treatment

The viscosity measurements for the tested bio-oils over the 8 hours at 125 and 135°C without pre-treatment are summarized and listed in Table A4.1 and Table A4.2 in Appendix A, respectively. Figure 4.1 to Figure 4.3 and Figure 4.4 to Figure 4.6 display the viscosity over time for all the tested blends before treatment at 125 and 135°C, respectively.

Based on these figures, the following observations are noted. First, the viscosity of the unmodified oakwood, switchgrass, and cornstover bio-oils (blends 1, 8 and 15, respectively) were very low due to the presence of water and volatile materials. Besides, some viscosity measurements at the first two hours were almost zero due to the presence of water and volatile materials. Second, there was no considerable difference between the viscosity measurements of the three unmodified bio-oils. Third, the rates of change of viscosity over time for most of the blends were not constant. In other words, the rate of change of viscosity at the first two hours was different than the rate of change of viscosity between 2 and 8 hours. During the first two hours, a significant amount of evaporation and boiling took place due to the water and volatile materials. This may be the reason that the rate of change of viscosity during the first two hours was less than the rate of change of viscosity between 2 and 8 hours. Fourth, the addition of the polymer modifier led to a significant increase in the viscosity of the unmodified bio-oils. However, no specific optimum content for polymer modifiers could be determined.

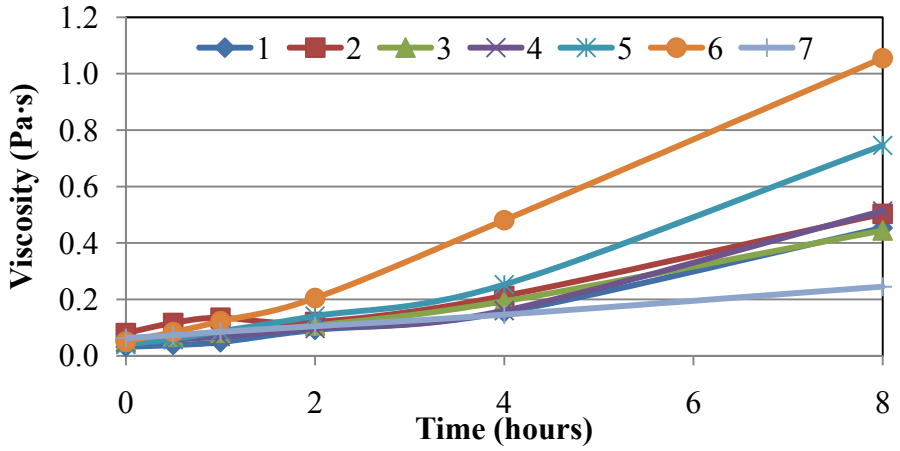


Figure 4.1. Viscosity over Time for Oakwood Blends before Treatment at 125°C

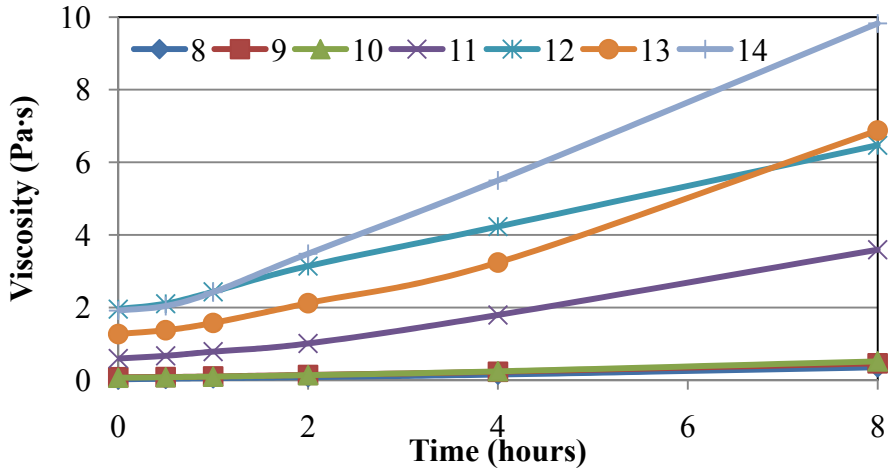


Figure 4.2. Viscosity over Time for Switchgrass Blends before Treatment at 125°C

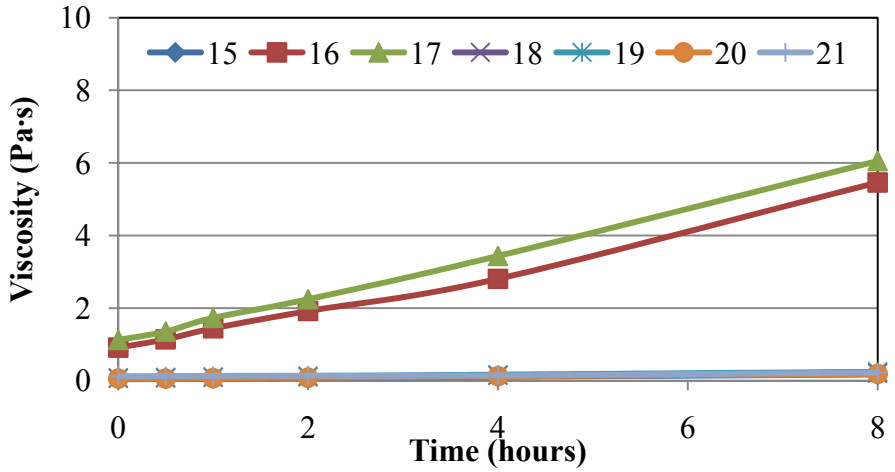


Figure 4.3. Viscosity over Time for Cornstover Blends before Treatment at 125°C

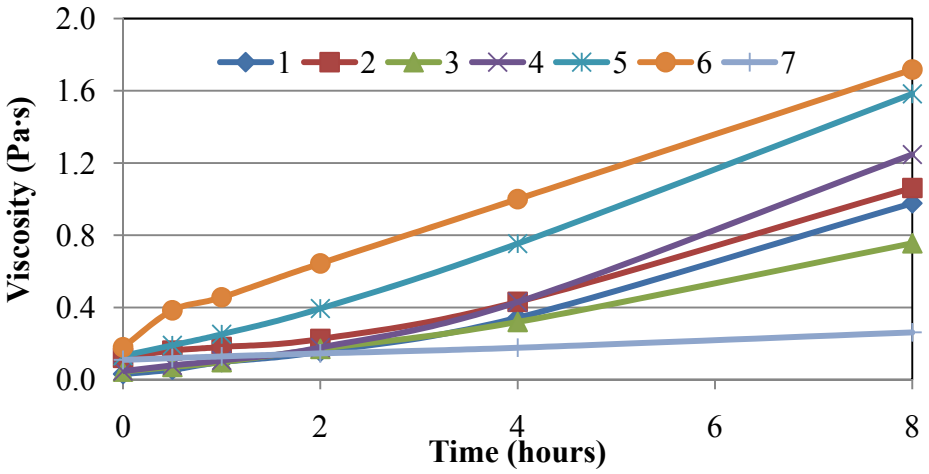


Figure 4.4. Viscosity over Time for Oakwood Blends before Treatment at 135°C

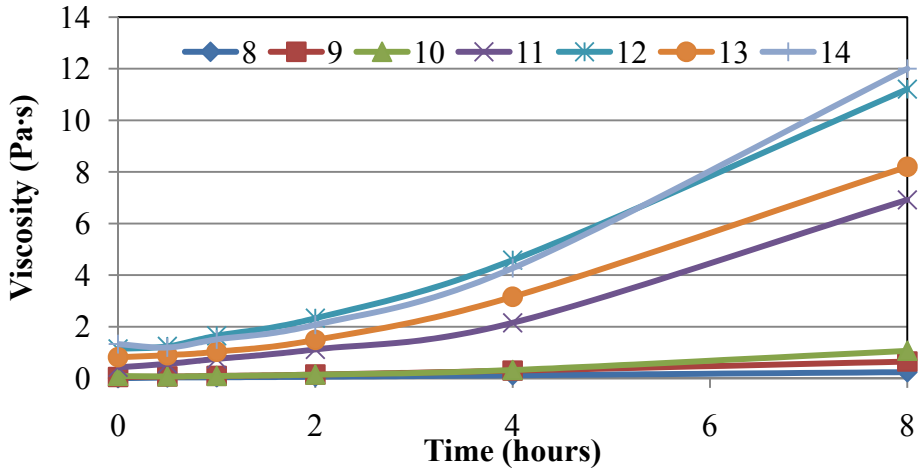


Figure 4.5. Viscosity over Time for Switchgrass Blends before Treatment at 135°C

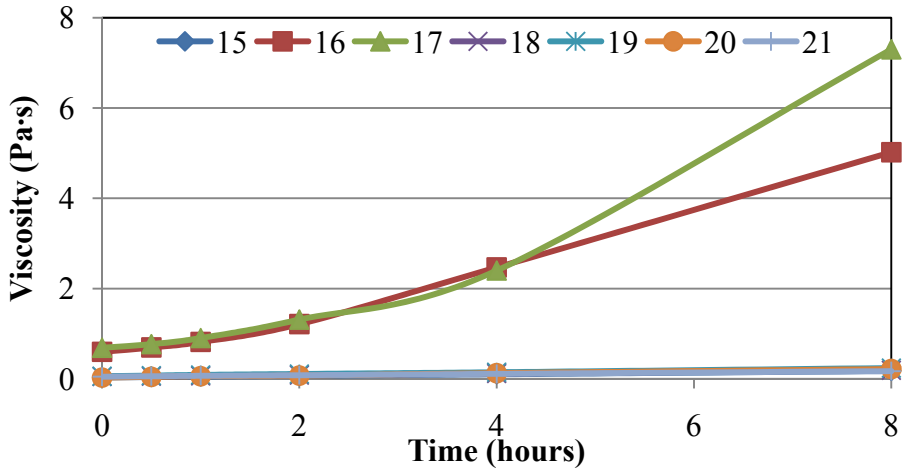


Figure 4.6. Viscosity over Time for Cornstover Blends before Treatment at 135°C

The aging indexes relative to zero and two hours were calculated and listed in Table 4.1 and Table 4.2 at 125 and 135°C, respectively. Figure 4.7 to Figure 4.9 and Figure 4.10 to Figure 4.12 display the aging indexes at 125°C for all the tested blends relative to zero and two hours, respectively. Figure 4.13 to Figure 4.15 and Figure 4.16 to Figure 4.18 represent the aging indexes at 135°C for all the tested blends relative to zero and two hours, respectively. Based on these values, the following conclusions could be made. First, the aging indexes after four hours were below 12 (the threshold value of bitumen binders) for all blends at 125°C and 135°C (except blend 8 at 135°C). In addition, the aging indexes after 8 hours were ranging between 1.78 and 20.75 and 3.46 and 32.00 for 125°C and 135°C, respectively. This indicated that increasing the temperature led to higher aging indexes and this was expected as the temperature is a significant factor in increasing the oxidation occurring in the bio-oils. However, when the aging indexes were determined relative to two hours, they were below 12 for all blends.

Therefore, it can be concluded that if the bio-oils were pre-treated/upgraded, the aging indexes of the bio-oils would decrease and become below the assumed limiting value (12) and would be comparable to bitumen binders. Second, the aging indexes relative to zero after 8 hours for the unmodified bio-oils were -in general- higher than 12 which indicated that significant amount of oxidation took place in the bio-oils due to the high content of oxygen present in the bio-oils. Third, the addition of polymer modifiers did not lead to a decrease in the aging indexes of the bio-oils. In other words, no specific trend could be noted in the aging indexes after the addition of a polymer modifier. Overall, it may be concluded that a pre-treatment/upgrading procedure was required for the bio-oils to stabilize them through decreasing the water and volatile materials content and consequently decrease the aging indexes.

Table 4.1. Aging Index Relative to Zero and Two Hours before Treatment at 125°C

Blend #	Aging Index relative to zero					Aging Index relative to two	
	0.5	1	2	4	8	4	8
1	1.21	1.53	2.89	4.87	14.32	1.68	4.95
2	1.44	1.67	1.48	2.63	6.23	1.77	4.19
3	1.31	1.58	2.08	3.74	8.60	1.80	4.13
4	1.28	1.52	2.15	3.56	11.41	1.66	5.31
5	1.50	2.17	3.52	6.31	18.65	1.79	5.30
6	1.66	2.41	4.03	9.46	20.75	2.35	5.15
7	1.16	1.35	1.67	2.32	3.89	1.39	2.33
8	1.63	2.44	3.74	6.81	15.63	1.82	4.18
9	1.09	1.29	1.83	2.93	5.90	1.60	3.23
10	1.23	1.47	2.10	3.71	7.94	1.76	3.77
11	1.13	1.32	1.70	3.02	6.04	1.78	3.56
12	1.08	1.24	1.61	2.16	3.31	1.35	2.06
13	1.08	1.24	1.67	2.55	5.42	1.53	3.24
14	1.07	1.26	1.82	2.87	5.13	1.58	2.82
15	1.25	1.58	1.93	2.70	4.25	1.40	2.21
16	1.25	1.58	2.10	3.07	5.98	1.46	2.84
17	1.20	1.54	2.00	3.05	5.38	1.53	2.69
18	1.15	1.38	1.62	2.26	3.20	1.40	1.98
19	1.19	1.31	1.63	2.10	3.10	1.29	1.91
20	1.00	1.17	1.42	2.08	3.12	1.47	2.20
21	1.04	1.08	1.12	1.16	1.78	1.04	1.59

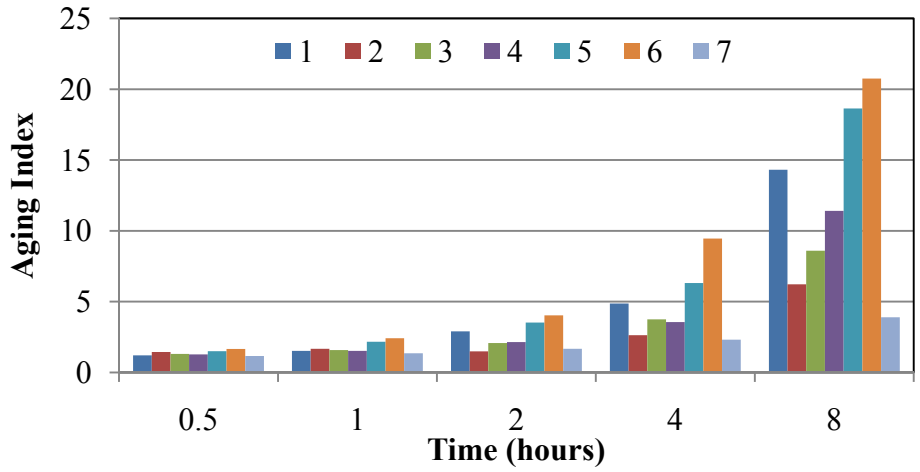


Figure 4.7. Aging Index Relative to Zero Hours for Oakwood Blends before Treatment at 125°C

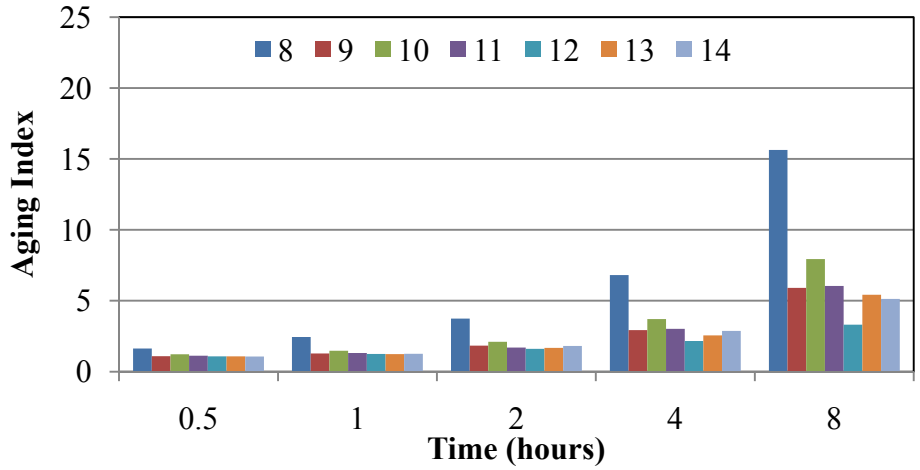


Figure 4.8. Aging Index Relative to Zero Hours for Switchgrass Blends before Treatment at 125°C

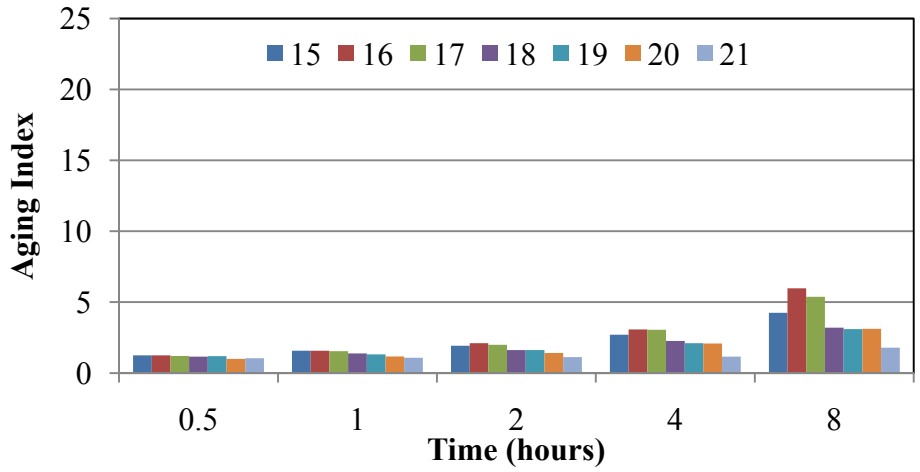


Figure 4.9. Aging Index Relative to Zero Hours for Cornstover Blends before Treatment at 125°C

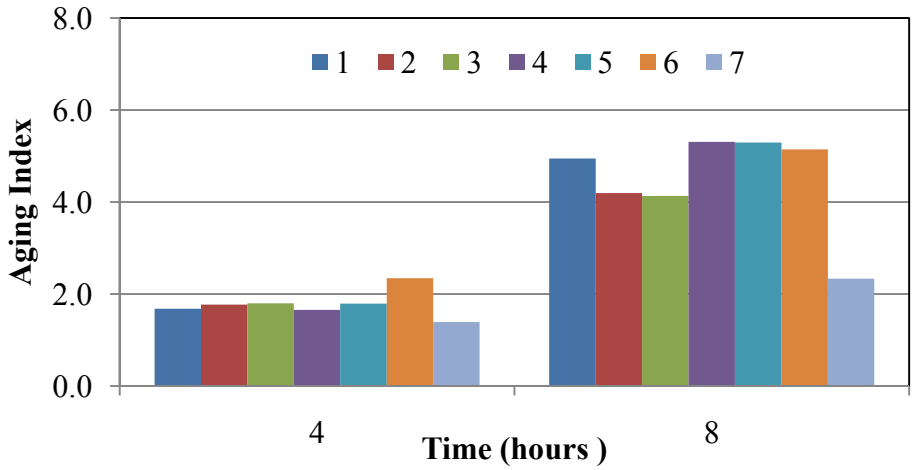


Figure 4.10. Aging Index Relative to Two Hours for Oakwood Blends before Treatment at 125°C

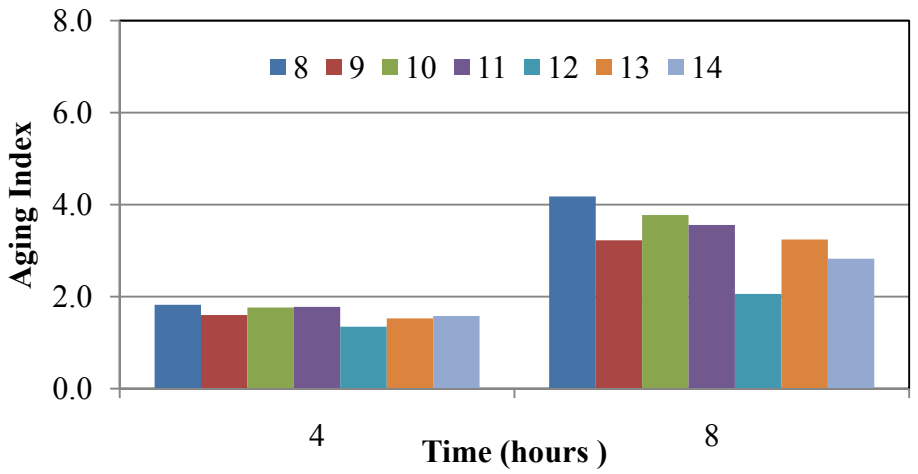


Figure 4.11. Aging Index Relative to Two Hours for Switchgrass Blends before Treatment at 125°C

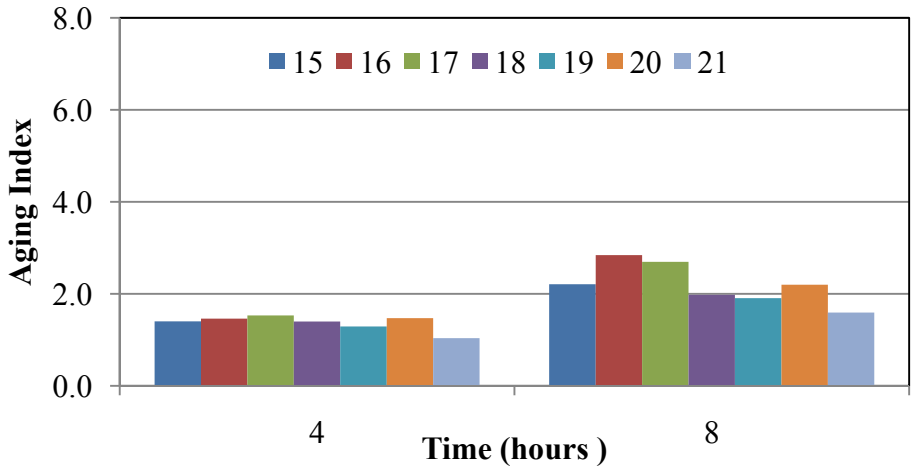


Figure 4.12. Aging Index Relative to Two Hours for Cornstover Blends before Treatment at 125°C

Table 4.2. Aging Index Relative to Zero and Two Hours before Treatment at 135°C

Blend #	Aging Index relative to zero					Aging Index relative to two	
	0.5	1	2	4	8	4	8
1	1.76	3.08	4.89	10.84	30.84	2.22	6.30
2	1.34	1.51	1.87	3.58	8.80	1.91	4.70
3	1.57	2.17	3.80	7.11	16.80	1.87	4.42
4	1.67	2.25	3.75	9.05	26.25	2.41	6.99
5	1.44	1.90	2.97	5.69	11.95	1.91	4.02
6	2.13	2.54	3.58	5.56	9.54	1.55	2.67
7	1.09	1.18	1.33	1.61	2.39	1.22	1.80
8	4.33	5.67	8.33	15.78	32.00	1.89	3.84
9	1.39	1.84	2.88	5.82	12.63	2.02	4.38
10	0.83	1.01	1.59	3.50	11.54	2.20	7.28
11	1.32	1.76	2.64	5.06	16.27	1.92	6.18
12	1.09	1.45	2.04	4.02	9.83	1.97	4.81
13	1.10	1.26	1.82	3.85	10.00	2.12	5.50
14	0.90	1.14	1.56	3.22	9.05	2.06	5.78
15	1.27	1.61	2.12	3.18	5.39	1.50	2.54
16	1.16	1.37	2.03	4.12	8.37	2.03	4.13
17	1.12	1.31	1.91	3.48	10.58	1.83	5.55
18	1.09	1.28	1.60	2.26	3.58	1.41	2.24
19	1.25	1.50	1.83	2.47	4.00	1.35	2.18
20	1.50	2.00	2.43	4.27	7.33	1.75	3.01
21	1.20	1.40	1.66	2.26	3.46	1.36	2.08

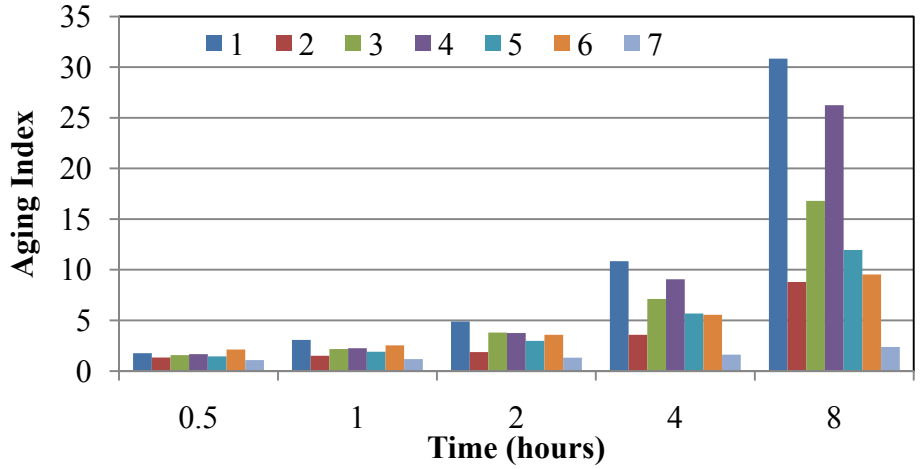


Figure 4.13. Aging Index Relative to Zero Hours for Oakwood Blends before Treatment at 135°C

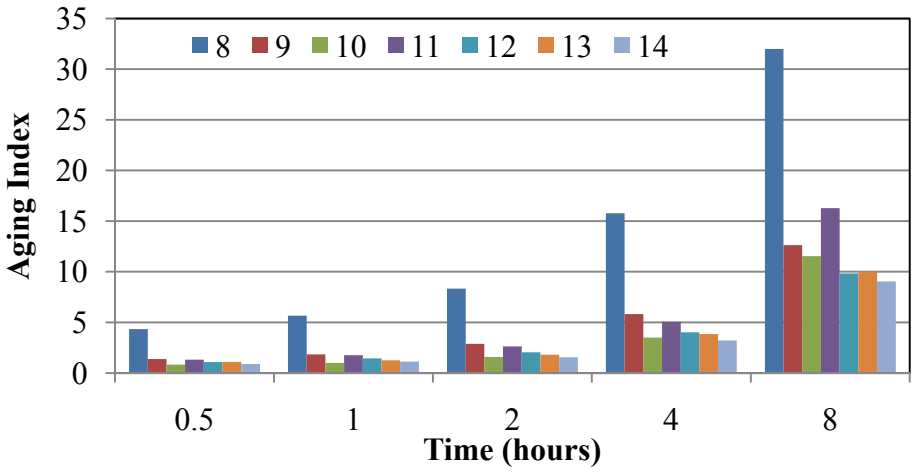


Figure 4.14. Aging Index Relative to Zero Hours for Switchgrass Blends before Treatment at 135°C

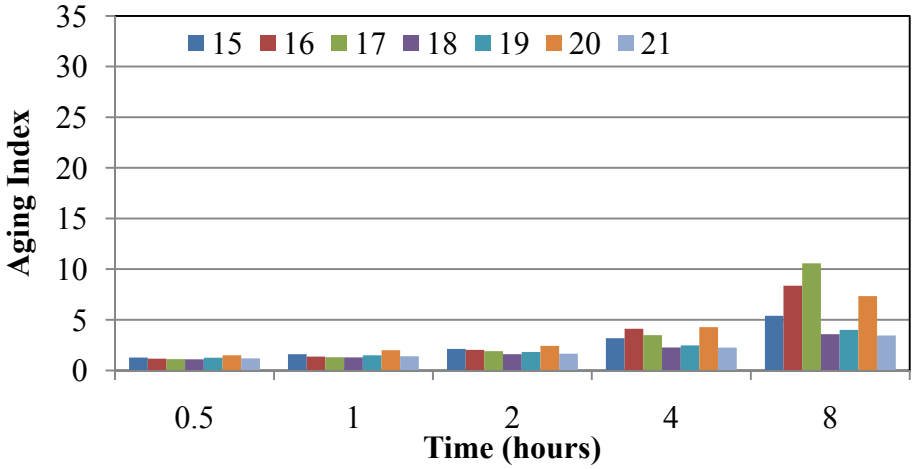


Figure 4.15. Aging Index Relative to Zero Hours for Cornstover Blends before Treatment at 135°C

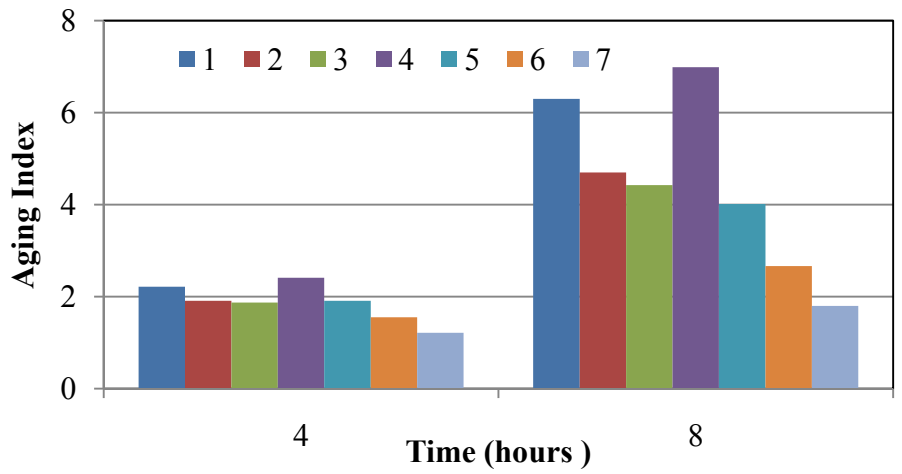


Figure 4.16. Aging Index Relative to Two Hours for Oakwood Blends before Treatment at 135°C

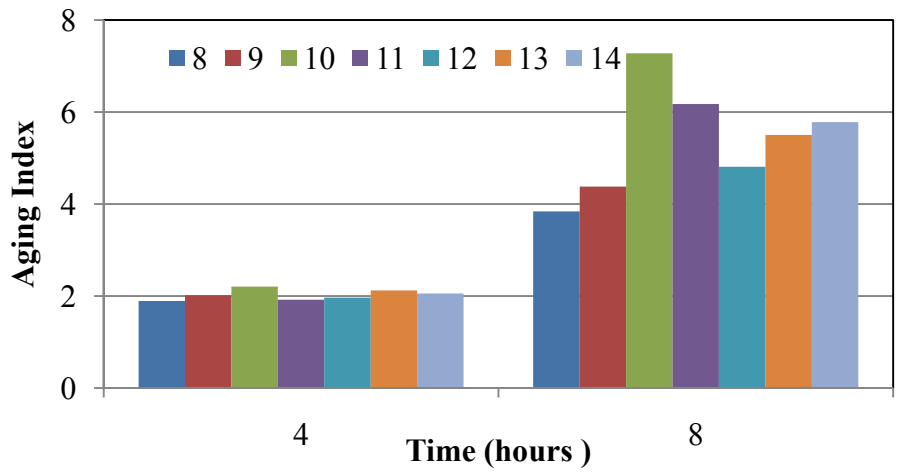


Figure 4.17. Aging Index Relative to Two Hours for Switchgrass Blends before Treatment at 135°C

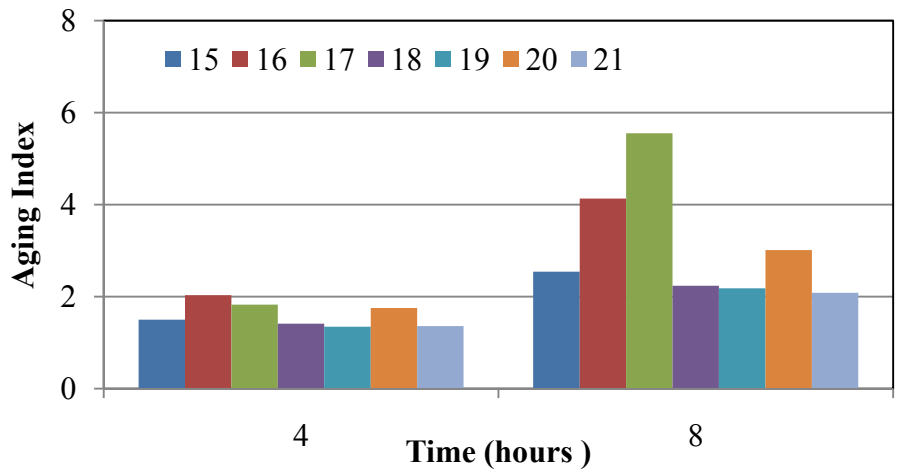


Figure 4.18. Aging Index Relative to Two Hours for Cornstover Blends before Treatment at 135°C

Having a global prospective, it was safe to conclude that since the bio-oils tested had a high content of water and volatile materials, the pre-treatment/upgrading temperature could be considered to be between 100 and 110°C, which is the temperature required for the evaporation of water. Importantly, the pre-treatment temperature should be below the decomposition temperature of the chemical constituents of bio-oils (cellulose, hemicellulose, and lignin). Significantly, it was noted that the rates of change of viscosity over 8 hours were variable and the aging and hardening of bio-oils after two hours were high, so the pre-treatment duration should be less than two hours because developing a bio-binder, initially, having a high viscosity may lead to mixing and pavement performance problems. Notably, the viscosity of the bio-oils after two-hours heating were below the viscosity specified by the Superpave at 140°C, which is 3 Pa·s. Therefore, the pre-treatment/upgrading duration could be considered to be a two-hour period.

Viscosity Measurements and Aging Index after Treatment

The viscosity measurements for the tested bio-oils over the 8 hours at 125°C and 135°C with pre-treatment are summarized and listed in Table A4.3 and Table A4.4 in Appendix A, respectively. Figure 4.19 to Figure 4.21 and Figure 4.22 to Figure 4.24 display the viscosity over time for all the tested blends after treatment at 125°C and 135°C, respectively. Based on these figures, the following observations could be noted.

First, the viscosity of the unmodified oakwood, switchgrass, and cornstover bio-oils (blends 1, 8 and 15, respectively) increased at 125°C and 135°C after treatment. This was expected as the treatment led to a decrease in the water and volatile materials contents. Second, no specific trend could be observed for the effect of treatment on the viscosity of the modified bio-oils at 125°C and 135°C. Precisely, the treatment procedure did not lead -in general- to an increase in the viscosity of the modified bio-oils. This may be due to the effect of the blending procedure of the polymer modifiers (polymer additives) with the bio-oils which incorporated heating for 30 minutes at 110-120°C; this blending procedure led to considerable variability in the viscosity of the modified bio-oils after treatment. Third, after treatment, the rates of change in viscosity over

time for most of the blends were constant. In other words, the rate of change in viscosity at the first two hours was the same rate of change of viscosity between 2 and 8 hours. Fourth, during the first two hours, the amount of evaporation and boiling took place due to the water and volatile materials decreased due to the treatment procedure. Fifth, the addition of the polymer modifier did not led to a specific trend in the sense of increasing the viscosity of the unmodified bio-oils. Therefore, no specific optimum content for polymer modifiers could be determined. In summary, it may be concluded that the treatment procedure was effective in increasing the viscosity of the unmodified bio-oils due to the evaporation of water and volatile materials and this at least in part lead to decrease the temperature susceptibility of the bio-binders developed from bio-oils.

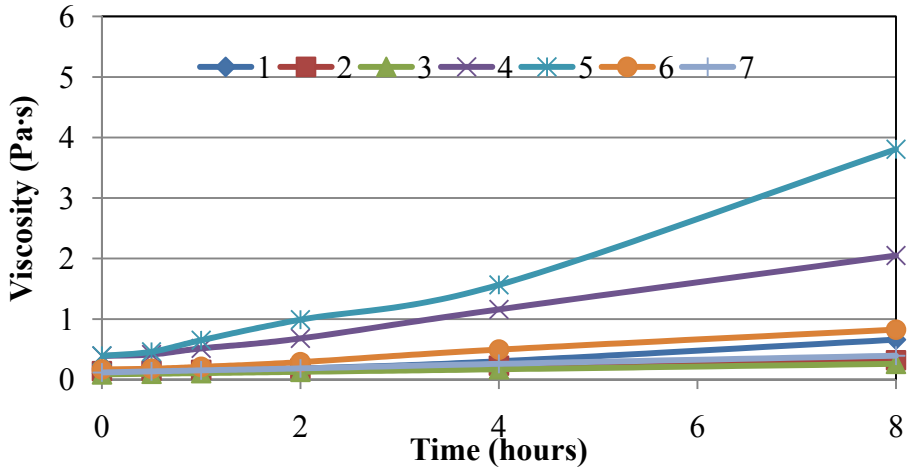


Figure 4.19. Viscosity over Time for Oakwood Blends after Treatment at 125°C

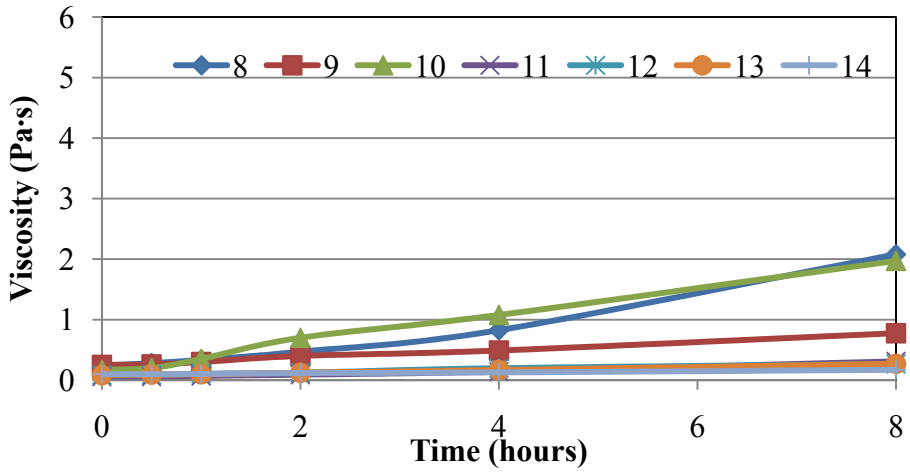


Figure 4.20. Viscosity over Time for Switchgrass Blends after Treatment at 125°C

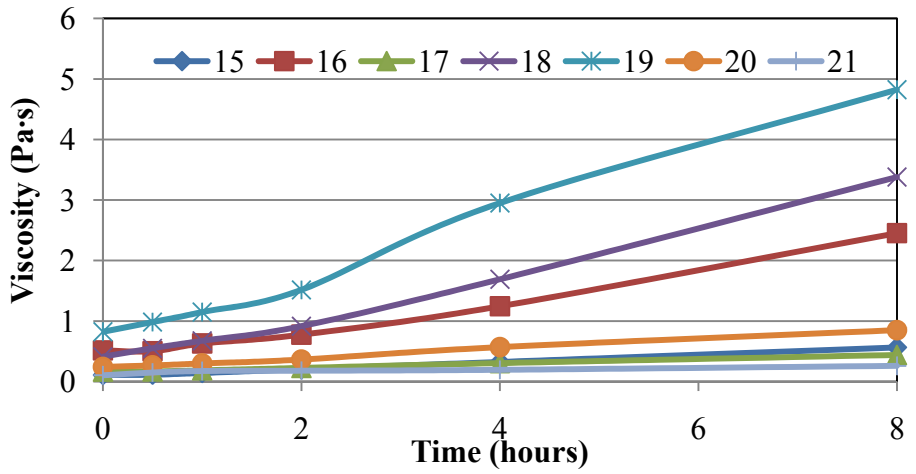


Figure 4.21. Viscosity over Time for Cornstover Blends after Treatment at 125°C

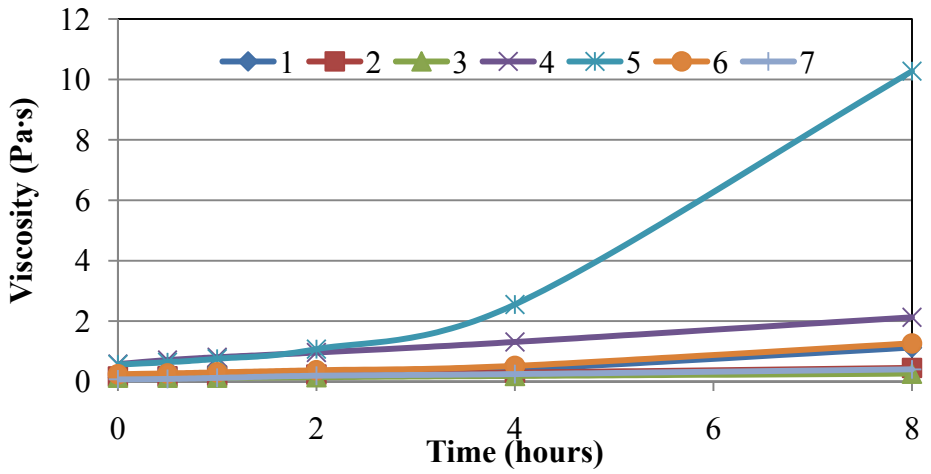


Figure 4.22. Viscosity over Time for Oakwood Blends after Treatment at 135°C

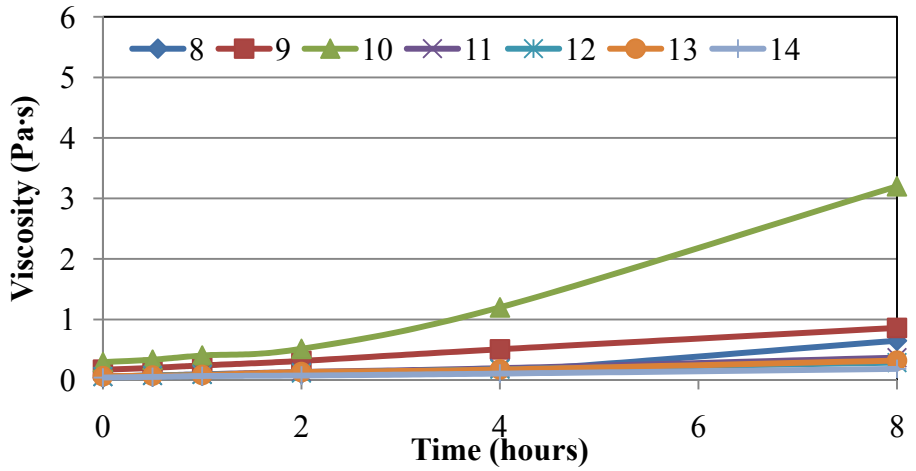


Figure 4.23. Viscosity over Time for Switchgrass Blends after Treatment at 135°C

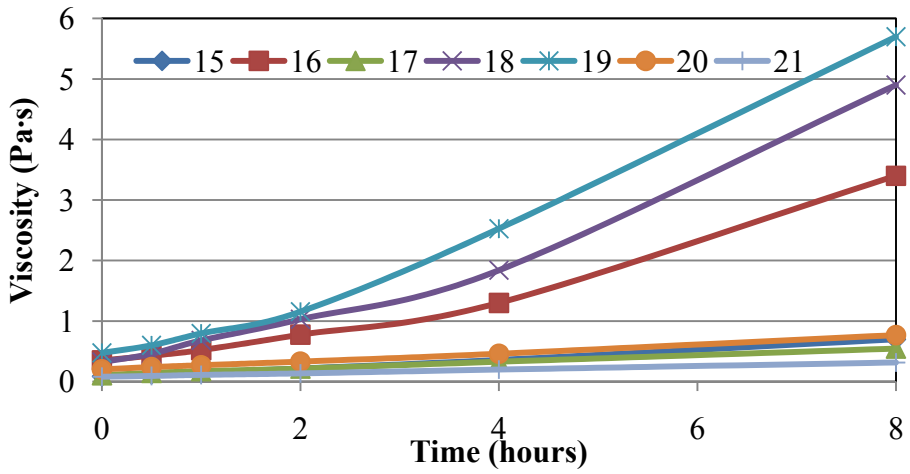


Figure 4.24. Viscosity over Time for Cornstover Blends after Treatment at 135°C

The aging indexes relative to zero hours were calculated and listed in Table 4.3 and Table 4.4 at 125°C and 135°C, respectively. Figure 4.25 to Figure 4.27 and Figure 4.28 to Figure 4.30 represent the aging indexes for all the tested blends relative to zero hours at 125°C and 135°C, respectively. Based on these values, the following conclusions can be made. First, the aging indexes relative to zero hours were decreased -in general- after treatment compared to the corresponding values of aging indexes before treatment. This may be due to the increase in viscosity of the bio-oils associated with the treatment procedure due to the loss of water and volatile materials. Second, there was variability in the aging indexes after the treatment, precisely the aging indexes for some blends increased after treatment. However, this variability was expected due to the variability associated with the blending procedure of the polymer modifier, and with the bio-oils itself as a material.

Table 4.3. Aging Index Relative to Zero Hours after Treatment at 125°C

Blend #	Aging Index relative to zero				
	0.5	1	2	4	8
1	1.14	1.29	1.74	2.89	6.29
2	1.04	1.14	1.29	1.64	2.29
3	1.12	1.25	1.50	2.00	3.06
4	1.06	1.32	1.74	2.97	5.26
5	1.17	1.65	2.52	3.98	9.68
6	1.07	1.25	1.71	2.95	4.91
7	1.15	1.30	1.57	2.21	3.36
8	1.18	1.41	1.97	3.47	8.73
9	1.03	1.19	1.58	1.94	3.06
10	1.18	2.06	4.12	6.34	11.59
11	1.00	1.17	1.50	2.38	5.17
12	1.06	1.26	1.44	2.32	3.15
13	1.12	1.18	1.49	2.03	3.27
14	1.00	1.03	1.18	1.28	1.70
15	1.06	1.32	1.90	3.01	5.23
16	0.98	1.22	1.51	2.42	4.76
17	1.02	1.12	1.36	1.85	2.67
18	1.34	1.64	2.23	4.12	8.24
19	1.19	1.39	1.84	3.58	5.86
20	1.10	1.23	1.50	2.35	3.50
21	1.43	1.67	1.71	1.86	2.48

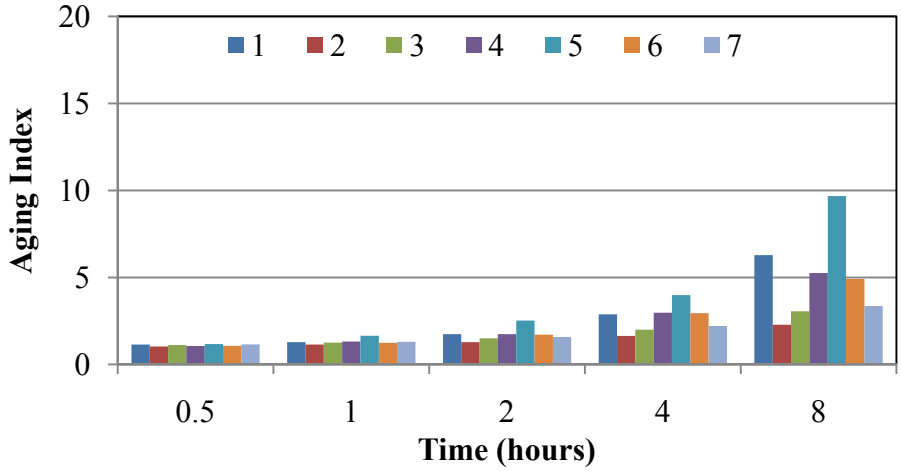


Figure 4.25. Aging Index Relative to Zero Hours for Oakwood Blends after Treatment at 125°C

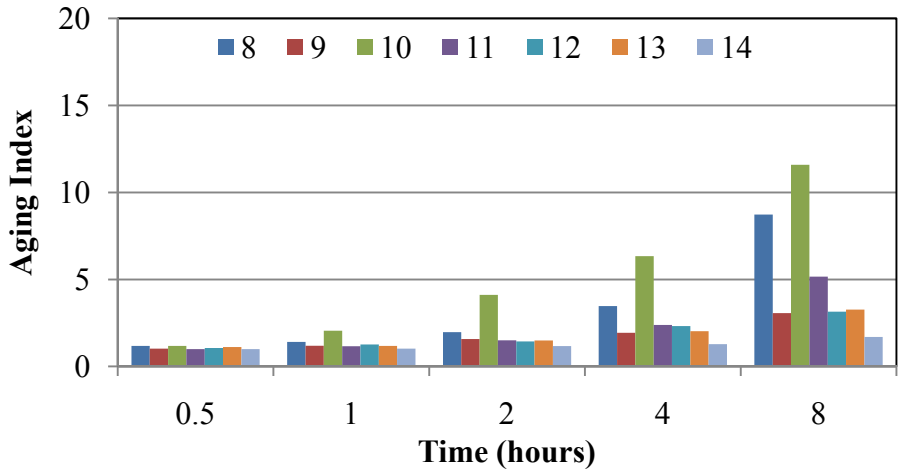


Figure 4.26. Aging Index Relative to Zero Hours for Switchgrass Blends after Treatment at 125°C

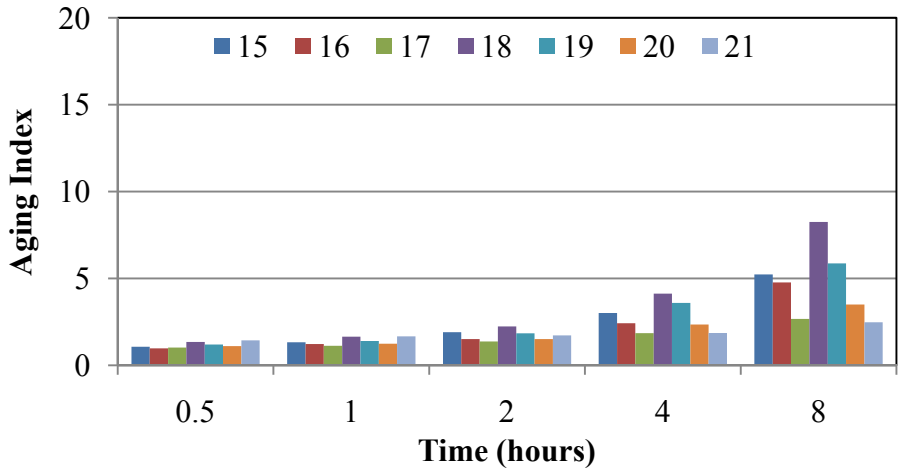


Figure 4.27. Aging Index Relative to Zero Hours for Cornstover Blends after Treatment at 125°C

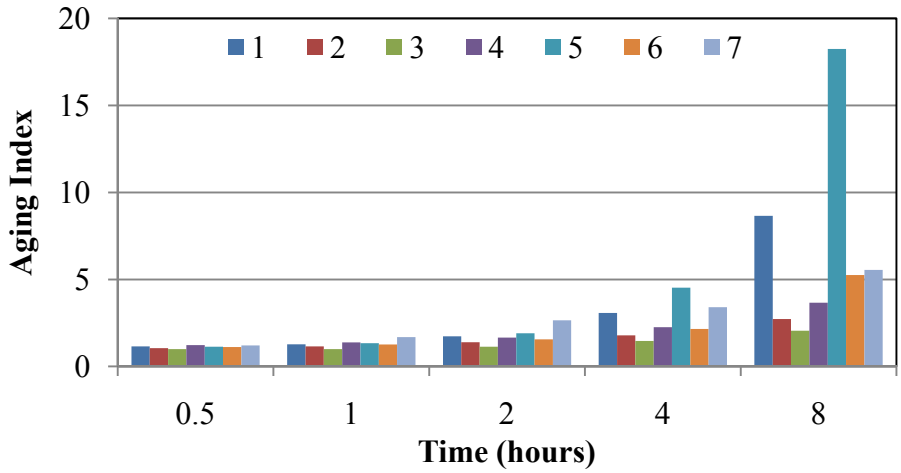


Figure 4.28. Aging Index Relative to Zero Hours for Oakwood Blends after Treatment at 135°C

Table 4.4. Aging Index Relative to Zero Hours after Treatment at 135°C

Blend #	Aging Index relative to zero				
	0.5	1	2	4	8
1	1.15	1.27	1.73	3.08	8.65
2	1.05	1.15	1.39	1.79	2.73
3	1.00	1.00	1.13	1.46	2.05
4	1.22	1.39	1.66	2.26	3.66
5	1.14	1.34	1.91	4.53	18.25
6	1.12	1.26	1.55	2.16	5.25
7	1.21	1.69	2.66	3.41	5.55
8	1.37	1.71	2.47	3.66	15.85
9	1.18	1.41	1.85	2.98	5.06
10	1.14	1.37	1.75	4.07	10.85
11	1.36	1.73	2.41	3.55	6.69
12	1.30	1.57	2.00	3.09	5.00
13	1.16	1.32	2.08	2.76	5.12
14	1.25	1.63	1.81	2.63	4.56
15	1.44	1.78	2.51	4.11	8.02
16	1.22	1.49	2.21	3.71	9.71
17	1.37	1.65	2.05	3.12	5.19
18	1.42	2.09	3.17	5.66	15.08
19	1.26	1.68	2.44	5.33	12.03
20	1.19	1.34	1.63	2.28	3.80
21	1.16	1.38	1.69	2.48	3.94

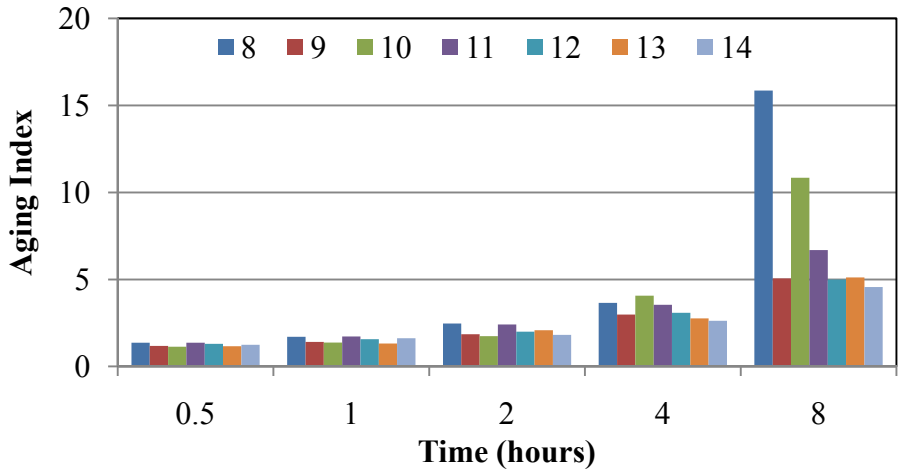


Figure 4.29. Aging Index Relative to Zero Hours for Switchgrass Blends after Treatment at 135°C

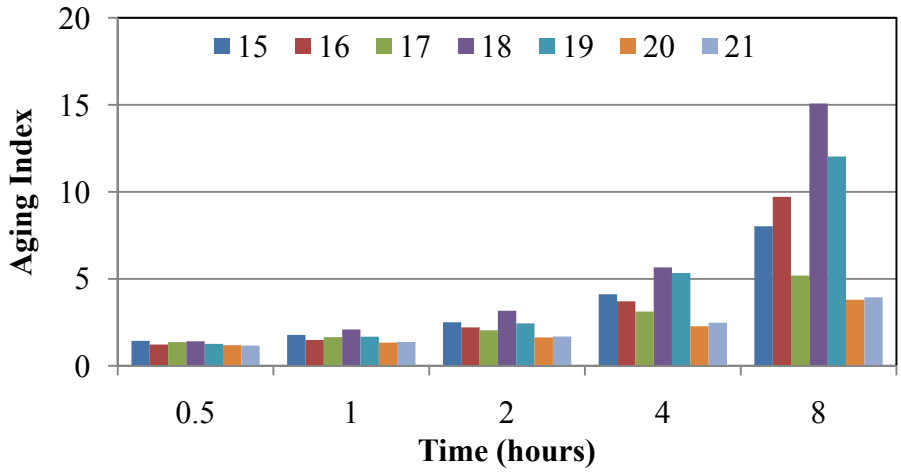


Figure 4.30. Aging Index Relative to Zero Hours for Cornstover Blends after Treatment at 135°C

Statistical Analysis

A statistical analysis was conducted, using the computer software JMP 7.0, to study the statistical difference between the viscosity over time and the aging indexes of the bio-oils. A one-way analysis of variance "ANOVA" using the method of least squares was performed for evaluating the effect of heat treatment. Type I error (α) of 0.05 was used for all statistical analysis as the confidence level was 95%. The p-values of the AVOVA for the viscosity over time and aging indexes for bio-oils were summarized and listed in Table 4.5 and

Table 4.6, respectively. As shown below, the statistical tests were grouped according to the binder type and the temperature.

Table 4.5. Effect of Heat Treatment on the Viscosity over Time of Bio-oils

Binder Type	Temp. (°C)	V0	V0.5	V1	V2	V4	V8
Oakwood	125	***0.0110****	***0.0207****	***0.0435****	0.0677	0.1042	0.2393
	135	***0.0588***	0.1638	0.2071	0.2781	0.4048	0.4038
Switchgrass	125	***0.0535***	***0.0506***	***0.0539***	***0.0622***	***0.0554***	***0.0515***
	135	***0.0541***	***0.0476****	***0.0458****	***0.0379****	***0.0349****	***0.0275****
Cornstover	125	0.9779	0.9186	0.8641	0.8626	0.9436	0.9799
	135	0.8935	0.7520	0.6226	0.6375	0.6964	0.7666

Bold, italic,*: statistically significant
Bold, italic: very close to be statistically significant

Table 4.6. Effect of Heat Treatment on Aging Index of Bio-oils

Binder Type	Temp. (°C)	AI0.5	AI1	AI2	AI4	AI8
Oakwood	125	***0.0029****	***0.0185****	***0.0578***	0.0620	***0.0180****
	135	***0.0048****	***0.0088****	***0.0129****	***0.0154****	0.0720
Switchgrass	125	0.2233	0.5255	0.7271	0.4937	0.3917
	135	0.5149	0.4518	0.3326	0.1447	0.0696
Cornstover	125	0.9398	0.9496	0.8526	0.3579	0.3875
	135	0.3387	0.3429	0.2082	0.2846	0.2859

Bold, italic,*: statistically significant
Bold, italic: very close to be statistically significant

Based on these results, the following conclusions can be established. First, the effect of the heat treatment on the viscosity over time and aging indexes were dependent on the type of the bio-oil. In other words, the viscosity over time and aging index for the bio-oils were not affected similarly due to heat treatment. From Table 4.5, the viscosity over time of the oakwood and switchgrass bio-oils was in general affected at 125°C and 135°C, respectively. From

Table 4.6, the aging index of the oakwood was the only bio-oil affected by the heat treatment. Second, no specific trend could be noted for the effect of the treatment on the viscosity over time and aging indexes of the bio-oils. This may be due to the low temperature (100-110°C) of the treatment which led to evaporate the water content and the volatile materials without affecting the physical and chemical properties of the bio-oils. In addition, no clear trend was observed for the effect of heat treatment on viscosity may be due to the difference in temperature between the heat treatment (100-110°C) and the temperature at which the viscosity was being measured (125°C and 135°C). Overall, the statistical analysis showed that the heat treatment procedure for the bio-oils had different effects on the viscosity over time and aging index and the degree of this effect was dependant on the type of the bio-oil. Also, the heat treatment procedure may not lead to significant changes in the physical and chemical properties of the bio-oils; however, the heat treatment procedure may be very important procedure to upgrade and stabilize the bio-oils through reducing the water and volatile materials content.

General Conclusions

Having a global prospective in the results, the following conclusions could be established. First, the viscosity of the unmodified oakwood, switchgrass, and cornstover bio-oils were very low due to the presence of high content of water and volatile materials. In addition, there was no considerable difference between the viscosity measurements of the three unmodified bio-oils. Importantly, it was observed that the rates of change in viscosity over time for most of the blends were not constant and a considerable amount of evaporation and boiling took place in the first 2 hours due to the high content of water and volatile materials. Second, the aging indexes relative to zero after 8 hours for the unmodified bio-oils were in general higher than the assumed limiting value (12) which indicate that a significant amount of oxidation took place in the bio-oils due to the high content of oxygen present in the bio-oils. Also, the results indicated that increasing the temperature led to higher aging indexes and this was expected as the temperature is a significant factor in increasing the oxidation occurring in the bio-oils. Therefore, it may be concluded that after the pre-treatment procedure, the water content and volatile materials would decrease and the aging indexes of the bio-oils would be below the assumed limiting value (12). Third, after treatment, the viscosity of the unmodified oakwood, switchgrass, and cornstover bio-oils (blends 1, 8 and 15, respectively) increased at 125°C and 135°C. This was expected as the treatment led to decrease the amount of water content and volatile materials. Fourth, no specific trend could be noted for the viscosity of the modified bio-oils after treatment at 125°C and 135°C. Precisely, the treatment procedure did not lead in general to an increase in the viscosity of the modified bio-oils. This may be due to the effect of the blending procedure of the polymer modifiers with the bio-oils which incorporated heating for 30 minutes at 110-120°C; this blending procedure led to considerable variability in the viscosity of the modified bio-oils after treatment. Fifth, the aging indexes relative to zero hours were generally decreased after treatment compared to the corresponding values of aging indexes before treatment. This may be due to the increase in viscosity of the bio-oils associated with the treatment procedure due to the loss of water and volatile materials. However, the statistical analysis showed that the effect of the heat treatment on the aging indexes were not statistically significant at all types of bio-oils. Overall, it is reasonable to conclude that the bio-oils needs heat treatment in order to be suitable to be used as a bio-binder in the pavement industry. Importantly, the heat treatment procedure may not lead to significant changes in the physical and chemical properties of the bio-oils; however, the heat treatment procedure may be very important procedure to upgrade the bio-oils through reducing the high water and volatile materials content. According to the bio-oils tested in this study, the heat treatment/upgrading procedure was established to be heating for 2 hours at 100-110°C.

CHAPTER 5. MODIFICATIONS OF SUPERPAVE TEST STANDARDS AND PROCEDURES

Introduction

The RTFO test procedure serves two purposes that can be stated as follows. The first is to provide an aged bituminous/asphalt binder that can be used for further testing of physical properties. The second is to determine the mass quantity of volatiles loss from the asphalt during the mixing and compaction processes. Volatile mass loss is an indication of the aging that may occur in the asphalt during mixing and compaction operations. Hence, the main objective of the RTFO test is to measure the effect of temperature and moving current of air on the properties of the semi-solid asphalt binders.

The Superpave specifications and standards were developed for the unmodified bituminous binders, but they are used for modified bituminous binders as well without any modifications. Since there is scarcity of data concerning using the bio-oils as a direct alternative (100% replacement) as a pavement material, there are no specifications or standards for determining the effect of temperature and moving current of air on the bio-oils. In other words, the RTFO test procedure for bio-oils is not developed and the current RTFO test procedure for bituminous binders could not be used without modifications for the bio-oils or the bio-binders derived from the bio-oils. As a result, the RTFO test procedure should be modified to comply with the properties of the bio-oils based upon different viscosities of bio-binders than standard paving bitumens. In this chapter, the Superpave specification or procedure for short-term and long-term aging through RTFO and PAV testing were modified to comply with the properties of the bio-binders developed from bio-oils. The proposed RTFO and PAV test procedures for bio-binders included changing the temperature and the duration specified by the Superpave specification.

Modifying the Superpave Procedure for Rolling Thin Film Oven Testing

The Superpave specification limits was initially established by consensus of the Federal Highway Administration Asphalt Binder Expert Task Group (ETG). The ETG group initially established the minimum limit of 1 kPa for unaged asphalt binders (original binders). As AC-10 asphalt cements were providing reasonable service in moderate climates from a rutting standpoint, AC-10 asphalt cements were tested in a DSR at 10 radians/second and their G*/sin(delta) values were approximately 1 kPa (Roberts *et al.* 1996). Therefore, the minimum limit of 1 kPa for the unaged asphalt binder was considered reasonable. The minimum limit of 2.2 kPa for the G*/sin(delta) value of RTFO aged asphalt binders was established based on the 1 kPa value of the unaged asphalt binder. RTFO test data on asphalt cements indicated that, on the average, the aging index (viscosity after RTFO/viscosity before RTFO) for asphalt cements ranged from 2 to 2.5. In other words, asphalt binders become from 2 to 2.5 times stiffer when aged according to the RTFO test procedure. Therefore, the average of the range, 2.2 was used to establish the 2.2 kPa minimum limit for RTFO aged asphalt binders (Roberts *et al.* 1996). Since there is scarcity of data concerning about the usage of bio-oils as a direct alternative to pavement materials, these specification limits are considered to be the same for bio-oils.

As concluded in Chapter 4, the bio-oils/bio-binders could not be treated at temperatures higher than 110-120°C, so the RTFO temperature was decreased from 160°C to 110-120°C. Likely, according to the Superpave specification for bituminous binders, the RTFO duration should be set to 80 minutes, which did not suit the properties of bio-oils/bio-binders. Therefore, the RTFO duration should be modified to comply with the properties of the bio-oils. In this section of the chapter, the duration for the RTFO test procedure will be determined through G*/sin(delta) for the unaged samples and the RTFO aged samples at 40°C. This temperature were selected as many bio-binders, such as blends 1, 2, 3, 11, and 15 were getting very low values of G*/sin(delta) at this temperature, which indicated that their performance grades were lower than 40°C. In addition, measuring the G*/sin(delta) and determining the high performance grade at temperatures lower than 40°C would be unfeasible and unpractical. The performance grade for the unaged samples could not be determined for the bio-oils/bio-binders without a pre-treatment procedure. Therefore, the performance grades for the bio-oils were determined after the treatment procedures which were previously discussed. The treatment procedures required heating the bio-oils at 110°C for 2 hours. The unaged treated/upgraded samples were considered as a base or control value. The RTFO aged samples consisted of three different aging durations in the RTFO, preciously 10-min, 20-min and 30-min. The G*/sin(delta) and performance grade for unaged, 10-min, 20-min and 30-min-RTFO samples were determined and listed in Table B5.1 to Table B5.4 in appendix B, respectively. The high temperature performance grade for these samples were summarized and listed in Table 5.1.

To determine the RTFO duration required for the testing procedure, the ratio between the G*/sin(delta) values for the unaged and the RTFO aged samples were determined through a value called the RTFO Index (as shown in Equation 5.1). The RTFO index is a value employed for the first time in this research work, so there is no limitation or threshold value for this index in the literature review.

$$RTFO\ Index = \frac{(G*/sindelta)_{aged}}{(G*/sindelta)_{unaged}} \qquad \text{Equation 5.1}$$

Table 5.1. Summary of High Temperature Performance Grade

Blend #	Sample I.D.	High Temperature Performance Grade (°C)			
		Unaged samples	10-min RTFO Samples	20-min RTFO Samples	30-min RTFO Samples
1	**OFP0B0**	-	47	50	64
2	**OFP1B2**	-	53	52	68
3	**OFP1B4**	-	56	55	67
4	**OFP2B2**	65	65	68	77
5	**OFP2B4**	57	71	76	79
6	**OFP3B2**	47	59	65	69
7	**OFP3B4**	49	60	65	71
8	**SGP0B0**	46	53	59	67
9	**SGP1B2**	47	58	59	66
10	**SGP1B4**	55	57	64	71
11	**SGP2B2**	-	41	53	59
12	**SGP2B4**	41	51	59	63
13	**SGP3B2**	42	48	59	67
14	**SGP3B4**	41	64	57	63
15	**CSP0B0**	-	48	60	60
16	**CSP1B2**	59	65	72	71
17	**CSP1B4**	46	50	71	71
18	**CSP2B2**	55	61	69	77
19	**CSP2B4**	57	65	73	81
20	**CSP3B2**	56	59	68	73
21	**CSP3B4**	44	51	57	66

There is scarcity of data to specify the ratio of G*/sin(delta) between the unaged and the RTFO aged samples for bituminous binders. Likely, the ratio between G*/sin(delta) for the unaged and RTFO aged bio-binders samples is not specified. Therefore, a threshold value for the RTFO index should be specified. The Superpave specifications specified values of 1.0 and 2.2 kPa for G*/sin(delta) as passing values for unaged and RTFO aged samples for bituminous binders, respectively. For example, the G*/sin(delta) value for an unaged sample should be higher than 1.0 kPa at a given temperature in order to be considered as its high temperature performance grade. On the other hand, the G*/sin(delta) value for an RTFO aged sample should be higher than 2.2 kPa at a given temperature in order to be considered as its high temperature performance grade. Therefore, the RTFO index for bituminous binders can be calculated according to the equation mentioned above. The RTFO index for bituminous binders was calculated to be 2.2. Using this value as a threshold for RTFO index, the RTFO index values for bio-oils/bio-binders can be calculated using the G*/sin(delta) of the unaged and the RTFO aged samples of the bio-oils/bio-binders. The RTFO index values for all bio-binders are summarized in

Table 5.2 and displayed in Figure 5.1.

Table 5.2. RTFO Index for All Bio-binders

Blend #	Sample I.D.	RTFO Index (%) 10-min RTFO Samples	20-min RTFO Samples	30-min RTFO Samples
1	**OFP0B0**	25	83	2002
2	**OFP1B2**	86	1001	7542
3	**OFP1B4**	16142	18520	272874
4	**OFP2B2**	2	4	51
5	**OFP2B4**	23	54	155
6	**OFP3B2**	6	59	13
7	**OFP3B4**	15	71	284
8	**SGP0B0**	10	31	99
9	**SGP1B2**	17	15	58
10	**SGP1B4**	4	15	61
11	**SGP2B2**	4	73	258
12	**SGP2B4**	20	115	219
13	**SGP3B2**	6	110	245
14	**SGP3B4**	66	65	275
15	**CSP0B0**	42	466	539
16	**CSP1B2**	8	48	39
17	**CSP1B4**	4	343	317
18	**CSP2B2**	11	55	275
19	**CSP2B4**	6	42	252
20	**CSP3B2**	4	36	104
21	**CSP3B4**	32	39	287

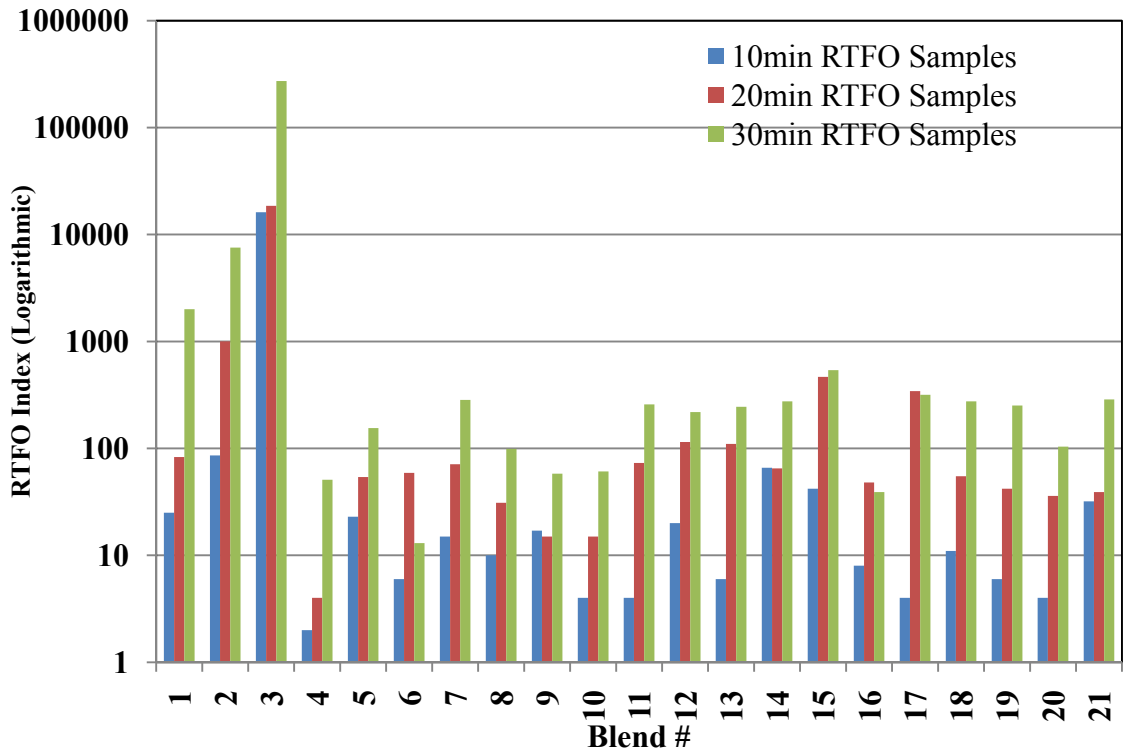


Figure 5.1. RTFO Index for all Bio-oils/Bio-Binders

From Table 5.2 and Figure 5.1, the following conclusions could be noted. First, the RTFO indexes for the bio-oils blends/bio-binders (modified and unmodified) were very high in comparison to the RTFO index of bituminous binders (2.2). This was expected as the amount of oxygen in the bio-oils was around 40% and much greater than the 1% in the bitumen. Therefore, the amount of oxidation taking place in bio-oils/bio-binders was significantly higher than that taking place in bitumen. Second, the RTFO duration for the treated bio-oils could not be more than 20 minutes because the RTFO indexes for 30-min RTFO samples were extremely high. In addition, there were some difficulties preparing the 30-min RTFO samples for testing in the DSR due to the excessive mass losses and oxidation in the samples. Importantly, the temperature performance grades due to 30-min duration were higher than temperature performance grades due to 20-min for all bio-binders blends (see Table B5.3 and Table B5.4 in appendix B); therefore, it is more conservative to use 20-min duration as the specified duration to determine the temperature performance grade of the bio-oils/bio-binders. Third, the unmodified oakwood, switchgrass, and cornstover bio-binders (1, 8 and 15) showed that 10-min duration would be fair enough to be considered as the duration that resembles the oxidation occurring due to mixing and compaction. However, 10-min as duration for mixing and compaction was not enough. As a result, it was more reasonable and appropriate to consider 20-min duration as a more feasible duration to resemble mixing and compaction. Significantly, no clear trend could be observed for the amount of oxidation taking place in the bio-binders. In other words, a threshold value for RTFO index for bio-binders could not be determined due to the large variability in the results of the RTFO indexes calculated above. Overall, the 20-min duration was established to be the duration to resemble the mixing and compaction duration.

Modifying the Superpave Procedure for Pressure Aging Vessel Testing

The PAV exposes the developed bio-binder to high pressure and temperature for 20 hours to simulate the effects of long-term in-situ aging, precisely 5-10 years of in-service aging (Bahia and Anderson, 1994). Generally, the PAV aged bio-binders were used to test the intermediate critical temperature with the DSR and then the low temperature performance grade using the BBR. Since pavement binders exposed to long-term aging have also been through the mixing and construction process, the PAV procedure was performed on RTFO-aged bio-binder residues.

According to Superpave specifications and standards for the PAV procedure, the PAV should operate under pressure of 2070 kPa and temperature of 90, 100 or 110°C for about 20 hours. As previously mentioned, the bio-binders could not be heated above 110-120°C; therefore, the pressure was not changed, the temperature was set to 100°C, and the duration initially varied to 2.5, 5.0, 10 and 20 hours in order to study the effect of duration on the stiffness of the bio-binders. Due to the large amount of oxidation occurring to the bio-binders after 5.0 hours, this led to the decay of the samples, and thus the stiffness at 5.0 hours could not be measured (as shown in Figure 5.2).

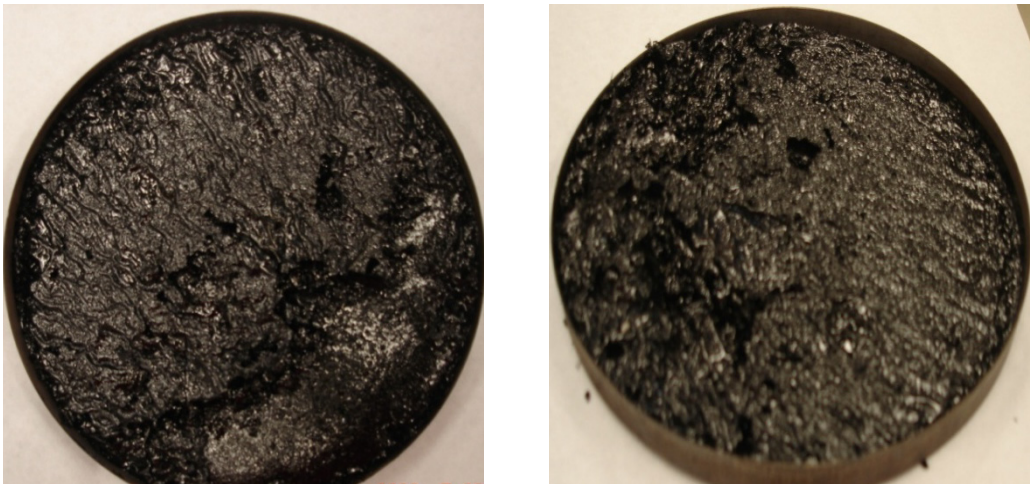


Figure 5.2. Pictorial View of Bio-binders after 5 Hours in PAV Oven

Notably, this considerable amount of oxidation was expected due to the large amount of oxygen present in the bio-binders, which reach up to 40%. Accordingly, the Superpave specifications for PAV procedure for bituminous binders should be modified to comply with the properties of the bio-binders. Precisely, the pressure and temperature were set to be the same but the duration was set to 2.5 hours instead of 20 hours. Then, after heating the bio-binders samples in the PAV oven for 2.5 hours, the bio-binders samples were transferred in the storage container and degassed in a 120°C for 30 minutes instead of 170°C as the bio-binders could not be heated above 110-120°C. The stiffness of unmodified oakwood, switchgrass and cornstover bio-binders (blends 1, 8 and 15, respectively) were measured at different temperatures (-12, -6 and 0°C) as listed in Table 5.3, and illustrated in Figure 5.3 and Figure 5.4.

Table 5.3. Stiffness of Unmodified Bio-binders at Different Temperatures

Temperature (°C)	Binder	Stiffness (MPa)	m-value
-12	AAM	174	0.23
	Blend 1	2450	0.03
	Blend 8	1520	0.14
	Blend 15	724	0.22
-6	AAM	78.1	0.32
	Blend 1	2200	0.08
	Blend 8	1710	0.15
	Blend 15	546	0.32
0	AAM	43	0.47
	Blend 1	1940	0.12
	Blend 8	594	0.19
	Blend 15	308	0.29

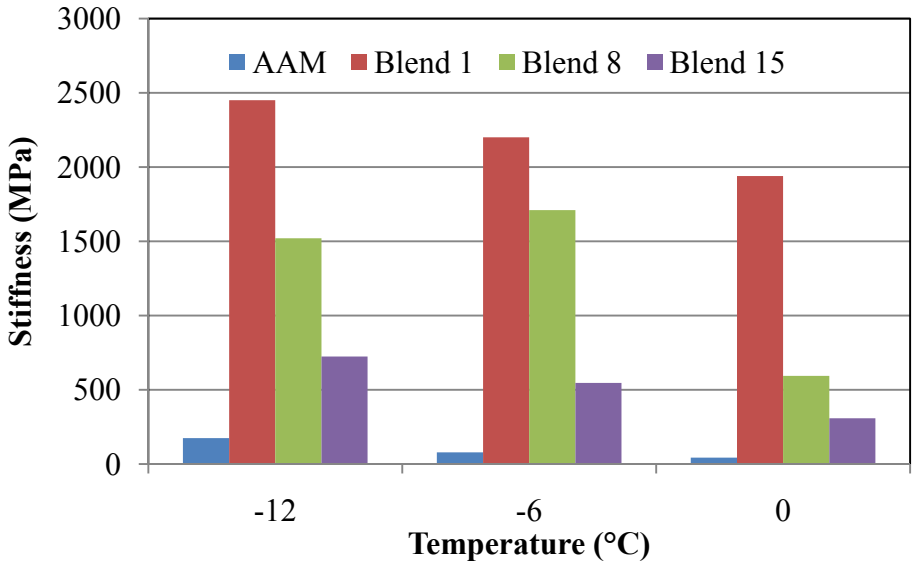


Figure 5.3. Stiffness of Unmodified Bio-binders at Different Temperatures

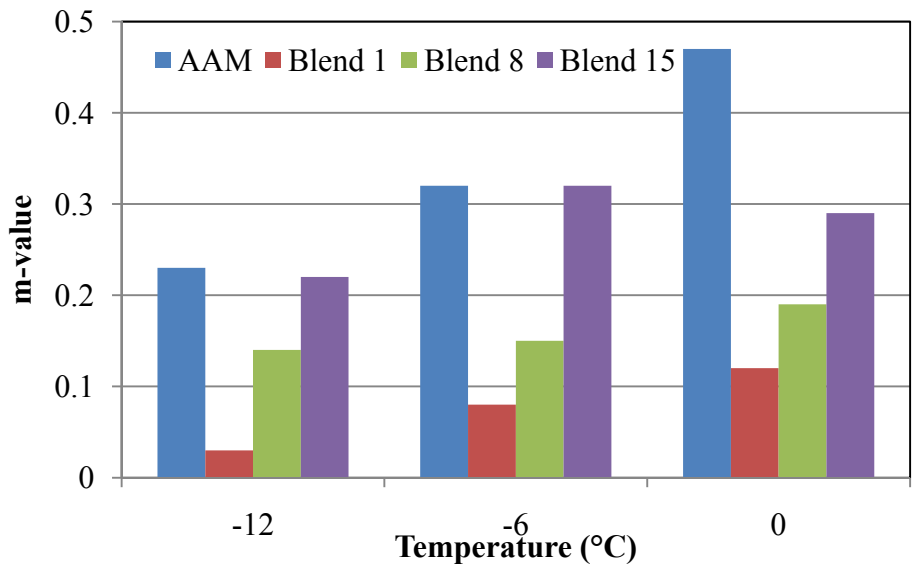


Figure 5.4. m-values of Unmodified Bio-binders at Different Temperatures

From the results, the following conclusions could be made. First, the stiffness of the bio-binders could not be measured after 2.5 hours aging in the PAV oven due to the deterioration of the samples. Second, the stiffness values of bio-binders were very high and m-values were very small compared to bitumen binders (AAM) at all temperatures although the PAV aging was set to 2.5 hours instead of 20 hours. This meant that the rate of oxidation of bio-binders occurred at a higher rate due to the large amount of oxygen in bio-binders. Third, stiffness values increased with measuring them at lower temperatures. In other words, the stiffness increased at low temperature which meant that the resistance to low temperature cracking was decreasing. In conclusion, the Superpave specification for PAV procedure should be modified to comply with the bio-binders properties. Precisely, the aging duration in PAV oven should be shortened to 2.5 hours instead of 20 hours and the temperature of the degassing container should be lowered to 120°C instead of 170°C.

CHAPTER 6. PHYSICAL AND CHEMICAL TESTING

Introduction

This chapter is divided into two sections. The first section is concerned about the physical testing which included the separation and the specific gravity tests. The second section is concerned about the chemical testing which included the determination of the possible functional groups available in the bio-binders and included the quantification of the amount of aging occurred in the bio-binders due to the different stages of aging (heat pre-treatment, RTFO aging with different durations, and PAV aging).

Physical Testing

The physical testing of the bio-binders is a significant phase before using the bio-oils/developed bio-binders as pavement materials. The separation test is important to determine how well the polymer modifier and the bio-binders are blended. The separation test was conducted according to ASTM 7173 (2005), which were previously discussed in details in Chapter 3. The specific gravity test is significant to determine the density of the bio-binders before designing the pavement material and quantifying the amount of the bio-binders that should be mixed with the aggregates. The specific gravity test was conducted according to ASTM D-70 (1997), which was discussed previously in detail in Chapter 3.

Separation Test

The separation data for all bio-binders is listed in Table 6.1 and is illustrated in Figure 6.1. The percent difference represented the difference in the G*/sin(delta) values between the top and the bottom portions with respect to the bottom portions. Therefore, the percent difference in some cases were negative values which indicated that the G*/sin(delta) of the top portion was higher than the G*/sin(delta) of the bottom portion.

Table 6.1. Separation Data for the Modified Bio-binders

Blend #	Portion	G*/sin(delta) @ T=52°C	Difference (%)
Blend 2	Top	6.5	73.47
	Bottom	3.747	
Blend 3	Top	4.6	89.85
	Bottom	2.423	
Blend 4	Top	69.91	-55.53
	Bottom	157.2	
Blend 5	Top	31.96	-39.02
	Bottom	52.41	
Blend 6	Top	11.8	63.46
	Bottom	7.219	
Blend 7	Top	1.3	18.18
	Bottom	1.1	
Blend 9	Top	4.43	9.82
	Bottom	4.034	
Blend 10	Top	20.87	16.01
	Bottom	17.99	
Blend 11	Top	0.6236	23.39
	Bottom	0.5054	
Blend 12	Top	1.005	20.78
	Bottom	0.8321	
Blend 13	Top	1.626	33.28
	Bottom	1.22	
Blend 14	Top	0.7665	13.56
	Bottom	0.675	
Blend 16	Top	25.53	-11.94
	Bottom	28.99	
Blend 17	Top	4.6	59.67
	Bottom	2.881	
Blend 18	Top	1.9	11.76
	Bottom	1.7	
Blend 19	Top	3.3	-5.71
	Bottom	3.5	
Blend 20	Top	11.05	-31.41
	Bottom	16.11	
Blend 21	Top	2.304	31.81
	Bottom	1.748	

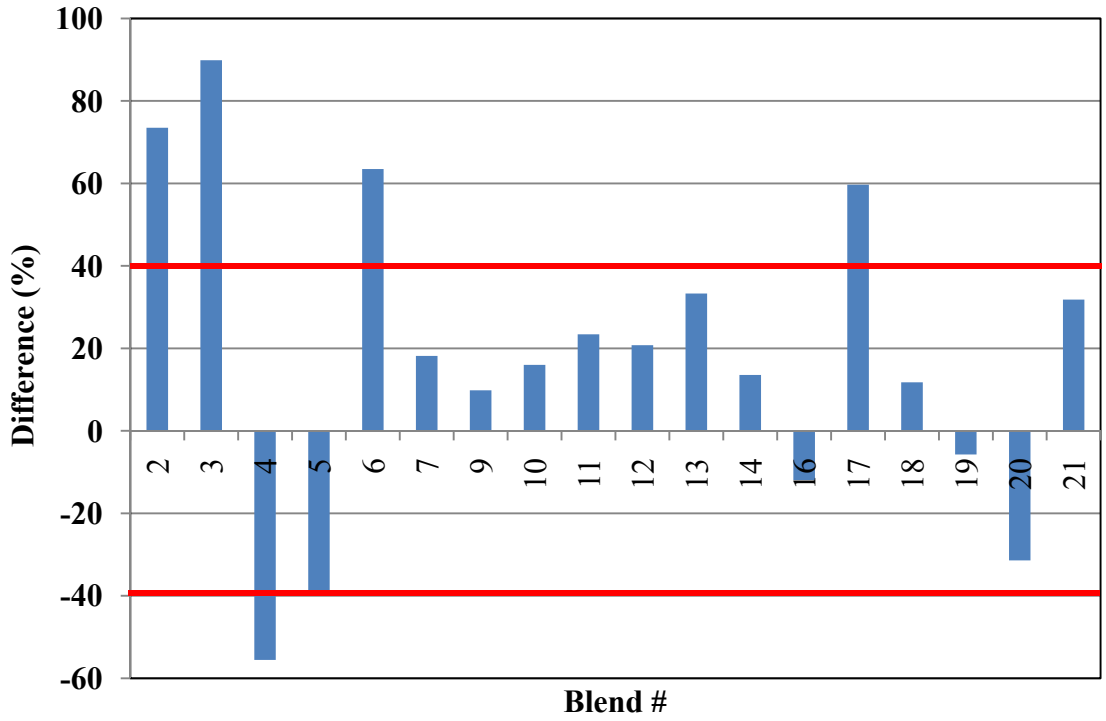


Figure 6.1. Separation Data for the Modified Bio-binders

According to the ASTM standards, there is no specification limit or threshold value to determine and specify exactly that the separation between the polymer modifier and the binder is occurred. Therefore, it is assumed that if the difference between the G*/sin(delta) values of the top and the bottom portions exceeds 40%, the separation between the polymer modifier and the binders will be considered to have occurred.

From the results shown above, it can be concluded that the oakwood bio-binders generally were more susceptible to separation with all types of the polymer modifiers used in this research in comparison to switchgrass and cornstover bio-binders. However, the oakwood bio-binders showed no separation when the amount of the blending ratio of the polymer modifiers (specifically polymers 2 and 3) increased from 2% to 4%. In summary, it is safe to conclude that the separation between the polymer modifier and the binder depends upon the chemical interaction between them and the blending ratio of the polymer modifier. Significantly, more care and caution should be taken when blending oakwood bio-binders with polymer modifiers in comparison to switchgrass and cornstover bio-binders due to its higher susceptibility to separation.

Specific Gravity Test

All the specific gravity values for the tested bio-binders are listed in Table 6.2 and summarized in Figure 6.2. From the results, the following observations can be noted. First, the specific gravity values of the bio-binders were higher than the specific gravity values of the bitumen binders which range between 1.02 and 1.08. Second, there was no significant difference between

the specific gravity values of the unmodified bio-binders (blends 1, 8 and 15). The difference between the specific gravity values can be considered minimal which may be attributed to the normal variability associated with the materials. Third, it can be concluded that the addition of the polymer modifiers to the switchgrass and cornstover -in general- led to a decrease in the specific gravity values. However, the oakwood bio-binders did not follow this trend as switchgrass and cornstover bio-binders. This may be attributed to the conclusion previously mentioned which was the oakwood bio-binders had higher separation susceptibility which meant that the polymers were not totally miscible with the bio-binders. This may reveal that the specific gravity values of the oakwood bio-binders were not measurably decreased upon the addition of polymers. Fourth, the blending procedure -in general- did not lead to an increase in the specific gravity values of the modified bio-binders since the blending procedure included heating at temperature between 110-120°C for 20-30 minutes, which meant that more water and volatile materials would be removed. In summary, it is safe to conclude that the addition of the polymer modifiers generally led to a decrease in the specific gravity values of the modified bio-binders in comparison to the unmodified bio-binders.

Table 6.2. Specific Gravity Values for All Binders

Blend #	Specific Gravity
Blend 1	1.30
Blend 2	1.29
Blend 3	1.27
Blend 4	1.33
Blend 5	1.29
Blend 6	1.35
Blend 7	1.32
Blend 8	1.28
Blend 9	1.26
Blend 10	1.28
Blend 11	1.23
Blend 12	1.23
Blend 13	1.24
Blend 14	1.23
Blend 15	1.29
Blend 16	1.30
Blend 17	1.26
Blend 18	1.25
Blend 19	1.27
Blend 20	1.24
Blend 21	1.23

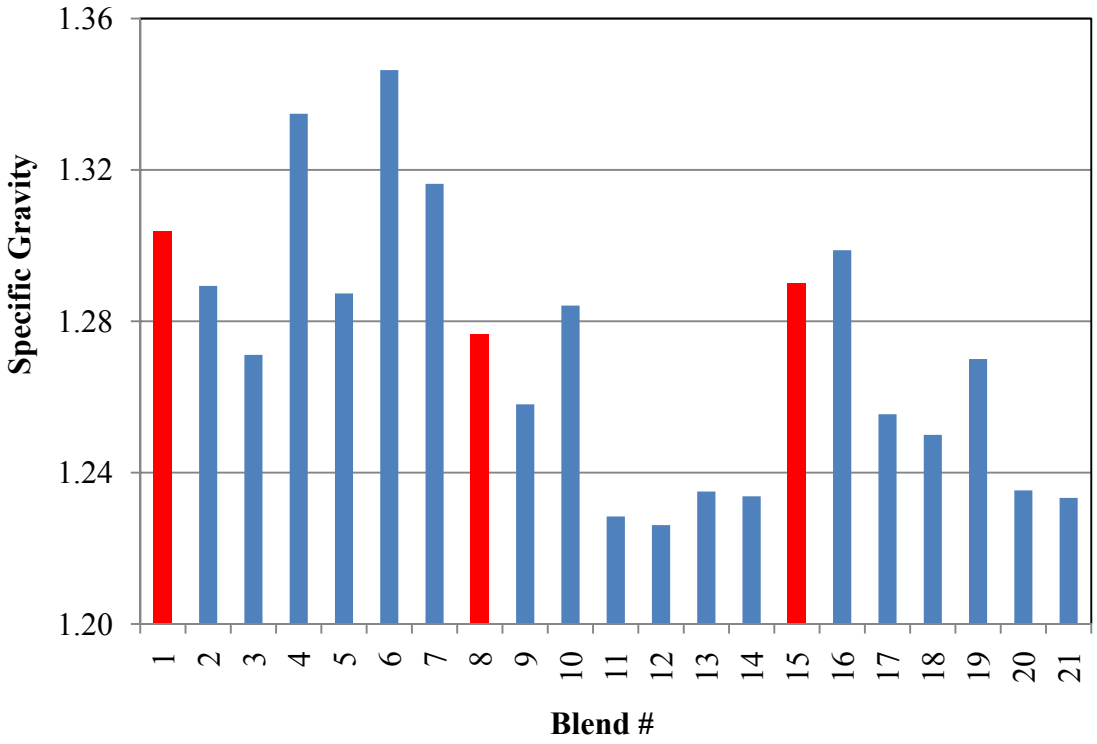


Figure 6.2. Specific Gravity Values for All Bio-binders

Chemical Testing Data

The chemical testing is concerned with studying the amount of aging occurring in the unmodified bio-binders at the various phases of heat treatment and aging processes; therefore, only the unmodified bio-binders (blends 1, 8 and 15) were tested. The chemical testing consisted of Gas Chromatography-Mass Spectrometry (GC/MS) and Fourier Transform Infrared Spectroscopy (FTIR) tests. The sample identification code for the tested samples is summarized in Table 6.3.

Due to the sacristy of data available on the usage of the bio-oils as bio-binders in the pavement industry, there is lack of information on the chemical compounds that should be studied that indicate the amount of aging occurring in the bio-binders. However, some previous investigations showed that the reaction of furfural and phenols compounds can be considered as a means to determine the aging (Chollar *et. al* 1992). Importantly, the role of the phenol compounds in the bio-binders is significant as the phenol compounds act as an antioxidant agent; therefore, it is crucial to determine the amount of the phenol compounds after the heat treatment and the aging processes. The weights in percentage for the furfural and phenol compounds in the unmodified bio-binders were summarized and are listed in Table 6.4 and are illustrated in Figure 6.3 (furfural compounds) and Figure 6.4 (phenol compounds).

Table 6.3. Sample Identification Code and Description

Sample I.D.	Blend #	Heat Treatment (@120°C for 2 hours)	Aging (Process and duration)
1-N1	Blend 1 (Unmodified Oakwood)	Untreated	Unaged
1-N2		Treated	Unaged
1-N3		Treated	RTFO Aged-10 min
1-N4		Treated	RTFO Aged-20 min
1-N5		Treated	RTFO Aged-30 min
1-N6		Treated	RTFO Aged-20 min and PAV Aged
8-N1	Blend 8 (Unmodified Switchgrass)	Untreated	Unaged
8-N2		Treated	Unaged
8-N3		Treated	RTFO Aged-10 min
8-N4		Treated	RTFO Aged-20 min
8-N5		Treated	RTFO Aged-30 min
8-N6		Treated	RTFO Aged-20 min and PAV Aged
15-N1	Blend 15 (Unmodified Cornstover)	Untreated	Unaged
15-N2		Treated	Unaged
15-N3		Treated	RTFO Aged-10 min
15-N4		Treated	RTFO Aged-20 min
15-N5		Treated	RTFO Aged-30 min
15-N6		Treated	RTFO Aged-20 min and PAV Aged

Table 6.4. GC/MS Data for the Unmodified Bio-binders

Blend #	Sample ID	Weight (%)	
		Furfural	Phenol
Blend 1	1-N1	0.06670	0.08894
	1-N2	0.04449	0.08899
	1-N3	0.04448	0.06672
	1-N4	0.00000	0.04452
	1-N5	0.00000	0.04443
	1-N6	0.00000	0.04443
Blend 8	8-N1	0.04443	0.26661
	8-N2	0.02205	0.17642
	8-N3	0.02283	0.22827
	8-N4	0.00000	0.09007
	8-N5	0.00000	0.13393
	8-N6	0.00000	0.11109
Blend 15	15-N1	0.02238	0.38042
	15-N2	0.02224	0.40026
	15-N3	0.00000	0.37784
	15-N4	0.00000	0.24449
	15-N5	0.00000	0.20047
	15-N6	0.00000	0.17793

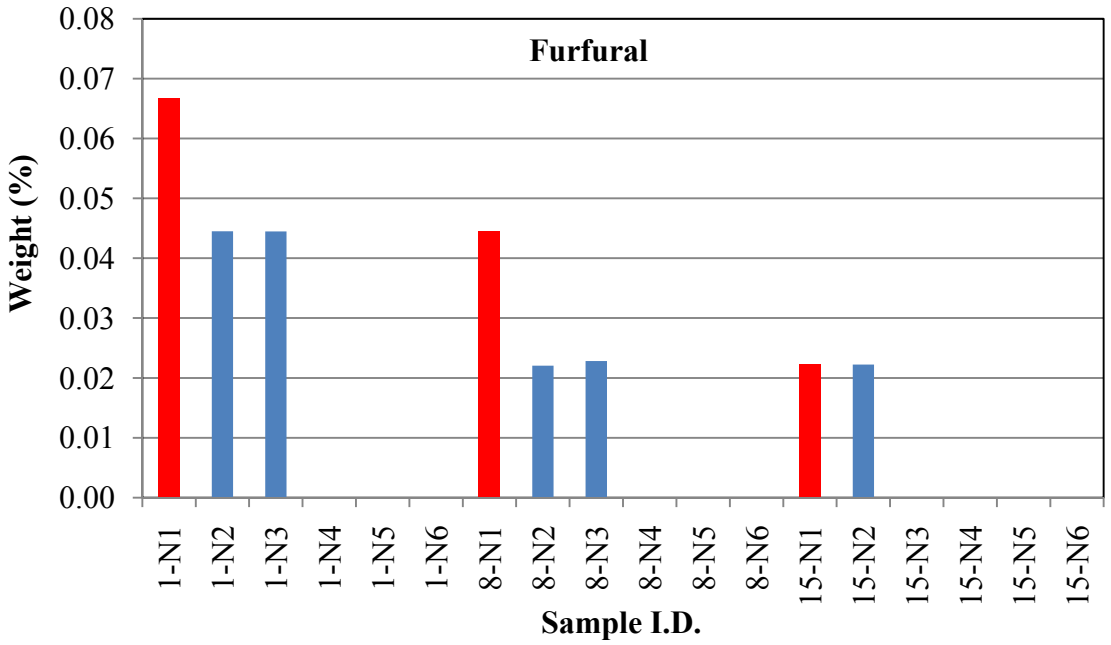


Figure 6.3. The Effect of Aging on the Furfural Compound

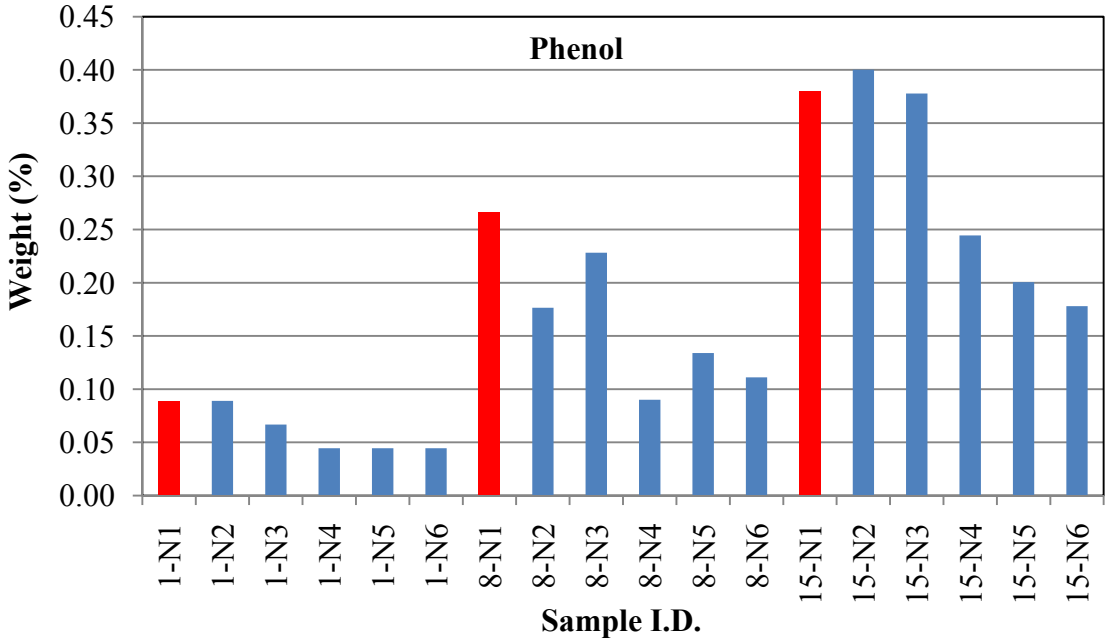


Figure 6.4. The Effect of Aging on the Phenol Compound

From the results above, the following remarks are made. First, after the heat treatment/upgrading procedure and the RTFO aging for 20 minutes, it was observed that the furfural compounds generally in all the unmodified binders vanished completely. On the other hand, it was observed that the phenol compounds in the unmodified bio-binders decreased after the heat treatment and the aging processes. This may be attributed to the reaction taking place between the furfural and

the phenol compounds and the formation of a new polymer. Second, the amount of the furfural compounds in the unmodified bio-binders was different. The unmodified oakwood bio-binders had the higher amount of the furfural compounds while the unmodified cornstover had the lowest furfural compounds (as shown in Figure 6.3). Third, the amount of the phenol compounds in the unmodified bio-binders was different. The unmodified oakwood bio-binders had the lowest amount of the phenol compounds while the unmodified cornstover had the highest furfural compounds (as shown in Figure 6.4). Fourth, after the heat treatment and the aging for 20 minutes in the RTFO, the phenol compounds did not show a specific trend. For example, for the oakwood bio-binders, the amount of the phenol compounds did not change while for the switchgrass and the cornstover, the amount of the phenol compounds changed without a specific trend. However, it can be concluded that the phenol compounds were -in general- decreasing as the amount of aging was increasing. In summary, it may be concluded that the furfural and the phenol compounds were reacting with each other and formed a new polymer due to the heat treatment and the aging processes; however, the phenol compounds, which are acting as an antioxidant agent, are still present, unlike the furfural compounds which vanished completely, after the heat treatment and the aging processes.

As previously mentioned, there is lack of information on the methods or means to quantify the amount of aging occurring in the bio-oils as pavement materials. Therefore, in this section, two new methods are employed for the first time. These two methods are the aging ratio and the aging index. There are three functional groups; two of them, i.e. CH_3-CH_2 and CH_2 were supposedly changing with aging, which were referred to as the "reacting groups" while the third one, i.e. O-H group, was not supposedly changing, which was referred to as the "neutral group". The aging ratios were calculated based on Equation 6.1. The ratios between different groups may be measured and then considered to be as means or methods to quantify the amount of aging occurring in the bio-oils. In addition, the aging indexes were calculated based on Equation 6.2.

$$\text{Aging Ratio} = \frac{\text{Intenisty of reacting group } (CH_2 \text{ and } CH_3-CH_2)}{\text{Intenisty of unreacting group } (O-H)}$$

Equation 6.1

$$\text{Aging Index} = 100 * \frac{(\text{Aging ratio of treated/aged sample}) - (\text{Aging ratio of untreated/unaged sample})}{\text{Aging ratio of untreated/unaged sample}}$$

Equation 6.2

Using the FTIR test data, the intensities of these groups are listed and then the aging ratios and indexes were calculated and then summarized as shown in Table 6.5. Figure 6.5 and Figure 6.6 show the aging ratios of these groups and Figure 6.7 and Figure 6.8 represent the aging indexes.

Table 6.5. FTIR Data, Aging Ratios and Aging Indexes for the Unmodified Binders

Sample ID	Groups			Aging Ratios		Aging Index	
	O-H	CH_3&CH_2	CH_2	CH_2/O-H	CH_3&CH_2/O-H	AI_{CH2}	$AI_{CH3-CH2}$
1-N1	53.29	66.18	65.92	1.24	1.24	-	-
1-N2	59.39	72.18	71.64	1.21	1.22	2.47	2.12
1-N3	63.25	74.52	70.60	1.12	1.18	9.76	5.13
1-N4	58.01	70.82	67.40	1.16	1.22	6.07	1.70
1-N5	61.56	71.19	68.10	1.11	1.16	10.55	6.87
1-N6	61.87	67.95	70.05	1.13	1.10	8.46	11.55
8-N1	63.14	62.88	67.11	1.06	1.00	-	-
8-N2	73.13	38.72	70.76	0.97	0.53	8.97	46.83
8-N3	63.42	60.94	67.84	1.07	0.96	-0.62	3.52
8-N4	64.71	67.55	67.11	1.04	1.04	2.44	-4.83
8-N5	70.62	46.27	69.04	0.98	0.66	8.03	34.21
8-N6	83.87	67.52	70.46	0.84	0.81	20.97	19.16
15-N1	65.59	65.89	69.62	1.06	1.00	-	-
15-N2	56.50	62.13	64.90	1.15	1.10	-8.23	-9.46
15-N3	56.09	59.01	62.71	1.12	1.05	-5.35	-4.73
15-N4	61.43	63.52	64.93	1.06	1.03	0.40	-2.93
15-N5	56.74	56.15	62.70	1.10	0.99	-4.11	1.50
15-N6	59.11	61.94	63.80	1.08	1.05	-1.69	-4.31

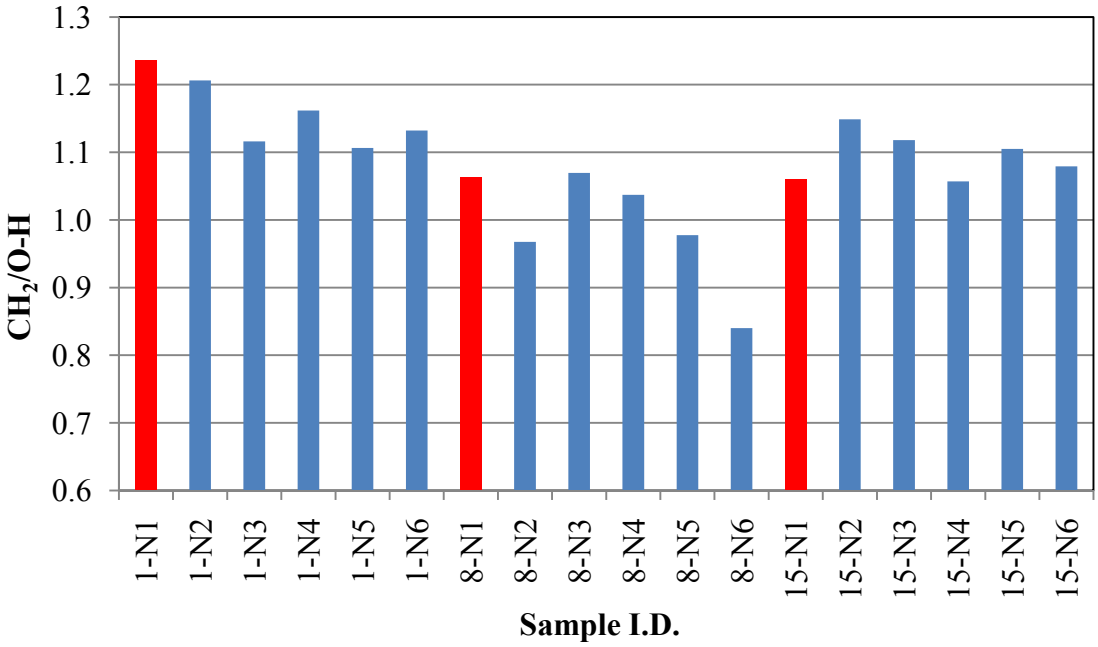


Figure 6.5. Aging Ratio of CH_2/O-H for the Unmodified Bio-binders

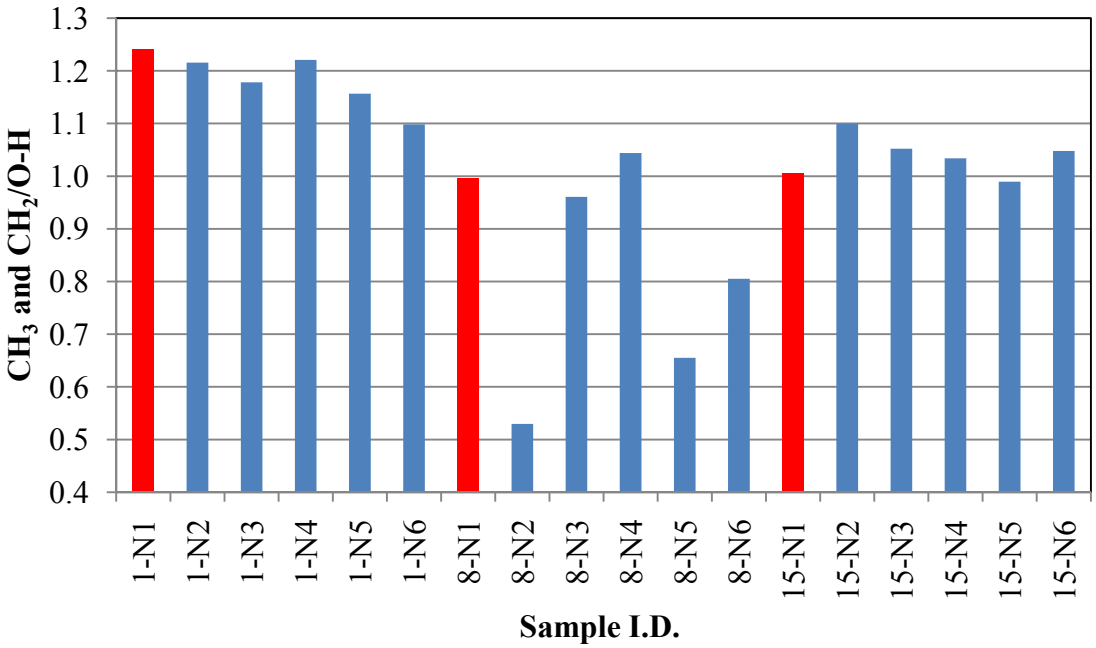


Figure 6.6. Aging Ratio of CH_3-CH_2/O-H for the Unmodified Bio-binders

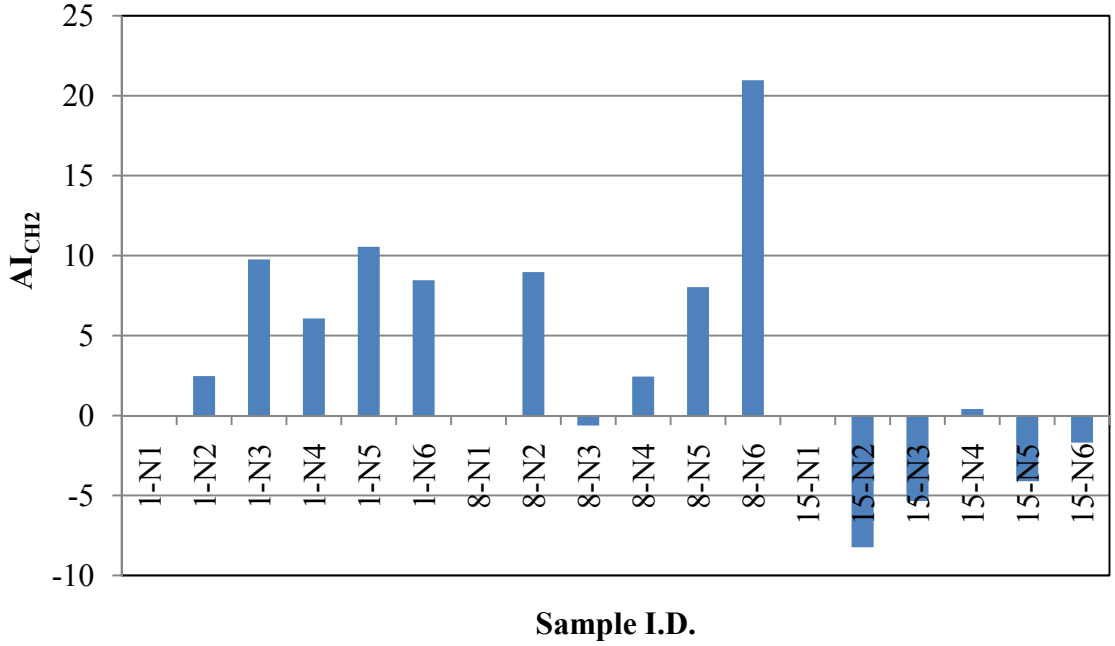


Figure 6.7. Aging Indexes of CH_2 for the Unmodified Bio-binders

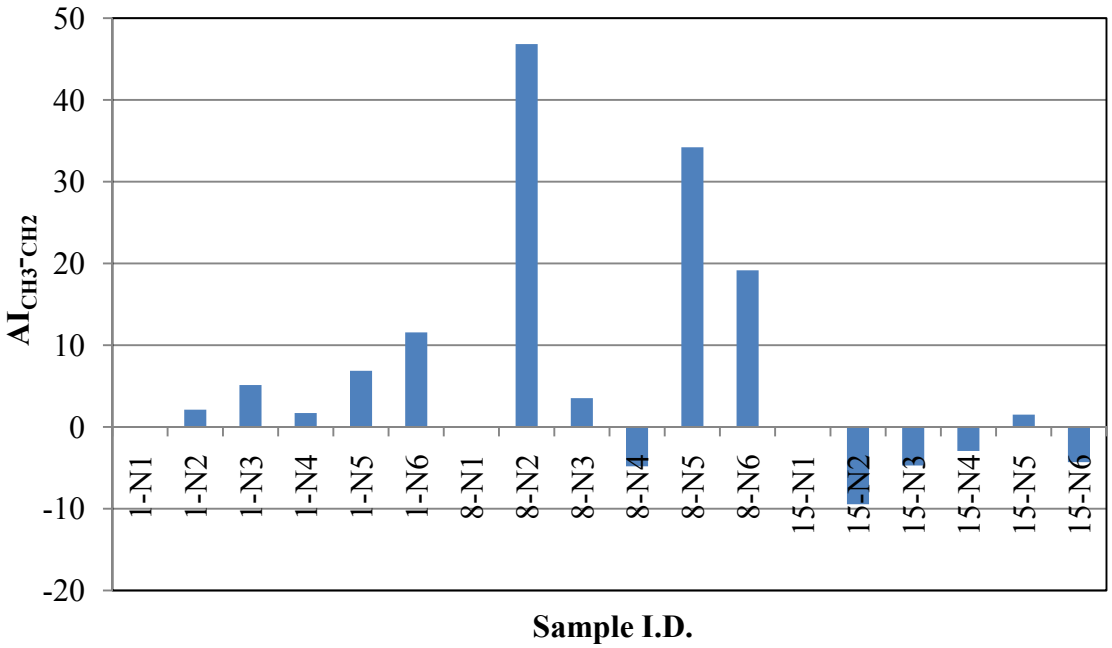


Figure 6.8. Aging Indexes of CH_3-CH_2 for the Unmodified Bio-binders

From the results shown above, the following observations can be made. First, the aging ratios for both reacting groups (CH_2 and CH_2-CH_3) with respect to the neutral O-H group were decreasing which meant that these reacting groups were decreasing upon heat treatment and aging. For the unmodified oakwood and switchgrass bio-binders, there was a clear trend that these reacting groups were generally decreasing but with no specific trend. However, for the unmodified cornstover bio-binders, the same decreasing trend could not be established. Second, for the aging indexes, upon heat treatment and aging of the unmodified bio-binders, the aging indexes were generally increasing but without a specific trend. For the unmodified oakwood and switchgrass bio-binders, the aging indexes were generally increasing; however, the same trend could not be established for the unmodified cornstover bio-binders. In summary, these two new means or methods, i.e. aging ratio and aging index, can be employed to quantify the amount of aging occurring for some of the bio-binders, such as oakwood and switchgrass, upon heat treatment and aging processes, but care should be taken before usage of these means or methods as their validity vary depending on the type of the bio-binders. Therefore, new means and methods to quantify the aging occurring in bio-binders should be studied extensively to establish a standard procedure or a criterion to chemically quantify the aging taking place.

CHAPTER 7. RHEOLOGICAL TESTING

Introduction

In this chapter, the rheological testing data for the tested bio-binders are listed and summarized according to the experimental plans. This chapter was subdivided into four main sections which can be summarized as follows. First, the relationship between viscosity of the tested bio-binders and shear rate were studied through determining the shear susceptibility values "SS". Second, the viscosity temperature susceptibility values "VTS" were calculated to study the relationship between viscosity of the tested bio-binders and the temperature. Third, the correlation between viscosity and the shear rate were modeled according to an Arrhenius-type model to determine "E_a" and "η_∞" values. Fourth, the relationship between viscosity and temperature were modeled according to a Power-law model to determine "n" and "K" values. The viscosity measurements (in centipoises) for all bio-binders at different shear rates (in rpm) and temperatures (in °C) are listed and summarized in Table C7.1 to

Table C7.23 in Appendix D. Based on these viscosity measurements, the SS, VTS, E_a, η_∞, n and K values were calculated.

Shear Susceptibility Values "SS"

In this section, the shear susceptibility values SS for all the bio-binders and the bitumens tested in this report were calculated according to the equation mentioned in Chapter 3. The determination of the SS values is significant to correlate the relationship between viscosity and shear rate as previously discussed.

Oakwood Bio-binders

The shear susceptibility values "SS" for oakwood bio-binders are summarized and listed in Table 7.1, in addition to SS values of AAM and AAD blends for comparison purposes. Figure 7.1 to Figure 7.5 show the linear logarithmic relationship between viscosity and shear rate at different temperatures for some blends (e.g. AAM, 1, 2, 4 and 7) as an example, while the rest of the blends were added to Appendix D (Figure C7.1 to Figure C7.4).

Table 7.1. Shear Susceptibility Values for Oakwood Blends

Temperature	Blend #								
(°C)	AAM	AAD	1	2	3	4	5	6	7
40	-	-	-0.09	-0.06	-0.06	-	-	-	-
50	-	-	-0.04	-0.06	-0.22	-	-	-	-
60	-	-	-0.13	-0.11	-0.33	-	-	-	-
70	-	-	-0.02	-0.11	-0.38	-	-	-0.13	-0.11
80	0.03	0.01	-0.06	-0.15	-0.43	-0.07	-0.16	-0.08	-0.05
90	-0.05	-0.01	0.04	-0.30	-0.48	-0.05	-0.09	-0.05	-0.02
100	-0.05	-0.01	-	-0.09	-0.10	-0.02	-0.04	-0.09	-0.03
110	-0.03	-0.01	-	-0.10	-0.12	-0.09	0.03	-0.05	0.00
120	-0.02	-0.02	-	-0.18	-0.22	-0.07	-0.02	-0.02	-0.13
130	-0.02	-0.01	-	-	-	-0.03	-0.11	-0.34	-0.04
140	-0.06	0.05	-	-	-	-0.09	-0.05	0.06	0.04
150	-0.04	0.05	-	-	-	-0.04	0.08	-	-
160	0.00	0.05	-	-	-	-0.02	0.06	-	-

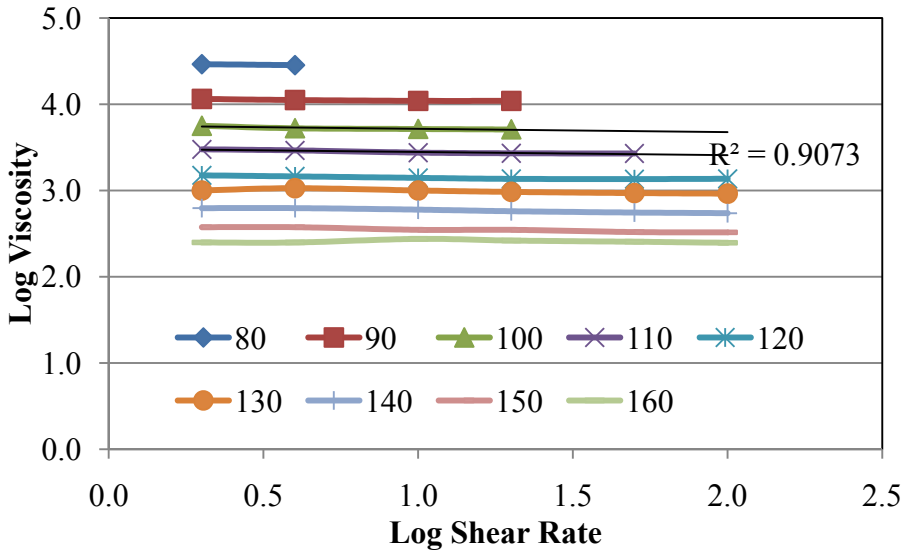


Figure 7.1. Log Viscosity versus Log shear Rate for AAM

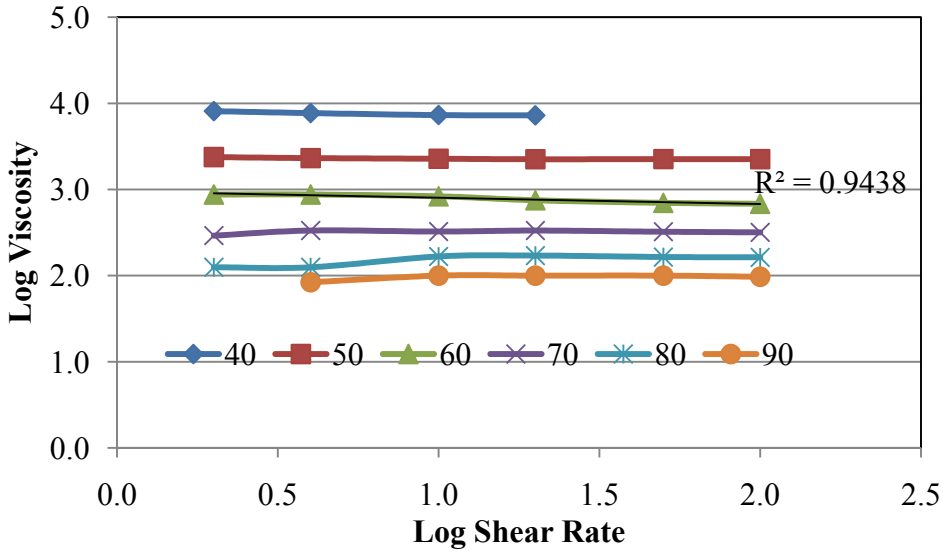


Figure 7.2. Log Viscosity versus Log shear Rate for Blend 1

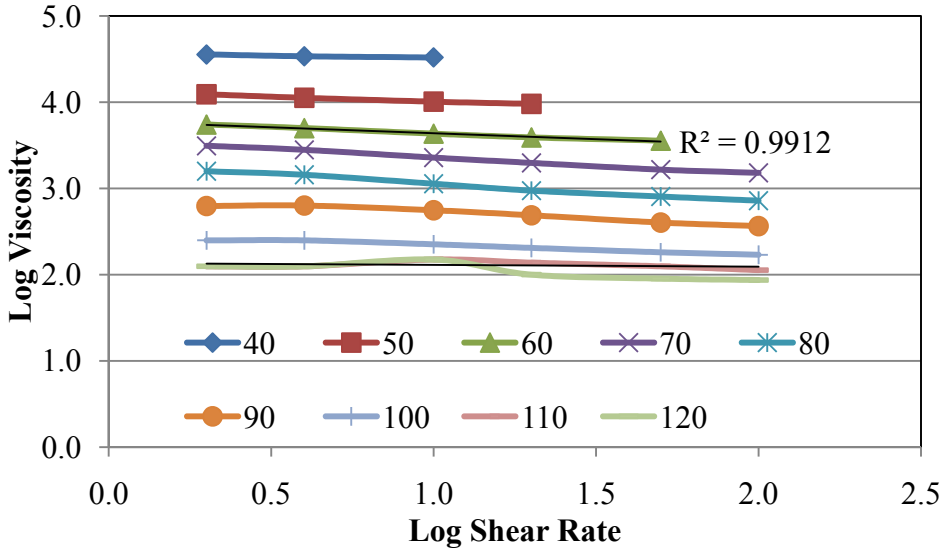


Figure 7.3. Log Viscosity versus Log shear Rate for Blend 2

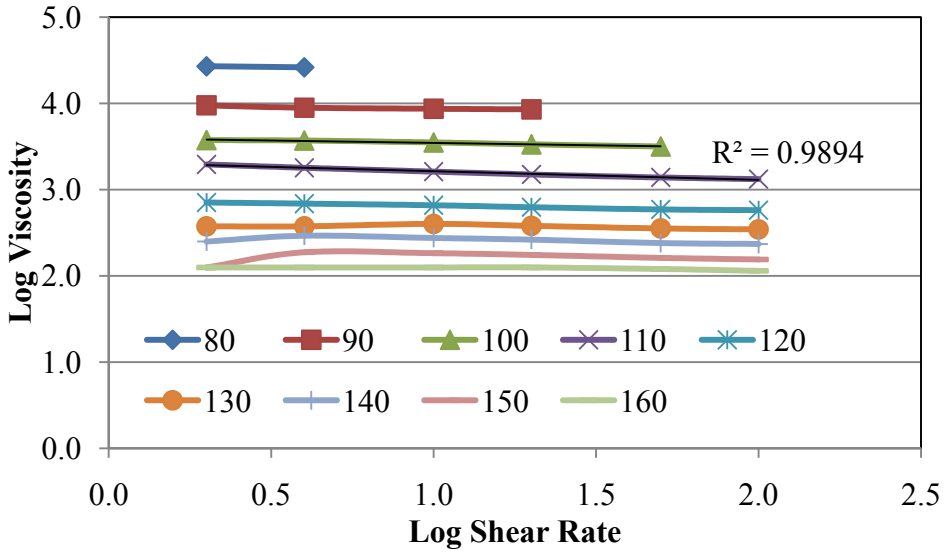


Figure 7.4. Log Viscosity versus Log shear Rate for Blend 4

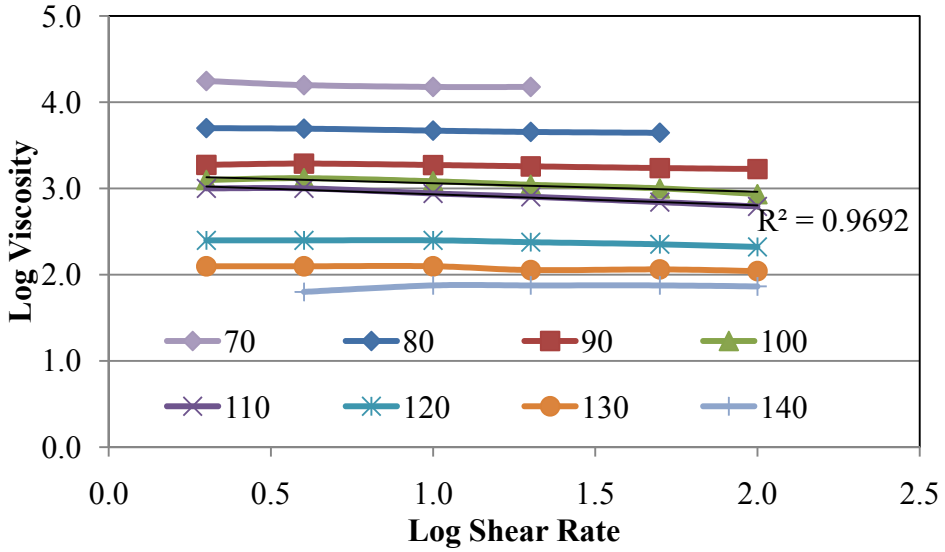


Figure 7.5. Log Viscosity versus Log shear Rate for Blend 7

Based on the SS values listed and demonstrated above, the following observations are noted. First, SS values had no specific trend that could be observed with increasing the temperature. In other words, the influence of temperature on the SS values cannot be described as one that exhibits a well-defined pattern. The effect can be considered as minimal. The variation in data was relatively small when noting that meaningful changes in the values were often observed in terms of changes in order of magnitude and not as fractional changes. Second, the temperature range for bitumen binders, e.g. AAM and AAD, were different than the temperature range for unmodified bio-binder (blend 1) and some modified bio-binders. For example, the bitumen binders had a temperature range between 80 and 160°C while the bio-binders had temperature ranges between 40 to 90°C, 40 to 120°C, 80 to 160°C, and 70 to 140°C for blend 1 (the

unmodified oakwood bio-binder), blends 2 and 3, blends 4 and 5, and blends 6 and 7, respectively. Importantly, the addition of polymer 2 led to a shift in the temperature range to match exactly the AAM binder. Therefore, it is safe to conclude that the addition of polymer modifiers to bio-binders (oakwood) led to changing the temperature range, but the effect of different types of polymer modifiers were not the same. Third, no clear trend or improvement could be established in the SS values of the oakwood bio-binders after the addition of the polymer modifiers. Fourth, there is scarcity of data to specify an accepted range or a threshold value for SS values at any temperature, therefore, the SS values for AAM and AAD blends can be considered as acceptable since these two bitumen binders are typical of ones that are widely used in the United States. Then, it can be concluded that the SS of bio-binders were comparable to bitumen binders with no significance difference between them.

Switchgrass Bio-binders

The shear susceptibility values "SS" for switchgrass bio-binders were summarized and listed in Table 7.2. Figure 7.6 and Figure 7.7 show the linear logarithmic relationship between viscosity and shear rate at different temperatures for blends 8 and 10 while blends 9, 11, 12, 13 and 14 were added to Appendix D (Figure C7.5 to Figure C7.9).

Table 7.2. Shear Susceptibility Values for Switchgrass Blends

Temperature	Blend #								
(°C)	AAM	AAD	8	9	10	11	12	13	14
50	-	-	-	-	-	-0.09	-0.18	-0.11	-0.09
60	-	-	-	-	-	-0.06	-0.24	-0.20	-0.11
70	-	-	-0.11	-0.13	-0.04	-0.11	-0.13	-0.25	-0.14
80	0.03	-	-0.20	-0.15	-0.07	-0.16	-0.16	-0.26	-0.10
90	-0.05	0.01	-0.20	-0.16	-0.13	-0.15	-0.30	-0.31	-0.07
100	-0.05	-0.01	-0.16	-0.17	-0.07	-0.21	-0.36	-0.35	-0.18
110	-0.03	-0.01	-0.19	-0.02	-0.10	-0.01	-0.12	-0.10	-0.33
120	-0.02	-0.01	-0.23	-0.01	-0.10	0.00	-0.08	0.00	-0.10
130	-0.02	-0.02	-0.69	-0.11	0.02	0.00	-0.17	-0.06	-0.06
140	-0.06	-0.01	-	-	-	-0.10	-0.20	0.00	-0.09
150	-0.04	0.05	-	-	-	-	-	-	-
160	0.00	0.05	-	-	-	-	-	-	-

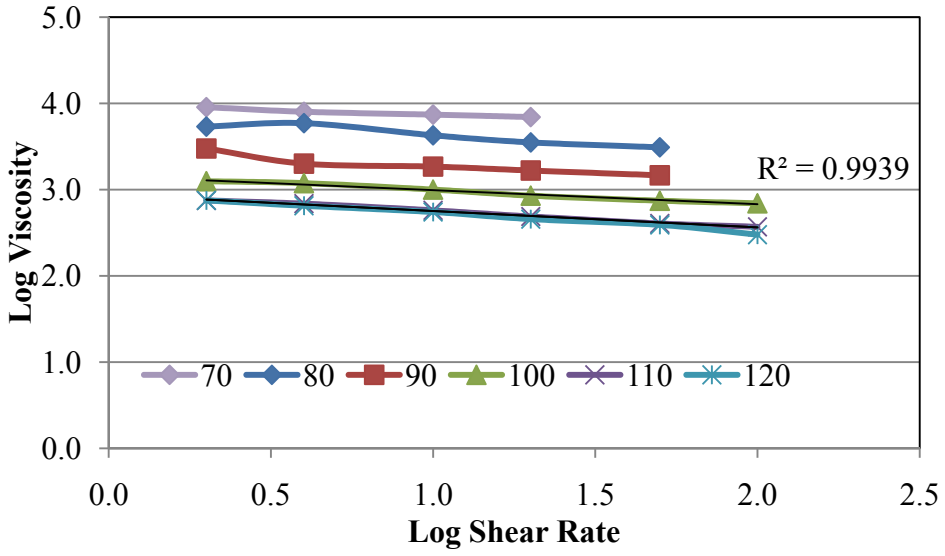


Figure 7.6. Log Viscosity versus Log shear Rate for Blend 8

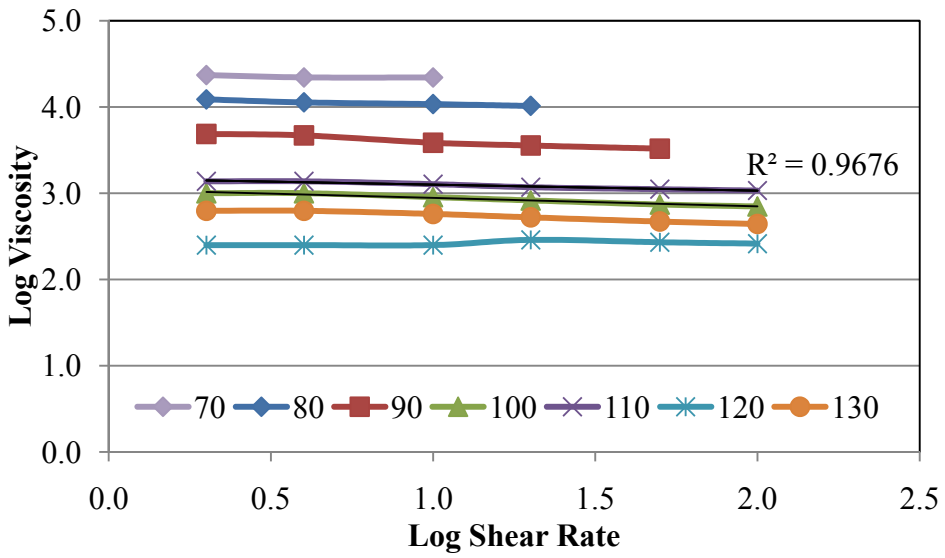


Figure 7.7. Log Viscosity versus Log shear Rate for Blend 10

Based on the results established above, the following observations are made. First, SS values for switchgrass bio-binders (modified and unmodified) were higher than the SS values for bitumen binders, AAM and AAD. Therefore, it may be concluded that the switchgrass bio-binders had high shear susceptibility in comparison to bitumen binders and oakwood bio-binders. Second, the temperature range for switchgrass bio-binders ranged between 70 to 130°C and 50 to 140°C which were lower than the range for bitumen binders. Third, like the oakwood bio-binders, the addition of different types of polymer modifiers led to different effects on the temperature range of the switchgrass bio-binders. For example, polymer 1 had no effect on temperature range while polymers 2 and 3 had a significant effect on the temperature range. However, no clear

improvement or trend could be established for decreasing the SS values for switchgrass bio-binders after the addition of the polymer modifiers.

Cornstover Bio-binders

The shear susceptibility values "SS" for cornstover bio-binders are summarized and listed in Table 7.3. Figure 7.8 and Figure 7.9 show the linear logarithmic relationship between viscosity and shear rate at different temperatures for blends 15 and 18 while blends 16, 17, 18, 19, 20 and 21 were added to Appendix D (Figure C7.10 to Figure C7.14).

Table 7.3. Shear Susceptibility Values for Cornstover Blends

Temperature	Blend #								
(°C)	AAM	AAD	15	16	17	18	19	20	21
40			-0.16	-	-	-	-	-	-
50	-	-	-0.24	-	-	-	-	-	-
60	-	-	-0.06	-	-	-	-	-	-
70	-	-	-0.03	-0.04	-0.24	-0.03	-0.10	-0.09	-0.21
80	0.03	-	-0.06	-0.07	-0.13	-0.09	-0.07	-0.08	-0.12
90	-0.05	0.01	-0.07	-0.13	-0.23	-0.08	-0.15	-0.10	-0.06
100	-0.05	-0.01	-0.08	-0.09	-0.18	-0.11	-0.08	-0.08	-0.06
110	-0.03	-0.01	-0.04	-0.07	-0.15	-0.10	-0.10	-0.07	-0.04
120	-0.02	-0.01	-0.03	-0.07	-0.09	-0.09	-0.10	-0.08	-0.08
130	-0.02	-0.02	-	-0.04	-0.04	-0.06	-0.10	-0.02	0.00
140	-0.06	-0.01	-	-0.15	-0.10	-0.11	-0.03	-0.12	-0.07
150	-0.04	0.05	-	-	-	-	-	-	-
160	0.00	0.05	-	-	-	-	-	-	-

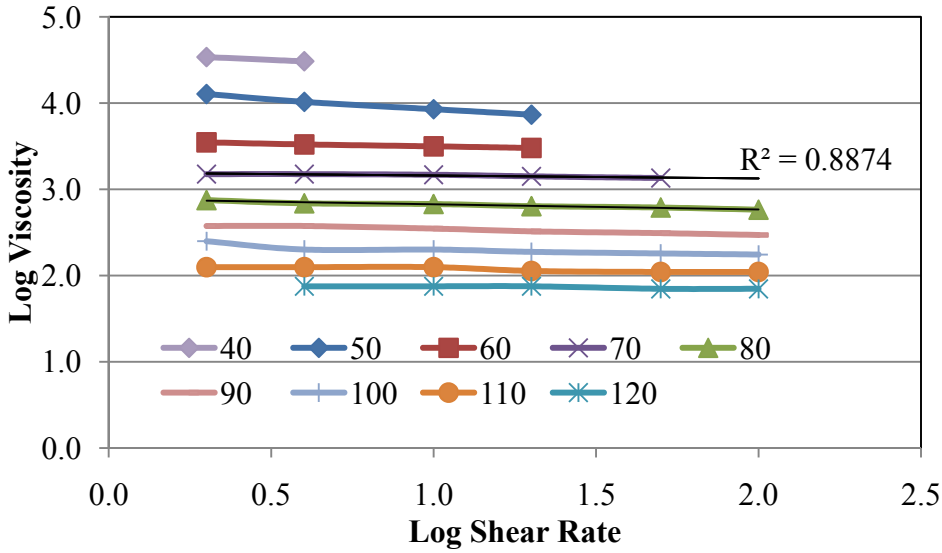


Figure 7.8. Log Viscosity versus Log shear Rate for Blend 15

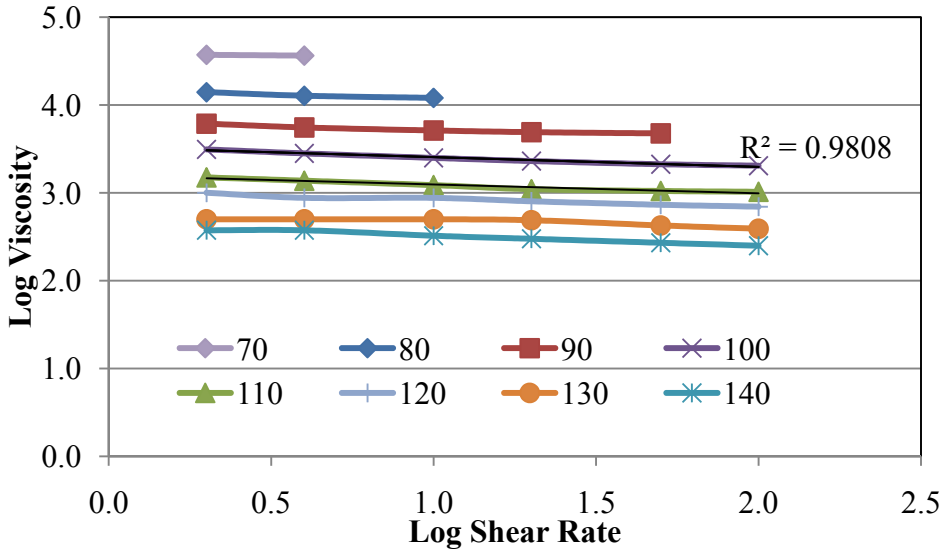


Figure 7.9. Log Viscosity versus Log shear Rate for Blend 18

Based on the SS values listed and demonstrated above, the following observations are made. First, SS values for cornstover bio-binders (unmodified and modified) were higher than the SS values for bitumen binders, AAM and AAD. Like switchgrass bio-binders, it may be concluded that the cornstover bio-binders had high shear susceptibility in comparison to oakwood bio-binders and the bitumen binders. Second, the temperature range for cornstover bio-binders ranged between 40 to 120°C (unmodified bio-binder 15) which is lower than the range for the bitumen binders. Third, unlike the oakwood and switchgrass bio-binders, the addition of different types of polymer modifiers led to the same effect on the temperature range of the cornstover bio-binders. For example, all polymer types changed the temperature range from 40-120°C to 70-140°C. However, no clear improvement or trend could be established for decreasing the SS values for cornstover bio-binders after the addition of the polymer modifiers as switchgrass bio-binders.

Statistical Analysis

A statistical analysis was conducted using the computer software JMP 7.0 to study the statistical difference between SS values of bio-binders and bitumen. A one-way analysis of variance "ANOVA" using the method of least squares was performed for examination to evaluate the binder types (bitumen and bio-oil/bio-binder), polymer modifier types (P1, P2, and P3), and blending percentages (2% and 4%). Type I error (α) of 0.05 was used for all statistical analysis as the confidence level was 95%. Three different statistical tests were conducted for each bio-binder type separately. These tests can be summarized and listed as follows: (1) test 1 was concerned about studying the statistical difference between the SS values of modified and unmodified bio-binders in order to emphasize the importance of the addition of polymer modifiers, (2) test 2 was to study the difference between the SS values of unmodified bio-binder and bitumen (AAM and AAD) and (3) test 3 was designed to compare between the SS values of modified bio-binders and bitumen binders. The p-values of the AVOVA for different tests were summarized and listed in

Table 7.4, Table 7.5, and Table 7.6 for oakwood, switchgrass, and cornstover bio-binders, respectively.

Table 7.4. Statistical Analysis for SS Values for Oakwood Bio-binders

Test #	Blends	Temp (°C)	Experimental Variable	SS F-Ratio	SS Prob >F
1	**1,2,3,4,5,6&7**	**80**	Polymer type	1.4609	0.3815
			Blending ratio	0.9601	0.3826
		90	Polymer type	10.8379	**0.0406***
			Blending ratio	0.1463	0.7216
2	**AAM,AAD,1**	**80**	Binder Type	21.3333	0.1357
		90		4.0833	0.2926
3	**AAM,AAD,2,3,4,5,6&7**	**80**	Binder Type	2.8165	0.1443
		90		0.9573	0.3657
		100		1.2741	0.3021
		110		0.6142	0.4630
		120		1.9241	0.2147

For the oakwood bio-binders, the following conclusions are made from Table 7.4. The polymer type may be a significant factor in changing the SS values (at 90°C) but the blending ratio was not a significant factor (at 80 and 90°C). Importantly, there was no significance difference between SS values of the unmodified bio-binder and the bitumens and modified bio-binders and the bitumens.

Table 7.5. Statistical Analysis for SS Values for Switchgrass Bio-binders

Test #	Blends	Temp (°C)	Experimental Variable	SS F-Ratio	SS Prob>F
1	8,9,10,11,12,13&14	70	Polymer type	1.2718	0.4240
			Blending ratio	1.2319	0.3293
		80	Polymer type	0.4589	0.7306
			Blending ratio	3.3103	0.1430
		90	Polymer type	0.1626	0.9150
			Blending ratio	0.2156	0.6666
		100	Polymer type	1.1685	0.4506
			Blending ratio	0.1581	0.7112
		110	Polymer type	1.0104	0.4967
			Blending ratio	3.1500	0.1506
		120	Polymer type	2.3283	0.2528
			Blending ratio	145.8000	**0.0003***
		130	Polymer type	14.7704	**0.0266***
			Blending ratio	0.0440	0.8442
2	AAM,AAD,8	90	Binder Type	24.0833	0.1280
		100		14.0833	0.1658
		110		96.3333	0.0646
3	AAM,AAD, 9,10,11,12,13&14	90	Binder Type	4.6278	0.0750
		100		5.2617	0.0616
		110		1.1713	0.3207
		120		0.5788	0.4756
		130		0.8553	0.3907

For the switchgrass bio-binders, the following conclusions are made from Table 7.5. Like the oakwood bio-binders, the polymer type and blending ratio—in general—were not a significant factor in changing the SS values. Importantly, there was no significant difference between SS values of unmodified switchgrass bio-binder and the bitumens and the modified switchgrass bio-binder and the bitumens.

Table 7.6. Statistical Analysis for SS Values for Cornstover Bio-binders

Test #	Blends	Temp (°C)	Experimental Variable	SS F-Ratio	SS Prob>F
1	15,16,17,18,19,20&21	70	Polymer type	0.5167	0.6994
			Blending ratio	7.8402	**0.0488***
		80	Polymer type	0.5306	0.6921
			Blending ratio	1.8824	0.2420
		90	Polymer type	1.5628	0.3613
			Blending ratio	0.7161	0.4451
		100	Polymer type	0.9878	0.5039
			Blending ratio	0.1221	0.7444
		110	Polymer type	1.4892	0.3757
			Blending ratio	0.2500	0.6433
		120	Polymer type	11.5714	**0.0372***
			Blending ratio	1.5000	0.2879
		130	Polymer type	7.4000	0.0692
			Blending ratio	0.0455	0.8416
		140	Polymer type	0.7982	0.5273
			Blending ratio	6.4800	0.0636
2	AAM,AAD,15	90	Binder Type	1.3333	0.4544
		100		2.0833	0.3857
		110		1.3333	0.4544
3	AAM,AAD, 16,17,18,19,20&21	80	Binder Type	32.7170	**0.0012***
		90		4.1977	0.0864
		100		4.5000	0.0781
		110		5.7700	0.0531
		120		69.1364	**0.0002***
		130		1.2075	0.3140
		140		5.1156	0.0644

FromTable 7.6, the following conclusions can be made for the cornstover bio-binders. Like the oakwood and switchgrass bio-binders, the polymer type and blending ratio -in general- were not a significant factor in changing the SS values although the polymer type showed significance at some temperatures (70 and 120°C). The influence of polymer type on the SS values cannot be described as one that has a well-defined pattern, so the effect can be considered as minimal. Likely, there was no significant difference between SS values of unmodified cornstover bio-binder and the bitumens and the modified cornstover bio-binders and the bitumens.

Based on Table 7.7, the relationship between viscosity and shear rates at different temperatures for the different types of bio-oils can be well described as a logarithmic linear relationship. For instance, the R^2 values for most of the bio-binders were high and exceeded 85% except for blends 5 and 9. Since the bio-oil blends and the bitumens had different temperature ranges, the coefficients of correlation could not be determined at the same temperature; therefore, they were determined at different temperatures as shown in Table 7.7. The relationship between viscosity and shear rates at different temperatures can be best described as a logarithmic linear relationship similar to bitumen binders.

Table 7.7. Coefficient of Correlation for Relationship between Viscosity and Shear Rate

Blend #	R^2 value	Blend #	R^2 value	Blend #	R^2 value
AAM	0.9073 (110)	AAD	0.8482 (110)		
1	0.9438 (60)	8	0.9939 (110)	15	0.9676 (80)
2	0.9912 (60)	9	0.2726 (110)	16	0.9936 (100)
3	0.9657 (60)	10	0.9676 (110)	17	0.9958 (100)
4	0.9894 (110)	11	0.9935 (80)	18	0.9808 (100)
5	0.7542 (110)	12	0.9503 (80)	19	0.9874 (100)
6	0.9561 (110)	13	0.8900 (80)	20	0.9402 (100)
7	0.9692 (110)	14	0.9066 (80)	21	0.8585 (100)

*correlation coefficient was measured at the temperature between the brackets in °C

General Conclusions

Having a broader examination of the overall results herein, it can be concluded that although the SS values of switchgrass and cornstover bio-binders yielded higher values than the bitumens, the statistical analysis showed that there were no statistical differences. In addition, the addition of polymer modifiers with different blending ratios did not lead to significant changes in SS values of all types of bio-binders. However, the polymer modifiers changed the temperature range of oakwood and switchgrass bio-binders only and had no effect on cornstover bio-binders. Precisely, some oakwood and switchgrass modified bio-binders yielded the same temperature range as bitumens (80 to 160°C). Therefore, it is worth noting that the addition of different types of polymer modifiers was not yielding the same effect for different types of bio-binders. Importantly, it is safe to conclude that the relationship between viscosity and shear rate at different temperatures, for different types of bio-binders, can be well described by a linear logarithmic relationship as bitumen.

Viscosity Temperature Susceptibility Values "VTS"

In this section, the temperature susceptibility values VTS for all the bio-binders and the bitumens tested in this report were calculated according to the equation mentioned in Chapter 3. The determination of the VTS values is significant to correlate the relationship between viscosity and temperature as previously discussed.

All Bio-binders

The viscosity temperature susceptibility values "VTS" for all bio-binders and bitumen are summarized and listed in Table 7.8. Figure 7.10 to Figure 7.19 show the linear logarithmic relationship between viscosity and temperature at different shear rates for some blends as an example, while the rest of the blends are in Appendix D (Figure C7.15 to Figure C7.27).

Table 7.8. Viscosity Temperature Susceptibility Values for All Binders

Blend #	Shear Rate (rpm)					
	2	4	10	20	50	100
AAM	-3.00	-2.97	-2.89	-2.92	-2.92	-2.92
AAD	-3.43	-3.32	-3.19	-3.18	-3.10	-3.03
1	-5.19	-4.91	-4.52	-4.48	-4.40	-4.14
2	-3.64	-3.59	-3.42	-3.64	-3.76	-3.79
3	-3.70	-4.22	-3.95	-4.22	-4.53	-4.62
4	-3.90	-3.67	-3.58	-3.58	-3.49	-3.53
5	-3.29	-3.27	-2.94	-3.00	-2.80	-2.70
6	-3.71	-4.13	-3.75	-4.10	-4.05	-3.98
7	-4.08	-4.36	-4.20	-4.25	-4.28	-4.44
8	-2.62	-2.70	-2.77	-2.92	-2.96	-2.63
9	-3.63	-3.65	-3.48	-3.53	-3.44	-3.16
10	-3.68	-3.63	-3.64	-3.57	-3.33	-2.93
11	-3.74	-4.18	-4.05	-4.07	-4.10	-4.11
12	-3.44	-3.34	-3.75	-3.70	-3.75	-3.90
13	-3.91	-3.89	-4.07	-4.14	-4.01	-4.01
14	-3.50	-3.86	-4.16	-4.12	-4.05	-4.05
15	-3.78	-3.81	-3.74	-3.74	-3.82	-3.81
16	-3.07	-3.03	-2.92	-2.83	-2.73	-2.92
17	-3.95	-3.58	-3.62	-3.56	-3.62	-3.55
18	-3.20	-3.11	-3.06	-3.00	-3.13	-3.12
19	-3.15	-3.11	-3.42	-3.46	-3.35	-3.30
20	-3.66	-3.59	-3.75	-3.75	-3.60	-3.71
21	-3.75	-3.99	-3.91	-3.68	-3.68	-3.69

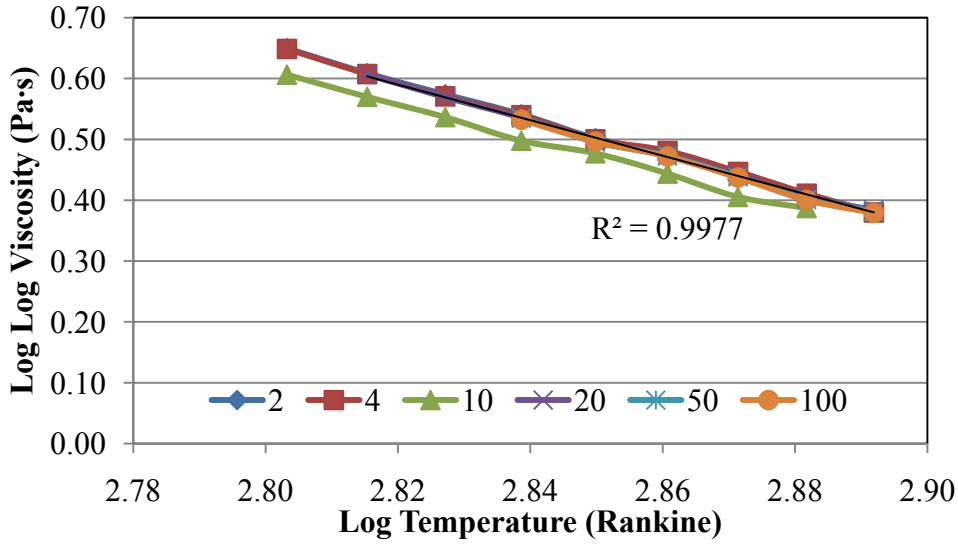


Figure 7.10. Log Log Viscosity versus Log Temperature for AAM

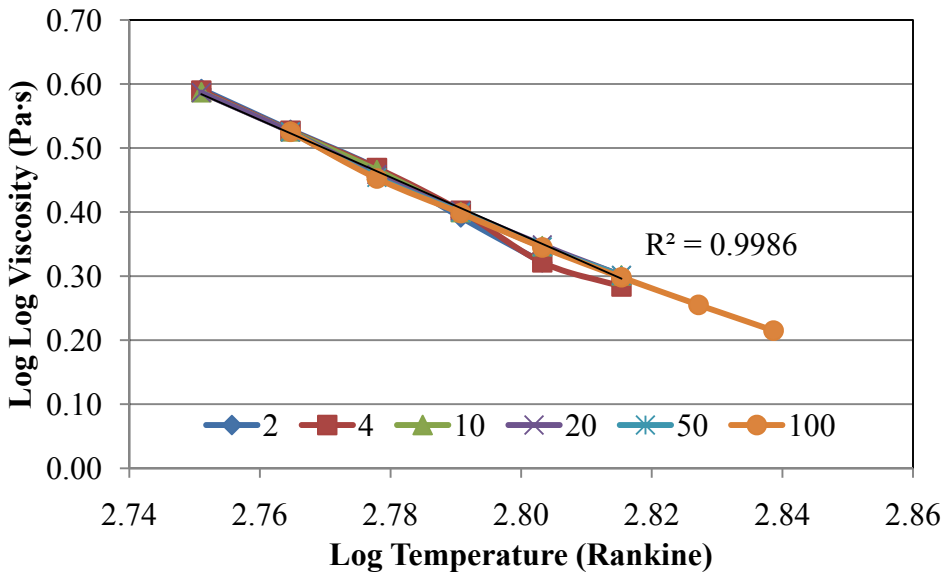


Figure 7.11. Log Log Viscosity versus Log Temperature for Blend 1

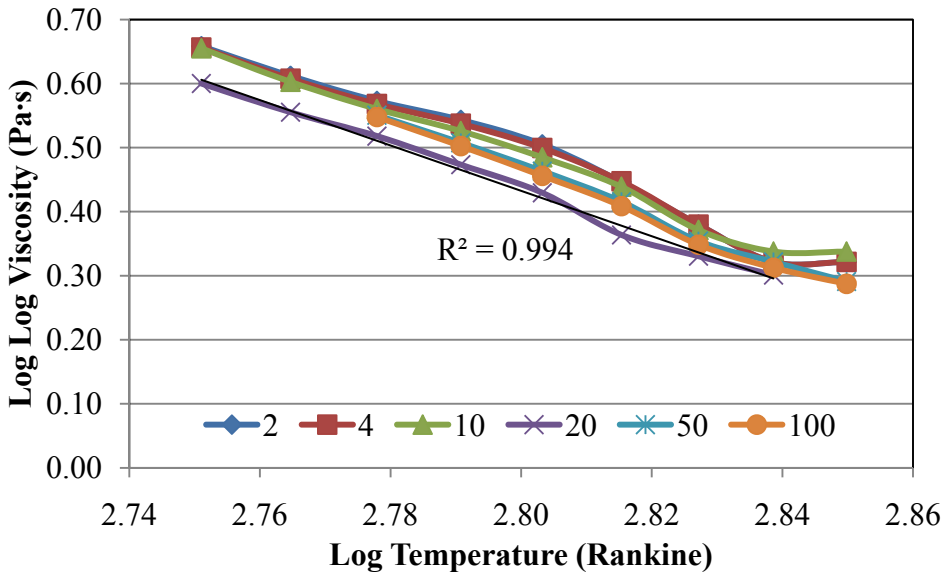


Figure 7.12. Log Log Viscosity versus Log Temperature for Blend 2

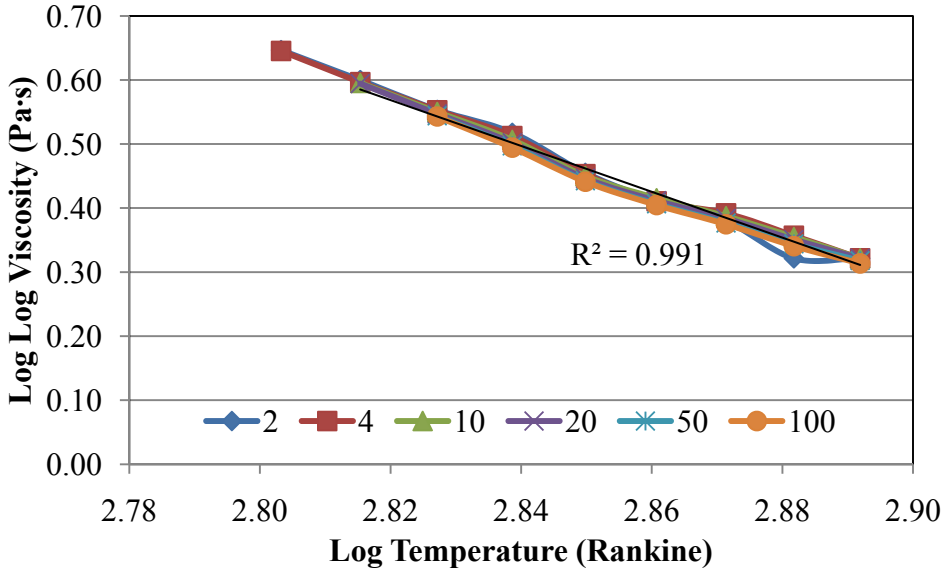


Figure 7.13. Log Log Viscosity versus Log Temperature for Blend 4

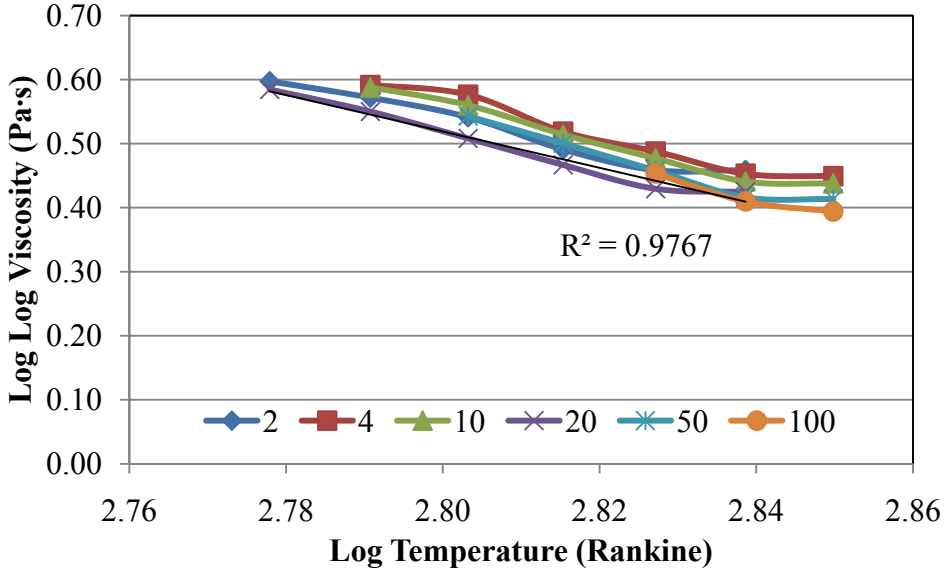


Figure 7.14. Log Log Viscosity versus Log Temperature for Blend 8

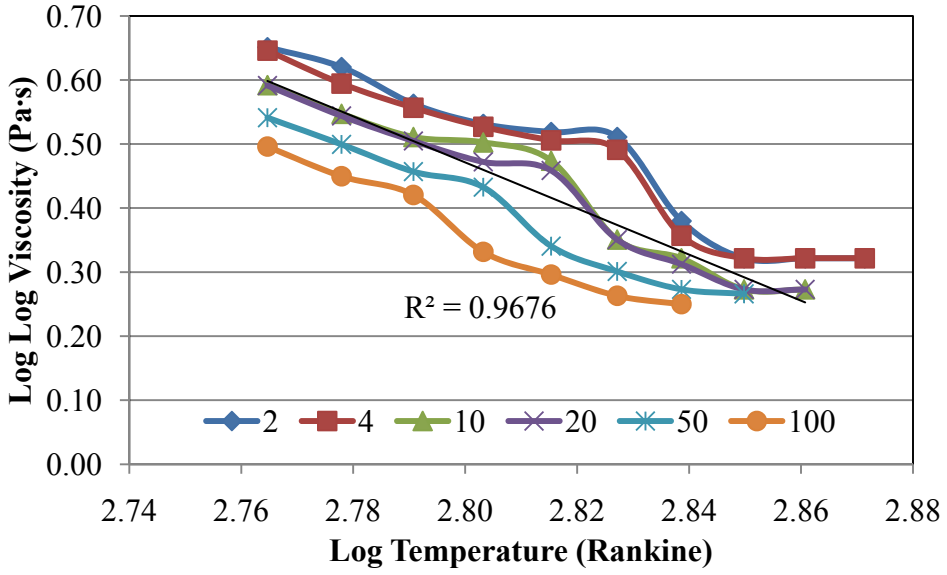


Figure 7.15. Log Log Viscosity versus Log Temperature for Blend 12

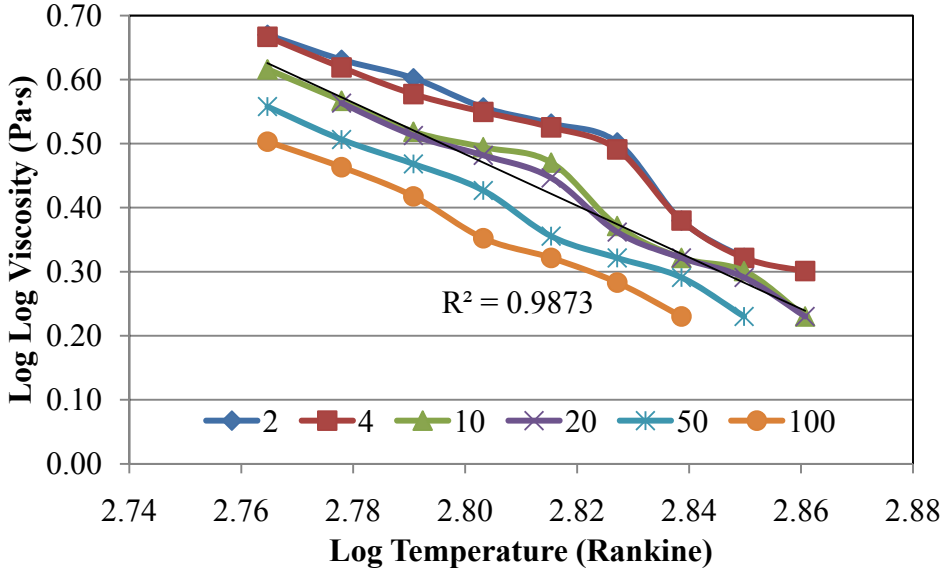


Figure 7.16. Log Log Viscosity versus Log Temperature for Blend 13

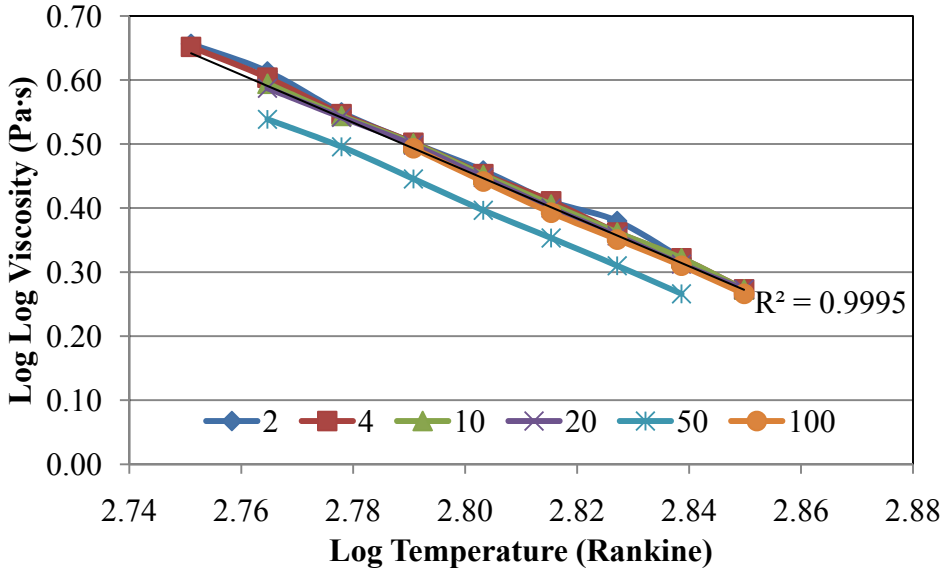


Figure 7.17. Log Log Viscosity versus Log Temperature for Blend 15

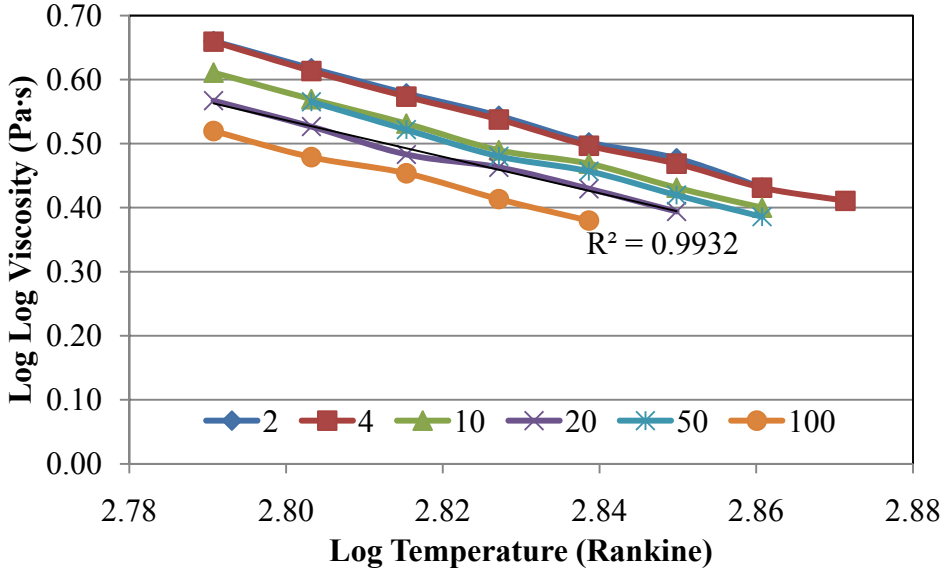


Figure 7.18. Log Log Viscosity versus Log Temperature for Blend 18

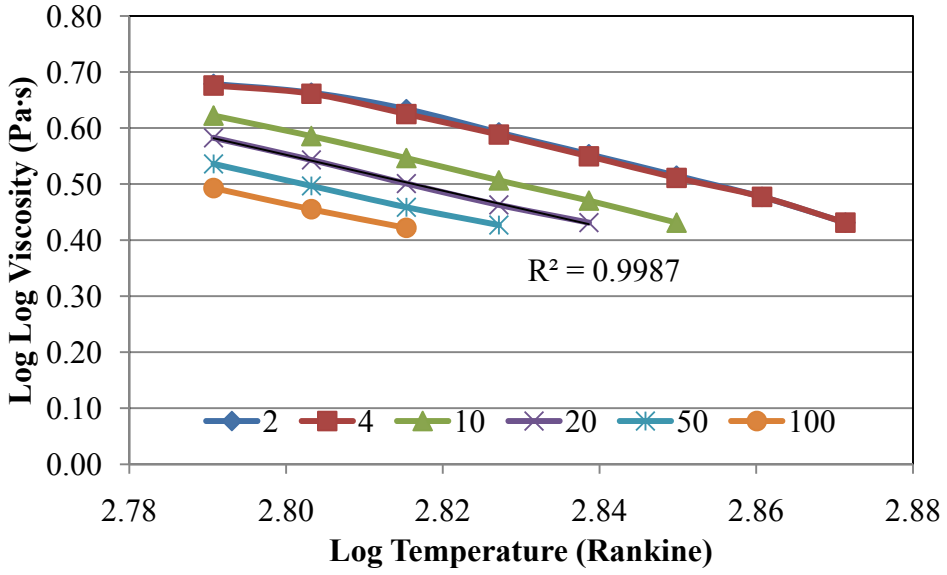


Figure 7.19. Log Log Viscosity versus Log Temperature for Blend 19

Based on the VTS values summarized above, the following conclusions are made. First, it was noted that increasing the shear rate led to a slight decrease in the VTS values for bitumen binders, e.g. AAM and AAD; however, the same trend could not be established for the all bio-binders. Yet, the significance between the viscosity measurements at different shear rates can be considered minimal. Second, the VTS values for the bio-binders in comparison to the corresponding values in AAM and AAD were -in general- higher and demonstrated that the bio-binders are more susceptible to temperature than the bitumen binders studied. Third, it can be concluded that the viscosity of the bio-binders and the bitumens were -significantly- more susceptible to the change in temperature than shear rate. This is mainly due to the higher VTS values in comparison to SS values. Fourth, it was observed that in some modified bio-binder blends, e.g. 12, 13, 18 and 19, increasing the shear rate led to a decrease in the viscosity measurements; however, the VTS values were -in general- the same.

Statistical Analysis

A statistical analysis was conducted, using the computer software JMP 7.0, to study the statistical difference between VTS values of bio-binders and bitumens. A one-way analysis of variance "ANOVA" using the method of least squares was performed to evaluate the binder types (bitumen and bio-oil/bio-binder), polymer modifier types (P1, P2, and P3), and blending percentages (2% and 4%). Type I error (α) of 0.05 was used for all statistical analysis as the confidence level was 95%. Two different statistical tests were conducted for each bio-binder type separately. These tests can be summarized and listed as follows: (1) test 1 was concerned about studying the statistical difference between the VTS values of unmodified bio-binders and bitumens (AAM and AAD) and (2) test 2 was to study the difference between the VTS values of unmodified and modified bio-binders in order to emphasize the importance of the addition of polymer modifiers. The p-values of the AVOVA for different tests were summarized and listed

in Table 7.9, Table 7.10, and Table 7.11 for oakwood, switchgrass, and cornstover bio-binders, respectively.

Based on the p-values reported in Table 7.9 for oakwood bio-binders, it was observed that there was no statistical significant difference between VTS values of the unmodified bio-binders and the bitumens although the VTS values for blend 1, AAM, and AAD were -4.48, -3.18 and -2.92, respectively. Importantly, test 2 yielded that the polymer type and blending ratios at almost all shear rates were not significant factors in changing the VTS values of unmodified and modified oakwood bio-binders (except at the 2 rpm shear rate). In summary, it may be concluded that there was no statistically significant difference between the unmodified and the modified oakwood bio-binders, and the bitumens.

Table 7.9. Statistical Analysis for VTS Values for Oakwood Bio-binders

Test #	Blends	Shear Rate (rpm)	Experimental Variable	SS	
				F-Ratio	Prob >F
1	**AAM,AAD,1**	**20**	Binder Type	39.7712	0.1001
2	**1,2,3,4,5,6&7**	**2**	Polymer Type	7.5091	0.0659
			Blending Ratio	10.5194	**0.0255***
		4	Polymer Type	5.0009	0.1095
			Blending Ratio	2.1904	0.2278
		10	Polymer Type	2.0859	0.2807
			Blending Ratio	1.2392	0.3812
		20	Polymer Type	2.8281	0.2080
			Blending Ratio	0.5428	0.6186
		50	Polymer Type	2.9424	0.1995
			Blending Ratio	0.3212	0.7424
		100	Polymer Type	2.0975	0.2792
			Blending Ratio	0.0942	0.9121

Based on the p-values listed in Table 7.10 for the switchgrass bio-binders, it can be concluded that there was no statistical significant difference between VTS values of unmodified switchgrass bio-binders and bitumen. This conclusion is in compliance with the aforementioned conclusion for oakwood bio-binders. Unlike oakwood bio-binders, test 2 yielded that the polymer type was a statistically significant factor in changing the VTS values for switchgrass bio-binders at intermediate and high shear rates. On the other hand, the blending ratio was a statistically significant factor in changing the VTS values for switchgrass bio-binders at low shear rates. In summary, it can be concluded that there was no statistical significant difference between the unmodified switchgrass bio-binders and the bitumens. Yet, the polymer type and blending ratio were significant factors in changing the VTS values for the modified switchgrass bio-binder, but their effect varied depending on the shear rate. Then, it is now safe to report that the effect of polymer modifier type and blending ratio on the rheological properties of the bio-binder, e.g. VTS values, depend on the type of the bio-binder. In other words, the same polymer modifier will yield different effects on the rheological properties of different bio-binders.

Table 7.10. Statistical Analysis for VTS Values for Switchgrass Bio-binders

Test #	Blends	Shear Rate (rpm)	Experimental Variable	SS	
				F-Ratio	Prob >F
1	**AAM,AAD,8**	**20**	Binder Type	0.3333	0.6667
2	**8,9,10,11,12,13&14**	**2**	Polymer Type	7.0809	0.0711
			Blending Ratio	27.6604	**0.0045***
		4	Polymer Type	2.8725	0.2046
			Blending Ratio	7.8945	**0.0409***
		10	Polymer Type	21.4793	**0.0157***
			Blending Ratio	5.4218	0.0726
		20	Polymer Type	15.6722	**0.0245***
			Blending Ratio	3.9664	0.1124
		50	Polymer Type	15.4984	**0.0249***
			Blending Ratio	2.3397	0.2124
		100	Polymer Type	45.2492	**0.0054***
			Blending Ratio	1.5508	0.3173

Based on the p-values summarized in Table 7.11 for the cornstover bio-binders, the statistical tests yielded that there was no statistically significant difference between VTS values of unmodified bio-binders and the bitumens although the VTS values for blend 15, AAM, and AAD were -3.74, -3.18 and -2.92, respectively. Importantly, it was noted that the polymer type and blending ratios at all shear rates were not significant factors in changing the VTS values of unmodified and modified cornstover bio-binders. This conclusion is in agreement with the aforementioned conclusion established for oakwood bio-binder. In summary, like the oakwood bio-binders, it may be reported that there was no statistically significant difference between the unmodified and the modified cornstover bio-binders, and the bitumens.

Table 7.11. Statistical Analysis for VTS Values for Cornstover Bio-binders

Test #	Blends	Shear Rate (rpm)	Experimental Variable	SS	
				F-Ratio	Prob >F
1	AAM,AAD,15	20	Binder Type	23.4339	0.1297
2	15, 16,17,18,19,20&21	2	Polymer Type	0.9513	0.5159
			Blending Ratio	0.8426	0.4950
		4	Polymer Type	2.7388	0.2150
			Blending Ratio	1.0270	0.4366
		10	Polymer Type	1.5979	0.3548
			Blending Ratio	1.2467	0.3795
		20	Polymer Type	1.1983	0.4427
			Blending Ratio	1.2716	0.3737
		50	Polymer Type	1.0429	0.4866
			Blending Ratio	1.9227	0.2600
		100	Polymer Type	2.1498	0.2729
			Blending Ratio	1.2577	0.3769

Considerably, the relationship between viscosity and temperature at different shear rates for the bio-binders and the bitumens were best described as a logarithmic linear relationship, as the relationship between viscosity and shear rates at different temperatures. The coefficients of correlation for the linear relationships were determined for all blends at 20 rpm as a reference and listed in Table 7.12. The R^2 values for this relationship for all bio-binders were very high (exceeding 96%) and comparable to the bitumens.

Table 7.12. Coefficient of Correlation for Relationship between Viscosity and Temperature

Blend #	R^2 value	Blend #	R^2 value	Blend #	R^2 value
AAM	0.9977	**AAD**	0.9989		
1	0.9986	**8**	0.9767	**15**	0.9995
2	0.9940	**9**	0.9971	**16**	0.9726
3	0.9695	**10**	0.9800	**17**	0.9964
4	0.9910	**11**	0.9777	**18**	0.9932
5	0.9640	**12**	0.9676	**19**	0.9987
6	0.9920	**13**	0.9873	**20**	0.9962
7	0.9670	**14**	0.9862	**21**	0.9740

*correlation coefficient was measured at the shear rate of 20 rpm

General Conclusions

Having a global look at the overall results herein, it can be concluded that the temperature was the main contributor to the viscosity of the bio-oils in comparison to shear rate. In other words, the effect of temperature in changing the viscosity of the bio-oils was more significant than the effect of shear rate. This kind of behavior showed that the bio-oil binders had the same behavior as bitumen binders. In addition, the relationship between viscosity and temperature at different

shear rates can be well described as a linear logarithmic relationship. Importantly, it was observed that the addition of polymer modifiers with different blending ratios did not lead to the same effect when blending with different bio-binders. Also, the effect of the addition of different types of polymer modifiers and the blending ratios on the VTS values was varied depending on the type of the bio-binder and the shear rate.

Power Law Model

In this section, the relationship between viscosity and shear rates at different temperatures is studied for all the bio-binders and the bitumens using the Power law model.

All Bio-binders

Figure 7.20 to Figure 7.22 display the Power-law relationship between viscosity and shear rates for oakwood, switchgrass, and cornstover bio-binders, respectively. Subsequently, the logarithmic linear relationship between log viscosity and log shear rate were plotted in Figure 7.23 to Figure 7.33, for some blends, e.g. AAM, 1, 2, 4, 7, 8, 11, 14, 15, 17, and 19, as an example while the rest of the blends were attached to Appendix D (Figure C7.28 to Figure C7.39). Based on the Power-law relationship between viscosity and shear rate, the *n* and *K* values for the unmodified and modified bio-binders and bitumens were calculated according to Equation 2.2 and were summarized in Table 7.13 to Table 7.18.

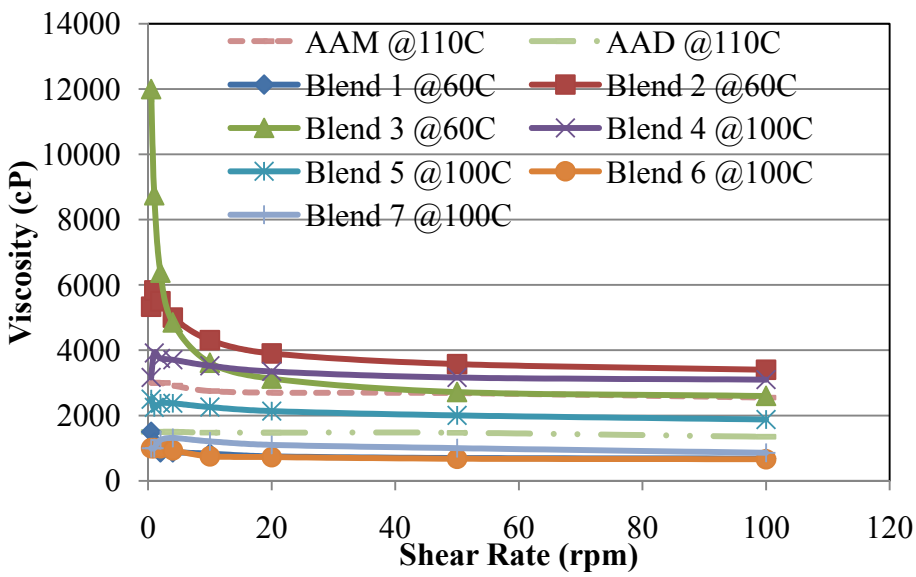


Figure 7.20. Viscosity versus Shear Rate for Oakwood Bio-binders at Different Temperatures

From Figure 7.20, the following conclusions could be established. First, the change in viscosity with the changing shear rate was insignificant for the control bitumen binders (e.g. AAM and AAD). In other words, the shear susceptibility was very minimal. However, some oakwood bio-binders, e.g. blends 2 and 3, showed significant shear susceptibility which indicated that the viscosity changed with a changing shear rate. On the other hand, some blends, e.g. blends 5, 6

and 7, did not show any shear susceptibility or dependence as the viscosity did not change with respect to the shear rate. Therefore, it is worth noting that the addition of the polymer led to an impact on the shear susceptibility, but the degree of impact depended upon the type of the polymer and the blending percentage. Second, the shear dependence or susceptibility could not be measured at the same temperature because some of the blends, e.g. 4, 5, 6 and 7, and AAM and AAD were solid at 60°C. This indicated that the addition of polymer modifiers led to change the temperature range for the oakwood bio-binders.

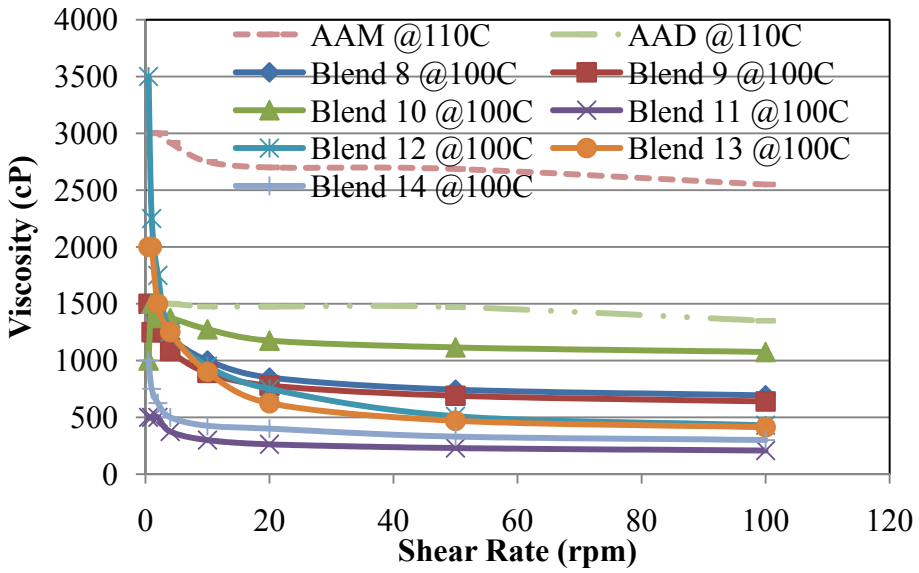


Figure 7.21. Viscosity versus Shear Rate for Switchgrass Bio-binders at Different Temperatures

Based on Figure 7.21, the following conclusions could be established. First, for the switchgrass bio-binders, the change in viscosity relative to the change in shear rate had -in general- the same trend as the bitumen blends. In other words, at low shear rates, the viscosity decreased as the shear rate increased, and then became constant at high shear rates. Second, it was observed that the viscosity of the switchgrass bio-binders were lower than the viscosity of the bitumen binders. Third, the change in viscosity with the changing shear rate was insignificant for the bitumen binders (blends AAM and AAD). In other words, the shear susceptibility was very minimal. However, some blends of the bio-oils, e.g. blends 9, 12 and 13, showed significant shear susceptibility which indicated that the viscosity changed with changing shear rate. On the other hand, some blends, e.g. blends 10, 11 and 14, did not show any shear susceptibility or dependence as the viscosity did not change with respect to the shear rate. Therefore, it is worth noting that the addition of the polymer led to an impact on the shear susceptibility, but the degree of impact depended upon the type of the polymer and the blending percentage, which was the same conclusion established for the oakwood bio-binders.

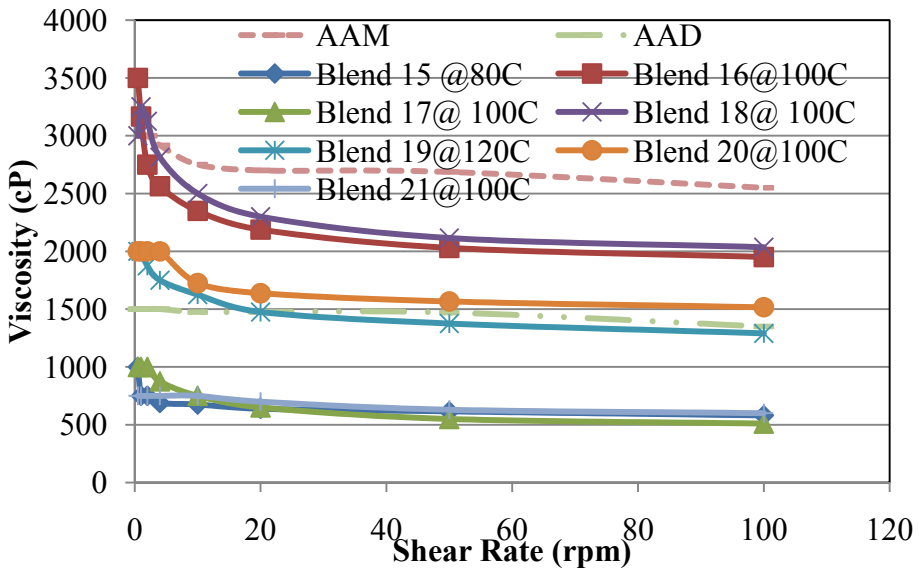


Figure 7.22. Viscosity versus Shear Rate for Cornstover Bio-binders at Different Temperatures

Based on Figure 7.22, the following observations could be noted for the cornstover bio-binders. First, the change in viscosity relative to the change in shear rate had -in general- the same trend as the bitumen blends. In other words, at low shear rates, the viscosity decreased as the shear rate increased, and then becomes constant at high shear rates. Second, it was observed that the viscosity of some cornstover bio-binders was lower than the viscosity of the AAM bitumen binder; however, some of the cornstover bio-binders showed higher viscosity than the AAD bitumen binder. Third, the change in viscosity with the changing shear rate was insignificant for the bitumen binders (blends AAM and AAD). In other words, the shear susceptibility was very minimal. However, some blends of the bio-binders, e.g. blends 16 and 18, showed significant shear susceptibility which indicated that the viscosity changed with the changing shear rate. Therefore, it is worth noting that the addition of the polymer led to an impact on the shear susceptibility, but the degree of impact depended upon the type of the polymer and the blending percentage, which was the same conclusion established for the oakwood and switchgrass bio-binders.

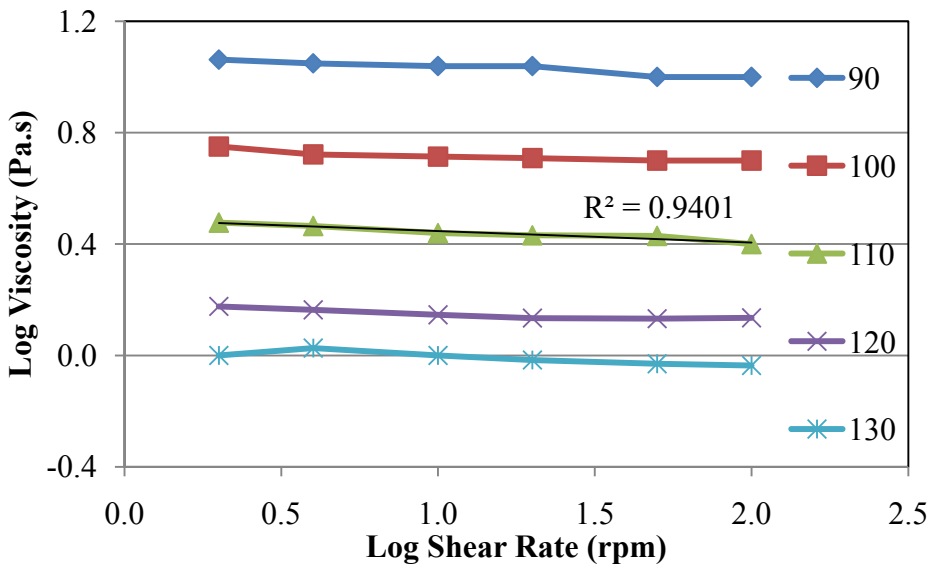


Figure 7.23. Power-law Model for AAM Blend

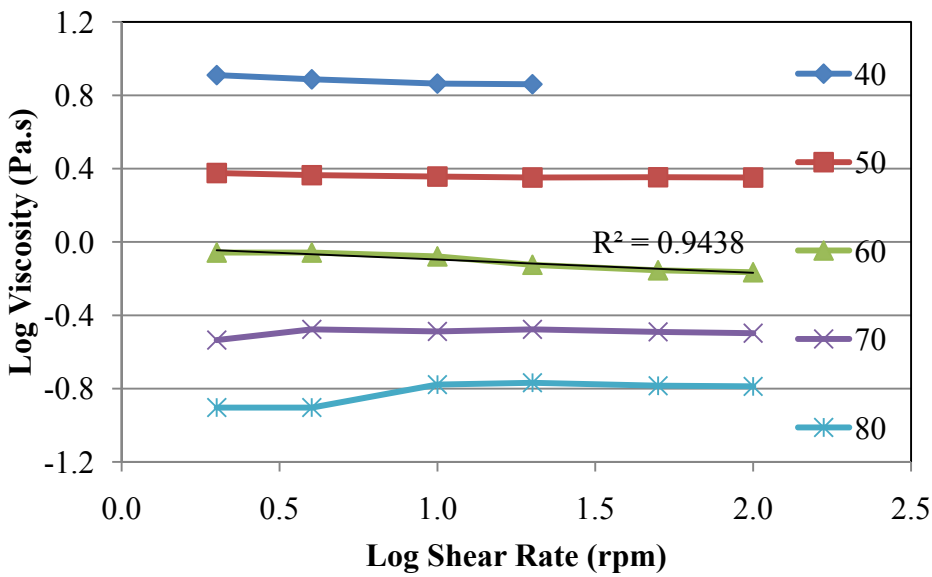


Figure 7.24. Power-law Relationship for Blend 1

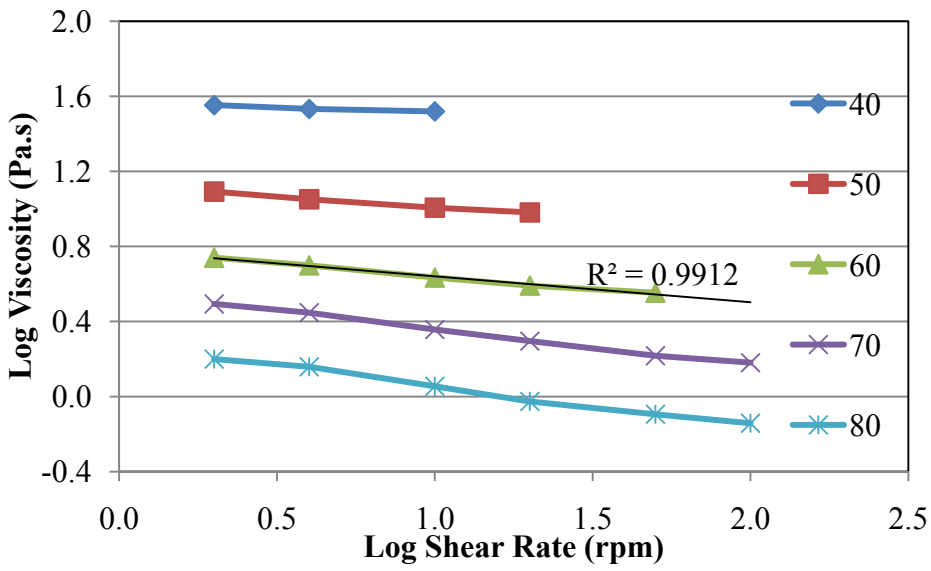


Figure 7.25. Power-law Relationship for Blend 2

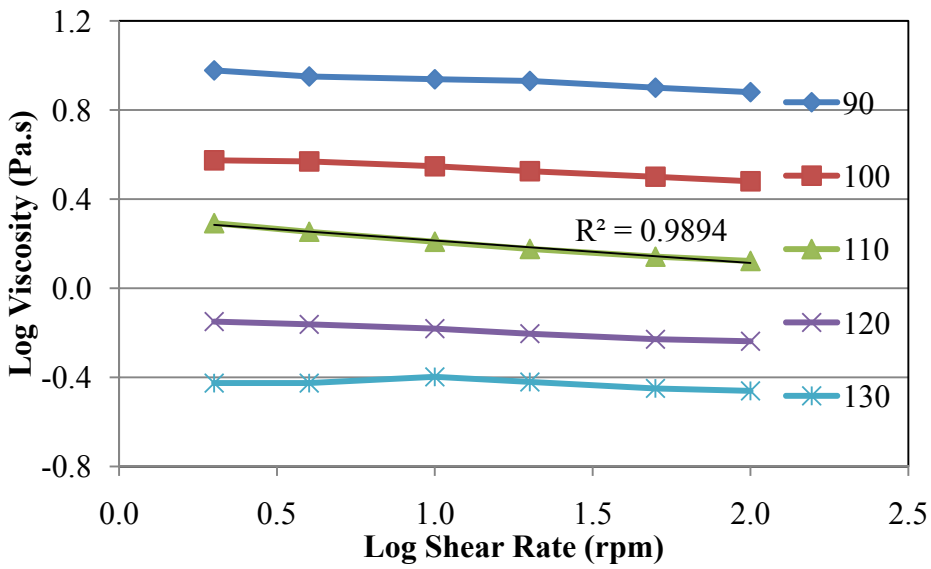


Figure 7.26. Power-law Relationship for Blend 4

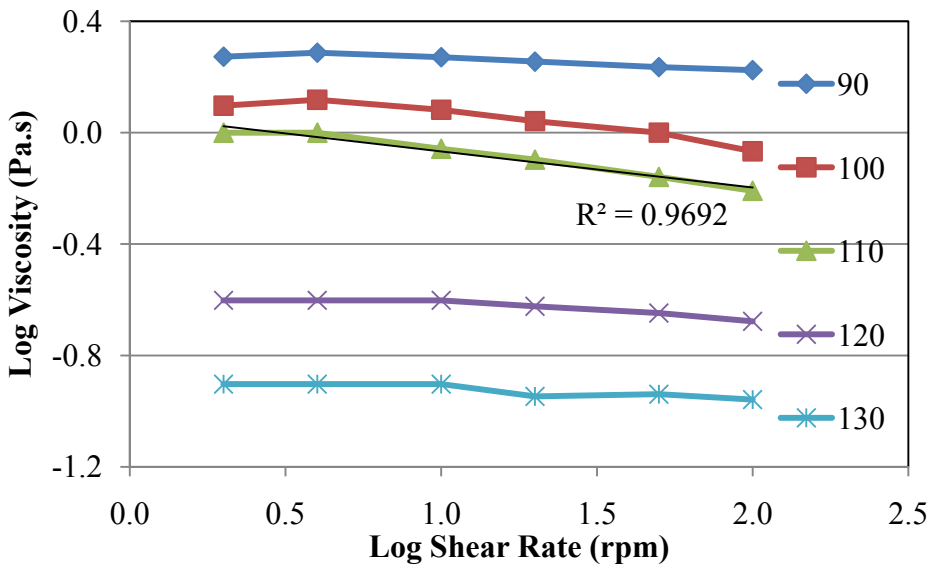


Figure 7.27. Power-law Relationship for Blend 7

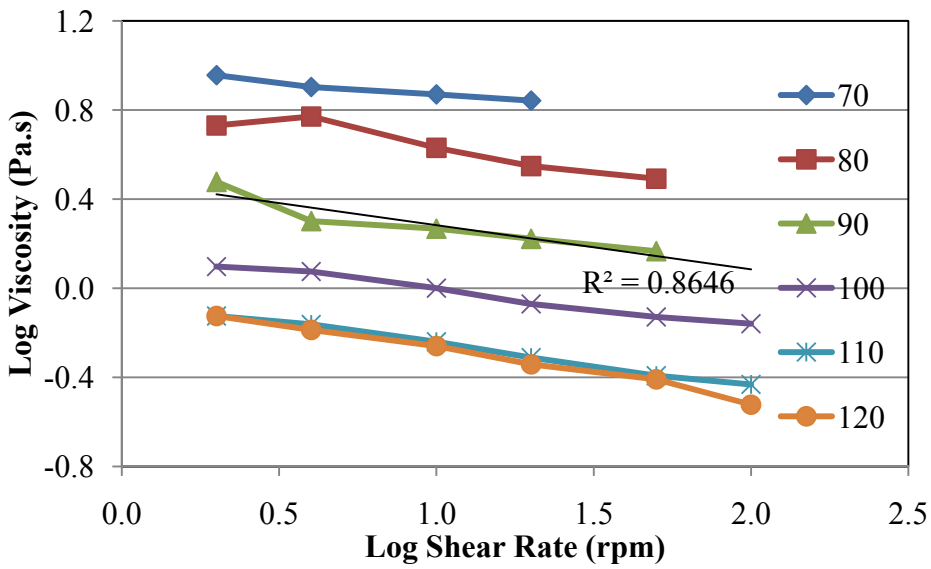


Figure 7.28. Power-law Relationship for Blend 8

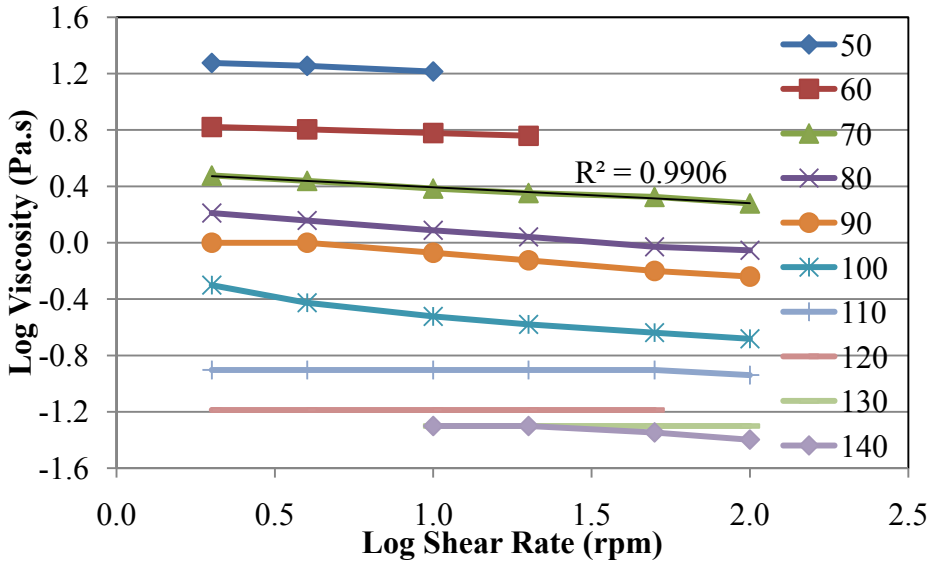


Figure 7.29. Power-law Relationship for Blend 11

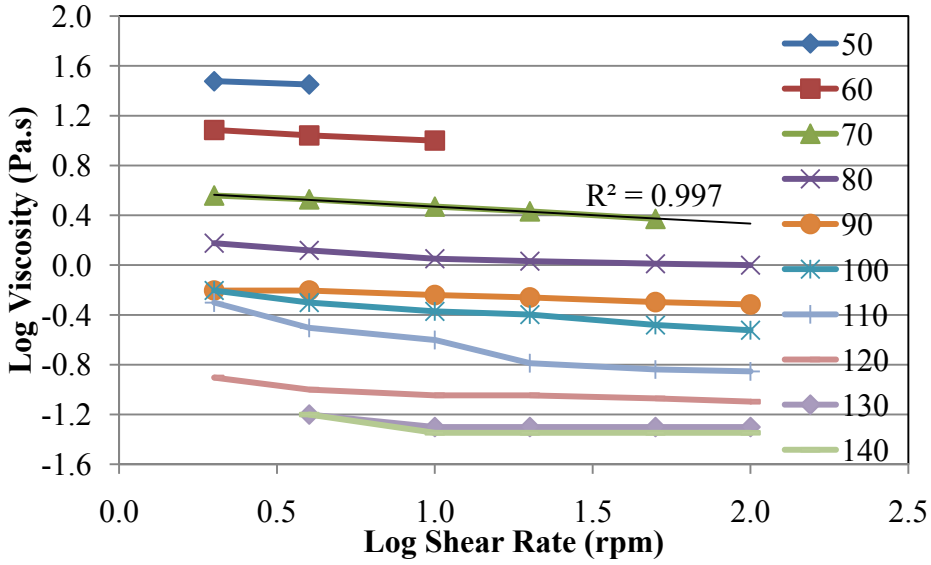


Figure 7.30. Power-law Relationship for Blend 14

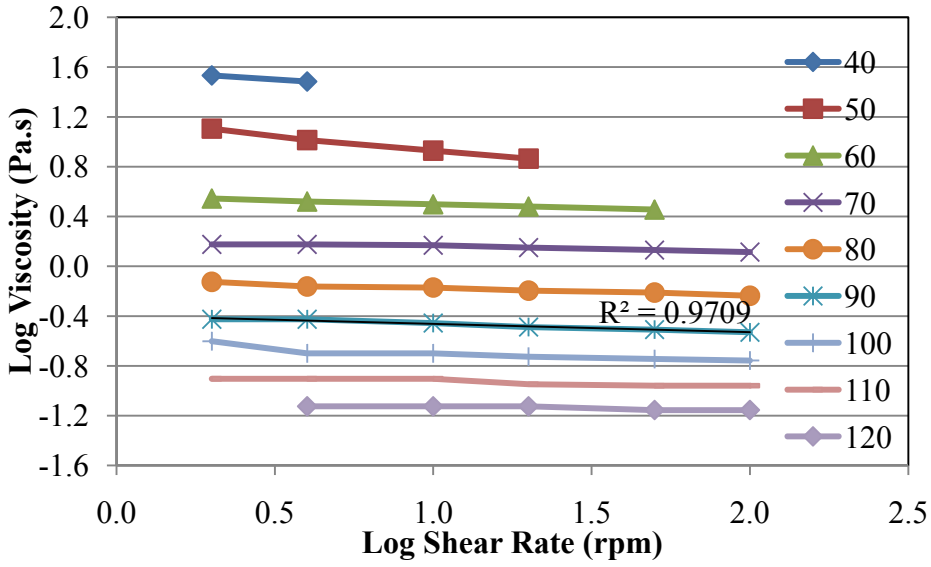


Figure 7.31. Power-law Relationship for Blend 15

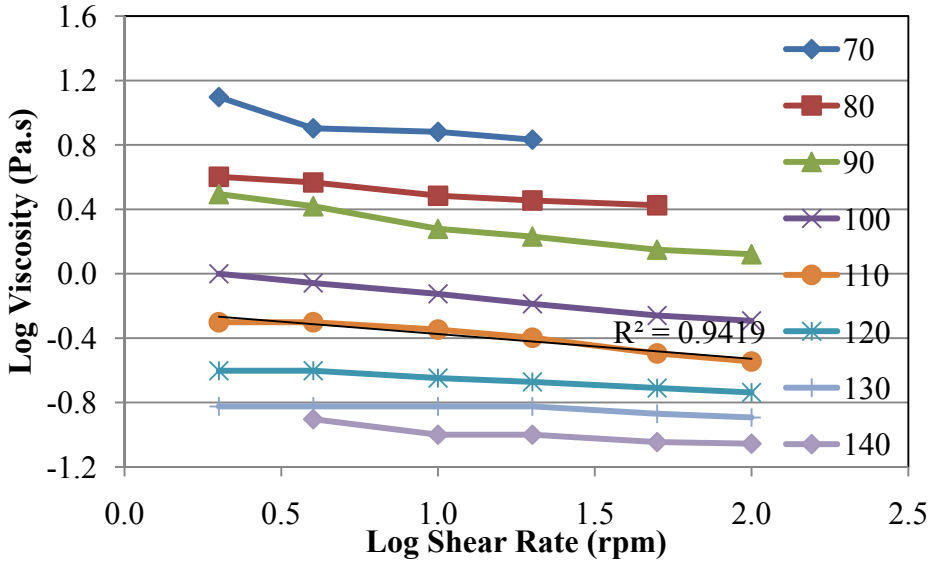


Figure 7.32. Power-law Relationship for Blend 17

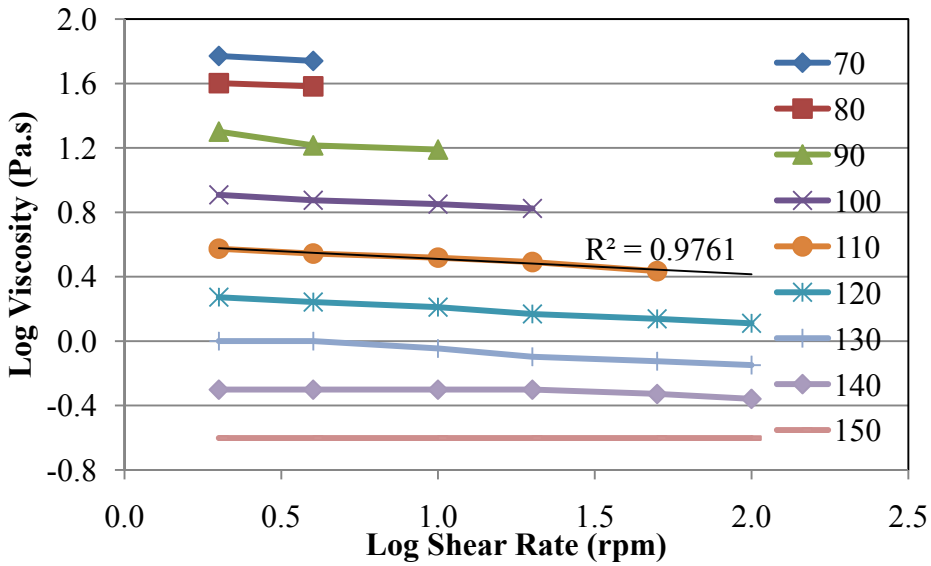


Figure 7.33. Power-law Relationship for Blend 19

Table 7.13. *n*-values for Oakwood Bio-binders

Temperature (°C)	Blend #								
	AAM	AAD	1	2	3	4	5	6	7
40	-	-	0.91	0.94	0.92	-	-	-	-
50	-	-	0.96	0.94	0.78	-	-	-	-
60	-	-	0.87	0.89	0.67	-	-	-	-
70	-	-	0.98	0.89	0.62	-	-	0.87	0.89
80	1.03	1.01	0.94	0.85	0.57	0.93	0.84	0.92	0.95
90	0.95	0.99	1.04	0.82	0.36	0.95	0.97	0.95	0.98
100	0.97	1.01	-	0.88	0.98	0.94	0.93	0.91	0.97
110	0.97	1.00	-	0.95	0.98	0.91	0.98	0.95	1.00
120	0.98	0.98	-	0.85	0.86	0.94	0.96	0.98	0.84
130	0.98	0.99	-	-	-	0.97	0.91	0.66	0.96
140	0.94	1.05	-	-	-	0.93	0.84	1.06	1.04
150	0.96	1.05	-	-	-	0.94	1.06	-	-
160	1.00	1.05	-	-	-	0.97	1.03	-	-

Table 7.14. *K*-values for Oakwood Bio-binders

Temperature	Blend #								
(°C)	AAM	AAD	1	2	3	4	5	6	7
40	-	-	9.10	37.81	32.73	-	-	-	-
50	-	-	2.59	11.81	14.25	-	-	-	-
60	-	-	1.14	5.53	8.51	-	-	-	-
70	-	-	0.34	2.69	5.53	-	-	17.17	19.79
80	28.40	13.57	0.19	1.49	4.32	28.71	16.11	5.56	5.31
90	12.30	6.48	0.09	0.82	4.04	9.70	4.34	1.80	2.07
100	5.72	2.93	-	0.30	0.14	4.07	2.62	1.01	1.60
110	3.00	1.50	-	0.15	0.07	2.02	0.78	0.55	1.23
120	1.49	0.95	-	0.17	0.08	0.75	0.54	0.12	0.28
130	1.02	0.49	-	-	-	0.41	0.43	0.49	0.13
140	0.69	0.26	-	-	-	0.32	0.51	0.07	0.06
150	0.39	0.17	-	-	-	0.21	0.13	-	-
160	0.26	0.12	-	-	-	0.13	0.14	-	-

From the results of the *n* and *K* values of the oakwood bio-binders, the following observations were noted. First, for the behavior index *n*, it could be concluded that increasing the temperature led to a more Newtonian behavior for all blends (*n* values were almost equal to unity). Also, all the blends at low temperatures had a pseudo-plastic behavior as their *n* values were less than unity. Second, the addition of a polymer modifier to the various blends led to a change in the rheological properties of the bio-oils. For most viscoelastic materials, it is well established that increasing the temperature leads to a more Newtonian behavior; however, polymer 1 may be the main reason that led to have a shear thickening or a dilatant behavior in blends 2 and 3 as the temperature increased. Third, for the consistency index *K*, it was observed that increasing the temperature led to a decrease in the viscous behavior for all blends. Fourth, if the *K* values of the bitumen binders assumed to represent the acceptable range, then the *K* values at low temperatures for all the bio-oils blends were acceptable and comparable to the bitumen binders. For example, blend 1 yielded 9.10 $Pa{\cdot}s^n$ while AAM and AAD yielded 12.31 $Pa{\cdot}s^n$ and 6.49 $Pa{\cdot}s^n$, respectively, which indicated that the viscous behavior of the bio-binders and bitumens, were similar. However, the temperature range for the bio-binders and bitumens was different. For instance, the temperature range for the bitumens was 90 to 160°C while it was 40 to 90°C (blends 1, 2 and 3) or 70 to 140°C (blends 6 and 7) for the bio-binders, excluding blend 4 which had the same temperature range as bitumen binders (90 to 160°C).

Table 7.15. *n*-values for Switchgrass Bio-binders

Temperature (°C)	AAM	AAD	8	9	10	11	12	13	14
50	-	-	-	-	-	0.91	0.82	0.89	0.91
60	-	-	-	-	-	0.94	0.76	0.80	0.88
70	-	-	0.89	0.87	0.96	0.89	0.87	0.75	0.86
80	1.03	1.01	0.80	0.85	0.93	0.84	0.84	0.74	0.90
90	0.95	0.99	0.80	0.84	0.87	0.85	0.70	0.69	0.93
100	0.97	1.01	0.84	0.83	0.93	0.79	0.64	0.65	0.82
110	0.97	1.00	0.81	0.98	0.90	0.99	0.88	0.90	0.67
120	0.98	0.98	0.77	0.99	0.90	1.00	0.92	1.00	0.90
130	0.98	0.99	0.89	0.89	1.02	1.00	0.83	0.94	0.94
140	0.94	1.05	-	-	0.99	0.90	0.80	1.00	0.91
150	0.96	1.05							
160	1.00	1.05							

Table 7.16. *K*-values for Switchgrass Bio-binders

Temperature (°C)	AAM	AAD	8	9	10	11	12	13	14
50	-	-	-	-	-	20.16	33.96	51.28	31.86
60	-	-	-	-	-	6.94	14.69	20.70	13.15
70	-	-	9.57	11.64	23.81	3.27	4.99	11.02	4.00
80	28.40	13.57	6.79	5.97	12.72	1.82	2.84	4.83	1.56
90	12.30	6.48	3.03	2.56	5.40	1.17	2.59	3.29	0.67
100	5.72	2.93	1.43	1.37	1.48	0.53	2.15	1.94	0.67
110	3.00	1.50	0.87	0.40	1.11	0.13	0.25	0.28	0.53
120	1.49	0.95	0.90	0.26	0.70	0.07	0.14	0.13	0.12
130	1.02	0.49	-	0.25	0.25	0.05	0.14	0.11	0.06
140	0.69	0.26	-	-	0.18	0.06	0.14	0.05	0.06
150	0.39	0.17	-	-	-	-	-	-	-
160	0.26	0.12	-	-	-	-	-	-	-

Based on Table 7.15 and Table 7.16, the following observations were noted for the switchgrass bio-binders. First, for the behavior index *n*, it could be concluded that increasing the temperature led to a more Newtonian behavior for all blends (*n* values were almost equal to unity). This was the same conclusion established for the oakwood bio-binders. In addition, all the switchgrass bio-binders at low temperatures had a pseudo-plastic behavior as their *n* values were less than unity, like the oakwood bio-binders. Second, for the consistency index *K*, it was observed that increasing the temperature led to a decrease in the viscous behavior of all switchgrass bio-binders, which was the same conclusion verified by the oakwood bio-binders.

Table 7.17. *n*-values for Cornstover Bio-binders

Temperature (°C)	AAM	AAD	15	16	17	18	19	20	21
40	-	-	0.84	-	-	-	-	-	-
50	-	-	0.76	-	-	-	-	-	-
60	-	-	0.94	-	-	-	-	-	-
70	-	-	0.96	0.96	0.76	0.97	0.90	0.91	0.87
80	1.03	1.01	0.94	0.93	0.87	0.91	0.93	0.94	0.90
90	0.95	0.99	0.93	0.87	0.77	0.92	0.85	0.90	0.94
100	0.97	1.01	0.92	0.91	0.82	0.89	0.92	0.92	0.94
110	0.97	1.00	0.96	0.93	0.85	0.90	0.90	0.93	0.96
120	0.98	0.98	0.97	0.93	0.91	0.91	0.90	0.92	0.92
130	0.98	0.99	-	0.96	0.96	0.94	0.90	0.98	1.00
140	0.94	1.05	-	0.85	0.90	0.89	0.97	0.88	0.93
150	0.96	1.05	-	-	-	-	-	-	-
160	1.00	1.05	-	-	-	-	-	-	-

Table 7.18 *K*-values for Cornstover Bio-binders

Temperature (°C)	AAM	AAD	15	16	17	18	19	20	21
40	-	-	38.18	-	-	-	-	-	-
50	-	-	14.72	-	-	-	-	-	-
60	-	-	3.64	-	-	-	-	-	-
70	-	-	1.54	37.14	13.10	38.16	63.29	34.31	10.19
80	28.40	13.57	0.77	15.51	4.34	14.75	41.88	13.31	3.27
90	12.30	6.48	0.40	8.40	3.64	6.28	21.55	4.63	1.34
100	5.72	2.93	0.24	2.90	1.12	3.29	8.50	2.13	0.82
110	3.00	1.50	0.13	1.62	0.60	1.57	4.03	1.09	0.54
120	1.49	0.95	0.08	0.81	0.27	1.04	2.00	0.55	0.21
130	1.02	0.49	-	0.56	0.16	0.55	1.10	0.26	0.10
140	0.69	0.26	-	0.60	0.14	0.42	0.52	0.27	0.12
150	0.39	0.17	-	-	-	-	-	-	-
160	0.26	0.12	-	-	-	-	-	-	-

From Table 7.17 and Table 7.18 for the cornstover bio-binders, the following observations can be made. First, the behavior of the cornstover bio-binders did not resemble the oakwood and switchgrass bio-binders in the sense that increasing the temperature did not lead to a Newtonian behavior because all *n* values were below unity. Second, unlike the oakwood and switchgrass bio-binders, all the cornstover bio-binders at low and high temperatures had a pseudo-plastic behavior (their *n* values were less than unity). On the other hand, for the consistency index *K*, it was observed that increasing the temperature led to a decrease in the viscous behavior of all cornstover bio-binders, which was the same conclusion established for the oakwood and switchgrass bio-binders.

Statistical Analysis

A statistical analysis was conducted, using the computer software JMP 7.0, to study the statistical difference between VTS values of bio-binders and bitumens. A one-way analysis of variance "ANOVA" using the method of least squares was performed for examination to evaluate the binder types (bitumen and bio-oil/bio-binder), polymer modifier types (P1, P2, and P3), and blending percentages (2% and 4%). Type I error (α) of 0.05 was used for all statistical analysis as the confidence level was 95%. Three different statistical tests were conducted for each bio-binder type separately. These tests can be summarized and listed as follows: (1) test 1 was concerned about studying the statistical difference between the *n* and *K* values of modified and unmodified bio-binders in order to emphasize the importance of the addition of polymer modifiers, (2) test 2 was to examine the difference between the *n* and *K* values of unmodified bio-binder and bitumen, e.g. AAM and AAD, and (3) test 3 was designed to compare between the *n* and *K* values of modified bio-binders and bitumen binders. The p-values of the AVOVA for different tests were summarized and listed in Table 7.19, Table 7.20, and Table 7.21 for oakwood, switchgrass, and cornstover bio-binders, respectively.

Based on the p-values reported in Table 7.19 for the oakwood bio-binders, for the *n* values, it was observed that the polymer type and blending ratios at almost all temperatures were not significant factors in changing the *n* values of the unmodified and modified oakwood bio-binders (except at temperature of 110°C). On the other hand, for the *K* values, the polymer type was not a significant factor in almost all temperatures except at 70, 100 and 120°C. Yet, the blending ratio was not a significant factor in changing the *K* values at all temperatures. Importantly, there was no statistical significant difference between *n* and *K* values of the unmodified bio-binders and bitumens. In addition, the binder type was not a statistically significant factor at all temperatures (except at temperature of 120°C) in affecting the *n* and *K* values for the modified oakwood bio-binders and bitumen. This may be due to the variability of the material that led to this inconsistency in the statistical analysis, so this result can be considered limited. In summary, it may be concluded that there was no statistically significant difference between the unmodified and modified oakwood bio-binders, and bitumens.

Table 7.19. Statistical Analysis for *n* and *K* Values for Oakwood Bio-binders

Test #	Blends	Temp (°C)	Experimental Variable	*n*		*K*	
				F-Ratio	Prob >F	F-Ratio	Prob >F
1	1,2,3,4,5,6&7	70	Polymer type	1.0027	0.4993	40.5233	***0.0241****
			Blending ratio	0.8527	0.4533	0.0722	0.8134
		80	Polymer type	1.4609	0.3815	6.4346	0.0803
			Blending ratio	0.9601	0.3826	0.1295	0.7371
		90	Polymer type	2.0657	0.2832	2.2064	0.2663
			Blending ratio	0.4254	0.5499	0.0462	0.8403
		100	Polymer type	0.0219	0.9785	12.1997	***0.0362****
			Blending ratio	4.6875	0.0963	0.0623	0.8152
		110	Polymer type	0.3373	0.7376	2.5245	0.2275
			Blending ratio	11.2500	***0.0285****	0.1041	0.7631
		120	Polymer type	1.3582	0.3802	12.1864	***0.0363****
			Blending ratio	0.4708	0.5303	0.0372	0.8565
		130	Polymer type	0.7222	0.4849	0.3723	0.6038
			Blending ratio	0.5842	0.5245	1.1992	0.3878
		140	Polymer type	12.8118	0.0700	13.5359	0.0666
			Blending ratio	0.2127	0.6900	0.1223	0.7600
2	AAM,AAD,1	80	Binder Type	21.3333	0.1357	2.6216	0.3522
		90		4.0833	0.2926	3.4045	0.3162
3	AAM,AAD, 2,3,4,5,6&7	80	Binder Type	2.8165	0.1443	1.6121	0.2512
		90		0.5338	0.4925	4.1451	0.0879
		100		3.5129	0.1100	4.3218	0.0829
		110		0.8855	0.3830	4.9579	0.0676
		120		2.6436	0.1551	14.4510	***0.0090****
		130		1.0123	0.3713	3.7288	0.1257
		140		0.1075	0.7595	1.2638	0.3238
		150		0.0044	0.9529	0.8832	0.4465
		160		0.4098	0.5876	0.6142	0.5153

Table 7.20. Statistical Analysis for *n* and *K* Values for Switchgrass Bio-binders

Test #	Blends	Temp (°C)	Experimental Variable	*n*		*K*	
				F-Ratio	Prob >F	F-Ratio	Prob >F
1	8,9,10,11, 12,13&14	50	Polymer type	0.5765	0.5270	1.4838	0.3474
			Blending ratio	0.5765	0.5270	0.0325	0.8736
		60	Polymer type	0.0103	0.9284	1.2756	0.3760
			Blending ratio	0.2941	0.6419	0.0002	0.9898
		70	Polymer type	1.2718	0.4240	2.0009	0.2917
			Blending ratio	1.2319	0.3293	0.1075	0.7595
		80	Polymer type	0.4589	0.7306	2.1433	0.2737
			Blending ratio	3.3103	0.1430	0.1611	0.7087
		90	Polymer type	0.1626	0.9150	0.6800	0.6205
			Blending ratio	0.2156	0.6666	0.1315	0.7353
		100	Polymer type	1.1685	0.4506	0.0093	0.9985
			Blending ratio	0.1581	0.7112	0.0670	0.8085
		110	Polymer type	1.0104	0.4967	1.6403	0.3471
			Blending ratio	3.1500	0.1506	1.8453	0.2459
		120	Polymer type	2.3283	0.2528	5.5910	0.0956
			Blending ratio	145.800	***0.0003****	0.7072	0.4477
		130	Polymer type	0.1528	0.9214	14377.68	***<.0001****
			Blending ratio	0.0440	0.8442	0.0272*	0.8771
		140	Polymer type	2.4365	0.2589	1.2462	0.3804
			Blending ratio	1.6335	0.3295	1.2462	0.3804
2	AAM,AAD,8	80	Binder Type	161.3333	***0.0500****	1.2216	0.4682
		90		24.0833	0.1280	1.5922	0.4266
		100		18.7500	0.1445	1.4356	0.4428
		110		45.3704	0.0938	1.1285	0.4808
3	AAM,AAD, 9,10,11,12, 13&14	80	Binder Type	12.1542	***0.0130****	11.7290	***0.0141****
		90		4.6278	0.0750	13.3228	***0.0107****
		100		6.4067	***0.0446****	13.1464	***0.0110****
		110		1.2953	0.2985	16.7509	***0.0064****
		120		0.5788	0.4756	20.5668	***0.0040****
		130		0.8553	0.3907	18.7085	***0.0050****
		140		1.7467	0.2568	8.6232	***0.0425****

Based on the p-values reported in Table 7.20 for the switchgrass bio-binders, it was observed that the polymer type and blending ratios at all temperatures were not -in general- significant factors in changing the *n* and *K* values of the unmodified and modified oakwood bio-binders (except at temperatures of 120°C and 130°C for blending ratio and polymer type, respectively). This conclusion was to a very large extent consistent with the conclusion aforementioned for the oakwood bio-binders. Importantly, there was no statistical significant difference between the *n* and *K* values of the unmodified bio-binders and bitumen although the binder type was a significant factor in affecting the *n* values at 80°C only. In addition, the binder type was not a statistically significant factor at all temperatures (except at temperatures of 80 and 100°C) between the *n* values of the modified oakwood bio-binders and bitumens. However, the binder

type was a significant factor in affecting the *K* values at all temperatures. In summary, it may be concluded that there was no statistically significant difference between the *n* values of the unmodified and modified oakwood bio-binders, and bitumens, but there was a significance difference between the *K* values of the modified switchgrass bio-binders and bitumens.

Based on the p-values reported in Table 7.21 for the cornstover bio-binders, it was observed that the polymer type and blending ratios at almost all temperatures were not significant factors in changing the *n* and K values of the unmodified and modified cornstover bio-binders (except at the temperature of 120°C). This conclusion was inconsistent with the conclusion established for the oakwood bio-binders. Importantly, like the oakwood bio-binders, there was no statistical significant difference between the *n* and *K* values of the unmodified bio-binders and bitumens. In addition, the binder type was not a statistically significant factor at all temperatures in affecting the *K* values for the modified oakwood bio-binders and bitumens. On the other hand, there was a statistically significant difference between the *n* values of the modified cornstover bio-binders and bitumens. In summary, it may be concluded that there was no statistically significant difference between the unmodified and modified oakwood bio-binders, and bitumens.

Table 7.21. Statistical Analysis for *n* and *K* Values for Cornstover Bio-binders

Test #	Blends	Temp (°C)	Experimental Variable	*n*		*K*	
				F-Ratio	Prob >F	F-Ratio	Prob >F
1	15,16,17, 18,19,20&21	70	Polymer type	0.4009	0.7637	2.0269	0.2882
			Blending ratio	4.9536	0.0900	0.1975	0.6797
		80	Polymer type	0.4082	0.7595	1.4160	0.3909
			Blending ratio	1.8824	0.2420	0.0241	0.8842
		90	Polymer type	1.5628	0.3613	1.2921	0.4191
			Blending ratio	0.7161	0.4451	0.1379	0.7292
		100	Polymer type	0.9878	0.5039	1.8995	0.3057
			Blending ratio	0.1221	0.7444	0.0777	0.7942
		110	Polymer type	1.4892	0.3757	1.7252	0.3326
			Blending ratio	0.2500	0.6433	0.0648	0.8117
		120	Polymer type	11.5714	***0.0372****	2.9872	0.1964
			Blending ratio	1.5000	0.2879	0.0020	0.9669
		130	Polymer type	7.4000	0.0692	2.7234	0.2117
			Blending ratio	0.0455	0.8416	0.0001	0.9926
		140	Polymer type	0.7982	0.5273	0.9525	0.4783
			Blending ratio	6.4800	0.0636	1.1101	0.3515
2	AAM,AAD,15	80	Binder Type	21.3333	0.1357	2.4774	0.3603
		90		1.3333	0.4544	3.1814	0.3253
		100		4.0833	0.2926	2.8583	0.3400
		110		0.9259	0.5122	2.6633	0.3500
3	AAM,AAD, 16,17,18,19, 20&21	80	Binder Type	28.9811	***0.0017****	0.2486	0.6358
		90		4.1977	0.0864	0.0993	0.7634
		100		7.4388	***0.0343****	0.2993	0.6041
		110		6.4248	***0.0444****	0.4357	0.5337
		120		69.1364	***0.0002****	0.6377	0.4550
		130		1.2075	0.3140	0.9787	0.3607
		140		5.1156	0.0644	0.5209	0.4976

Considerably, the relationship between viscosity and shear rate at different temperatures for the bio-binders and bitumens were following a power-law relationship. The coefficients of correlation for this power-law model were determined for all blends at different temperatures and listed in Table 7.22. The R^2 values for this relationship for all bio-binders were very high (exceeding 80%, except for only blend 5) and comparable to the bitumens.

Table 7.22. Coefficient of Correlation for Power-law Model

Blend #	R^2 value	Blend #	R^2 value	Blend #	R^2 value
AAM	0.9401 (110)	**AAD**	0.6282 (110)		
1	0.9438 (60)	**8**	0.8646 (90)	**15**	0.9709 (80)
2	0.9912 (60)	**9**	0.9755 (90)	**16**	0.9657 (110)
3	0.9657 (60)	**10**	0.9685 (90)	**17**	0.9419 (110)
4	0.9894 (110)	**11**	0.9906 (70)	**18**	0.9534 (110)
5	0.7542 (110)	**12**	0.9448 (70)	**19**	0.9761 (110)
6	0.9561 (110)	**13**	0.8326 (70)	**20**	0.8805 (110)
7	0.9692 (110)	**14**	0.9970 (70)	**21**	0.8585 (100)

*correlation coefficient was measured at the temperature between the brackets in °C

General Conclusions

For the behavior index *n*, it can be concluded that increasing the temperature led to a more Newtonian behavior for the oakwood and switchgrass bio-binders (*n* values were almost equal to unity), but the cornstover bio-binders did not follow the same behavior. Also, all the bio-binders at low temperatures had a pseudo-plastic behavior as their *n* values were less than unity. For the consistency index *K*, it was observed that increasing the temperature led to a decrease in the viscous behavior of all types of the bio-binders.

From the statistical analysis, it may be concluded that the addition of polymer modifiers with different blending percentages to all types of bio-binders did not lead -in general- to a significant change in the *n* and *K* values. Significantly, there was no statistically significant difference between the *n* and *K* values of the unmodified bio-binders and the bitumens. In addition, there was no significant difference between the *n* and *K* values of the modified oakwood bio-binders and the bitumens. On the other hand, there was no significance difference between the *n* values of the modified switchgrass bio-binders and bitumens, but there was significance difference between the *K* values of the modified switchgrass and bitumens. For the cornstover bio-binders, for the *n* values, there was significant difference between the modified cornstover bio-binders and bitumens, but there was no significance difference between the *K* values of the modified cornstover bio-binders and bitumens. Therefore, it is worth noting that the effect of the polymer modifiers on the *n* and *K* values vary according to the type of the bio-binders. Considerably, the relationship between viscosity and shear rate at different temperatures for the bio-binders and bitumens were following a power-law relationship.

Arrhenius-type Model

In this section, the relationship between viscosity and temperature at different shear rates is studied for all the bio-binders and the bitumens using the Arrhenius-type model. The Arrhenius-type model is always employed at temperatures higher than the glass transition temperature of the materials. Therefore, it was assumed that the temperatures at which the materials were tested are higher than the glass transition temperature, so the Arrhenius-type model could be employed.

All bio-binders

Based on the Arrhenius type relationship between viscosity and temperature, the E_a and η_∞ values for the unmodified and modified bio-binders and bitumens were calculated according to Equation 2.3 and are summarized in Table 7.23. Figure 7.37 to Figure 7.47 displaying the Arrhenius-type relationship between viscosity and temperature for some blends, e.g. AAM, AAD, 1, 4, 5, 8, 9, 14, 15, 16, and 21, as an example while the rest of the blends are attached to Appendix D (Figure C7.40 to Figure C7.51).

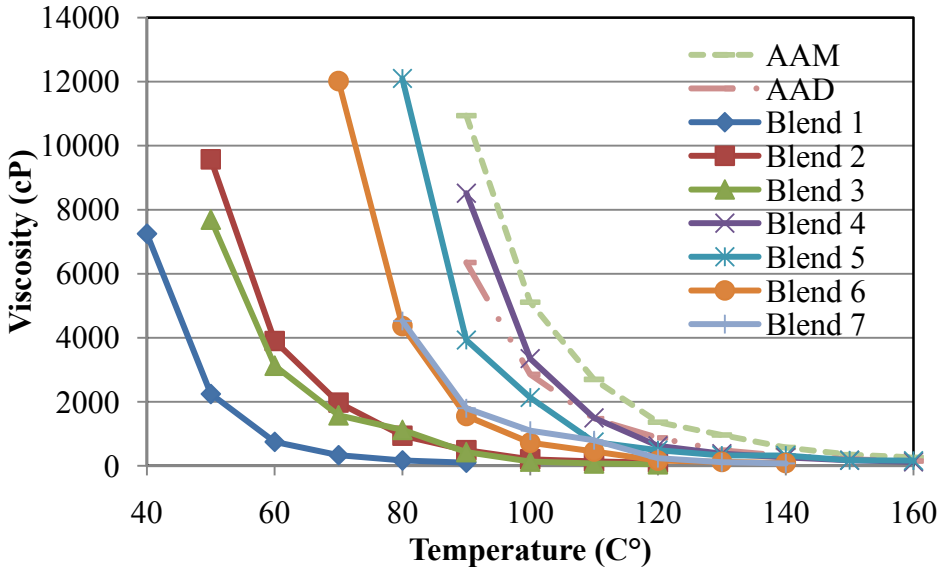


Figure 7.34. Viscosity versus Temperature for Oakwood Bio-binders at 20 rpm

Based on Figure 7.34, the following observations could be made. First, the relationship between viscosity and temperature was the same for all the blends including the bitumens (AAM and AAD). Specifically, the viscosity measurements were decreasing exponentially with increasing temperatures. Second, the ranges of temperature for this exponential relationship were different. For example, blend 1 (the unmodified oakwood bio-binder) had this exponential relationship at temperature range between 40 and 90°C, while AAM and AAD (bitumens) had the same exponential behavior at temperature range between 90 and 160°C. Third, the addition of polymer modifiers may be the main reason for the change in the temperature range; the same exponential relationship was observed but shifted to the right side. For example, the behaviors of blends 2 and 3 (the modified oakwood bio-binders with polymer 1) were shifted which led to increase the low and high temperatures. Precisely, the low temperature changed from 40°C to 50°C and the high temperature increased from 90°C to 120°C. In addition, blends 4 and 5 (the modified oakwood bio-binder with polymer 2) had almost the same exponential relationship between viscosity and temperature at the same temperature range in comparison with the bitumens (AAM and AAD). Fourth, increasing the blending percentage of polymer modifier from 2% (blend 6) to 4% (blend 7) did not lead to a significant difference in the viscosity measurements between them. Therefore, it is worth noting that the addition of a high percentage of polymer modifiers did not guarantee an enhancement in the properties of the bio-binders.

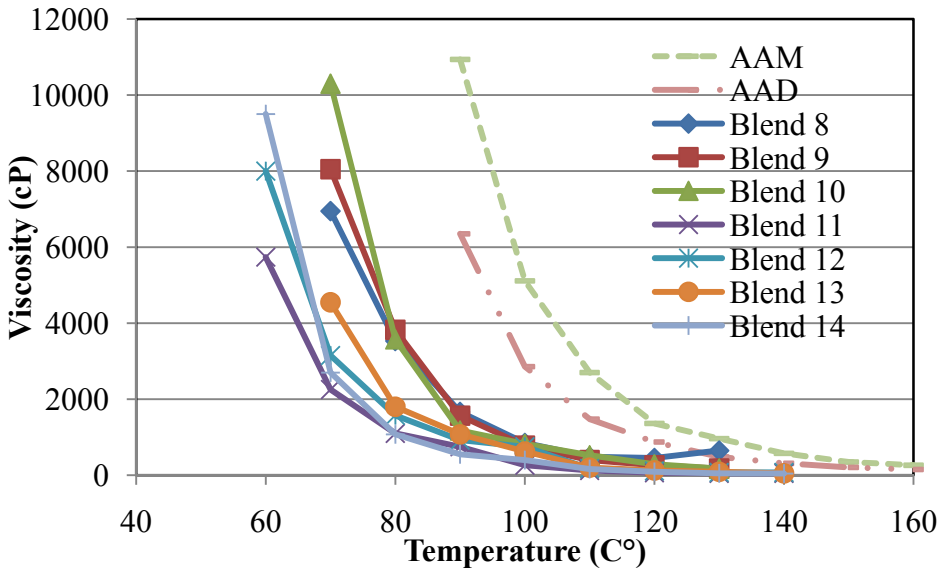


Figure 7.35. Viscosity versus Temperature for Switchgrass Bio-binders at 20 rpm

From Figure 7.35, the following observations are noted. First, like the oakwood bio-binders, the relationship between viscosity and temperature was the same for all the switchgrass bio-binders including the bitumens (AAM and AAD). Significantly, the viscosity measurements were decreasing exponentially with increasing temperatures as the oakwood bio-binders. Second, the ranges of temperature for this exponential relationship were different as previously mentioned. Third, the addition of polymer modifiers may be the main reason for the change in the temperature range; the same exponential relationship was observed but shifted to the left side. For example, the behavior of switchgrass bio-binders, e.g. blends 11 to 14 (the modified bio-oil with polymers 2 and 3, respectively) were shifted which led to increase the low and high temperatures. Precisely, the low temperature changed from 70°C to 50°C and the high temperature increased from 120°C to 140°C. Fourth, like the oakwood bio-binders, increasing the blending percentage of polymer modifier from 2% (blends 11 and 13) to 4% (blends 12 and 14) did not lead to a significant difference in the temperature ranges for the bio-binders.

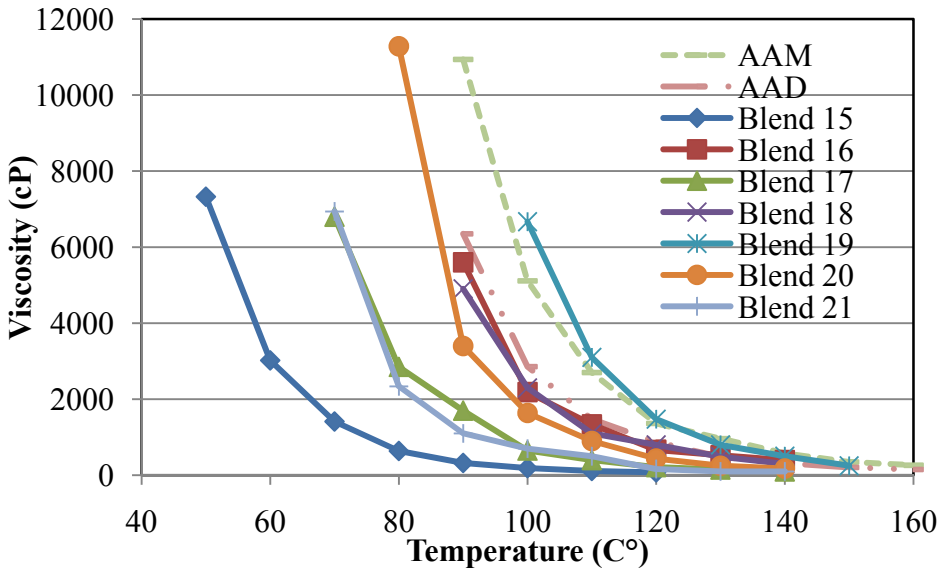


Figure 7.36. Viscosity versus Temperature for Cornstover Bio-binders at 20 rpm

Based on Figure 7.36, the following conclusions could be established. First, like the oakwood and switchgrass bio-binders, the relationship between viscosity and temperature was the same for all the cornstover bio-binders including the bitumens (AAM and AAD). Specifically, the viscosity measurements were decreasing exponentially with increasing temperatures as the oakwood and switchgrass bio-binders. Second, the ranges of temperature for this exponential relationship were different. Third, the addition of polymer modifiers may be the main reason for the change in the temperature range; the same exponential relationship was observed but shifted to the left side. For example, the behavior of cornstover bio-binders, e.g. blends 16, 18 and 20 (the modified bio-binder with polymers 1, 2 and 3, respectively) were shifted which led to increase the low and high temperatures. Precisely, the low temperature changed from 40°C to 70°C and the high temperature increased from 120°C to 140°C. Fourth, like the oakwood and switchgrass bio-binders, increasing the blending percentage of polymer modifier from 2% (blends 11 and 13) to 4% (blends 12 and 14) did not lead to a significant difference in the temperature ranges for bio-binders.

Based on the results in Table 7.23, the following observations were noted. First, for the activation energy E_a values, all bio-binder blends showed the same trend as the bitumens in the sense of increasing the shear rate led to decrease in the E_a values. Second, the E_a values for the bio-binders in comparison to the corresponding values in bitumens were -in general- higher which indicated that the bio-oils were more susceptible to temperature than the bitumens. Third, it was noted that increasing the shear rate led to increasing the η_∞ values for some of the bio-binders and the bitumens (e.g. AAM, AAD, 1, 7, 8, 13, 14, 15, 17, and 20), but the influence cannot be described as one that had a well-defined pattern. Fourth, it was observed that the E_a values of the unmodified oakwood bio-binder (blend 1) at a shear rate of 20 rpm were higher than the E_a values of the bitumens and the unmodified switchgrass and cornstover bio-binders (blends 8 and 15). Precisely the E_a values at shear rate of 20 rpm for AAM, AAD, blend 1, 8 and 15 were 3.64E+03, 3.65E+03, 4.25E+03, 3.41E+03, and 3.65E+03, respectively. Fifth, no clear trend could be observed for the effect of the addition of polymer modifiers on the E_a and η_∞ values. In general, the temperature susceptibility of oakwood binders was higher than the

bitumens, but the temperature susceptibility of the switchgrass and cornstover bio-binders were very close and comparable to the bitumens.

Table 7.23. E_a and η_∞ Values for all Blends

Blend #	Parameter	Shear Rate (rpm)					
		2	4	10	20	50	100
AAM	E_a	3.88E+03	3.83E+03	3.61E+03	3.64E+03	3.41E+03	3.29E+03
	η_∞	2.45E-10	3.18E-10	1.10E-09	9.14E-10	3.09E-09	5.97E-09
AAD	E_a	4.00E+03	3.89E+03	3.65E+03	3.65E+03	3.33E+03	3.23E+03
	η_∞	6.07E-11	1.18E-10	4.71E-10	4.77E-10	2.90E-09	5.06E-09
1	E_a	5.02E+03	4.58E+03	4.29E+03	4.25E+03	3.93E+03	3.44E+03
	η_∞	7.14E-16	1.61E-14	1.24E-13	1.59E-13	1.27E-12	3.53E-11
2	E_a	3.67E+03	3.77E+03	3.91E+03	4.07E+03	3.82E+03	3.85E+03
	η_∞	6.09E-11	2.68E-11	9.01E-12	2.76E-12	1.20E-11	9.08E-12
3	E_a	2.77E+03	2.79E+03	2.35E+03	3.87E+03	3.38E+03	4.29E+03
	η_∞	3.57E-08	2.60E-08	3.66E-07	1.39E-10	1.90E-10	3.73E-13
4	E_a	4.64E+03	4.43E+03	4.12E+03	4.11E+03	3.79E+03	3.43E+03
	η_∞	1.48E-12	2.53E-16	2.98E-11	3.14E-11	1.69E-10	1.19E-09
5	E_a	3.79E+03	3.75E+03	3.06E+03	3.10E+03	2.77E+03	2.31E+03
	η_∞	1.60E-10	2.05E-10	1.17E-08	8.34E-09	5.08E-08	6.00E-07
6	E_a	4.28E+03	4.43E+03	4.13E+03	4.39E+03	4.11E+03	3.82E+03
	η_∞	3.63E-12	1.34E-12	8.74E-12	1.52E-12	7.68E-12	3.95E-11
7	E_a	4.61E+03	4.65E+03	4.52E+03	4.38E+03	4.33E+03	4.26E+03
	η_∞	5.29E-13	4.04E-13	8.79E-13	1.92E-12	2.44E-12	3.36E-12
8	E_a	3.23E+03	3.28E+03	3.31E+03	3.41E+03	3.30E+03	2.68E+03
	η_∞	3.40E-09	2.20E-09	1.62E-09	7.37E-10	1.24E-09	4.32E-08
9	E_a	4.17E+03	4.13E+03	3.91E+03	3.93E+03	3.66E+03	3.04E+03
	η_∞	7.48E-12	8.88E-12	3.12E-11	2.65E-11	1.24E-10	4.25E-09
10	E_a	4.55E+03	4.47E+03	4.47E+03	4.04E+03	3.74E+03	3.08E+03
	η_∞	1.30E-12	2.13E-12	1.96E-12	6.53E-12	1.34E-10	6.07E-09
11	E_a	4.09E+03	4.29E+03	4.17E+03	4.07E+03	3.91E+03	3.82E+03
	η_∞	4.13E-12	9.96E-13	1.96E-12	3.38E-12	8.44E-12	1.41E-11
12	E_a	3.80E+03	3.64E+03	3.75E+03	3.69E+03	3.56E+03	3.51E+03
	η_∞	4.97E-11	1.17E-10	4.71E-11	6.12E-11	1.16E-10	1.38E-10
13	E_a	4.53E+03	4.33E+03	4.14E+03	3.98E+03	3.84E+03	3.64E+03
	η_∞	5.56E-13	1.72E-12	4.76E-12	1.07E-11	2.38E-11	7.33E-11
14	E_a	4.00E+03	4.02E+03	3.99E+03	3.71E+03	3.61E+03	3.45E+03
	η_∞	9.73E-12	7.74E-12	7.79E-12	3.80E-11	6.34E-11	1.58E-10
15	E_a	4.15E+03	3.98E+03	3.69E+03	3.65E+03	3.54E+03	3.38E+03
	η_∞	1.59E-12	4.49E-12	2.67E-11	3.33E-11	6.08E-11	1.61E-10
16	E_a	4.03E+03	3.97E+03	3.69E+03	3.41E+03	3.11E+03	3.27E+03
	η_∞	5.64E-11	7.80E-11	3.95E-10	1.80E-09	9.23E-09	3.16E-09
17	E_a	4.44E+03	3.88E+03	3.85E+03	3.76E+03	3.62E+03	3.40E+03
	η_∞	1.38E-12	3.98E-11	4.15E-11	6.77E-11	1.36E-10	4.59E-10
18	E_a	4.06E+03	4.03E+03	3.76E+03	3.54E+03	3.65E+03	3.46E+03
	η_∞	4.53E-11	5.21E-11	2.26E-10	7.80E-10	3.79E-10	1.04E-09
19	E_a	4.46E+03	4.38E+03	4.53E+03	4.42E+03	4.12E+03	3.91E+03
	η_∞	8.40E-12	1.31E-11	5.09E-12	9.28E-12	4.71E-11	1.49E-10
20	E_a	4.51E+03	4.41E+03	4.33E+03	4.33E+03	3.93E+03	3.87E+03
	η_∞	1.90E-12	3.43E-12	4.81E-12	4.59E-12	4.61E-11	6.23E-11
21	E_a	4.23E+03	4.23E+03	4.11E+03	3.80E+03	3.58E+03	3.55E+03
	η_∞	3.53E-12	3.40E-12	6.78E-12	4.71E-11	1.57E-10	1.86E-10

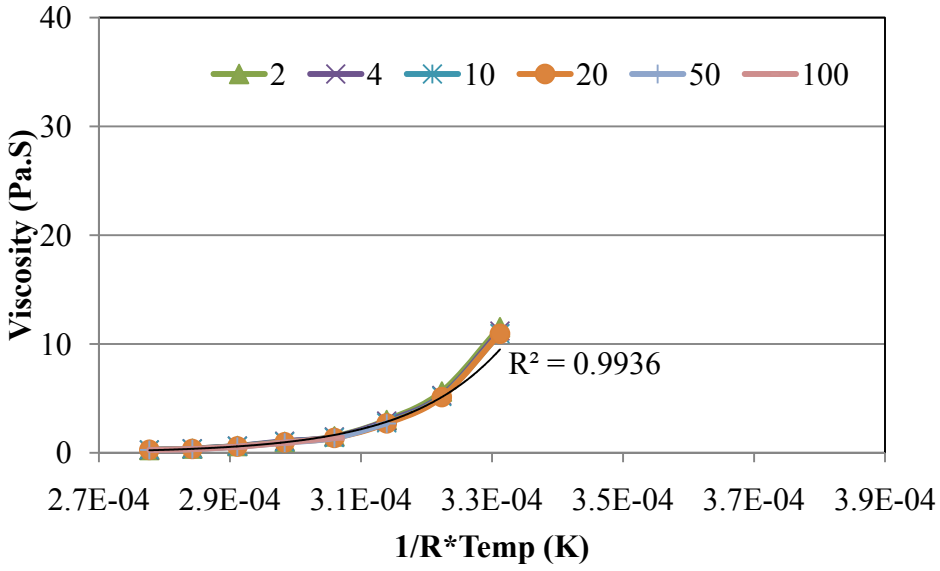


Figure 7.37. Arrhenius –type Model for AAM Blend

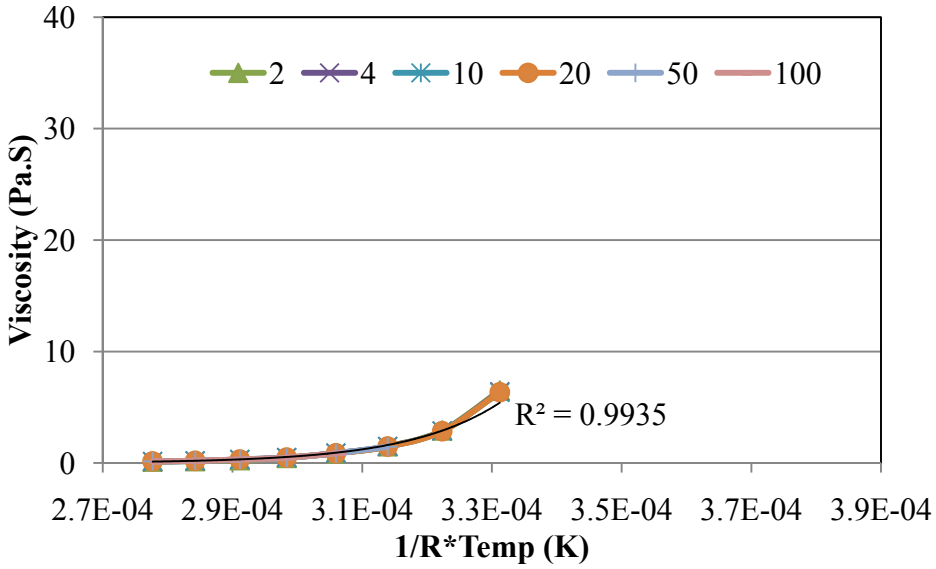


Figure 7.38. Arrhenius –type Model for AAD Blend

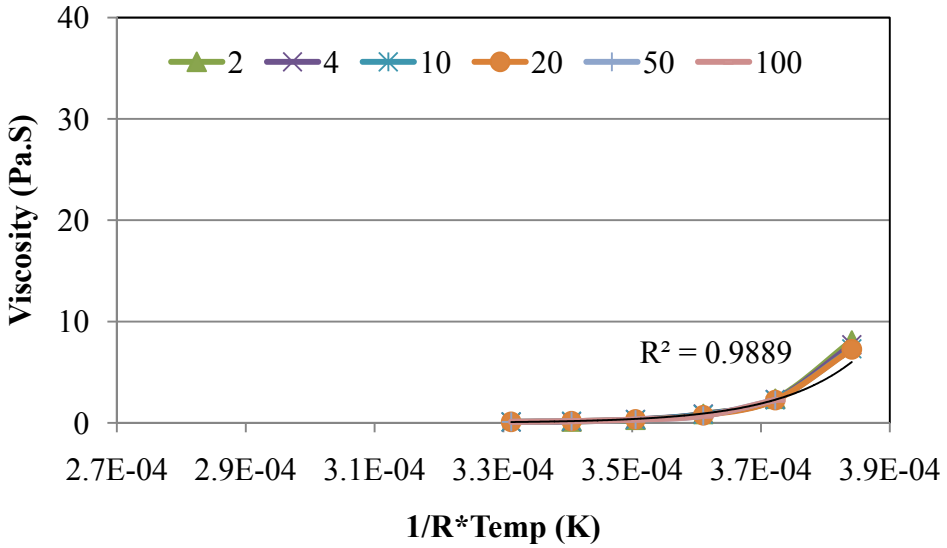


Figure 7.39. Arrhenius –type Model for Blend 1

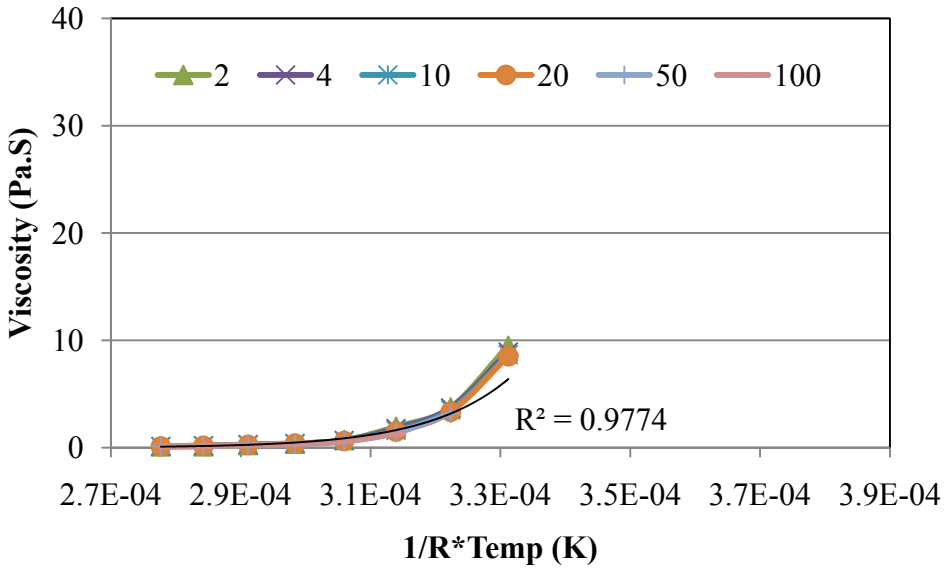


Figure 7.40. Arrhenius –type Model for Blend 4

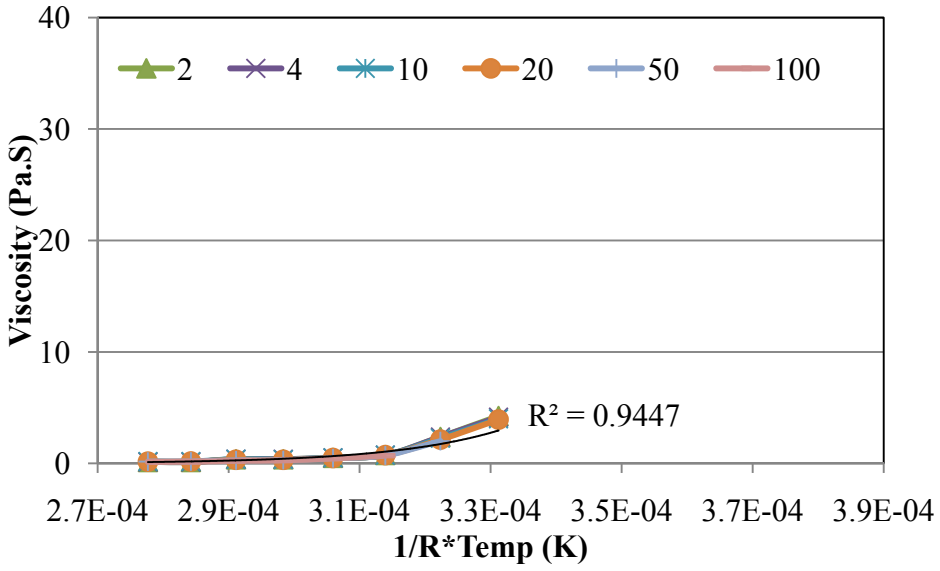


Figure 7.41. Arrhenius –type Model for Blend 5

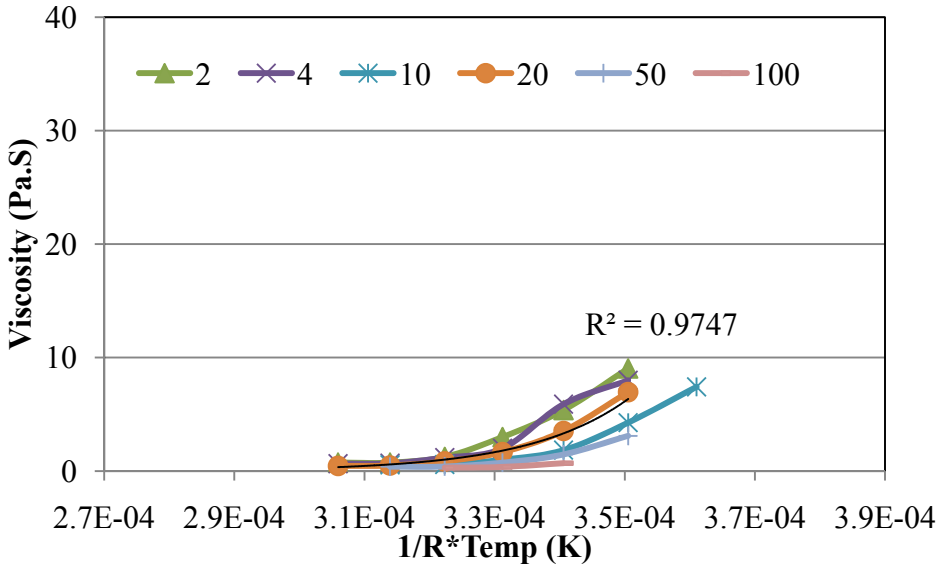


Figure 7.42. Arrhenius –type Model for Blend 8

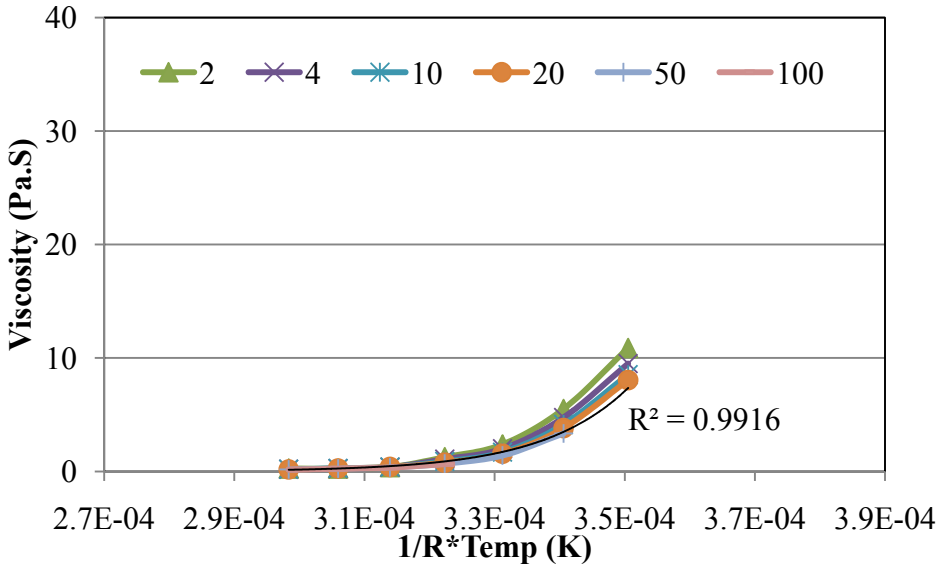


Figure 7.43. Arrhenius –type Model for Blend 9

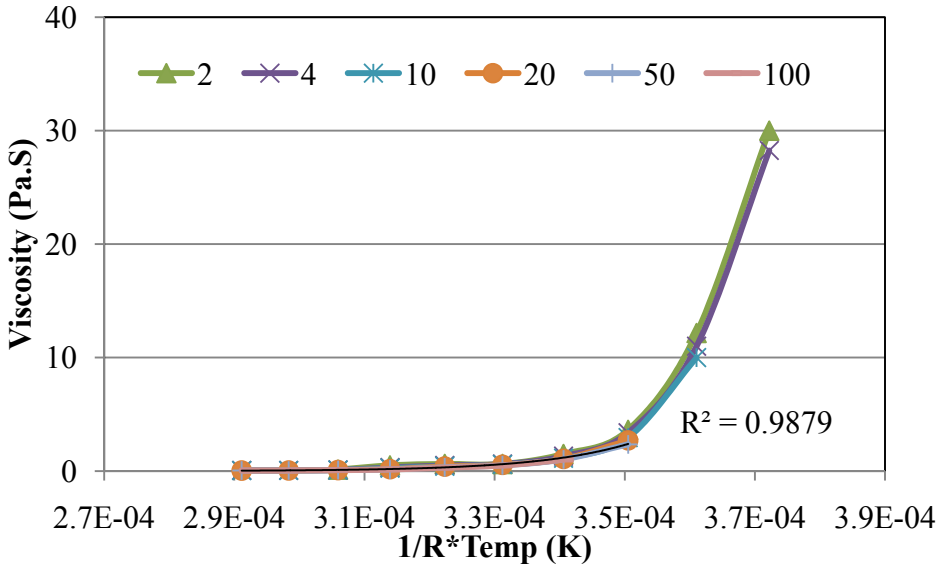


Figure 7.44. Arrhenius –type Model for Blend 14

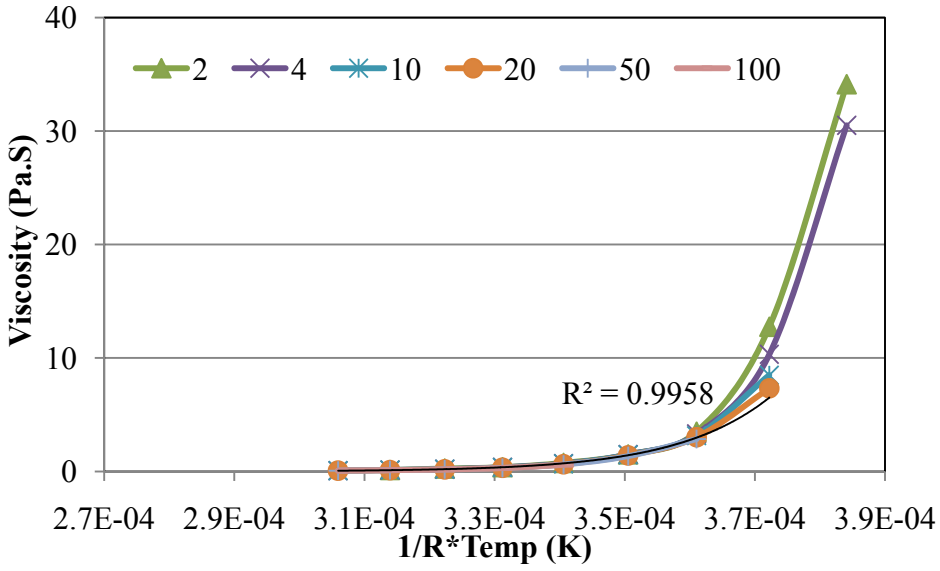


Figure 7.45. Arrhenius –type Model for Blend 15

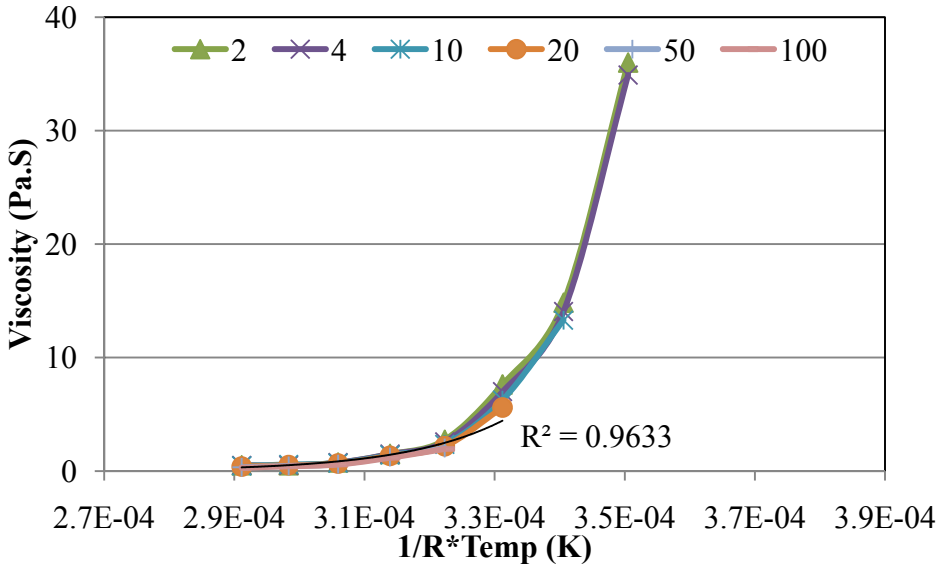


Figure 7.46. Arrhenius –type Model for Blend 16

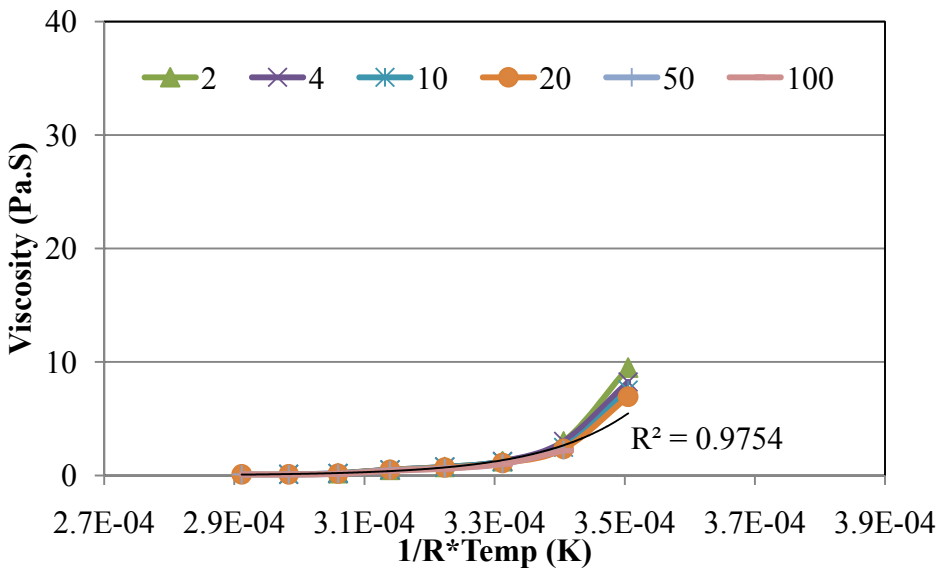


Figure 7.47. Arrhenius –type Model for Blend 21

Statistical Analysis

A statistical analysis was conducted, using the computer software JMP 7.0, to study the statistical difference between E_a and η_∞ values of bio-binders and bitumens. A one-way analysis of variance "ANOVA" using the method of least squares was performed for examination to evaluate the binder types (bitumen and bio-oil/bio-binder), polymer modifier types (P1, P2, and P3), and blending percentages (2% and 4%). Type I error (α) of 0.05 was used for all statistical analysis as the confidence level was 95%. Three different statistical tests were conducted for each bio-binder type separately. These tests can be summarized and listed as follows: (1) test 1 was concerned about studying the statistical difference between the E_a and η_∞ values of modified and unmodified bio-binders in order to emphasize the importance of the addition of polymer modifiers, (2) test 2 was to study the difference between the E_a and η_∞ values of unmodified bio-binder and bitumen, e.g. AAM and AAD, and (3) test 3 was designed to compare between the E_a and η_∞ values of modified bio-binders and bitumen binders. The p-values of the AVOVA for different tests were summarized and listed in Table 7.19, Table 7.205, and Table 7.216 for the oakwood, switchgrass, and cornstover bio-binders, respectively.

Table 7.24. Statistical Analysis for E_a and η_∞ Values for Oakwood Bio-binders

Test #	Blends	Shear Rate (rpm)	Experimental Variable	E_a		η_∞	
				F-Ratio	Prob >F	F-Ratio	Prob >F
1	1,2,3,4,5,6&7	2	Polymer type	3.2397	0.1801	0.7165	0.6047
			Blending ratio	1.1917	0.3927	0.5776	0.6021
		4	Polymer type	2.6505	0.2223	0.7127	0.6063
			Blending ratio	0.6577	0.5663	0.5841	0.5990
		10	Polymer type	0.9546	0.5148	0.6961	0.6135
			Blending ratio	0.9246	0.4677	0.6279	0.5792
		20	Polymer type	1.2614	0.4266	0.7151	0.6053
			Blending ratio	0.6900	0.5528	0.5971	0.5930
		50	Polymer type	1.4955	0.3744	0.7214	0.6026
			Blending ratio	0.4645	0.6585	0.5747	0.6034
		100	Polymer type	2.3327	0.2524	0.7199	0.6032
			Blending ratio	0.0381	0.9630	0.5696	0.6058
2	AAM,AAD,1	2	Binder Type	108.0000	0.0611	0.9171	0.5138
		4		192.0000	***0.0459****	1.5839	0.4274
		10		363.0000	***0.0334****	2.0787	0.3861
		20		4880.333	***0.0091****	3.3758	0.3173
		50		65.3333	0.0784	331.0220	***0.0350****
		100		12.0000	0.1789	48.3470	0.0909
3	AAM,AAD, 2,3,4,5,6&7	2	Binder Type	0.0014	0.9711	0.2892	0.6101
		4		0.0460	0.8373	0.2767	0.6177
		10		0.0073	0.9349	0.3154	0.5947
		20		0.9221	0.3740	0.0819	0.7843
		50		0.6291	0.4579	0.1286	0.7322
		100		0.5342	0.4924	0.2692	0.6224

Based on the p-values listed in Table 7.24, the following observations could be noted. First, it can be observed that neither polymer type nor the blending ratios affected the E_a and η_∞ values of the oakwood bio-binders. Since the activation energy represented the temperature susceptibility of the binder, this conclusion indicated that the temperature susceptibility of the oakwood bio-binders was not affected by the polymer type and the blending percentage. Second, for test 2, there was statistical significant difference between the E_a values of the bitumen and the unmodified oakwood bio-binder at intermediate shear rate (4, 10 and 20 rpm); however, the η_∞ values were not affected. Third, there was no statistical difference between the E_a and η_∞ values of the bitumen and the modified oakwood bio-binders. Therefore, it is worth noting that the temperature susceptibility of the unmodified oakwood bio-binders was higher than the temperature susceptibility of the bitumens, but there was no significant difference between temperature susceptibility of the modified oakwood bio-binders and the bitumens.

Table 7.25. Statistical Analysis for E_a and η_∞ Values for Switchgrass Bio-binders

Test #	Blends	Shear Rate (rpm)	Experimental Variable	E_a		η_∞	
				F-Ratio	Prob >F	F-Ratio	Prob >F
1	8,9,10,11, 12,13&14	2	Polymer type	3.8439	0.1490	8948.277	***<.0001****
			Blending ratio	3.9958	0.1113	14456.85	***<.0001****
		4	Polymer type	2.3918	0.2463	600.6270	***0.0001****
			Blending ratio	3.8506	0.1169	964.6715	***<.0001****
		10	Polymer type	2.1475	0.2732	1520.564	***<.0001****
			Blending ratio	3.2158	0.1470	2555.694	***<.0001****
		20	Polymer type	2.0039	0.2913	194.1162	***0.0006****
			Blending ratio	5.8903	0.0643	488.4798	***<.0001****
		50	Polymer type	1.6777	0.3406	175.9985	***0.0007****
			Blending ratio	7.6332	***0.0431****	219.6972	***<.0001****
		100	Polymer type	13.2144	***0.0310****	902.2374	***<.0001****
			Blending ratio	2.3023	0.2161	83.6299	***0.0005****
2	AAM,AAD,8	2	Binder Type	46.6759	0.0925	413.8975	***0.0313****
		4		124.5926	0.0569	130.9441	0.0555
		10		85.3333	0.0686	2.3469	0.3682
		20		736.3333	***0.0235****	0.0120	0.9305
		50		1.0208	0.4967	113.7590	0.0595
		100		124.5926	0.0569	2286.615	***0.0133****
3	AAM,AAD, 9,10,11,12, 13&14	2	Binder Type	1.2472	0.3068	9.5088	***0.0216****
		4		1.7060	0.2393	11.1600	***0.0156****
		10		5.6618	0.0548	26.7126	***0.0021****
		20		4.4169	0.0803	41.3726	***0.0007****
		50		11.5566	***0.0145****	2338.958	***<.0001****
		100		0.5011	0.5056	3.4537	0.1125

From Table 7.25, the following conclusions could be established. First, like the oakwood bio-binders, it was observed that neither polymer type nor the blending ratios affected the E_a of the switchgrass bio-binders. On the other hand, unlike the oakwood bio-binders, it was observed that the polymer type and blending ratio were significant factors in changing the η_∞ values between the unmodified and modified switchgrass bio-binders. Importantly, it is worth noting that the temperature susceptibility of the switchgrass bio-binders was not affected by the polymer type and the blending percentage like the oakwood bio-binders. Second, for test 2, there was no statistical significant difference -in general- between the E_a values of the bitumens and the unmodified oakwood bio-binder (except at 20 rpm). In addition, the η_∞ values were affected by the binder type at low and high shear rates only. Third, there was no statistical difference between the E_a values of the bitumens and the modified switchgrass bio-binders. This conclusion is in agreement with the conclusion established for the oakwood bio-binders. However, there was statistical significance difference between the η_∞ values between modified switchgrass bio-binders and bitumen. Therefore, it is safe to state that the temperature susceptibility of the unmodified and modified switchgrass bio-binders were not statistically different than the temperature susceptibility of the bitumens.

Table 7.26. Statistical Analysis for E_a and η_∞ Values for Cornstover Bio-binders

Test #	Blends	Shear Rate (rpm)	Experimental Variable	E_a		η_∞	
				F-Ratio	Prob >F	F-Ratio	Prob >F
1	15,16,17, 18,19,20&21	2	Polymer type	0.1822	0.9022	0.5111	0.7023
			Blending ratio	0.7141	0.5430	1.9387	0.2578
		4	Polymer type	2.3297	0.2527	2.4918	0.2365
			Blending ratio	0.2105	0.8186	0.9089	0.4727
		10	Polymer type	1.0212	0.4933	0.5935	0.6606
			Blending ratio	0.7969	0.5113	1.5765	0.3127
		20	Polymer type	0.5204	0.6974	0.5472	0.6836
			Blending ratio	0.3266	0.7389	1.4277	0.3405
		50	Polymer type	1.0176	0.4945	0.7131	0.6061
			Blending ratio	0.3037	0.7537	0.6143	0.5853
		100	Polymer type	1.2989	0.4175	0.8449	0.5535
			Blending ratio	0.2730	0.7742	0.9475	0.4604
2	AAM,AAD,15	2	Binder Type	4.0833	0.2926	0.8981	0.5171
		4		5.3333	0.2601	1.5196	0.4339
		10		3.0000	0.3333	1.9404	0.3964
		20		0.3333	0.6667	3.0616	0.3305
		50		6.0208	0.2464	317.9882	***0.0357****
		100		5.3333	0.2601	46.1544	0.0930
3	AAM,AAD, 16,17,18,19, 20&21	2	Binder Type	4.7257	0.0727	7.9931	***0.0301****
		4		3.0471	0.1315	12.7211	***0.0118****
		10		2.7349	0.1493	12.3324	***0.0126****
		20		0.5673	0.4798	0.1965	0.6731
		50		1.3398	0.2911	0.2313	0.6476
		100		2.6659	0.1536	26.2257	***0.0022****

From the p-values listed in Table 7.26, the following remarks could be made. First, like the oakwood bio-binders, it was observed that neither polymer type nor the blending ratios affected the E_a and η_∞ values of the cornstover bio-binders. Importantly, it is worth noting that the temperature susceptibility of the switchgrass bio-binders was not affected by the polymer type and the blending percentage like the oakwood and switchgrass bio-binders. Second, there was no statistical significant difference between the E_a values of the bitumens and the unmodified oakwood bio-binder. In addition, like the unmodified oakwood and switchgrass bio-binders, the η_∞ values were not affected -in general- by the binder type (except at 50 rpm). Third, like the modified switchgrass bio-binders, there was no statistical difference between the E_a values of the bitumens and the modified switchgrass bio-binders. This conclusion was in agreement with the previous conclusion mentioned for the oakwood and switchgrass bio-binders. However, there was statistical significance difference between the η_∞ values between the modified switchgrass bio-binders and the bitumens. Therefore, it is worth noting that the temperature susceptibility of the unmodified and modified cornstover bio-binders was not statistically different than the temperature susceptibility of bitumen.

Considerably, the relationship between viscosity and shear rate at different temperatures for the bio-binders and the bitumens were following an Arrhenius-type relationship. The coefficients of correlation for this Arrhenius-type model were determined for all blends at the same shear rate (20 rpm) and listed in Table 7.27. The R^2 values for this relationship for all bio-binders were very high (exceeding 90%) and comparable to the bitumens. This indicated that the correlation coefficients for the bio-oil blends were close to the correlation coefficients of the bitumens. Therefore, it could be concluded that the relationship between viscosity and shear rate was well described by the Arrhenius-type model.

Table 7.27. Coefficient of Correlation for Arrhenius-type Model

Blend #	R^2 value	Blend #	R^2 value	Blend #	R^2 value
AAM	0.9935	**AAD**	0.9935		
1	0.9889	**8**	0.9747	**15**	0.9958
2	0.9991	**9**	0.9916	**16**	0.9633
3	0.9816	**10**	0.9742	**17**	0.9918
4	0.9774	**11**	0.9788	**18**	0.9887
5	0.9447	**12**	0.9732	**19**	0.9973
6	0.9845	**13**	0.9895	**20**	0.9869
7	0.9784	**14**	0.9879	**21**	0.9754

*correlation coefficient was measured at the shear rate of 20 rpm

General Conclusions

Having a global prospective at the overall results herein, it can be concluded that the temperature susceptibility of the unmodified oakwood bio-binders was higher than the temperature susceptibility of the bitumens, but there was no significant difference between temperature susceptibility of modified oakwood bio-binders and bitumen. However, for the switchgrass and cornstover bio-binders, the temperature susceptibility of the unmodified and modified switchgrass and cornstover bio-binders was not statistically different than the temperature susceptibility of bitumen. In addition, it was observed that neither polymer type nor the blending ratios affected the E_a values of the oakwood, switchgrass and cornstover bio-binders. Overall, for all types of bio-binders, the lowest η_∞ took place at the highest speed, and vice versa. Significantly, the relationship between viscosity and shear rate was well described by the arrhenius-type model.

CHAPTER 8. PERFORMANCE TESTING

Introduction

In this chapter, the performance testing for the tested bio-binders are listed and summarized according to the experimental plans. This chapter was subdivided into three main sections which can be summarized as follows. First, the mixing and compaction temperatures for all blends were determined according to Superpave specifications and requirements which were aforementioned in Chapter 3. Second, based on the rheological testing previously analyzed, it is worth noting that the temperature ranges for bio-binders were different from each other and from the bitumens tested; therefore, the temperature range for all blends were determined and summarized hereafter. Third, the high, intermediate and low temperature performance grades testing for all blends were measured according to Superpave specifications and standards.

Mixing and Compaction Temperatures

The viscosity measurements at shear rate of 20 rpm for oakwood, switchgrass, and cornstover bio-binders were listed and summarized in Table 8.1 to Table 8.3, respectively. Figure 8.1 to Figure 8.3 display the viscosity versus temperature for all the tested bio-binders.

Table 8.1. Viscosity Measurements at 20 rpm for Oakwood Bio-binders

Temperature	Viscosity (Pa·s)/Blend #						
(°C)	1	2	3	4	5	6	7
40	7.25	-	-	-	-	-	-
50	2.25	9.58	7.69	-	-	-	-
60	0.75	3.90	3.13	-	-	-	-
70	0.33	1.98	1.58	-	-	12.02	15.02
80	0.17	0.94	1.13	-	12.10	4.37	4.53
90	0.10	0.49	0.43	8.52	3.93	1.56	1.80
100	-	0.20	0.13	3.35	2.14	0.73	1.10
110	-	0.14	0.08	1.50	0.75	0.45	0.80
120	-	0.10	0.05	0.63	0.49	0.16	0.24
130	-	-	-	0.38	0.33	0.13	0.11
140	-	-	-	0.26	0.33	0.09	0.08
150	-	-	-	0.18	0.18	-	-
160	-	-	-	0.13	0.16	-	-

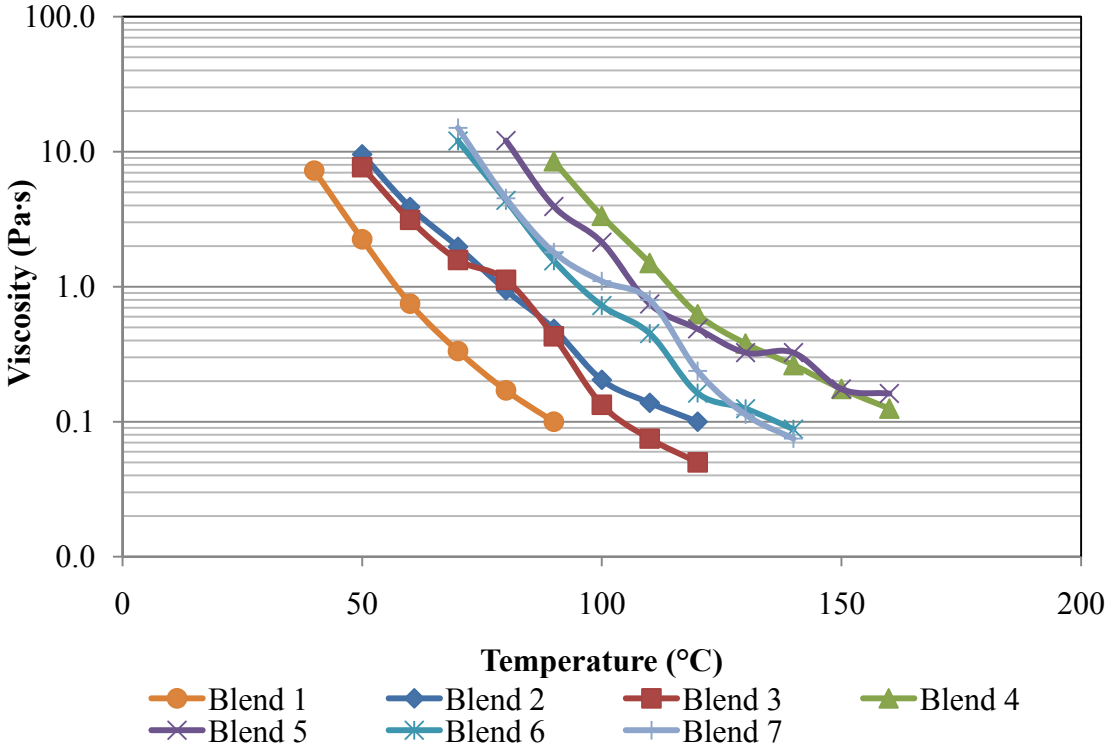


Figure 8.1. Viscosity versus Temperature for Oakwood Bio-binders

Table 8.2. Viscosity Measurements at 20 rpm for Switchgrass Bio-binders

Temperature	Viscosity (Pa·s)/Blend #						
(°C)	8	9	10	11	12	13	14
60	-	-	-	5.74	8.00	-	9.50
70	6.95	8.05	-	2.25	3.15	4.55	2.70
80	3.53	3.83	10.30	1.10	1.58	1.80	1.08
90	1.67	1.57	3.58	0.75	0.93	1.08	0.55
100	0.85	0.78	1.18	0.26	0.75	0.63	0.40
110	0.49	0.40	0.83	0.13	0.18	0.20	0.16
120	0.70	0.26	0.53	0.07	0.11	0.13	0.09
130	-	0.18	0.29	0.05	0.08	0.09	0.05
140	-	-	0.18	-	-	0.05	-

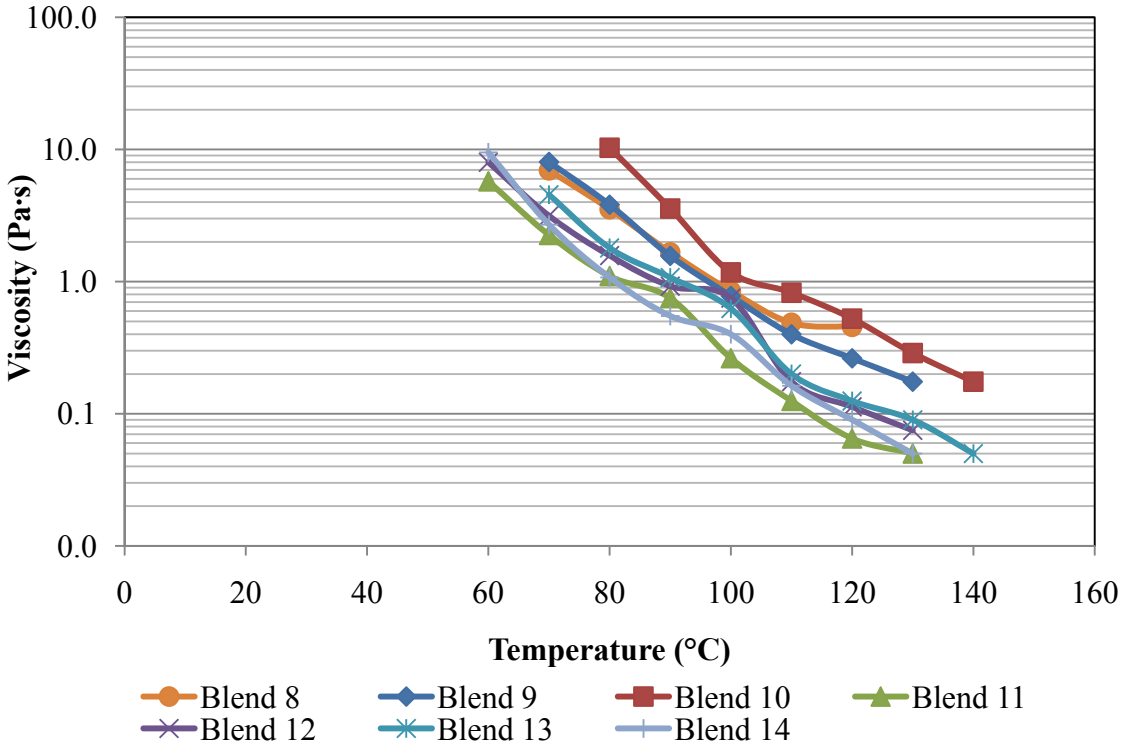


Figure 8.2. Viscosity versus Temperature for Switchgrass Bio-binders

Table 8.3. Viscosity Measurements at 20 rpm for Cornstover Bio-binders

Temperature (°C)	Viscosity (Pa·s)/Blend #						
	15	**16**	**17**	**18**	**19**	**20**	**21**
50	7.33	-	-	-	-	-	-
60	3.02	-	-	-	-	-	-
70	1.41	-	6.80	-	-	-	6.94
80	0.64	-	2.85	-	-	11.28	2.34
90	0.33	5.60	1.70	4.90	-	3.40	1.10
100	0.19	2.19	0.65	2.30	6.67	1.64	0.70
110	0.11	1.34	0.40	1.10	3.10	0.90	0.50
120	0.08	0.66	0.21	0.80	1.48	0.44	0.16
130	-	0.53	0.15	0.49	0.80	0.25	0.10
140	-	0.40	0.10	0.30	0.50	0.18	0.10

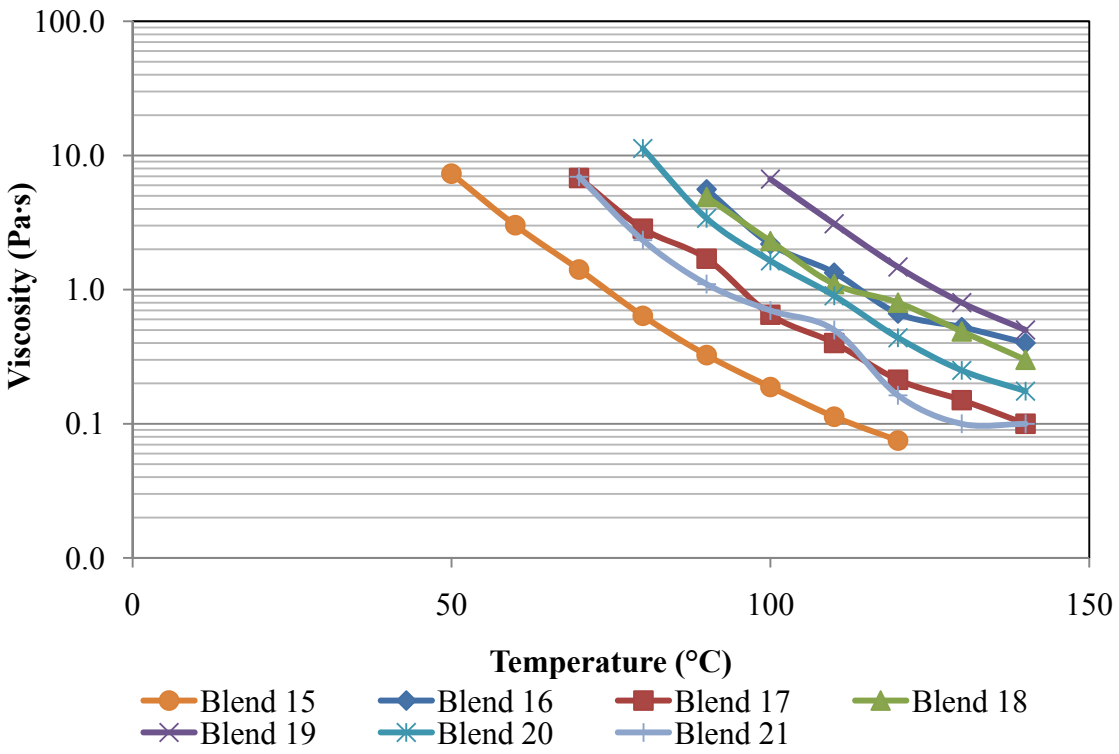


Figure 8.3. Viscosity versus Temperature for Cornstover Bio-binders

Based on the above results, the mixing and compaction temperatures could be determined and listed hereafter in Table 8.4. According to the Superpave specifications and requirements discussed in Chapter 3, determining the temperature range that corresponded to viscosity values of 0.17±0.02 Pa·s and 0.28±0.03 were the range of mixing and compaction temperatures, respectively.

Table 8.4. Mixing and Compaction Temperatures for All Bio-binders

Blend #	Mixing Range (°C)		Compaction Range (°C)	
1	78.8	81.6	73.1	75.6
2	105.1	108.7	97.8	101.0
3	99.7	102.9	93.1	96.0
4	145.8	149.8	137.7	141.3
5	147.2	151.7	137.8	141.9
6	122.7	126.0	115.8	118.8
7	124.5	127.7	117.9	120.8
8	129.2	133.3	120.8	124.5
9	124.8	128.4	117.2	120.5
10	134.6	138.3	127.1	130.4
11	106.1	109.5	99.1	102.2
12	113.6	117.1	106.3	109.5
13	117.3	121.0	109.6	113.0
14	109.0	112.3	102.1	105.1
15	101.2	104.8	93.8	97.0
16	149.5	154.0	140.0	144.2
17	124.3	128.2	116.3	119.8
18	147.1	151.5	138.1	142.1
19	153.9	157.5	146.4	149.7
20	134.6	138.1	127.4	130.5
21	123.4	127.2	115.3	118.9

Based on Table 8.4, the following conclusions could be established. First, for the oakwood bio-binders, it was observed that the mixing and compaction temperatures were lower than the bitumen ones. Precisely, the mixing and compaction temperatures for the unmodified oakwood bio-binder ranged between 78.8 and 81.6°C, and 73.1 and 75.6°C, respectively, which were lower than the typical mixing and compaction temperatures for bitumen, 135 and 165°C, respectively. Second, the addition of polymer modifiers led to a change in the mixing and compaction temperatures. For the oakwood bio-binders, it was observed that the mixing and compaction temperatures were increased, but the amount of increase varied according to the type of polymer modifier and the blending ratio. Third, the optimum amount of polymer modifier could not be determined because no clear trend could be observed after the addition of different types of polymer modifiers with different percentages. Fourth, for the switchgrass bio-binders, it was noted that the mixing and compaction temperatures were higher than the ones observed for oakwood bio-binders, but still lower than the typical bitumen ones. Fifth, like the oakwood bio-binders, the addition of polymer modifiers led to change the mixing and compaction temperatures. However, unlike oakwood bio-binders, the addition of polymer modifiers had various effects on the temperature and compaction temperatures. For example, polymers 2 and 3 led to a decrease in the mixing and compaction temperatures in comparison to the unmodified switchgrass bio-binders. In addition, the amount of the polymer modifier led to a change in the mixing and compaction temperatures without a clear trend that could be noted. For instance, the addition of 2% of polymer 1 led to a decrease in the mixing and compaction temperatures (blend 9) while the addition of 4% of polymer 1 led to an increase in the mixing and compaction temperatures (blend 10). Sixth, for the cornstover bio-binders, it was observed that the mixing

and compaction temperatures were in-between the mixing and compaction temperatures determined for the unmodified oakwood and switchgrass bio-binders. Specifically, for the unmodified cornstover bio-binder (blend 15), the temperature ranges for mixing and compaction were 101.2-104.8°C and 93.8-97°C, respectively. Seventh, like the oakwood bio-binders, the addition of polymer modifiers led to an increase in the temperature ranges for mixing and compaction. However, the optimum polymer modifier could not be determined due to the variability of the effect of polymer modifiers with different percentages on the bio-binders. In summary, it is safe to conclude that the mixing and compaction temperatures for the different types of bio-binders tested in this research were below the typical mixing and compaction temperatures of bitumen. Significantly, the addition of polymer modifier led to change the mixing and compaction temperatures' ranges, but the effect varied with respect to the type of the bio-binder and the amount of the polymer modifier added.

Temperature Range

From the rheological testing performed and discussed in Chapter 7, it was observed that the temperature range for the bio-binders were different from the bitumen binders. The low temperature represented the lowest temperature at which the viscosity measurements were measured because the bio-binders were solid below this temperature. On the other hand, the high temperature represented the highest temperature at which the viscosity measurements could not be measured because the viscosity of the bio-binder was very low. The temperature ranges for all bio-binders tested in this research are listed in Table 8.5.

From Table 8.5, the following observations could be made. First, the temperature ranges for the unmodified bio-binders were different than the bitumen binders. For example, the temperature ranges for the oakwood, switchgrass and cornstover bio-binders were 40-90°C, 70-120°C, and 40-120°C, respectively. Second, no clear trend could be observed for the effect of the polymer modifier and the blending ratio on changing the temperature ranges. However, the effect of polymer modifier on the temperature ranges varied according to the type of the bio-binder. For instance, the addition of the polymer modifiers on the cornstover led to an increase in the high temperature range by 20°C, but the same trend could not be observed for the other types of bio-binders. Overall, it may be concluded that due to the difference in the chemical composition and structure between the bio-binders and the bitumen, their temperature ranges were different.

Table 8.5. Temperature Range for the Tested Bio-binders

Blend #	Temperature Range
AAM	90 - 160
AAD	90 - 160
Blend 1	40 - 90
Blend 2	40 - 120
Blend 3	40 - 120
Blend 4	90 - 160
Blend 5	90 - 160
Blend 6	70 - 140
Blend 7	70 - 140
Blend 8	70 - 120
Blend 9	70 - 130
Blend 10	70 - 130
Blend 11	50 - 140
Blend 12	50 - 140
Blend 13	50 - 140
Blend 14	50 - 140
Blend 15	40 - 120
Blend 16	70 - 140
Blend 17	70 - 140
Blend 18	70 - 140
Blend 19	70 - 140
Blend 20	70 - 140
Blend 21	70 - 140

Performance Grade Testing

In this section, the high, intermediate, and low temperature performance grades of the treated bio-binders blends were determined. All bio-binders (unmodified and modified) were performance graded according to ASTM D6373 (1999) and AASHTO M 320 (2002), previously discussed in Chapter 3. According to the Superpave specifications, the high temperature performance grades were determined based on the unaged and RTFO aged samples. The G*/sin(delta) for both the unaged and the RTFO aged samples were determined and the lower value were considered as the high temperature performance grade. The intermediate and low temperature performance grades were determined based on PAV aged samples. Each bio-binder blend was also tested in duplicate for proper estimation of the performance grade.

Unaged Bio-binders

Initially, all samples were tested unaged in a dynamic shear rheometer. The G*/sin(delta) values were recorded for all bio-binders at different temperatures, starting at 40°C until the failure temperature was achieved (see Table B5.1 in Appendix B). The high temperature performance grades for all blends, based on unaged samples, were determined and listed in Table 8.6. Based on these results, the following conclusions could be made. First, the high temperature

performance grades for the unmodified bio-binders (blends 1 and 15) could not be determined as their performance grades were below 40°C. Second, the high performance grades for the modified bio-binders were higher than the performance grade of the unmodified bio-binders. Third, for the unmodified bio-binders, it was observed that the unaged high temperature performance grade for switchgrass was higher than oakwood and cornstover bio-binders. Fourth, it may be concluded that the increase in percentage of the polymer modifier did not guarantee an increase in the high temperature performance grade. For example, for oakwood and cornstover bio-binders, the high temperature performance grade decreased from 65°C to 57°C (blends 4 and 5) and from 59°C to 46°C (blends 16 and 17) although the amount of the polymer modifier was increased from 2% to 4%. Fifth, the effect of the polymer modifiers was not the same on the different types of bio-binders. For example, polymer modifier 1 increased the performance grade when it was added to cornstover bio-binders (blends 16 and 17), but did not show improvement in performance grade when it was added to oakwood bio-binders (blends 2 and 3) and switchgrass (blends 9 and 10). Sixth, all bio-binder (unmodified and modified blends) yielded, in general, lower high temperature performance grade compared to bitumen binders, which had a performance grade of 64°C. Overall, it is safe to report that the high temperature performance grade for the bio-binders were lower than bitumen. Importantly, it is worth noting that the high temperature performance grade could not be determined using the unaged samples, so it is more feasible and reliable to determine the high temperature performance grade of the bio-binders through the G*/sin(delta) of the RTFO aged samples.

Table 8.6. High Temperature Performance Grade for Unaged Bio-binders

Blend #	Sample I.D.	Performance Grade (°C)
1	**OFP0B0**	- (<40)
2	**OFP1B2**	- (<40)
3	**OFP1B4**	- (<40)
4	**OFP2B2**	65
5	**OFP2B4**	57
6	**OFP3B2**	47
7	**OFP3B4**	49
8	**SGP0B0**	46
9	**SGP1B2**	47
10	**SGP1B4**	55
11	**SGP2B2**	- (<40)
12	**SGP2B4**	41
13	**SGP3B2**	42
14	**SGP3B4**	41
15	**CSP0B0**	- (<40)
16	**CSP1B2**	59
17	**CSP1B4**	46
18	**CSP2B2**	55
19	**CSP2B4**	57
20	**CSP3B2**	56
21	**CSP3B4**	44

RTFO Aged Bio-binders

After the bio-binders were individually short-term aged in the RTFO, they were again tested with the dynamic shear rheometer. For bituminous binders, Superpave specifications require that the mass loss after RTFO aging to be less than one percent (The Asphalt Institute 2003). Since bio-binders -in general- have more volatile materials than bituminous binders, the Superpave specification limit for the mass loss was not attained. The mass losses due to RTFO aging for all bio-binders were calculated and summarized in Table 8.7.

Table 8.7. RTFO Mass Losses for All Bio-binders

Blend #	Sample I.D.	RTFO Mass Loss (%)
1	OFP0B0	9.5
2	OFP1B2	9.5
3	OFP1B4	11.6
4	OFP2B2	10.4
5	OFP2B4	5.6
6	OFP3B2	6.2
7	OFP3B4	4.6
8	SGP0B0	6.3
9	SGP1B2	5.7
10	SGP1B4	4.4
11	SGP2B2	6.2
12	SGP2B4	8.4
13	SGP3B2	9.0
14	SGP3B4	8.6
15	CSP0B0	13.9
16	CSP1B2	8.5
17	CSP1B4	7.7
18	CSP2B2	4.8
19	CSP2B4	3.8
20	CSP3B2	5.4
21	CSP3B4	7.1

From the mass losses results, the following observations could be made. First, the switchgrass bio-binders yielded the lowest mass losses in comparison to oakwood and cornstover bio-binders. Consequently, it may be concluded that switchgrass bio-binders had the lowest volatile materials. Second, no clear trend could be established after adding the polymer modifiers in the sense of enhancement or decreases in the mass losses due to RTFO aging. Although it was observed that the mass losses -in general- were decreased after the addition of polymer modifiers, there was no clear evidence that this was due to the effect of the polymer modifier and it may be due to the blending procedure (heating the bio-binder and polymer modifier in a shear mill for 30 minutes). Therefore, it is worth noting that the blending procedure may be the main reason that led to decreases in the mass losses of the modified bio-binders. Third, it is safe to conclude that the Superpave specification limit for mass losses due to RTFO aging would be higher than 1% for bituminous binders.

The high temperature performance grades for the RTFO aged bio-oil samples were determined after aging in the RTFO for 20 minutes (based on the modifications added to Superpave test criteria for short-term aging of bio-binders in RTFO which were previously discussed in Chapter 5). The RTFO aged samples were tested the same as the unaged samples. The bio-binders were tested at different temperatures, starting at 40°C until failure and each blend was tested in duplicate. However, since RTFO aged samples were aged by oxidation, the failure criterion was different as the stiffer the asphalt, the larger the G*/sin(delta) value. Following the Superpave specifications for bituminous binders, 2.2 kPa was used as the failure criterion (The Asphalt Institute 2003). The high temperature performance grades for 20min-RTFO samples are summarized and listed in Table 8.8.

Table 8.8. High Temperature Performance Grade for 20-min RTFO Aged Bio-binders

Blend #	Sample I.D.	Performance Grade (°C)
1	**OFP0B0**	50
2	**OFP1B2**	52
3	**OFP1B4**	55
4	**OFP2B2**	68
5	**OFP2B4**	76
6	**OFP3B2**	65
7	**OFP3B4**	65
8	**SGP0B0**	59
9	**SGP1B2**	59
10	**SGP1B4**	64
11	**SGP2B2**	53
12	**SGP2B4**	59
13	**SGP3B2**	59
14	**SGP3B4**	57
15	**CSP0B0**	60
16	**CSP1B2**	72
17	**CSP1B4**	71
18	**CSP2B2**	69
19	**CSP2B4**	73
20	**CSP3B2**	68
21	**CSP3B4**	57

Based on Table 8.8, the following observations are made. First, the high temperature performance grades for the unmodified switchgrass and cornstover bio-binders were higher than the unmodified oakwood bio-binder. Specifically, the unmodified oakwood bio-binder (blend 1) had a lower high temperature performance grade (50°C) in comparison to the unmodified switchgrass and cornstover bio-binders (blends 8 and 15) which had high temperature performance grades of 59 and 60°C, respectively. Second, the addition of polymer modifiers led to enhancement in the high temperature performance grade of bio-binders. However, the amount of increase in the high temperature performance grade varied depending on the type and the percentage of the polymer modifier. For the oakwood blends (blends 1 to 7), the performance grade ranged between 50°C (unmodified bio-binder blend 1) and 76°C (polymer modified bio-

binder blend 5). The highest performance grade was achieved after adding polymer 2 with 4% blending ratio. For the switchgrass blends (blends 8 to 14), the performance grade ranged between 53°C (blend 11) and 64°C (blend 10). The highest performance grade achieved after adding polymer 1 with 4% blending ratio while the lowest performance grade achieved after adding polymer 2 with 2% blending ratio. For the cornstover blends (blends 15 to 21), the performance grade ranged between 57°C (blend 21) and 73°C (blend 19). The highest performance grade achieved after adding polymer 2 with 4% blending ratio while the lowest performance grade, surprisingly, achieved after adding polymer 3 with 4% blending ratio. Since the interaction between the type of the bio-binder and the type of the polymer modifier played a significant role in enhancing the performance grade, it may be concluded that different polymer modifiers with different blending ratios should be thoroughly blended with bio-binders to enhance their performance grade. Third, it was observed that unmodified bio-binders had lower high temperature performance grades in comparison to the bituminous binders. In summary, the high temperature performance grade for unmodified bio-binders were lower than the bitumen performance grade; however, after the addition of different types of polymer modifier with different blending ratios, the high temperature performance grade of the modified bio-binders were increased significantly and exceeded the bitumen high performance grade.

PAV Aged Bio-binders

Using 20-min RTFO aged residues, long term aging through PAV was conducted. Then, the bio-binders were then tested with the DSR. Consequently, PAV aged samples were used to determine the intermediate and low critical temperatures that were summarized and listed hereafter.

Intermediate Temperature Performance Grade

The response produced by the DSR for PAV aged samples was G*sin(delta) rather than G*/sin(delta) according to Superpave specifications and standards. Using a failure criterion of 5000 kPa and semi-log regression equations, the intermediate critical temperatures were determined for all bio-binders (unmodified and modified blends) and listed in Table 8.9.

Table 8.9. Intermediate Temperature Performance Grade for PAV Aged Samples

Blend #	Sample I.D.	Performance Grade (°C)
1	**OFP0B0**	18
2	**OFP1B2**	20
3	**OFP1B4**	34
4	**OFP2B2**	26
5	**OFP2B4**	17
6	**OFP3B2**	34
7	**OFP3B4**	31
8	**SGP0B0**	25
9	**SGP1B2**	32
10	**SGP1B4**	29
11	**SGP2B2**	25
12	**SGP2B4**	29
13	**SGP3B2**	23
14	**SGP3B4**	17
15	**CSP0B0**	30
16	**CSP1B2**	29
17	**CSP1B4**	29
18	**CSP2B2**	38
19	**CSP2B4**	37
20	**CSP3B2**	18
21	**CSP3B4**	26

From the intermediate critical temperature results, the following observations could be made. First, the unmodified oakwood bio-binder (blend 1) yielded the lowest intermediate temperature (18°C) in comparison to the unmodified switchgrass and cornstover bio-binders (blends 8 and 15), which yielded 25 and 30°C, respectively. This meant that the switchgrass and the cornstover bio-binders were stiffer compared to the oakwood binders which may result in better resistance to fatigue cracking. Second, for all types of bio-binders, the addition of polymer modifiers to the bio-binders led to enhancement in intermediate critical temperatures as all polymer modified blends -in general- yielded higher intermediate temperatures compared to the unmodified blends. However, no clear trend could be established for the type of the polymer modifier and the blending ratio that should be used to achieve higher intermediate temperature. For example, for the oakwood bio-binders (blends 1 to 7), higher intermediate temperatures were yielded by using polymer 1 with blending ratio of 4% or polymer 3 with 2% blending ratio. On the other hand, for switchgrass bio-binders (blends 8 to 14), higher intermediate temperature were yielded when using polymer 1 with blending ratio of 2%. In addition, for the cornstover bio-binders, the highest temperature performance grade were yielded using polymer 2 with blending ratios of 2 or 4%. Therefore, it is safe to conclude that the effect of the polymer modifiers on the intermediate temperature performance grade differ according to the type of the bio-binder. Third, in comparison with bitumen binders which had -in general- an intermediate temperature of 20°C, the unmodified oakwood and switchgrass bio-binders yielded almost the same intermediate temperatures, e.g. 20°C and 25°C, respectively. On the other hand, the unmodified cornstover bio-binder (blend 15) had an intermediate temperature of 30°C which was higher than the

bitumen binders. Overall, it can be concluded that the intermediate performance temperatures for unmodified and modified bio-binders were generally higher than the bitumen intermediate temperatures.

Low Temperature Performance Grade

Accordingly, the low critical temperatures for all bio-binders were determined using a bending beam rheometer. As previously mentioned, the BBR test produces two responses: stiffness and the m-value. According to Superpave specifications, a sample can fail at a given temperature if the stiffness is greater than 300 MPa or if the m-value is less than 0.300. Generally, in this study, the stiffness was the limiting value. The low critical temperatures for all samples were listed in Table 8.10.

Table 8.10. Low Temperature Performance Grade for PAV Aged Samples

Blend #	Sample I.D.	Performance Grade (°C)
1	**OFP0B0**	2
2	**OFP1B2**	2
3	**OFP1B4**	-4
4	**OFP2B2**	8
5	**OFP2B4**	8
6	**OFP3B2**	2
7	**OFP3B4**	2
8	**SGP0B0**	2
9	**SGP1B2**	-4
10	**SGP1B4**	2
11	**SGP2B2**	-4
12	**SGP2B4**	-4
13	**SGP3B2**	-4
14	**SGP3B4**	-4
15	**CSP0B0**	-4
16	**CSP1B2**	-4
17	**CSP1B4**	-4
18	**CSP2B2**	-4
19	**CSP2B4**	-4
20	**CSP3B2**	-4
21	**CSP3B4**	-4

From the low temperature performance grades, the following could be concluded. First, all bio-binders had higher low temperature performance grades, ranging from 8 to -4°C, compared to bituminous binders which had low temperature performance grades of -16°C and -22°C for AAM and AAD, respectively. This meant that the tested bio-binders (unmodified and modified blends) have low resistance to low temperature cracking compared to bitumen binders. This may be due to the stiffening effect of the high oxygen content of the bio-binders tested in this research (35, 45, and 46% for oakwood, switchgrass and cornstover, respectively) compared to the

bitumen binders which had low oxygen content (<1%). Therefore, it is safe to conclude that these bio-binders should not be used in cold climatic conditions. Second, it was observed that the effect of polymer modifiers was not significant in enhancing the low temperature performance grade for oakwood and cornstover bio-binders. In other words, no clear trend could be observed for the effect of polymer modifiers on the low temperature performance grade of the bio-binders. On the other hand, polymers 2 and 3 generally led to an improvement in the low temperature cracking of the switchgrass bio-binders, precisely the temperature decreased from 2 to -4°C. However, the blending ratio was not significant in lowering the low temperature grade. For example, blends 11 and 12 (polymer modified switchgrass with polymer 2) yielded the same low temperature grade although they had different blending ratio and also blends 13 and 14 (polymer modified switchgrass with polymer 3) had the same conclusion. Overall, it is worth noting that due to the high oxygen content in bio-binders, the low temperature performance grade of the tested bio-binders were higher than the low temperature performance grade of the commonly bitumen binders used in most of the US market. Significantly, it may be concluded that these bio-binders should not be used in cold climates regions.

Statistical Analysis

A one-way analysis of variance "ANOVA" using the method of least squares was conducted, using the computer software JMP 7.0, to study the effect of the polymer type and blending ratio on the temperature performance grade of the bio-binders. Type I error (α) of 0.05 was used as the confidence level was 95%. The p-values of the AVOVA for different bio-binders were summarized and listed in Table 8.11.

Table 8.11. Summary of p-values for the Effect of Polymer Type and Blending Ration on Temperature Performance Grade

Bio-binder Type	Variable	Temperature					
		High		Intermediate		Low	
Oakwood	Polymer Type	13.8415	***0.0291****	1.3317	0.4098	4.7143	0.1175
	Blending Ratio	0.9656	0.4548	0.5324	0.6237	0.1429	0.8711
Switchgrass	Polymer Type	0.9604	0.5128	3.7681	0.1524	1.8571	0.3119
	Blending Ratio	0.5486	0.6158	0.0677	0.9356	2.2857	0.2178
Cornstover	Polymer Type	2.3458	0.2510	7.4220	0.0669	NA	NA
	Blending Ratio	0.8737	0.4844	0.0632	0.9397	NA	NA

Based on Table 8.11, the following conclusions could be established. First, for the high temperature performance grade, the polymer type was significant in changing the high temperature performance grade for only the cornstover bio-binders. On the other hand, the blending ratio was not significant in changing the performance grade for all types of bio-binders. Second, neither the polymer type nor the blending ratio was significant in changing the intermediate and low temperature performance grade for all types of bio-binders. Overall, the effect of the polymer type on changing the high temperature performance grade for the bio-binders was significant but this effect may vary with respect to the type of the bio-binder.

General Conclusion

The performance grade for all bio-binders tested in this research are summarized and listed in Table 8.12. Since the high temperature performance grade for some bio-binders (blends 1, 2, 3, 11 and 15) could not be measured using unaged samples and the high mass losses due to RTFO aging were yielded for bio-binders, it is more feasible and reliable to determine the high temperature performance grade of the bio-binders through the G*/sin(delta) of the RTFO aged samples. Precisely, in this study, the high temperature performance grades for bio-binders (unmodified and modified) were determined using 20-min RTFO aging residues. The addition of polymer modifiers was significant in changing the high temperature performance grade for bio-binders. Significantly, the Superpave specification limit for mass losses due to RTFO aging should be increased from 1% for bituminous binders to 10-15% for bio-binders. Generally, it is worth noting that bio-binders can yield the same or even higher high temperature performance grade in comparison to the bitumen binders. For the intermediate temperature performance grade, it can be concluded that the unmodified and modified bio-binders had generally higher grades than the bitumen intermediate temperature performance grade. In addition, it is worth noting that due to the high oxygen content in bio-binders, the low temperature performance grade of the tested bio-binders were higher than the low temperature performance grade of common bitumen binders used in the US market. No clear trend could be observed for the effect of the addition of polymer modifiers in changing the intermediate and low temperature performance grade for bio-binders. Importantly, it was established that the tested bio-binders should not be used in cold climates regions.

Table 8.12. Summary of Temperature Performance Grade for All Bio-binders

Blend #	Sample I.D.	Temperature Performance Grade (°C)		
		High (RTFO Aged)	Intermediate (PAV Aged)	Low (PAV Aged)
1	**OFP0B0**	50	18	2
2	**OFP1B2**	52	20	2
3	**OFP1B4**	55	34	-4
4	**OFP2B2**	68	26	8
5	**OFP2B4**	76	17	8
6	**OFP3B2**	65	34	2
7	**OFP3B4**	65	31	2
8	**SGP0B0**	59	25	2
9	**SGP1B2**	59	32	-4
10	**SGP1B4**	64	29	2
11	**SGP2B2**	53	25	-4
12	**SGP2B4**	59	29	-4
13	**SGP3B2**	59	23	-4
14	**SGP3B4**	57	17	-4
15	**CSP0B0**	60	30	-4
16	**CSP1B2**	72	29	-4
17	**CSP1B4**	71	29	-4
18	**CSP2B2**	69	38	-4
19	**CSP2B4**	73	37	-4
20	**CSP3B2**	68	18	-4
21	**CSP3B4**	57	26	-4

CHAPTER 9. DEVELOPING MASTER CURVE FOR BIO-BINDERS

Introduction

In this chapter, the master curves for all the tested bio-binders (unmodified and modified) and bitumen (AAM and AAD) were developed according to Richard's curve that was previously discussed in Chapter 2. For each binder, the complex moduli were determined at different temperatures. At high temperatures, the viscosity of the binder were measured at different temperatures and shear rates and then converted to complex modulus using equations 3.6 to 3.10 in Chapter 3. At intermediate temperatures, the complex moduli were determined at different temperatures and shear rates using 8mm plate samples in a DSR. At low temperatures, the stiffness moduli were measured at different temperatures and shear rates using a BBR and then converted to complex modulus using equations 3.2 to 3.5 in Chapter 3. Consequently, Microsoft Excel Solver was used to fit the master curve for each set of data. This method used the Generalized Reduced Gradient nonlinear optimization approach to find the parameters that gave the "best fit" between the equation and the data. The nonlinear regression algorithm solved for the values of the parameters that minimized the sum of the squared differences between the values of the observed and predicted values of the complex modulus. Finally, the master curves were plotted having the complex modulus on the Y-axis and the reduced frequency on the X-axis. The reduced frequency represents the temperature, or in other words, low reduced frequency values represents high temperatures and vice versa.

Master Curves for Bio-binders and Bitumen

After using the Microsoft Solver, the four parameters of Richard's model (α, β, δ, and γ) were calculated and are listed in Table 9.1, in addition to the sum of difference square, which represented the sum of the squared differences between the values of the observed and predicted values of the complex modulus.

Table 9.1. Richard's Model's Parameters for All Binders

Blend #	α	β	δ	γ	∑(Difference)^2
AAM	-8.172	3.921	7.475	-0.707	0.264
AAD	-16.451	2.297	9.048	-0.239	0.005
1	-13.023	-0.296	9.341	-0.285	0.063
2	-16.130	1.853	10.243	-0.227	0.040
3	-13.030	-0.109	8.781	-0.330	0.173
4	-11.023	1.143	9.022	-0.489	0.241
5	-25.596	2.774	8.870	-0.170	0.201
6	-23.632	2.540	8.969	-0.173	0.237
7	-15.909	1.319	8.998	-0.241	0.257
8	-18.123	1.537	9.678	-0.169	0.194
9	-17.661	0.979	8.841	-0.204	0.177
10	-88.315	4.267	8.729	-0.124	0.190
11	-11.023	2.544	8.220	-0.362	0.379
12	-9.906	1.734	8.226	-0.397	0.364
13	-10.504	1.937	8.223	-0.311	0.559
14	-11.266	-0.124	8.236	-0.355	0.499
15	-64.699	1.907	13.224	-0.087	0.623
16	-29.405	2.109	11.146	-0.136	0.043
17	-10.099	2.007	8.167	-0.512	1.530
18	-11.426	1.189	9.052	-0.409	0.151
19	-18.266	2.304	9.659	-0.200	0.012
20	-211.568	4.850	8.338	-0.127	0.430
21	-21.765	1.392	10.116	-0.175	0.278

From Table 9.1, the following observations could be noted. First, the sum of difference square was not substantially high which meant that the models were able to predict the complex modulus of the bio-binders. Second, for the α parameter, the unmodified bio-binders had the same or higher α values compared to bitumen; however, for the modified bio-binders, no specific trend was observed. For example, for bitumen, the α parameter were -8.172 and -16.451 for AAM and AAD, respectively, while for oakwood, switchgrass and cornstover bio-binders, the α parameter were ranging between -11.023 to -25.596, -9.906 to -88.315, and -10.099 and -211.568, respectively. Third, for the β parameter of the unmodified and modified bio-binders, the values were -in general- lower than the range of values of bitumen (2.297 to 3.921). Fourth, for the δ parameter, the values of the unmodified and modified bio-binder and bitumen were close to each other and comparable. Fifth, for the γ parameter, there is no specific trend observed but the values were consistent (low variability). Overall, since there is no threshold value or standard range for these parameters for bitumen, it is difficult to compare between Richard's parameters for bitumen and bio-binders and to relate these parameters to physical properties of the bio-binders. However, it is safe to conclude that the master curve of bio-binders (unmodified and modified) can be modeled using Richard's model.

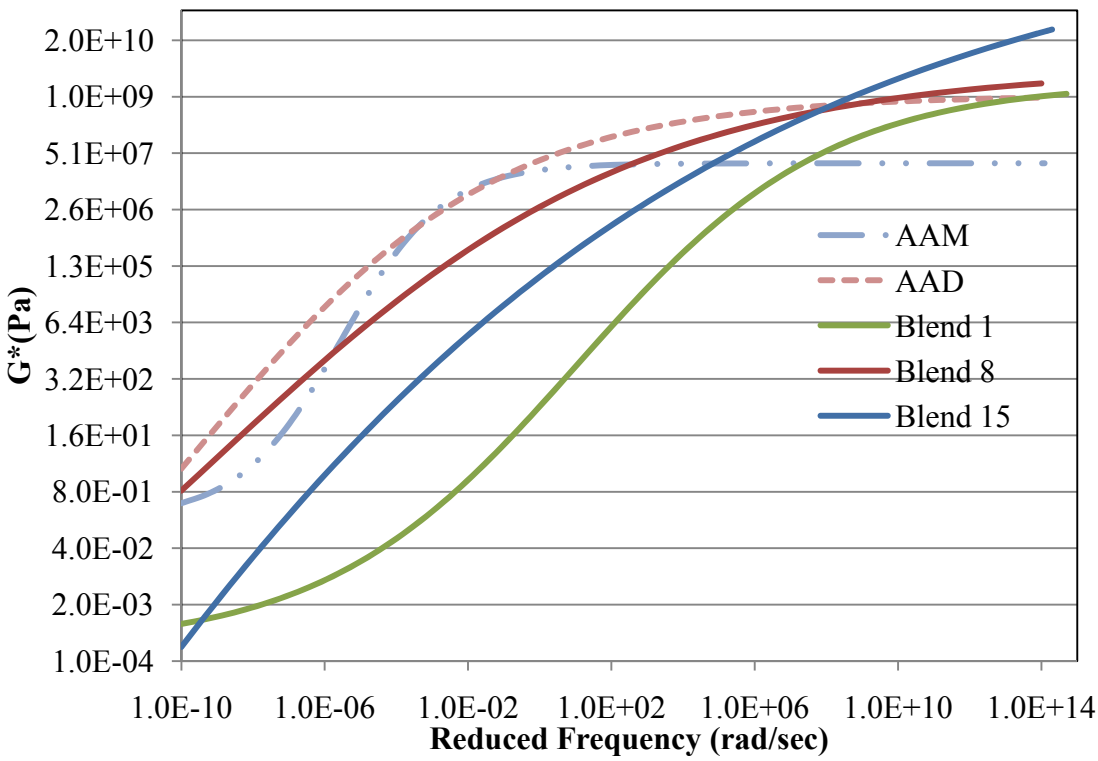


Figure 9.1. Master Curve for Unmodified Bio-binders versus Bitumen

Based on Figure 9.1 which represents the master curves of the unmodified bio-binders and bitumen, the following conclusions could be established. First, it was noted that at high and intermediate temperatures (low and intermediate reduced frequency, respectively), the complex moduli of the unmodified bio-binders (oakwood, switchgrass and cornstover) were -in general- lower than the bitumen. However, at the low temperatures (high reduced frequency), the complex moduli of the unmodified bio-binders were higher than the corresponding values in bitumen. The high complex moduli at low temperatures may be due to the oxidation taking place within the bio-binders after pre-treatment, RTFO aging and PAV aging due to the considerable amount of oxygen present in bio-binders in comparison with the bitumen. Consequently, it may be concluded that the unmodified bio-binder presented (blend 1) may not be used in cold climates and it is more feasible to be used in warm climates. However, the complex moduli of blend 8, which is the unmodified switchgrass bio-binder, showed that it may be used in cold climates. Second, it was observed that the shapes of the master curve were changing with respect to the type of the bio-binder. For example, the master curve of the unmodified oakwood bio-binder (blend 1) were following the same trend/shape as the AAM blend while the unmodified switchgrass and cornstover bio-binders (blends 8 and 15, respectively) were following the same trend/shape as the AAD. In summary, it may be concluded that the behavior of the bio-binders varied with respect to their type and their behavior may be different from bitumen at high, intermediate, and low temperatures (low, intermediate, and high reduced frequencies, respectively).

Based on Figure 9.2 which showed the master curves of the unmodified and modified oakwood bio-binders and bitumen, the following conclusions could be made. First, it was observed that at

high and intermediate temperatures, the complex moduli of the unmodified oakwood bio-binders were lower than the bitumen. However, at the low temperatures, the complex moduli of the unmodified bio-binders were higher than the corresponding values in bitumen. As mentioned previously, this may be due to the large oxidation taking place within the bio-binders after the pre-treatment and aging processes. Second, upon the addition of polymer modifiers to the oakwood bio-binders, the same trend was observed in the sense of having low complex moduli at low and intermediate temperatures and high complex moduli at low temperatures in comparison with bitumen except for blends 5 and 6, which had high complex moduli at high temperatures in comparison with bitumen. Therefore, no specific trend was observed after the addition of different types of polymer modifiers with different blending ratios. Third, it was observed that the shapes of the master curves changed with respect to the type of the polymer modifier and the blending ratio. For example, the master curves of blends 1, 3, and 4 followed the same trend/shape as the AAM binder while blends 2, 5, 6, and 7 followed the trend/shape as the AAD binder. Consequently, it can be concluded that the addition of different types of polymer modifiers with different blending ratios changed the behavior of the oakwood bio-binders. In summary, it may be concluded that the behavior of the unmodified oakwood bio-binder would not be suitable for cold climates and their behaviors varied upon the addition of different types of polymer modifiers with different blending ratios, and in some blends are suitable for cold climates.

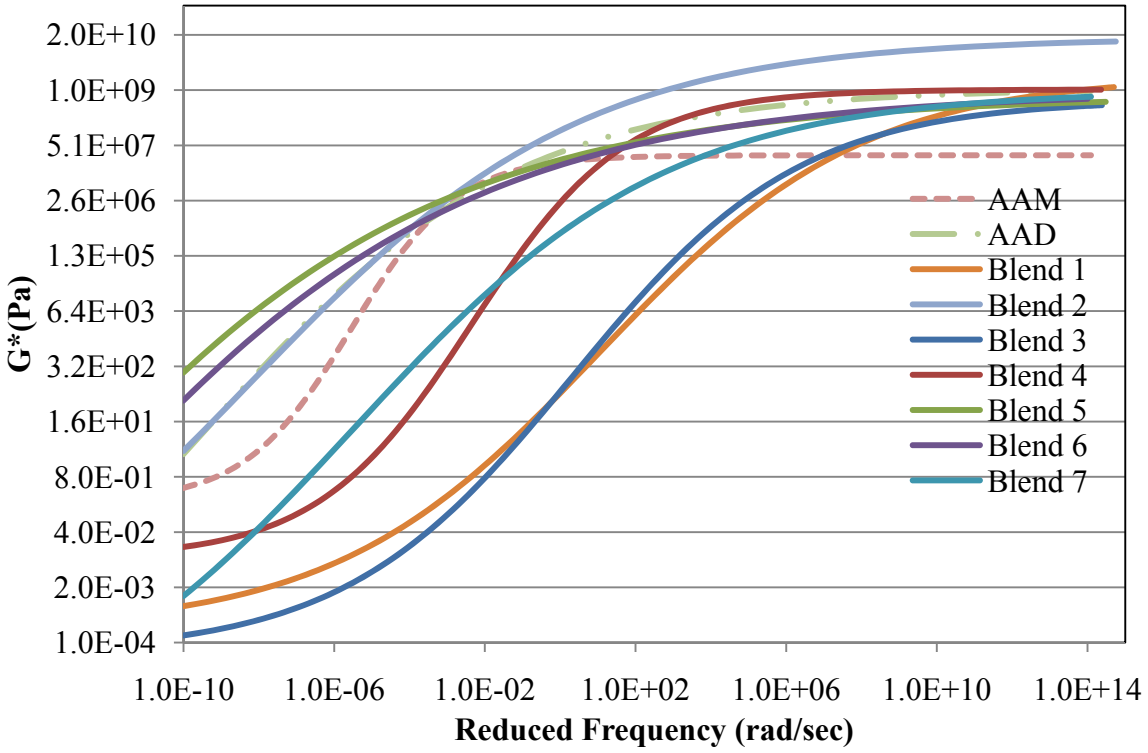


Figure 9.2. Master Curve for Oakwood Bio-binders versus Bitumen

Based on Figure 9.3 which showed the master curves of the unmodified and modified switchgrass bio-binders and bitumen, the following observations were noted. First, at high temperatures (low reduced frequency), it was observed that the complex moduli of the unmodified switchgrass bio-binders were in-between the complex moduli for the AAM and

AAD bitumen binders. However, at the intermediate temperatures, the complex moduli for the unmodified switchgrass bio-binder were lower than the complex moduli of the bitumens. In addition, at the low temperatures, the complex moduli of the unmodified switchgrass bio-binders were higher than the corresponding values in the bitumen binders. Second, no specific trend was observed after the addition of different types of polymer modifiers, but it is safe to note that the complex modulus -in general- was increased. For example, the complex moduli at high and intermediate temperatures of the modified switchgrass (blend 10) increased considerably with respect to the bitumen binders while the complex moduli at low temperatures did not change significantly. Third, it was observed that the shapes of the master curve were changing with respect to the type of the polymer modifier and the blending ratio. Overall, like the oakwood bio-binders, it may be concluded that the behavior of the switchgrass bio-binders would not be suitable for cold climates and their behaviors varied upon the addition of different types of polymer modifiers with different blending ratios.

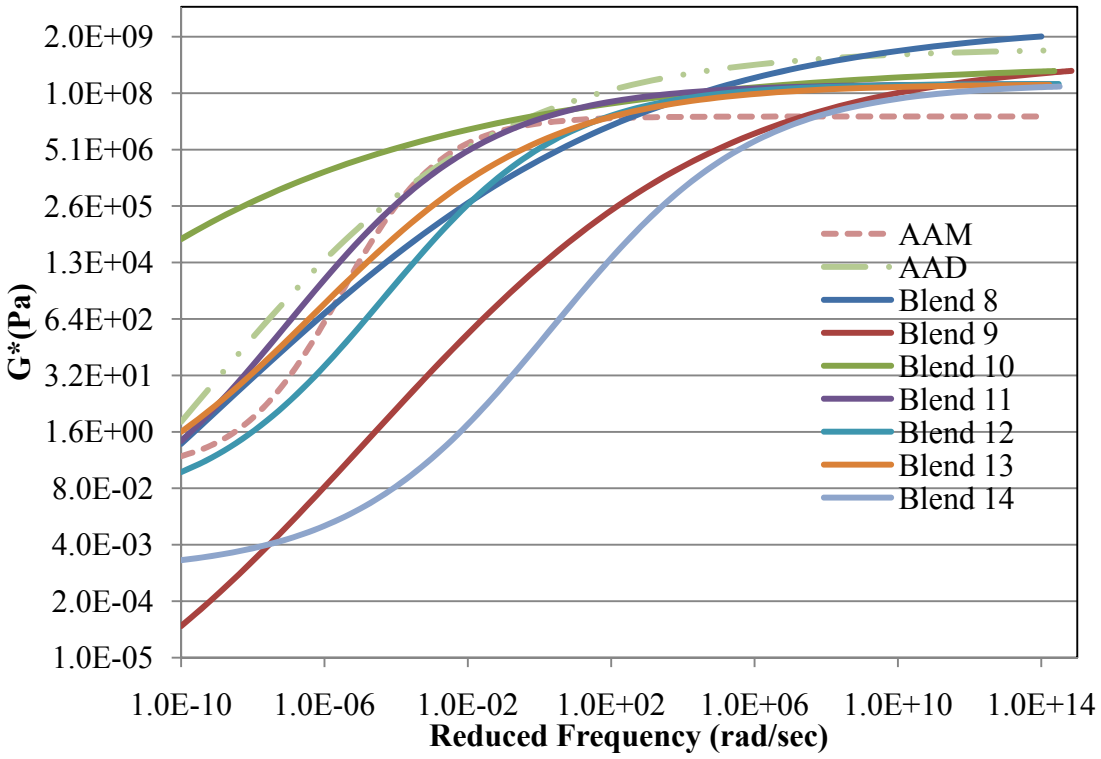


Figure 9.3. Master Curve for Switchgrass Bio-binders versus Bitumen

Based on Figure 9.4 which displays the master curves of the unmodified and modified cornstover bio-binders and bitumen, the following remarks are noted. First, as oakwood bio-binders, it was observed that at high and intermediate temperatures, the complex moduli of the unmodified cornstover bio-binders were lower than the bitumen binders. However, at the low temperatures, the complex moduli of the unmodified bio-binders were higher than the corresponding values in the bitumen binders. Second, no specific trend was observed after the addition of different types of polymer modifiers with different blending ratios. For example, upon the addition of polymer modifier P1 with 2% blending ratio (blend 16), the complex moduli decreased at high and intermediate temperatures (low and intermediate reduced frequency) and increased at low temperatures (high reduced frequency) while upon the addition of polymer 3 with 4% blending

ratio (blend 21), the complex moduli increased at the high and intermediate temperatures while remained -in general- the same at low temperatures. Third, it was observed that the shapes of the master curves were changing with respect to the type of the polymer modifier and the blending ratio. Overall, like oakwood and switchgrass bio-binders, it may be concluded that the behavior of the cornstover bio-binders varied upon the addition of different types of polymer modifiers with different blending ratios.

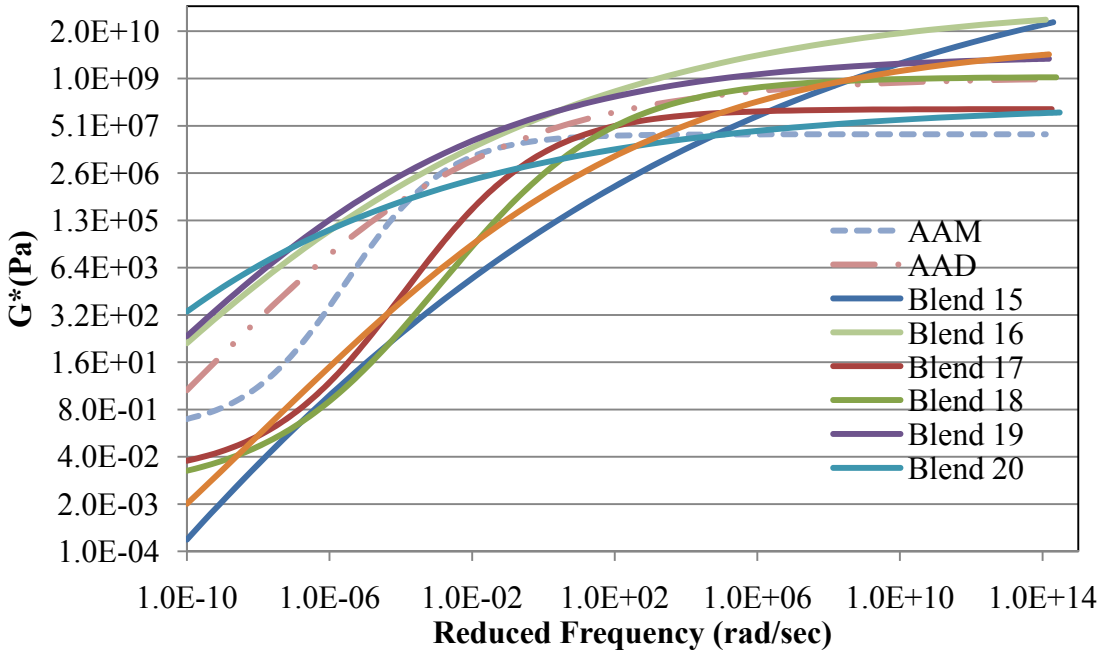


Figure 9.4. Master Curve for Cornstover Bio-binders versus Bitumen

General Conclusion

Having a global perspective on the master curves of the different types of unmodified and modified bio-binders, it was safe to note that behavior of the bio-binders were different compared to the two bitumen binders. Generally, the tested bio-binders had higher complex moduli at low temperatures/high reduced frequencies compared to the corresponding values of bitumen. This meant that the resistance of bio-binders to thermal cracking would be a main concern in utilizing bio-binders as a pavement material in cold climates. Importantly, the addition of different types of polymer modifiers with different blending ratios led to a change in the shape/trend of the master curve and hence changed the behavior of the bio-binder. Consequently, before utilizing the bio-binders in pavement applications, different types of polymer modifiers with different blending ratios should be tested until the required/specified behavior achieved. Overall, the master curves for different types of bio-binders can be well developed and predicted using Richard's model.

CHAPTER 10. SUMMARY, CONCLUSIONS, TESTING PROTOCOL, AND RECOMMENDATIONS

Summary

Most bituminous adhesives or binders that are used for pavement materials are derived mainly from fossil fuels. Nevertheless, with petroleum oil reserves becoming depleted and the subsequent urge to reduce fossil fuel usage, there is a drive to develop and produce binders from alternative sources, especially from biorenewable resources. Importantly, the United States is working to establish a bio-based economy which generates energy from renewable organic matter rather than fossil fuels. Due to the availability of large quantities of biorenewable 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. Recently, through the application of scientific research and development, a range of different vegetable oils have been investigated to determine their physical and chemical properties to study their applicability to be used as bio-binders in the pavement industry.

Currently, the state of the art for the utilization of bio-oils is concentrated on its uses as biorenewable fuels to replace fossil fuels. However, there is a limited amount of research that has been conducted to investigate the applicability of using bio-oils as a bitumen modifier or extender. Based on the conclusion of these investigations, the utilization of bio-oils as a bitumen modifier is very promising. On the other hand, there has been no research conducted until now that studies the applicability of the utilization of bio-oils as a bitumen replacement (100% replacement) to be used in the pavement industry. As a result, there is scarcity of data that illustrate the procedure to develop bio-binders from bio-oils. Bio-binders (synthetic binders) can be utilized in three different ways to decrease the demand for fossil fuel based bituminous binders summarized as follows: (1) as a bitumen modifier (<10% bitumen replacement), (2) as a bitumen extender (25% to 75% bitumen replacement), and (3) as a direct alternative binder (100% replacement).

The main objectives of this report can be summarized as follows. First, the rheological properties of fast pyrolysis liquid co-products (bio-oils) were investigated to determine the heat pre-treatment/upgrading procedure required for developing bio-binders from bio-oils. The second objective included the modification of Superpave test criterion to comply with the properties of the developed bio-binders. Third, the chemical characterization of the developed bio-binders was studied using Gas Chromatography-Mass Spectrometry (GC/MS) and Fourier Transform Infrared Spectroscopy (FTIR) in addition to the physical characterization that included the specific gravity and the separation tests. Fourth, the utilization of bio-oils as bio-binders in the pavement industry was explored through determining the temperature and shear susceptibilities of the developed bio-binders (unmodified and polymer modified) and comparing them with commonly used bitumen binders. Fifth, the temperature performance grades for the developed bio-binders were measured in addition to the determination of the mixing and the compaction temperatures. Sixth, using Richard's curve, the master curves for the developed bio-binders were studied and compared to commonly used bitumen binders. Seventh, an outline or a protocol to optimize bio-oils to be used as bio-binders was developed and will be discussed hereafter in detail.

Conclusions

The conclusions of this report are divided into two main sections. The first section is concerned about the general conclusions about the applicability of using the bio-oils as pavement materials. The second section is concerned about the conclusions and findings that were established based on testing the bio-oils provided by the Center for Sustainable Environmental Technologies at Iowa State University.

General Conclusions

The overall conclusions about the applicability of using bio-oils as bio-binders in the pavement industry can be summarized as follows:

- The bio-oils cannot be used as bio-binders/pavement materials without any heat pre-treatment/upgrading procedure due to the presence of water and volatile contents in considerable amounts.
- The heat treatment/upgrading procedure for deriving bio-binders from bio-oils should be determined for each type of bio-oil separately. This is mainly due to the significant difference between the different types of bio-oils. For example, the chemical composition of the different types of bio-oils vary significantly based on many factors, e.g. the process by which the bio-oils were derived and the type of the biorenewable resource from which the bio-oils were derived.
- The current testing standards and specifications, especially Superpave specifications, should be modified to comply with the properties of the bio-binders derived from bio-oils. This is mainly due to the difference in the chemical structure and composition between bio-oils and crude-petroleum binders. Importantly, due to the considerable amount of oxygen in the bio-oils, new specifications and testing procedures should be developed for the bio-binders derived from bio-oils.
- The temperature range of the viscous behavior for the bio-oils should be determined precisely as the temperature ranges for the different bio-binders vary depending on the type of the bio-oil and the type of the polymer modifier used. In general, the temperature range for bio-oils may be lower than that of bitumen binders by about 30-40°C.
- The rheological properties, i.e. temperature and shear susceptibilities, of the unmodified bio-binders derived from bio-oils vary in comparison to bitumen binders, but upon adding polymer modifiers, the rheological properties of these modified bio-binders change significantly.
- The polymer modifiers should be chosen with care and caution because the temperature range of the developed bio-binders is different than the polymer modifiers commonly used in the bitumen industry.
- The high temperature performance grade for the developed bio-binders may not vary significantly from the bitumen binders; however, the low temperature performance grade may vary significantly due to the high oxygen content in the bio-binders compared to the bitumen binders.

Addressing Objectives and Hypotheses

In this section, the conclusions addressing the objectives and hypotheses are summarized, based on testing the bio-oils provided. Therefore, these conclusions are limited for these types of bio-oils.

For the heat treatment/upgrading procedure, the following conclusions were established. First, the viscosity of the untreated and unmodified oakwood, switchgrass, and cornstover bio-binders were very low due to the presence of high content of water and volatile materials. In addition, there was no considerable difference between the viscosity measurements of the three untreated and unmodified bio-oils. Second, the results indicated that increasing the temperature led to higher aging indexes as temperature is a significant factor in increasing the oxidation occurring in the bio-oils. Third, the aging indexes relative to zero hours were generally decreased after the heat pre-treatment/upgrading procedure compared to the corresponding values of aging indexes before the heat pre-treatment/upgrading procedure. Fourth, the bio-oils tested showed that a heat treatment/upgrading procedure is significantly required in order to be able to use bio-oils as bio-binders in the pavement industry. Precisely, according to the bio-oils tested in this study, the heat treatment/upgrading procedure was established to be heating for 2 hours at 100-110°C. Importantly, the heat treatment procedure may not lead to significant changes in the physical and chemical properties of the bio-oils; however, the heat pre-treatment/upgrading procedure may be a very important procedure to upgrade the bio-oils through reducing the high water and volatile materials content. Importantly, the developed bio-binders could not be treated with temperatures higher than 120°C due to the high oxygen content which will lead to a considerable amount of oxidation with higher temperatures.

Since there was considerable difference between the properties of the bio-oils and asphalt at the same temperatures, the Superpave test criterion should be modified. Precisely, the Superpave specifications for RTFO and PAV procedures should be modified to comply with the bio-binders properties. Based on the tested bio-oils, the following suggestions were made. First, the RTFO temperature should be modified to 110-120°C instead of 163°C. Also, the 20-min duration was established to be the duration to resemble the mixing and compaction duration. Second, the aging duration in the PAV oven should be shortened to 2.5 hours instead of 20 hours and the temperature of the degassing container should be lowered to 120°C instead of 170°C.

For the physical testing, the following observations were noted. First, the oakwood bio-binders generally were more susceptible to separation with all types of the polymer modifiers used in this research in comparison to switchgrass and cornstover bio-binders. Therefore, more care and caution should be taken when blending oakwood bio-binders with polymer modifiers. Second, the specific gravity values of the bio-binders were higher than the specific gravity values of the bitumen binders. Third, there was no significant difference between the specific gravity values of the unmodified bio-binders (oakwood, switchgrass and cornstover). Fourth, the addition of the polymer modifiers to the switchgrass and cornstover -in general- led to a decrease in the specific gravity values; however, the same trend could not be observed for oakwood bio-binders. Fifth, the blending procedure -in general- did not lead to an increase in the specific gravity values of the modified bio-binders since the blending procedure included heating at temperatures between 110-120°C for 20-30 minutes.

For the chemical testing, the following remarks are made. First, it was observed that the furfural and the phenol compounds might be reacting with each other and forming a new polymer due to the heat treatment/upgrading procedure and the aging processes; however, the phenol compounds, which are acting as an antioxidant agent, are still present, unlike the furfural compounds which were completely removed, after the heat pre-treatment/upgrading procedure and the aging processes. Second, the aging ratios for both reacting groups (CH_2 and CH_2-CH_3) with respect to the neutral O-H group were decreasing which meant that these reacting groups were decreasing upon heat pre-treatment/upgrading procedure and aging processes. Third, for the aging indexes, upon heat pre-treatment/upgrading procedure and aging processes of the unmodified bio-binders, the aging indexes were generally increasing but without a specific trend. Importantly, these two new means or methods, i.e. aging ratio and aging index, can be employed to quantify the amount of aging occurring on some of the bio-binders, such as oakwood and switchgrass, upon heat treatment and aging processes, but care should be taken before usage of these means or methods as their validity vary depending on the type of the bio-binders.

For the rheological testing, the overall conclusions, which included shear and temperature susceptibilities, behavior index n, consistency index K, and activation energy E_a can be summarized as follows. First for the shear susceptibility (SS), although the SS values of the switchgrass and cornstover bio-binders yielded higher values than the bitumen binders tested, the statistical analysis showed that there was no statistical difference. In addition, the addition of polymer modifiers with different blending ratios did not lead to significant changes in the SS values of all types of the bio-binders. However, the polymer modifiers changed the temperature range of the oakwood and switchgrass bio-binders only and had no effect on the cornstover bio-binders. Moreover, the addition of different types of polymer modifiers was not yielding the same effect on the different types of bio-binders. Importantly, the relationship between viscosity and shear rate at different temperatures, for different types of bio-binders, can be well described by a similar linear logarithmic relationship as bitumen binders.

Second, for the temperature susceptibility, it can be concluded that the temperature was the main contributor to the viscosity of the bio-oils in comparison to shear rate. In other words, the effect of temperature in changing the viscosity of the bio-oils was more significant than the effect of shear rate. This kind of behavior showed that the bio-oil binders had the same behavior as bitumen binders. In addition, the relationship between viscosity and temperature at different shear rates can be well described as a linear logarithmic relationship. Importantly, it was observed that the addition of polymer modifiers with different blending ratios did not lead to the same effect when blending with different bio-binders. Also, the effect of the addition of different types of polymer modifiers and the blending ratios on the VTS values was varied depending on the type of the bio-binder and the shear rate.

Third, for the behavior index n, it can be concluded that increasing the temperature led to a more Newtonian behavior for the oakwood and switchgrass bio-binders (n values were almost equal to unity), but the cornstover bio-binders were not following the same behavior. Also, all the bio-binders at low temperatures had a pseudo-plastic behavior as their n values were less than unity. Fourth, for the consistency index K, it was observed that increasing the temperature led to a decrease in the viscous behavior of all types of bio-binders. Based on the statistical analysis conducted, it may be concluded that the addition of polymer modifiers with different blending percentages to all types of bio-binders did not generally lead to a significant change in the n and

K values. Significantly, there was no statistically significant difference between *n* and *K* values of the unmodified bio-binders and bitumen. In addition, there was no significant difference between *n* and *K* values of modified oakwood bio-binders and the bitumens. On the other hand, there was no significant difference between *n* values of modified switchgrass and the bitumens, but there was significance difference between *K* values of modified switchgrass and bitumen. For the cornstover bio-binders, for the *n* values, there was a significant difference between the modified cornstover bio-binders and the bitumens, but there was no significant difference between *K* values of the modified cornstover bio-binders and the bitumens. Therefore, it is worth noting that the effect of the polymer modifiers on the *n* and *K* values vary according to the bio-binder type. Considerably, the relationship between viscosity and shear rate at different temperatures for the bio-binders and bitumen were following a power-law relationship.

Fifth, for the activation energy E_a, which represents the susceptibility of bio-binders to temperature, the following observations can be noted. First, the temperature susceptibility of the unmodified oakwood bio-binders was higher than the temperature susceptibility of the bitumen binders, but there was no significant difference between temperature susceptibility of the modified oakwood bio-binders and the bitumen binders. However, for the switchgrass and cornstover bio-binders, the temperature susceptibility of the unmodified and modified switchgrass and cornstover bio-binders was not statistically different than the temperature susceptibility of the bitumen binders. Second, neither polymer type nor the blending ratios affected the E_a values of the oakwood, switchgrass and cornstover bio-binders. Third, the relationship between viscosity and temperature at different shear rates was well described by the Arrhenius-type model.

For the performance grade testing, the following findings were established based on the performance grade and the mixing and compaction temperatures summarized in Table 10.1. First, it is more feasible and reliable to determine the high temperature performance grade of the bio-binders through the G*/sin(delta) of the RTFO aged samples. Precisely, in this study, the high temperature performance grades for bio-binders (unmodified and modified) were determined using 20-min RTFO aging residues at 115°C. Generally, it is worth noting that bio-binders can yield the same or even a greater high temperature performance grade in comparison to the bitumen binders. Second, for the intermediate temperature performance grade, it can be concluded that the unmodified and modified bio-binders had generally higher grades than the bitumen intermediate temperature performance grade. Third, it is worth noting that due to the high oxygen content in bio-binders, the low temperature performance grade of the tested bio-binders were higher than the low temperature performance grade of the commonly bitumen binders used in the US market. No clear trend could be observed for the effect of the addition of polymer modifiers in changing the intermediate and low temperature performance grade for bio-binders. Importantly, it was established that the tested bio-binders should be limited in their use in cold climate regions until their low temperature properties are improved. Fourth, the results revealed that the mixing and compaction temperatures for the bio-binders generally were lower than the typical mixing and compaction temperatures for the bitumen binders commonly used.

For developing master curves for bio-oils, the following conclusions can be made. First, the behavior of the bio-binders (unmodified and polymer modified) varied with respect to their type; therefore, their behavior generally may be different from bitumen. First, the bio-binders had higher complex moduli at low temperature/high reduced frequency compared to the

corresponding values of bitumen. This meant that the resistance of bio-binders to thermal cracking would be a main concern in utilizing bio-binders as pavement materials in cold climates. Second, the addition of different types of polymer modifiers with different percentages led to a change in the shape/trend of the master curve and hence changes the behavior of the bio-binder. Consequently, before utilizing the bio-binders in pavement applications, different types of polymer modifiers with different percentages should be tested until the required/specified behavior is achieved. Overall, the master curves for different types of bio-binders can be well constructed and predicted using Richard's curve.

Table 10.1. Summary of Performance Testing

Blend #	Sample I.D.	Performance Grade (°C)			Performance Temperature (°C)			
		High	Intermediate	Low	Mixing Range		Compaction Range	
1	**OFP0B0**	50	18	2	78.8	81.6	73.1	75.6
2	**OFP1B2**	52	20	2	105.1	108.7	97.8	101.0
3	**OFP1B4**	55	34	-4	99.7	102.9	93.1	96.0
4	**OFP2B2**	68	26	8	145.8	149.8	137.7	141.3
5	**OFP2B4**	76	17	8	147.2	151.7	137.8	141.9
6	**OFP3B2**	65	34	2	122.7	126.0	115.8	118.8
7	**OFP3B4**	65	31	2	124.5	127.7	117.9	120.8
8	**SGP0B0**	59	25	2	129.2	133.3	120.8	124.5
9	**SGP1B2**	59	32	-4	124.8	128.4	117.2	120.5
10	**SGP1B4**	64	29	2	134.6	138.3	127.1	130.4
11	**SGP2B2**	53	25	-4	106.1	109.5	99.1	102.2
12	**SGP2B4**	59	29	-4	113.6	117.1	106.3	109.5
13	**SGP3B2**	59	23	-4	117.3	121.0	109.6	113.0
14	**SGP3B4**	57	17	-4	109.0	112.3	102.1	105.1
15	**CSP0B0**	60	30	-4	101.2	104.8	93.8	97.0
16	**CSP1B2**	72	29	-4	149.5	154.0	140.0	144.2
17	**CSP1B4**	71	29	-4	124.3	128.2	116.3	119.8
18	**CSP2B2**	69	38	-4	147.1	151.5	138.1	142.1
19	**CSP2B4**	73	37	-4	153.9	157.5	146.4	149.7
20	**CSP3B2**	68	18	-4	134.6	138.1	127.4	130.5
21	**CSP3B4**	57	26	-4	123.4	127.2	115.3	118.9

Testing Protocol

In this section, a testing protocol/procedure is recommended and suggested to develop bio-binders from bio-oils and to investigate the applicability of using these developed bio-binders as pavement materials. The testing protocol/procedure can be summarized as follows:

- Step 1: The viscosity of the virgin/untreated bio-oil should be measured versus time at different temperatures. The suggested times are at 0, 0.5, 1, 2, 4 and 8 hours and the suggested temperatures are 110°C, 120°C, and 130°C. The viscosity versus time at different temperatures should be plotted and named as plot 1. The y-axis and the x-axis represent the viscosity and time, respectively.

- Step 2: the aging index at varying durations should be measured using the following equation. Since there is no threshold value for the aging index even for bitumen binders, it is recommended to be taken as 12.

$$\text{Aging Index} = \frac{\text{Viscosity of Aged Binder}}{\text{Viscosity of original Binder}}$$

- Step 3: the pre-treatment/upgrading procedure should be determined based on steps 1 and 2. From plot 1, the pre-treatment duration is the point at which the slope of the viscosity-time relationship is changing. The pre-treatment temperature should be determined based on the measured viscosity after 8 hours. It is preferred to have viscosity of less than 3.0 Pa·s and an aging index of less than the threshold value (12) after 8 hours. It is recommended to have a pre-treatment temperature higher than 100°C to be sure that most of the volatile materials and water content be evaporated.
- Step 4: the viscosity at different temperatures and shear rates should be measured to determine the relationship between viscosity, and temperature and shear rate. The recommended temperature range is between 70°C and 160°C while the recommended shear rate range is between 20 and 100 rpm. The relationships between viscosity (y-axis) and temperature (x-axis) at the same shear rate (preferred to be 20 rpm) should be plotted and named as plot 2. The relationship between viscosity and temperature at the same shear rate of the commonly used bitumen binders should be included in this plot. The relationships between viscosity (y-axis) and shear rate at different temperatures (x-axis) should be plotted and named as plot 3.
- Step 5: the pre-treated/upgraded bio-oil should be blended with different types of polymer modifiers with different percentages. The relationship between viscosity and temperature for the modified bio-binders should be measured and added to plot 2 and renamed as plot 4. Based on plot 4, the bio-binder that resembles commonly used bitumen binders is preferred to be used. Otherwise, the bio-binder to be used as a pavement material should be chosen based on pavement design criteria.
- Step 6: the mixing and compaction temperatures for the bio-binder should be determined based on plot 4 from step 5.
- Step 7: the bio-binder should undergo RTFO and PAV aging in order to simulate in-situ aging during the mixing and compaction process (short term), and in-service period (long term). The RTFO procedure should be modified to comply with the bio-binders properties. The recommended temperature for the RTFO is 110-120°C. The RTFO duration should range between 10 minutes and 40 minutes and the recommended duration, based on this research, is 20 minutes. Using the DSR, the G*/sin(delta) values for 25-mm sample plates for the RTFO-aged bio-binders should be determined at varying durations. Then, the RTFO indexes based on the following equation should be calculated and compare them to RTFO index of bitumen binders (2.2) in order to determine the appropriate RTFO duration. The PAV temperature may not be modified because it is in the range of 90°C and 110°C; however, the temperature of the degassing equipment should be modified to comply with the properties of the bio-binders. The degassing temperature recommended based on this research is 120°C.

$$\text{RTFO Index} = \frac{(\text{G}*/\text{sindelta})_{\text{aged}}}{(\text{G}*/\text{sindelta})_{\text{unaged}}}$$

- Step 8: the amount of evaporation occurring due to RTFO aging should be calculated accurately based on the following equation. This step is crucial as it will be considered in the process of designing the pavement mixture.

$$\text{Mass change} = \frac{\text{Aged mass} - \text{Original mass}}{\text{Original mass}} \text{ x } 100$$

- Step 9: the performance grade should be determined including the high, intermediate, and low temperature performance grade. The high temperature performance grade should be determined based on the unaged and the RTFO-aged bio-binders using 25-mm samples in the DSR. The intermediate temperature performance grade should be determined based on 8-mm samples on the DSR after the bio-binders undergo RTFO and PAV aging. The low temperature performance grade should be determined after the bio-binders undergo RTFO and PAV aging using the BBR without changing or modifying the Superpave procedure.
- Step 10: using Richard's curve, the master curve for the developed bio-binders should be plotted and named as plot 5. The master curve for the bitumen binder should be included in plot 5. This plot is important to compare between the overall behavior of the developed bio-binder and bitumen binders at different temperatures and frequencies. The following guidelines are recommended to be followed to construct the master curves for the bio-binders:
    - Rotational viscometer: conducts test at four or five high temperatures (pre-treated/upgraded and unaged residues).
    - DSR: conduct tests using a 8mm plate for two or three intermediate temperatures with different frequency sweeps (pre-treated/upgraded, and RTFO and PAV aged residues).
    - BBR: conduct tests at two or three low temperatures (pre-treated/upgraded, and RTFO and PAV aged residues).

Recommendations

The extensive testing in this report has brought to light many issues that are involved in the applicability of the utilization of bio-oils as bio-binders in the pavement industry. The recommendations for future work can be summarized as follows:

- More investigation is required to study the applicability of using the bio-oils as bio-binders through studying and testing other bio-oils derived from different sources of biomasses.
- The effect of different types of polymer modifiers on the different types of bio-oils should be studied extensively. Particularly, the effect of molecular weight of the polymer modifiers on the rheological properties of the bio-binders.
- The thermal expansion coefficient of the developed bio-binders may be investigated particularly at low temperatures.
- More research effort should be conducted to study the applicability of using bio-oils as a direct alternative binder (100% replacement) in the pavement industry including mix designs and subsequent performance testing of mixes containing bio-binders.
- More investigation is needed to validate the heat pre-treatment/upgrading procedure recommended in this report. The new investigation should include different types of bio-oils derived from different biomasses.
- More research is required to validate the modifications of the Superpave test criterion and procedures recommended in this report.

- The resistance of the developed bio-binders against water and moisture intrusion should be studied. Moreover, the effect of water and moisture intrusion on the rheological properties should be investigated before the usage of the developed bio-binders as pavement materials.
- New means and methods to quantify the aging occurring in bio-binders should be studied extensively to establish a standard procedure or a specification to chemically quantify the aging taking place.

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APPENDIX A. DATA FOR CHAPTER 4

Table A4.1. Measurements of Viscosity Testing Over Time before Treatment at 125°C

Blend #	Sample I.D.	Time (hrs.)/Viscosity (Pa·s)					
		0	0.5	1	2	4	8
1	OFP0B0	0.03	0.04	0.05	0.09	0.15	0.45
2	OFP1B2	0.08	0.12	0.14	0.12	0.21	0.50
3	OFP1B4	0.05	0.07	0.08	0.11	0.19	0.44
4	OFP2B2	0.05	0.06	0.07	0.10	0.16	0.51
5	OFP2B4	0.04	0.06	0.09	0.14	0.25	0.75
6	OFP3B2	0.05	0.08	0.12	0.21	0.48	1.06
7	OFP3B4	0.06	0.07	0.09	0.11	0.15	0.25
8	SGP0B0	0.02	0.04	0.06	0.08	0.15	0.35
9	SGP1B2	0.08	0.09	0.10	0.14	0.23	0.46
10	SGP1B4	0.07	0.08	0.10	0.14	0.24	0.52
11	SGP2B2	0.60	0.67	0.79	1.01	1.80	3.59
12	SGP2B4	1.96	2.11	2.43	3.14	4.23	6.47
13	SGP3B2	1.27	1.38	1.58	2.12	3.24	6.88
14	SGP3B4	1.92	2.04	2.42	3.48	5.50	9.83
15	CSP0B0	0.04	0.05	0.06	0.08	0.11	0.17
16	CSP1B2	0.91	1.14	1.44	1.92	2.81	5.46
17	CSP1B4	1.13	1.36	1.73	2.25	3.44	6.05
18	CSP2B2	0.07	0.08	0.09	0.11	0.15	0.21
19	CSP2B4	0.08	0.10	0.11	0.13	0.17	0.25
20	CSP3B2	0.06	0.06	0.07	0.09	0.13	0.19
21	CSP3B4	0.13	0.13	0.14	0.14	0.15	0.22

Table A4.2. Measurements of Viscosity Testing Over Time before Treatment at 135°C

Blend #	Sample I.D.	Time (hrs.)/Viscosity (Pa·s)					
		0	0.5	1	2	4	8
1	OFP0B0	0.03	0.06	0.10	0.16	0.34	0.98
2	OFP1B2	0.12	0.16	0.18	0.23	0.43	1.06
3	OFP1B4	0.05	0.07	0.10	0.17	0.32	0.76
4	OFP2B2	0.05	0.08	0.11	0.18	0.43	1.25
5	OFP2B4	0.13	0.19	0.25	0.39	0.75	1.58
6	OFP3B2	0.18	0.38	0.46	0.64	1.00	1.72
7	OFP3B4	0.11	0.12	0.12	0.14	0.17	0.26
8	SGP0B0	0.01	0.03	0.04	0.06	0.12	0.24
9	SGP1B2	0.05	0.07	0.10	0.15	0.30	0.65
10	SGP1B4	0.09	0.08	0.09	0.15	0.32	1.07
11	SGP2B2	0.43	0.56	0.75	1.12	2.15	6.92
12	SGP2B4	1.14	1.24	1.65	2.33	4.58	11.21
13	SGP3B2	0.82	0.90	1.04	1.49	3.16	8.20
14	SGP3B4	1.33	1.19	1.51	2.07	4.27	12
15	CSP0B0	0.03	0.04	0.05	0.07	0.11	0.18
16	CSP1B2	0.60	0.70	0.82	1.22	2.47	5.02
17	CSP1B4	0.69	0.77	0.91	1.32	2.40	7.30
18	CSP2B2	0.05	0.06	0.07	0.09	0.12	0.19
19	CSP2B4	0.06	0.08	0.09	0.11	0.15	0.24
20	CSP3B2	0.03	0.05	0.06	0.07	0.13	0.22
21	CSP3B4	0.05	0.06	0.07	0.08	0.11	0.17

Table A4.3. Measurements of Viscosity Testing Over Time after Treatment at 125°C

Blend #	Sample I.D.	Time (hrs.)/Viscosity (Pa·s)					
		0	0.5	1	2	4	8
1	OFP0B0	0.11	0.12	0.14	0.18	0.30	0.66
2	OFP1B2	0.14	0.15	0.16	0.18	0.23	0.32
3	OFP1B4	0.09	0.10	0.11	0.13	0.17	0.26
4	OFP2B2	0.39	0.42	0.52	0.68	1.16	2.05
5	OFP2B4	0.39	0.46	0.65	0.99	1.57	3.81
6	OFP3B2	0.17	0.18	0.21	0.29	0.50	0.83
7	OFP3B4	0.12	0.14	0.15	0.19	0.26	0.40
8	SGP0B0	0.24	0.28	0.34	0.47	0.83	2.08
9	SGP1B2	0.25	0.26	0.30	0.40	0.49	0.78
10	SGP1B4	0.17	0.20	0.35	0.70	1.08	1.97
11	SGP2B2	0.06	0.06	0.07	0.09	0.14	0.31
12	SGP2B4	0.09	0.09	0.11	0.12	0.20	0.27
13	SGP3B2	0.08	0.09	0.10	0.12	0.17	0.27
14	SGP3B4	0.10	0.10	0.10	0.12	0.13	0.17
15	CSP0B0	0.11	0.12	0.14	0.21	0.33	0.57
16	CSP1B2	0.52	0.50	0.63	0.78	1.25	2.45
17	CSP1B4	0.17	0.17	0.19	0.23	0.31	0.44
18	CSP2B2	0.41	0.55	0.67	0.92	1.69	3.38
19	CSP2B4	0.82	0.98	1.15	1.52	2.95	4.82
20	CSP3B2	0.24	0.27	0.30	0.37	0.57	0.85
21	CSP3B4	0.11	0.15	0.18	0.18	0.20	0.26

Table A4.4. Measurements of Viscosity Testing Over Time after Treatment at 135°C

Blend #	Sample I.D.	Time (hrs.)/Viscosity (Pa·s)					
		0	0.5	1	2	4	8
1	OFP0B0	0.13	0.15	0.17	0.23	0.40	1.13
2	OFP1B2	0.17	0.17	0.19	0.23	0.30	0.45
3	OFP1B4	0.13	0.13	0.13	0.15	0.19	0.26
4	OFP2B2	0.58	0.71	0.81	0.96	1.31	2.13
5	OFP2B4	0.56	0.64	0.75	1.07	2.55	10.27
6	OFP3B2	0.24	0.27	0.30	0.37	0.52	1.26
7	OFP3B4	0.07	0.09	0.12	0.19	0.25	0.40
8	SGP0B0	0.04	0.06	0.07	0.10	0.15	0.65
9	SGP1B2	0.17	0.20	0.24	0.32	0.51	0.86
10	SGP1B4	0.30	0.34	0.41	0.52	1.20	3.20
11	SGP2B2	0.06	0.08	0.10	0.13	0.20	0.37
12	SGP2B4	0.06	0.08	0.09	0.12	0.18	0.29
13	SGP3B2	0.06	0.07	0.08	0.13	0.17	0.32
14	SGP3B4	0.04	0.05	0.07	0.07	0.11	0.18
15	CSP0B0	0.09	0.13	0.16	0.22	0.36	0.70
16	CSP1B2	0.35	0.43	0.52	0.78	1.30	3.40
17	CSP1B4	0.11	0.14	0.17	0.22	0.33	0.55
18	CSP2B2	0.33	0.46	0.68	1.03	1.84	4.90
19	CSP2B4	0.47	0.60	0.80	1.16	2.53	5.70
20	CSP3B2	0.20	0.24	0.27	0.33	0.46	0.77
21	CSP3B4	0.08	0.09	0.11	0.14	0.20	0.32

APPENDIX B. DATA FOR CHAPTER 5 AND 8

Table B5.1. G*/sin(delta) for Unaged Samples

Blend #	Sample I.D.	Temperature (°C)/G*/sin(delta)					
		40	46	52	58	64	70
0	AAM						
1	OFP0B0	0.094	-	-	-	-	-
2	OFP1B2	0.354	-	-	-	-	-
3	OFP1B4	0.006	-	-	-	-	-
4	OFP2B2	273.567	54.270	14.193	4.050	1.243	0.410
5	OFP2B4	39.193	10.303	3.053	0.967	-	-
6	OFP3B2	6.415	1.973	0.646	-	-	-
7	OFP3B4	7.749	2.399	0.795	-	-	-
8	SGP0B0	2.905	1.058	0.507	-	-	-
9	SGP1B2	3.824	1.274	0.521	-	-	-
10	SGP1B4	13.190	4.203	1.509	0.666	-	-
11	SGP2B2	0.565	-	-	-	-	-
12	SGP2B4	1.140	0.487	-	-	-	-
13	SGP3B2	1.611	0.571	-	-	-	-
14	SGP3B4	1.202	0.454	-	-	-	-
15	CSP0B0	0.271	-	-	-	-	-
16	CSP1B2	25.337	7.869	2.833	1.191	0.601	-
17	CSP1B4	3.447	1.293	0.702	-	-	-
18	CSP2B2	12.840	4.150	1.487	0.667	-	-
19	CSP2B4	39.193	10.303	3.053	0.967	-	-
20	CSP3B2	21.265	6.135	2.082	0.825	-	-
21	CSP3B4	2.203	0.739	-	-	-	-

Table B5.2. G*/sin(delta) for 10min-RTFO Samples

Blend #	Sample I.D.	Temperature (°C)/G*/sin(delta)						
		40	46	52	58	64	70	76
1	OFP0B0	11.953	3.073	0.943	-	-	-	-
2	OFP1B2	30.637	8.798	2.829	1.384	-	-	-
3	OFP1B4	99.977	21.793	5.536	1.612	-	-	-
4	OFP2B2	695.533	158.800	38.327	10.413	3.067	0.967	-
5	OFP2B4	931.9	279.9	81.7	24.98	8.1	2.821	1.149
6	OFP3B2	51.74	18.24	6.468	2.316	0.873	-	-
7	OFP3B4	122.500	39.810	12.420	3.951	1.347	-	-
8	SGP0B0	30.675	9.216	3.023	1.107	-	-	-
9	SGP1B2	67.83	19.83	5.863	1.988	0.753	-	-
10	SGP1B4	53.585	16.235	5.260	2.000	-	-	-
11	SGP2B2	2.767	0.998	-	-	-	-	-
12	SGP2B4	23.345	6.603	2.080	-	-	-	-
13	SGP3B2	10.270	3.330	1.176	-	-	-	-
14	SGP3B4	79.695	28.670	9.595	7.459	1.340	-	-
15	CSP0B0	11.530	3.371	1.208	-	-	-	-
16	CSP1B2	204.550	55.780	17.025	5.881	2.276	1.076	-
17	CSP1B4	15.855	4.863	1.719	-	-	-	-
18	CSP2B2	144.200	37.940	11.445	4.029	1.538	-	-
19	CSP2B4	265.050	66.120	18.945	6.335	2.411	1.018	-
20	CSP3B2	92.465	24.240	7.315	2.610	1.057	-	-
21	CSP3B4	71.125	56.740	37.310	2.160	-	-	-

Table B5.3. G*/sin(delta) for 20min-RTFO Samples

Blend #	Sample I.D.	Temperature (°C)/G*/sin(delta)							
		40	46	52	58	64	70	76	82
1	OFP0B0	7.87	2.37	0.66	-	-	-	-	-
2	OFP1B2	30.64	8.80	2.83	1.38	-	-	-	-
3	OFP1B4	114.71	23.94	5.64	1.29	-	-	-	-
4	OFP2B2	1221	322.37	72.27	18.83	5.44	1.70	-	-
5	OFP2B4	2119.67	683.03	203.20	64.84	19.88	6.64	2.30	0.90
6	OFP3B2	446.60	129.57	37.48	11.13	3.56	1.16	-	-
7	OFP3B4	556.10	144.58	38.09	10.45	3.21	1.14	-	-
8	SGP0B0	90.55	26.63	7.90	2.58	1.01	-	-	-
9	SGP1B2	58.5	20.06	6.928	2.531	0.991	-	-	-
10	SGP1B4	198.40	59.31	17.62	5.71	2.10	0.98	-	-
11	SGP2B2	41.30	11.53	3.74	1.37	-	-	-	-
12	SGP2B4	132.15	33.51	9.19	2.93	1.07	-	-	-
13	SGP3B2	177.97	35.47	9.42	2.88	1.07	-	-	-
14	SGP3B4	78.52	24.79	7.23	2.21	0.84	-	-	-
15	CSP0B0	126.45	33.21	9.48	3.09	1.16	-	-	-
16	CSP1B2	1229.00	321.10	83.48	24.84	8.18	-	-	-
17	CSP1B4	1185.50	304.65	79.35	23.08	7.37	-	-	-
18	CSP2B2	708.75	183.60	51.61	15.54	5.30	2.10		
19	CSP2B4	1673.50	413.55	104.70	30.95	10.10	3.80	1.69	
20	CSP3B2	779.60	179.40	47.21	14.04	4.81	1.86		
21	CSP3B4	87.84	21.40	6.02	2.05				

Table B5.4. G*/sin(delta) for 30min-RTFO Samples

Blend #	Sample I.D.	Temperature (°C)/G*/sin(delta)							
		40	46	52	58	64	70	76	82
1	OFP0B0	187.93	104.77	33.76	8.84	2.32	0.54	-	-
2	OFP1B2	2667.67	527.47	107.10	25.30	6.70	1.97	-	-
3	OFP1B4	1690.00	344.37	68.49	16.54	4.54	1.41	-	-
4	OFP2B2	14173.33	4039.00	871.00	171.57	40.43	10.60	3.02	0.98
5	OFP2B4	6088.00	2243.50	627.95	167.25	46.75	13.60	4.29	1.50
6	OFP3B2	102.7	67.38	30.76	12.23	4.73	1.808	-	-
7	OFP3B4	500.5	132.7	39.89	13.94	5.557	2.643	0.841	-
8	SGP0B0	287.70	93.49	27.74	8.52	2.90	1.36	-	-
9	SGP1B2	223.90	94.61	29.60	9.67	3.34	1.29	-	-
10	SGP1B4	807.10	263.23	78.28	24.24	7.96	2.88	1.22	-
11	SGP2B2	146.03	36.62	10.50	3.47	1.29	-	-	-
12	SGP2B4	249.8	70.3	20.49	6.077	1.953	-	-	-
13	SGP3B2	395.10	130.80	37.93	11.45	3.86	1.44	-	-
14	SGP3B4	331.23	81.24	20.11	5.75	1.99	-	-	-
15	CSP0B0	145.97	38.03	10.97	3.60	1.33	-	-	-
16	CSP1B2	1009.63	278.97	75.86	22.86	7.60	2.89	1.31	-
17	CSP1B4	1095.50	297.45	79.19	23.18	7.48	2.71	1.12	-
18	CSP2B2	3538.00	917.10	229.15	66.78	20.53	6.98	2.63	1.21
19	CSP2B4	9889.00	2722.00	693.20	180.45	52.95	16.94	6.11	2.48
20	CSP3B2	2232.50	613.35	145.20	39.24	11.97	4.11	1.64	
21	CSP3B4	633.40	140.05	34.74	10.02	3.29	1.24		

APPENDIX C. DATA FOR CHAPTER 7

Table C7.1. Viscosity Measurements for AAM

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
80	25567	32083	29167	28395				
90	13000	12500	11542	11187	10942	10938		
100	6000	5750	5625	5271	5175	5113		
110	3000	3000	3000	2917	2750	2700	2687	2550
120	1500	1500	1500	1459	1400	1362	1355	1365
130	1000	1000	1000	1063	1000	963	933	920
140	500	750	625	625	600	575	555	546
150	0	417	375	375	350	350	330	327
160	0	250	250	250	275	263	255	248

Table C7.2. Viscosity Measurements for AAD

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
80	13500	13500	13708	13832				
90	6500	6500	6500	6400	6325	6350		
100	3000	3000	2917	2875	2867	2858		
110	1500	1500	1500	1500	1475	1475	1470	1350
120	1000	1000	875	875	900	875	875	868
130	500	500	458	500	475	484	480	480
140	0	250	250	313	325	313	315	318
150	0	83	167	188	200	205	210	207
160	0	0	125	125	150	150	150	150

Table C7.3. Viscosity Measurements for Blend 1

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
40	10500	8750	8125	7708	7308	7250		
50	3000	2500	2375	2313	2275	2246	2253	2246
60	1500	1167	875	875	833	750	700	683
70	500	250	292	334	325	334	323	318
80	250	250	125	125	167	171	164	163
90	0	0	0	84	100	100	100	97
100								63
110								44

Table C7.4. Viscosity Measurements for Blend 2

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
40	40000	37750	35750	34104	33083	33083		
50	11833	11417	12375	11250	10150	9575		
60	5333	5833	5500	5000	4308	3900	3573	3400
70	2500	2250	3117	2800	2275	1975	1650	1515
80	1500	1283	1583	1440	1133	942	805	720
90	833	5167	625	633	558	488	402	365
100		250	250	250	225	204	182	170
110		250	125	125	150	138	125	113
120		250	125	125	150	100	90	87

Table C7.5. Viscosity Measurements for Blend 3

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
40	32000	37333	30000	28687	27917	27917		
50	16500	14750	12250	10063	8475	7693		
60	12000	8750	6375	4850	3617	3130	2720	2600
70	8333	5833	4067	2904	2000	1579	1267	1137
80	6167	4417	2958	2425	1583	1125	775	660
90	2750	2000	1792	1479	1308	430	375	203
100		250	125	125	133	134	123	118
110			125	63	75	75	65	63
120			125	63	75	50	50	44

Table C7.6. Viscosity Measurements for Blend 4

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
80	30667	28250	26958	26229				
90	10500	9417	9500	8917	8667	8516		
100	3167	3917	3750	3709	3525	3350	3165	3100
110	2000	2083	1958	1792	1617	1500	1385	1325
120	1000	667	708	688	658	625	590	578
130		417	375	375	400	379	355	346
140		417	250	292	275	263	240	234
150		250	125	188	183	175	162	155
160			125	125	125	125	120	114

Table C7.7. Viscosity Measurements for Blend 5

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	105000	87000	75000					
80	18500	15667	14125	13083	12300	12100		
90	6000	4500	4250	4146	4000	3929	3868	
100	2500	2250	2375	2375	2258	2135	2003	1878
110	500	750	750	750	750	746	720	700
120	500	500	500	500	500	488	465	445
130		500	375	375	350	325	295	279
140		250	375	375	375	325	270	228
150		0	125	125	175	175	170	160
160			125	125	175	162	165	145

Table C7.8. Viscosity Measurements for Blend 6

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	19500	17000	15000	14046	12592	12017		
80	6000	5500	5208	4896	4692	4367	4102	
90	2000	1750	1667	1709	1633	1559	1528	1493
100	1000	1000	1000	938	750	725	675	660
110	500	500	500	500	450	450	412	392
120	0	250	125	125	150	163	165	164
130	0	500	375	313	275	125	125	115
140	0	0	0	63	100	88	85	85

Table C7.9. Viscosity Measurements for Blend 7

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	22000	20083	17625	15771	15017	15017		
80	5833	5083	5000	4938	4683	4525	4420	
90	2000	1750	1875	1938	1867	1800	1720	1677
100	1000	1000	1250	1313	1208	1100	1000	858
110	500	750	1000	1000	875	800	693	618
120	500	500	250	250	250	238	225	210
130	0	0	125	125	125	113	115	110
140	0	0	0	63	75	75	75	73

Table C7.10. Viscosity Measurements for Blend 8

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	9000	10000	9042	8000	7417	6950		
80	13833	5583	5375	5896	4267	3533	3100	
90	5500	4500	3000	2000	1850	1667	1467	
100	1500	1500	1250	1188	1000	850	743	693
110	1500	1000	750	688	575	488	405	370
120	1000	750	750	650	550	455	390	300

Table C7.11. Viscosity Measurements for Blend 9

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	13500	12583	10875	9500	8533	8050		
80	7500	6750	5500	4750	4150	3825	3348	
90	3000	2500	2375	2000	1700	1567	1402	
100	1500	1250	1250	1084	892	779	690	640
110	500	500	375	375	400	400	360	340
120	0	250	250	250	275	263	250	238
130	0	250	250	200	200	175	175	153

Table C7.12. Viscosity Measurements for Blend 10

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	28000	26000	23500	22063	22025			
80	15667	13833	12250	11313	10800	10300		
90	7500	5000	4875	4688	3850	3575	3285	
100	1000	1500	1375	1375	1275	1175	1115	1075
110	1000	1000	1000	1000	900	825	740	703
120	0	625	625	625	575	525	470	440
130	0	0	250	250	250	288	270	260
140	0	0	0	175	175	175	170	170

Table C7.13. Viscosity Measurements for Blend 11

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
50	24667	20000	18875	18000	16400			
60	13000	9000	6625	6375	6000	5737		
70	3500	3000	3000	2750	2425	2254	2113	1900
80	2500	2000	1625	1438	1225	1100	935	883
90	1000	1000	1000	1000	850	750	630	575
100	500	500	500	375	300	263	230	208
110	0	0	125	125	125	125	125	115
120	0	0	0	65	65	65	65	65
130	0	0	0	0	50	50	50	50
140	0	0	0	0	50	50	45	40

Table C7.14. Viscosity Measurements for Blend 12

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
50	40500	35250	30000	26500				
60	21500	17833	14750	8500	8100	8000		
70	10500	6500	4500	4000	3350	3150	2995	
80	4000	3000	2500	2313	1750	1575	1440	1360
90	4000	2750	2000	1600	1517	925	730	655
100	3500	2250	1750	1250	950	750	510	430
110	500	250	250	188	175	175	155	140
120	0	250	125	125	125	113	100	95
130	0	250	125	125	75	75	75	68
140	0	0	125	125	75	75	70	60

Table C7.15. Viscosity Measurements for Blend 13

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
50	57000	53000	47500	44000				
60	23000	20250	18875	14421	13500			
70	14500	12000	10000	6000	4900	4550	4100	
80	6500	5500	4000	3500	2000	1800	1620	1530
90	5000	3250	2500	2250	1325	1075	870	805
100	2000	2000	1500	1250	900	625	470	413
110	1000	1000	250	250	225	200	185	178
120	0	0	125	125	125	125	125	125
130	0	0	0	100	100	90	90	83
140	0	0	0	0	50	50	50	50

Table C7.16. Viscosity Measurements for Blend 14

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
50	35000	32750	30000	28250				
60	16000	14333	12167	11000	10000	9500		
70	5000	4250	3625	3375	2950	2700	2350	
80	1750	1750	1500	1313	1125	1075	1025	998
90	1000	750	625	625	575	550	505	483
100	1000	750	625	500	425	400	330	300
110	500	500	500	313	250	163	145	140
120	0	0	125	100	90	90	85	80
130	0	0	0	63	50	50	50	50
140	0	0	0	63	45	45	45	45

Table C7.17. Viscosity Measurements for Blend 15

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
40	49500	40500	34125	30500				
50	21000	16500	12750	10320	8483	7325		
60	4000	3500	3500	3313	3150	3021	2855	
70	2000	1750	1500	1500	1475	1413	1350	1300
80	1000	750	750	688	675	638	615	580
90	500	375	375	375	350	325	310	295
100	0	250	250	200	200	188	180	175
110	0	0	125	125	125	113	110	110
120	0	0	0	75	75	75	70	70

Table C7.18. Viscosity Measurements for Blend 16

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	39000	37250	36000	34896				
80	17000	15583	14833	14063	13292			
90	9000	8000	7625	7001	6250	5600		
100	3500	3167	2750	2563	2350	2188	2030	1951
110	2000	1500	1500	1500	1408	1338	1235	1169
120	1000	750	750	750	700	663	610	575
130	500	500	500	500	575	525	460	418
140	500	500	500	500	450	400	330	285

Table C7.19. Viscosity Measurements for Blend 17

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	19000	13000	12500	8000	7600	6800		
80	6000	4750	4000	3688	3050	2850	2660	
90	4000	3750	3125	2625	1900	1700	1410	1320
100	1000	1000	1000	875	750	650	550	510
110	500	500	500	500	450	400	320	285
120	0	250	250	250	225	213	195	183
130	0	0	150	150	150	150	135	128
140	0	0	0	125	100	100	90	88

Table C7.20. Viscosity Measurements for Blend 18

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	50167	40500	37333	36521				
80	24000	16500	14000	12750	12058			
90	7000	6500	6125	5542	5125	4904	4748	
100	3000	3250	3125	2813	2500	2300	2115	2035
110	1500	1500	1500	1375	1225	1100	1050	1028
120	1000	1000	1000	875	875	800	730	695
130	500	500	500	500	500	488	425	389
140	500	500	375	375	325	300	270	250

Table C7.21. Viscosity Measurements for Blend 19

Temperature	Viscosity (cP)/Shear Rate (rpm)							
(°C)	0.5	1.0	2.0	4.0	10.0	20.0	50.0	100.0
70	68000	62000	59000	55000				
80	52000	42000	40000	38208				
90	22500	21750	20000	16437	15475			
100	9500	9500	8100	7500	7092	6670		
110	4000	4000	3750	3500	3300	3100	2720	
120	2000	2000	1875	1750	1625	1475	1375	1290
130	1000	1000	1000	1000	900	800	750	710
140	500	500	500	500	500	500	470	438

Table C7.22. Viscosity Measurements for Blend 20

Temperature (°C)	Viscosity (cP)/Shear Rate (rpm)							
	0.5	**1.0**	**2.0**	**4.0**	**10.0**	**20.0**	**50.0**	**100.0**
70	44000	40000	32125	30083				
80	15667	13833	13000	12000	11342			
90	5000	4750	4625	3846	3558	3400	3322	
100	2000	2000	2000	2000	1725	1638	1567	1517
110	1000	1000	1000	1000	1000	900	835	786
120	500	500	500	500	500	438	400	380
130	0	250	250	250	250	250	243	223
140	0	250	250	250	175	175	175	160

Table C7.23. Viscosity Measurements for Blend 21

Temperature (°C)	Viscosity (cP)/Shear Rate (rpm)							
	0.5	**1.0**	**2.0**	**4.0**	**10.0**	**20.0**	**50.0**	**100.0**
70	11500	10000	9500	8238				
80	4500	3750	3000	3000	2475			
90	1500	1250	1250	1250	1200	1100	1045	
100	750	750	750	750	750	700	630	600
110	0	500	500	500	500	500	460	412
120	0	250	200	188	175	163	150	145
130	0	0	0	100	100	100	100	100
140	0	0	0	0	0	100	90	90

Table C7.24. Shear Susceptibility Values for AAM

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	**0.00**	**0.30**	**0.60**	**1.00**	**1.30**	**1.70**	**2.00**	
80	4.41	4.51	4.46	4.45					0.03
90	4.11	4.10	4.06	4.05	4.04	4.04			-0.05
100	3.78	3.76	3.75	3.72	3.71	3.71			-0.05
110	3.48	3.48	3.48	3.46	3.44	3.43	3.43		-0.03
120	3.18	3.18	3.18	3.16	3.15	3.13	3.13	3.14	-0.02
130	3.00	3.00	3.00	3.03	3.00	2.98	2.97	2.96	-0.02
140		2.88	2.80	2.80	2.78	2.76	2.74	2.74	-0.06
150			2.57	2.57	2.54	2.54	2.52	2.51	-0.04
160			2.40	2.40	2.44	2.42	2.41	2.39	0.00

Table C7.25. Shear Susceptibility Values for AAD

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
80	4.13	4.13	4.14	4.14					0.01
90	3.81	3.81	3.81	3.81	3.80	3.80			-0.01
100	3.48	3.48	3.46	3.46	3.46	3.46			-0.01
110	3.18	3.18	3.18	3.18	3.17	3.17	3.17		-0.01
120	3.00	3.00	2.94	2.94	2.95	2.94	2.94	2.94	-0.02
130	2.70	2.70	2.66	2.70	2.68	2.68	2.68	2.68	-0.01
140		2.40	2.40	2.50	2.51	2.50	2.50	2.50	0.05
150			2.22	2.27	2.30	2.31	2.32	2.32	0.05
160			2.10	2.10	2.18	2.18	2.18	2.18	0.05

Table C7.26. Shear Susceptibility Values for Blend 1

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
40	4.02	3.94	3.91	3.89	3.86	3.86			**-0.09**
50	3.48	3.40	3.38	3.36	3.36	3.35	3.35	3.35	**-0.04**
60	3.18	3.07	2.94	2.94	2.92	2.88	2.85	2.83	**-0.13**
70	2.70	2.40	2.46	2.52	2.51	2.52	2.51	2.50	**-0.02**
80	2.40	2.40	2.10	2.10	2.22	2.23	2.22	2.21	**-0.06**
90				1.92	2.00	2.00	2.00	1.99	**0.04**

Table C7.27. Shear Susceptibility Values for Blend 2

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
40	4.60	4.58	4.55	4.53	4.52	4.52			**-0.06**
50	4.07	4.06	4.09	4.05	4.01	3.98			**-0.06**
60	3.73	3.77	3.74	3.70	3.63	3.59	3.55		**-0.11**
70	3.40	3.35	3.49	3.45	3.36	3.30	3.22	3.18	**-0.11**
80	3.18	3.11	3.20	3.16	3.05	2.97	2.91	2.86	**-0.15**
90	2.92	3.71	2.80	2.80	2.75	2.69	2.60	2.56	**-0.30**
100		2.40	2.40	2.40	2.35	2.31	2.26	2.23	**-0.09**
110		2.40	2.10	2.10	2.18	2.14	2.10	2.05	**-0.10**
120		2.40	2.10	2.10	2.18	2.00	1.95	1.94	**-0.18**

Table C7.28. Shear Susceptibility Values for Blend 3

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	**0.00**	**0.30**	**0.60**	**1.00**	**1.30**	**1.70**	**2.00**	
40	4.51	4.57	4.48	4.46	4.45	4.45			**-0.06**
50	4.22	4.17	4.09	4.00	3.93	3.89			**-0.22**
60	4.08	3.94	3.80	3.69	3.56	3.50	3.43		**-0.33**
70	3.92	3.77	3.61	3.46	3.30	3.20	3.10	3.06	**-0.38**
80	3.79	3.65	3.47	3.38	3.20	3.05	2.89	2.82	**-0.43**
90	3.44	3.30	3.25	3.17	3.12	2.63	2.57	2.31	**-0.48**
100		2.40	2.10	2.10	2.12	2.13	2.09	2.07	**-0.10**
110			2.10	1.80	1.88	1.88	1.81	1.80	**-0.12**
120			2.10	1.80	1.88	1.70	1.70	1.64	**-0.22**

Table C7.29. Shear Susceptibility Values for Blend 4

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	**0.00**	**0.30**	**0.60**	**1.00**	**1.30**	**1.70**	**2.00**	
80	4.49	4.45	4.43	4.42					**-0.07**
90	4.02	3.97	3.98	3.95	3.94	3.93			**-0.05**
100	3.50	3.59	3.57	3.57	3.55	3.53	3.50		**-0.02**
110	3.30	3.32	3.29	3.25	3.21	3.18	3.14	3.12	**-0.09**
120	3.00	2.82	2.85	2.84	2.82	2.80	2.77	2.76	**-0.07**
130		2.62	2.57	2.57	2.60	2.58	2.55	2.54	**-0.03**
140		2.62	2.40	2.47	2.44	2.42	2.38	2.37	**-0.09**
150		2.40	2.10	2.27	2.26	2.24	2.21	2.19	**-0.04**
160			2.10	2.10	2.10	2.10	2.08	2.06	**-0.02**

Table C7.30. Shear Susceptibility Values for Blend 5

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	**0.00**	**0.30**	**0.60**	**1.00**	**1.30**	**1.70**	**2.00**	
80	4.27	4.19	4.15	4.12					**-0.16**
90	3.78	3.65	3.63	3.62	3.60	3.59			**-0.09**
100	3.40	3.35	3.38	3.38	3.35	3.33	3.30		**-0.04**
110	2.70	2.88	2.88	2.88	2.88	2.87	2.86	2.85	**0.03**
120	2.70	2.70	2.70	2.70	2.70	2.69	2.67	2.65	**-0.02**
130		2.70	2.57	2.57	2.54	2.51	2.47	2.45	**-0.11**
140		2.40	2.57	2.57	2.57	2.51	2.43	2.36	**-0.05**
150			2.10	2.10	2.24	2.24	2.23	2.20	**0.08**
160			2.10	2.10	2.24	2.21	2.22	2.16	**0.06**

Table C7.31. Shear Susceptibility Values for Blend 6

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.29	4.23	4.18	4.15	4.10	4.08			**-0.13**
80	3.78	3.74	3.72	3.69	3.67	3.64	3.61		**-0.08**
90	3.30	3.24	3.22	3.23	3.21	3.19	3.18	3.17	**-0.05**
100	3.00	3.00	3.00	2.97	2.88	2.86	2.83	2.82	**-0.09**
110	2.70	2.70	2.70	2.70	2.65	2.65	2.61	2.59	**-0.05**
120		2.40	2.10	2.10	2.18	2.21	2.22	2.22	**-0.02**
130		2.70	2.57	2.50	2.44	2.10	2.10	2.06	**-0.34**
140				1.80	2.00	1.94	1.93	1.93	**0.06**

Table C7.32. Shear Susceptibility Values for Blend 7

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.34	4.30	4.25	4.20	4.18	4.18			**-0.11**
80	3.77	3.71	3.70	3.69	3.67	3.66	3.65		**-0.05**
90	3.30	3.24	3.27	3.29	3.27	3.26	3.24	3.22	**-0.02**
100	3.00	3.00	3.10	3.12	3.08	3.04	3.00	2.93	**-0.03**
110	2.70	2.88	3.00	3.00	2.94	2.90	2.84	2.79	**0.00**
120		2.70	2.40	2.40	2.40	2.38	2.35	2.32	**-0.13**
130			2.10	2.10	2.10	2.05	2.06	2.04	**-0.04**
140				1.80	1.88	1.88	1.88	1.86	**0.04**

Table C7.33. Shear Susceptibility Values for Blend 8

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	3.95	4.00	3.96	3.90	3.87	3.84			**-0.11**
80	4.14	3.75	3.73	3.77	3.63	3.55	3.49		**-0.20**
90	3.74	3.65	3.48	3.30	3.27	3.22	3.17		**-0.20**
100	3.18	3.18	3.10	3.07	3.00	2.93	2.87	2.84	**-0.16**
110	3.18	3.00	2.88	2.84	2.76	2.69	2.61	2.57	**-0.19**
120		2.88	2.88	2.81	2.74	2.66	2.59	2.48	**-0.23**
130			3.55	3.42	2.99	2.81	2.78	2.30	**-0.69**

Table C7.34. Shear Susceptibility Values for Blend 9

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.13	4.10	4.04	3.98	3.93	3.91			**-0.13**
80	3.88	3.83	3.74	3.68	3.62	3.58	3.52		**-0.15**
90	3.48	3.40	3.38	3.30	3.23	3.19	3.15		**-0.16**
100	3.18	3.10	3.10	3.03	2.95	2.89	2.84	2.81	**-0.17**
110	2.70	2.70	2.57	2.57	2.60	2.60	2.56	2.53	**-0.02**
120		2.40	2.40	2.40	2.44	2.42	2.40	2.38	**-0.01**
130			2.40	2.30	2.30	2.24	2.24	2.18	**-0.11**

Table C7.35. Shear Susceptibility Values for Blend 10

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.45	4.41	4.37	4.34	4.34				**-0.04**
80	4.19	4.14	4.09	4.05	4.03	4.01			**-0.07**
90	3.88	3.70	3.69	3.67	3.59	3.55	3.52		**-0.13**
100	3.00	3.18	3.14	3.14	3.11	3.07	3.05	3.03	**-0.07**
110	3.00	3.00	3.00	3.00	2.95	2.92	2.87	2.85	**-0.10**
120		2.80	2.80	2.80	2.76	2.72	2.67	2.64	**-0.10**
130			2.40	2.40	2.40	2.46	2.43	2.41	**0.02**

Table C7.36. Shear Susceptibility Values for Blend 11

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
50	4.39	4.30	4.28	4.26	4.21				**-0.09**
60	4.11	3.95	3.82	3.80	3.78	3.76			**-0.06**
70	3.54	3.48	3.48	3.44	3.38	3.35	3.32	3.28	**-0.11**
80	3.40	3.30	3.21	3.16	3.09	3.04	2.97	2.95	**-0.16**
90	3.00	3.00	3.00	3.00	2.93	2.88	2.80	2.76	**-0.15**
100	2.70	2.70	2.70	2.57	2.48	2.42	2.36	2.32	**-0.21**
110			2.10	2.10	2.10	2.10	2.10	2.06	**-0.01**
120				1.81	1.81	1.81	1.81	1.81	**0.00**
130					1.70	1.70	1.70	1.70	**0.00**
140					1.70	1.70	1.65	1.60	**-0.10**

Table C7.37. Shear Susceptibility Values for Blend 12

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
50	4.61	4.55	4.48	4.42					**-0.18**
60	4.33	4.25	4.17	3.93	3.91	3.90			**-0.24**
70	4.02	3.81	3.65	3.60	3.53	3.50	3.48		**-0.13**
80	3.60	3.48	3.40	3.36	3.24	3.20	3.16	3.13	**-0.16**
90	3.60	3.44	3.30	3.20	3.18	2.97	2.86	2.82	**-0.30**
100	3.54	3.35	3.24	3.10	2.98	2.88	2.71	2.63	**-0.36**
110	2.70	2.40	2.40	2.27	2.24	2.24	2.19	2.15	**-0.12**
120		2.40	2.10	2.10	2.10	2.05	2.00	1.98	**-0.08**
130		2.40	2.10	2.10	1.88	1.88	1.88	1.83	**-0.17**
140			2.10	2.10	1.88	1.88	1.85	1.78	**-0.20**

Table C7.38. Shear Susceptibility Values for Blend 13

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
50	4.76	4.72	4.68	4.64					**-0.11**
60	4.36	4.31	4.28	4.16	4.13				**-0.20**
70	4.16	4.08	4.00	3.78	3.69	3.66	3.61		**-0.25**
80	3.81	3.74	3.60	3.54	3.30	3.26	3.21	3.18	**-0.26**
90	3.70	3.51	3.40	3.35	3.12	3.03	2.94	2.91	**-0.31**
100	3.30	3.30	3.18	3.10	2.95	2.80	2.67	2.62	**-0.35**
110	3.00	3.00	2.40	2.40	2.35	2.30	2.27	2.25	**-0.10**
120			2.10	2.10	2.10	2.10	2.10	2.10	**0.00**
130				2.00	2.00	1.95	1.95	1.92	**-0.06**
140					1.70	1.70	1.70	1.70	**0.00**

Table C7.39. Shear Susceptibility Values for Blend 14

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
50	4.54	4.52	4.48	4.45					**-0.09**
60	4.20	4.16	4.09	4.04	4.00	3.98			**-0.11**
70	3.70	3.63	3.56	3.53	3.47	3.43	3.37		**-0.14**
80	3.24	3.24	3.18	3.12	3.05	3.03	3.01	3.00	**-0.10**
90	3.00	2.88	2.80	2.80	2.76	2.74	2.70	2.68	**-0.07**
100	3.00	2.88	2.80	2.70	2.63	2.60	2.52	2.48	**-0.18**
110	2.70	2.70	2.70	2.50	2.40	2.21	2.16	2.15	**-0.33**
120			2.10	2.00	1.95	1.95	1.93	1.90	**-0.10**
130				1.80	1.70	1.70	1.70	1.70	**-0.06**
140				1.80	1.65	1.65	1.65	1.65	**-0.09**

Table C7.40. Shear Susceptibility Values for Blend 15

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
40	4.69	4.61	4.53	4.48					**-0.16**
50	4.32	4.22	4.11	4.01	3.93	3.86			**-0.24**
60	3.60	3.54	3.54	3.52	3.50	3.48			**-0.06**
70	3.30	3.24	3.18	3.18	3.17	3.15	3.13		**-0.03**
80	3.00	2.88	2.88	2.84	2.83	2.80	2.79	2.76	**-0.06**
90	2.70	2.57	2.57	2.57	2.54	2.51	2.49	2.47	**-0.07**
100		2.40	2.40	2.30	2.30	2.27	2.26	2.24	**-0.08**
110			2.10	2.10	2.10	2.05	2.04	2.04	**-0.04**
120				1.88	1.88	1.88	1.85	1.85	**-0.03**

Table C7.41. Shear Susceptibility Values for Blend 16

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.59	4.57	4.56	4.54					**-0.04**
80	4.23	4.19	4.17	4.15	4.12				**-0.07**
90	3.95	3.90	3.88	3.85	3.80	3.75			**-0.13**
100	3.54	3.50	3.44	3.41	3.37	3.34	3.31	3.29	**-0.09**
110	3.30	3.18	3.18	3.18	3.15	3.13	3.09	3.07	**-0.07**
120	3.00	2.88	2.88	2.88	2.85	2.82	2.79	2.76	**-0.07**
130	2.70	2.70	2.70	2.70	2.76	2.72	2.66	2.62	**-0.04**
140	2.70	2.70	2.70	2.70	2.65	2.60	2.52	2.45	**-0.15**

Table C7.42. Shear Susceptibility Values for Blend 17

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.28	4.11	4.10	3.90	3.88	3.83			**-0.24**
80	3.78	3.68	3.60	3.57	3.48	3.45	3.42		**-0.13**
90	3.60	3.57	3.49	3.42	3.28	3.23	3.15	3.12	**-0.23**
100	3.00	3.00	3.00	2.94	2.88	2.81	2.74	2.71	**-0.18**
110	2.70	2.70	2.70	2.70	2.65	2.60	2.51	2.45	**-0.15**
120		2.40	2.40	2.40	2.35	2.33	2.29	2.26	**-0.09**
130			2.18	2.18	2.18	2.18	2.13	2.11	**-0.04**
140				2.10	2.00	2.00	1.95	1.94	**-0.10**

Table C7.43. Shear Susceptibility Values for Blend 18

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.70	4.61	4.57	4.56					**-0.03**
80	4.38	4.22	4.15	4.11	4.08				**-0.09**
90	3.85	3.81	3.79	3.74	3.71	3.69	3.68		**-0.08**
100	3.48	3.51	3.49	3.45	3.40	3.36	3.33	3.31	**-0.11**
110	3.18	3.18	3.18	3.14	3.09	3.04	3.02	3.01	**-0.10**
120	3.00	3.00	3.00	2.94	2.94	2.90	2.86	2.84	**-0.09**
130	2.70	2.70	2.70	2.70	2.70	2.69	2.63	2.59	**-0.06**
140	2.70	2.70	2.57	2.57	2.51	2.48	2.43	2.40	**-0.11**

Table C7.44. Shear Susceptibility Values for Blend 19

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.83	4.79	4.77	4.74					**-0.10**
80	4.72	4.62	4.60	4.58					**-0.07**
90	4.35	4.34	4.30	4.22	4.19				**-0.15**
100	3.98	3.98	3.91	3.88	3.85	3.82			**-0.08**
110	3.60	3.60	3.57	3.54	3.52	3.49	3.43		**-0.10**
120	3.30	3.30	3.27	3.24	3.21	3.17	3.14	3.11	**-0.10**
130	3.00	3.00	3.00	3.00	2.95	2.90	2.88	2.85	**-0.10**
140	2.70	2.70	2.70	2.70	2.70	2.70	2.67	2.64	**-0.03**

Table C7.45. Shear Susceptibility Values for Blend 20

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	0.00	0.30	0.60	1.00	1.30	1.70	2.00	
70	4.64	4.60	4.51	4.48					**-0.09**
80	4.19	4.14	4.11	4.08	4.05				**-0.08**
90	3.70	3.68	3.67	3.59	3.55	3.53	3.52		**-0.10**
100	3.30	3.30	3.30	3.30	3.24	3.21	3.19	3.18	**-0.08**
110	3.00	3.00	3.00	3.00	3.00	2.95	2.92	2.90	**-0.07**
120	2.70	2.70	2.70	2.70	2.70	2.64	2.60	2.58	**-0.08**
130		2.40	2.40	2.40	2.40	2.40	2.39	2.35	**-0.02**
140		2.40	2.40	2.40	2.24	2.24	2.24	2.20	**-0.12**

Table C7.46. Shear Susceptibility Values for Blend 21

Temperature (°C)	Log(Viscosity)/Log (Shear Rate)								Shear Susceptibility Values "SS"
	-0.30	**0.00**	**0.30**	**0.60**	**1.00**	**1.30**	**1.70**	**2.00**	
70	4.06	4.00	3.98	3.92					**-0.21**
80	3.65	3.57	3.48	3.48	3.39				**-0.12**
90	3.18	3.10	3.10	3.10	3.08	3.04	3.02		**-0.06**
100	2.88	2.88	2.88	2.88	2.88	2.85	2.80	2.78	**-0.06**
110		2.70	2.70	2.70	2.70	2.70	2.66	2.61	**-0.04**
120		2.40	2.30	2.27	2.24	2.21	2.18	2.16	**-0.08**
130				2.00	2.00	2.00	2.00	2.00	**0.00**
140						2.00	1.95	1.95	**-0.07**

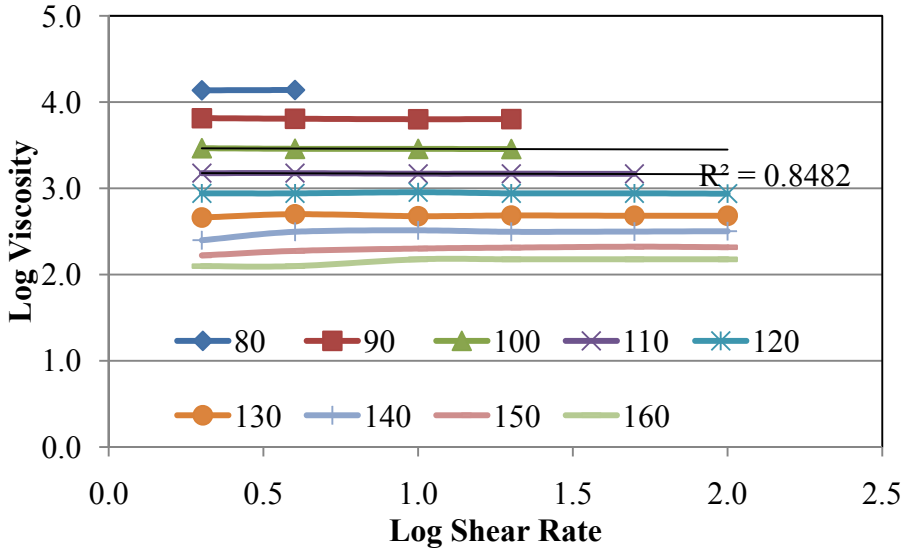

Figure C7.1 Log Viscosity versus Log Shear Rate for AAD

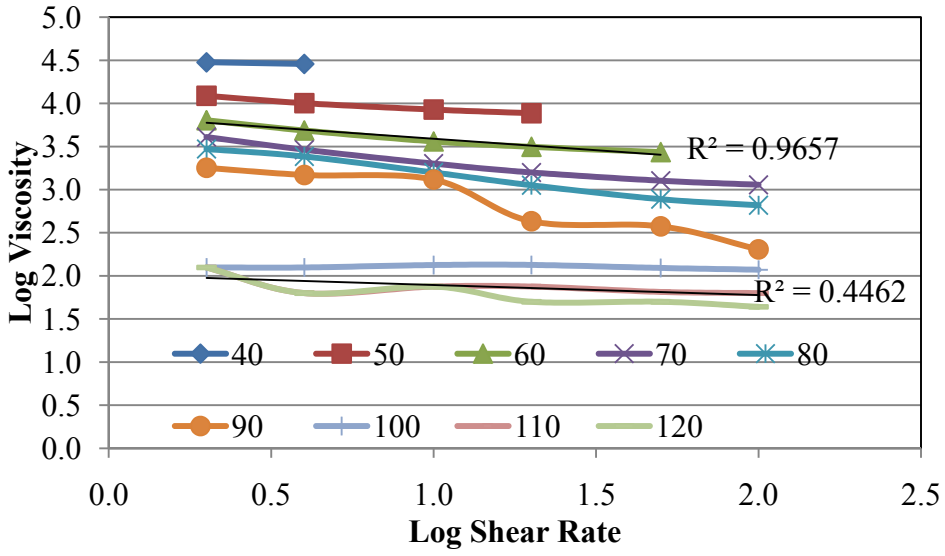

Figure C7.2 Log Viscosity versus Log Shear Rate for Blend 3

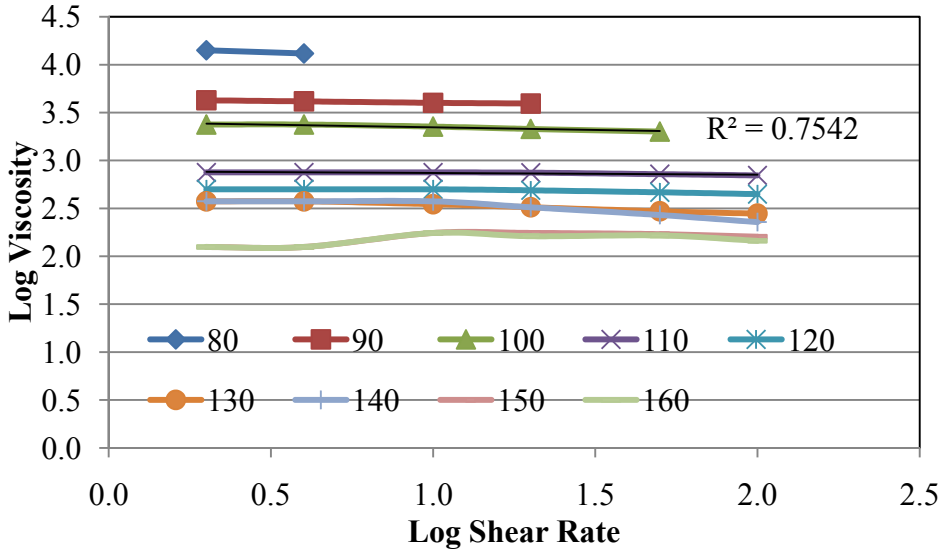

Figure C7.3. Log Viscosity versus Log Shear Rate for Blend 5

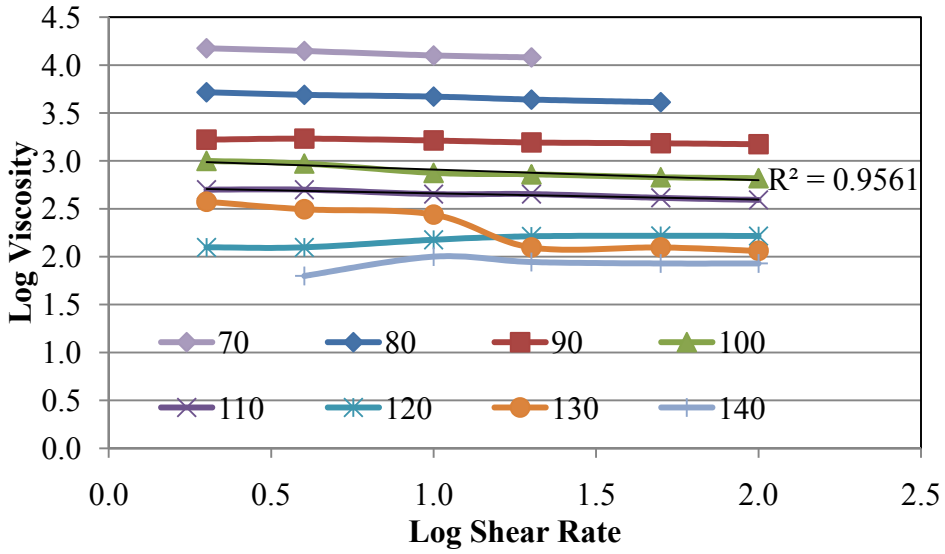

Figure C7.4. Log Viscosity versus Log Shear Rate for Blend 6

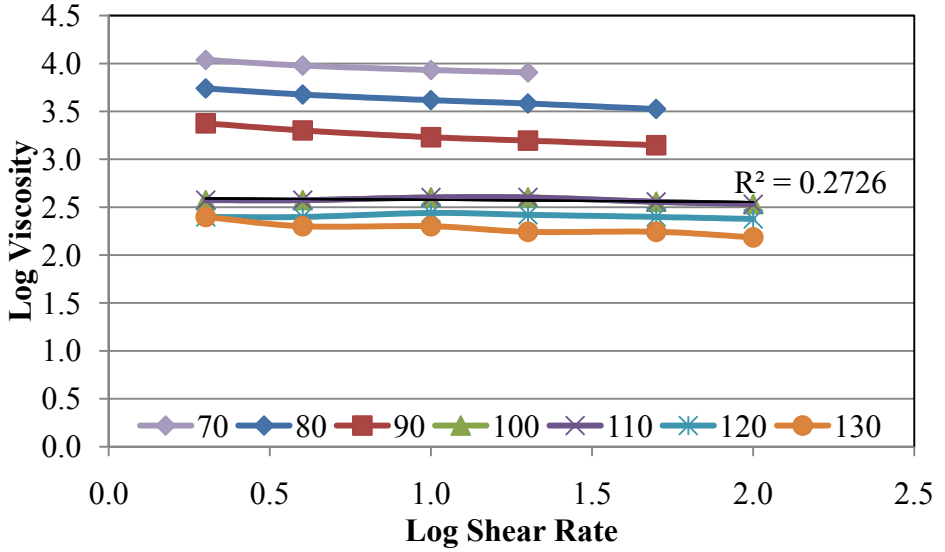

Figure C7.5. Log Viscosity versus Log Shear Rate for Blend 9

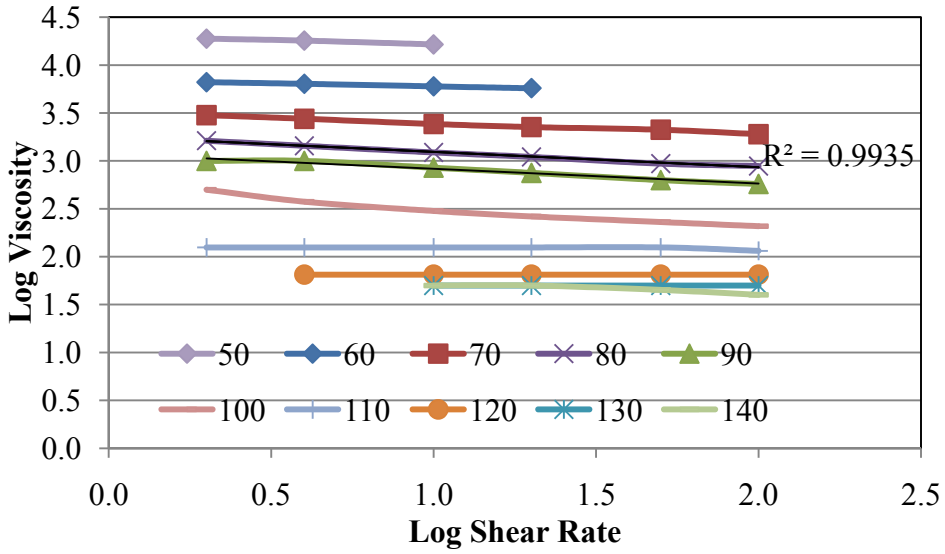

Figure C7.6. Log Viscosity versus Log Shear Rate for Blend 11

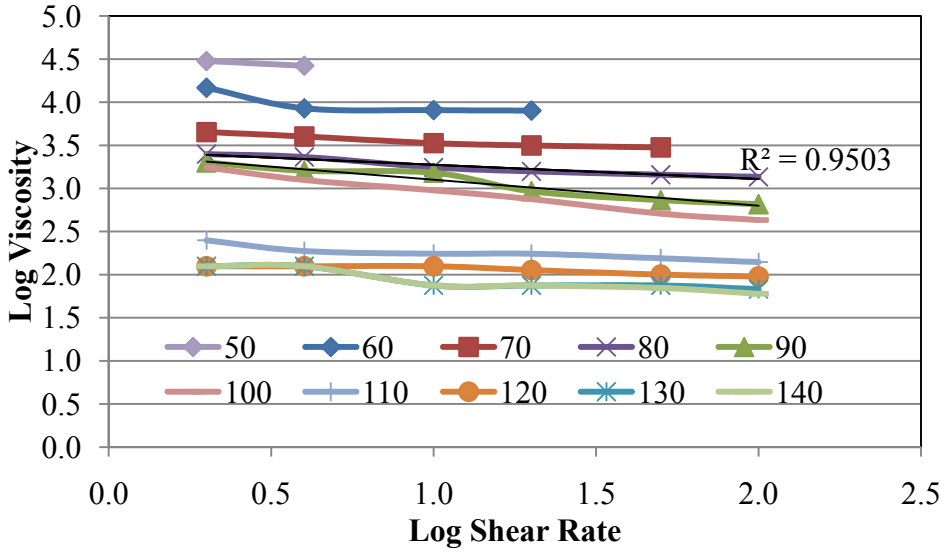

Figure C7.7. Log Viscosity versus Log Shear Rate for Blend 12

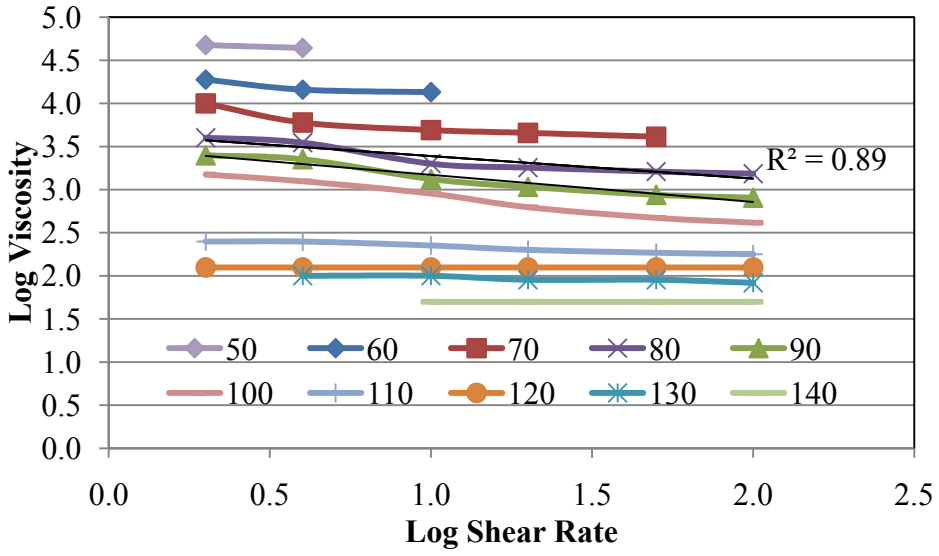

Figure C7.8. Log Viscosity versus Log Shear Rate for Blend 13

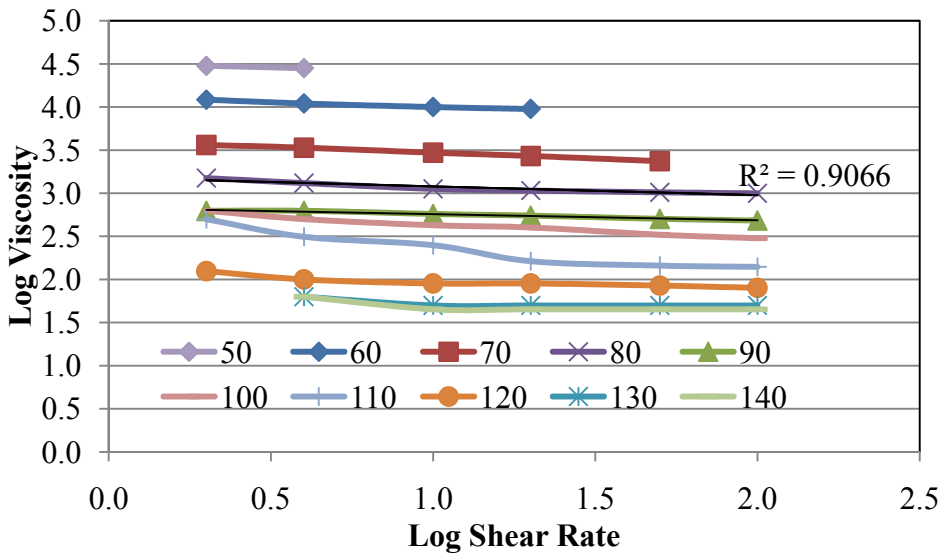

Figure C7.9. Log Viscosity versus Log Shear Rate for Blend 14

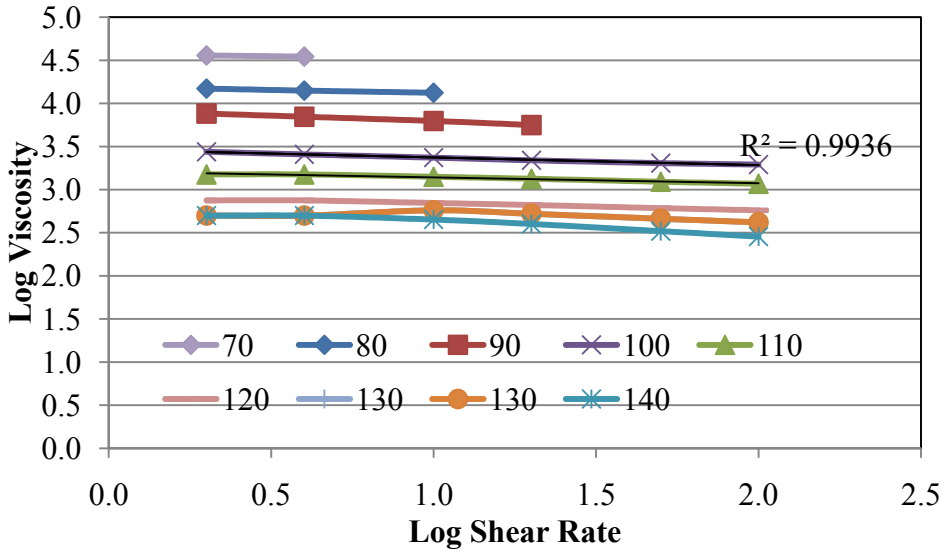

Figure C7.10. Log Viscosity versus Log Shear Rate for Blend 16

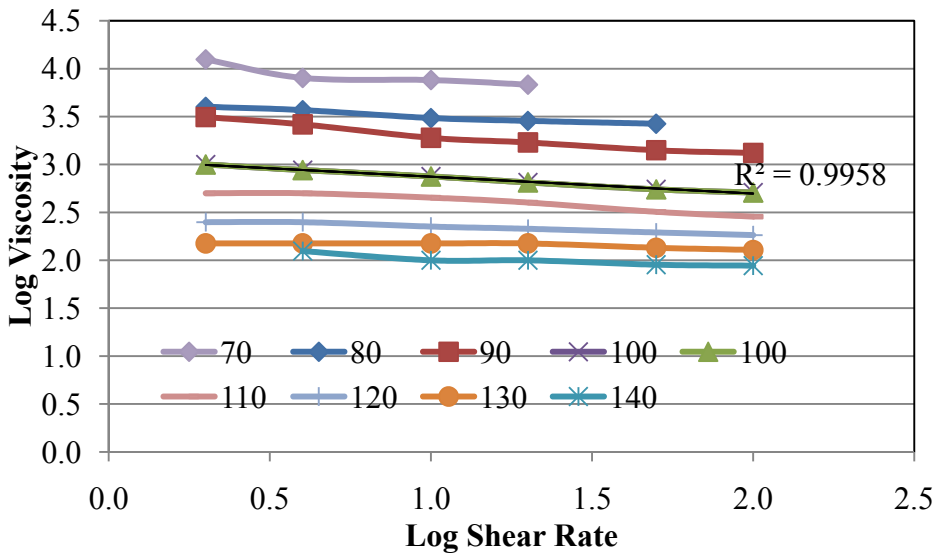

Figure C7.11. Log Viscosity versus Log Shear Rate for Blend 17

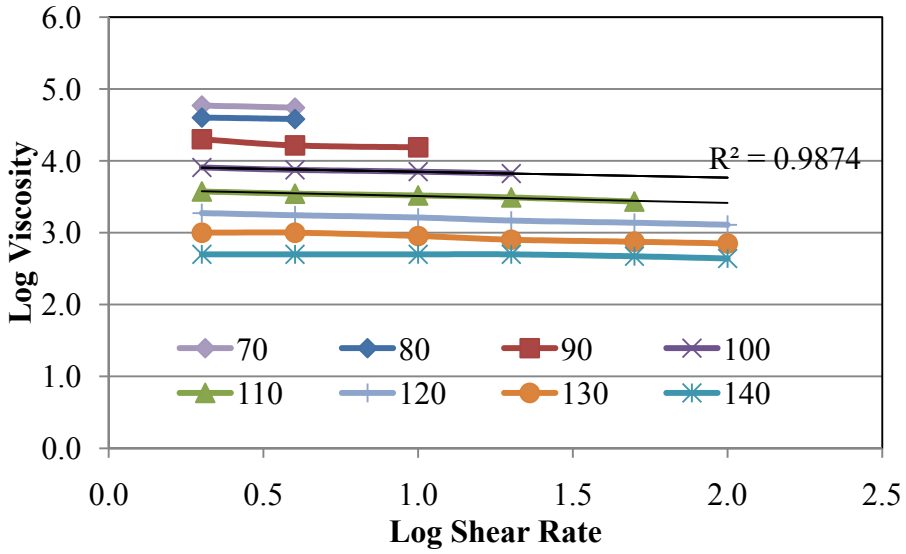

Figure C7.12. Log Viscosity versus Log Shear Rate for Blend 19

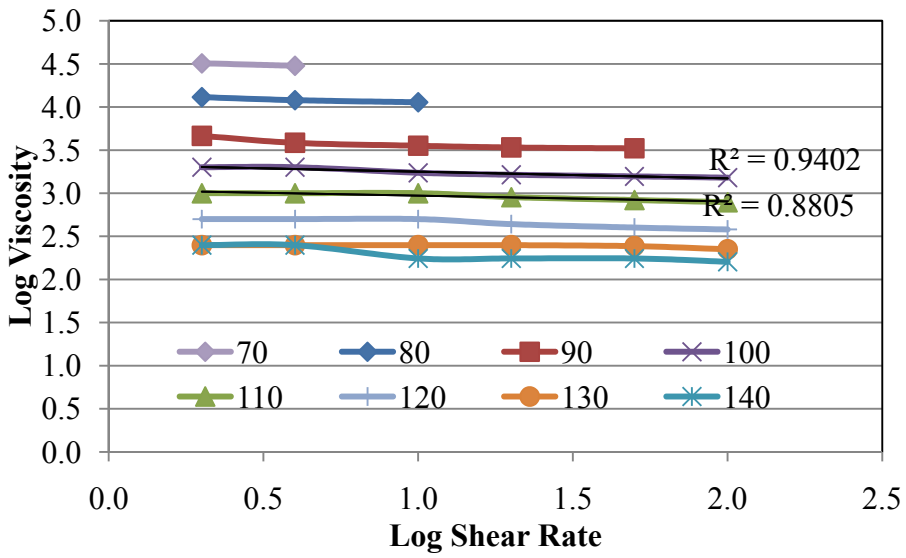

Figure C7.13. Log Viscosity versus Log Shear Rate for Blend 20

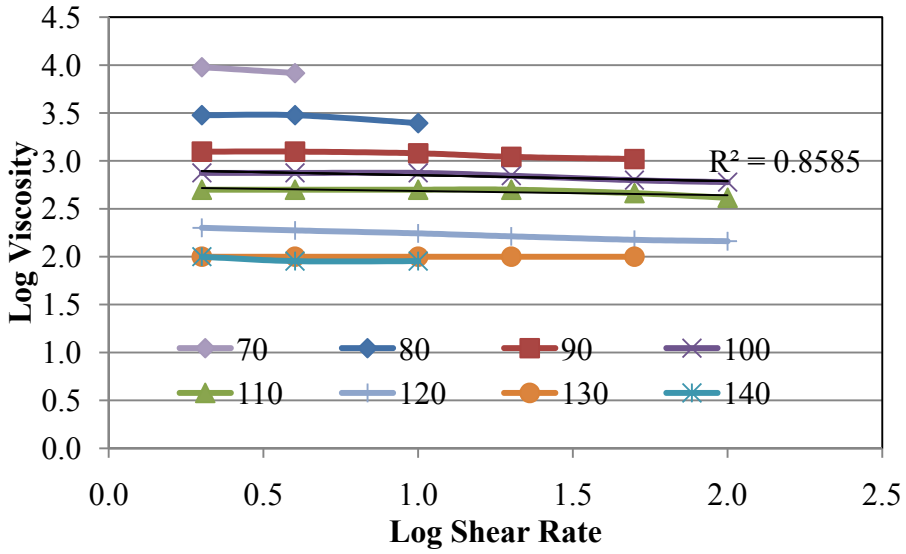

Figure C7.14. Log Viscosity versus Log Shear Rate for Blend 21

Table C7.47. Viscosity Temperature Susceptibility for Blend 1

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.75	0.60	0.60	0.59	0.59	0.59	0.59		
2.76	0.54	0.53	0.53	0.53	0.53	0.53	0.53	0.53
2.78	0.50	0.49	0.47	0.47	0.47	0.46	0.45	0.45
2.79	0.43	0.38	0.39	0.40	0.40	0.40	0.40	0.40
2.80	0.38	0.38	0.32	0.32	0.35	0.35	0.35	0.34
2.82				0.28	0.30	0.30	0.30	0.30
2.83								0.26
2.84								0.21
"VTS" Values	**-4.28**	**-4.47**	**-5.19**	**-4.91**	**-4.52**	**-4.48**	**-4.40**	**-4.14**

Table C7.48. Viscosity Temperature Susceptibility for Blend 2

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.75	0.66	0.66	0.66	0.66	0.66	0.66		
2.76	0.61	0.61	0.61	0.61	0.60	0.60		
2.78	0.57	0.58	0.57	0.57	0.56	0.56	0.55	0.55
2.79	0.53	0.53	0.54	0.54	0.53	0.52	0.51	0.50
2.80	0.50	0.49	0.51	0.50	0.48	0.47	0.46	0.46
2.82	0.47	0.57	0.45	0.45	0.44	0.43	0.42	0.41
2.83		0.38	0.38	0.38	0.37	0.36	0.35	0.35
2.84		0.38	0.32	0.32	0.34	0.33	0.32	0.31
2.85		0.38	0.32	0.32	0.34	0.30	0.29	0.29
"VTS" Values	**-3.01**	**-2.91**	**-3.64**	**-3.59**	**-3.42**	**-3.64**	**-3.76**	**-3.79**

Table C7.49. Viscosity Temperature Susceptibility for Blend 3

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.75	0.65	0.66	0.65	0.65	0.65	0.65		
2.76	0.63	0.62	0.61	0.60	0.59	0.59		
2.78	0.61	0.60	0.58	0.57	0.55	0.54	0.54	0.53
2.79	0.59	0.58	0.56	0.54	0.52	0.50	0.49	0.49
2.80	0.58	0.56	0.54	0.53	0.51	0.48	0.46	0.45
2.82	0.54	0.52	0.51	0.50	0.49	0.42	0.41	0.36
2.83		0.38	0.32	0.32	0.33	0.33	0.32	0.32
2.84			0.32	0.26	0.27	0.27	0.26	0.26
2.85			0.32	0.26	0.27	0.23	0.23	0.21
"VTS" Values	**-1.65**	**-3.01**	**-3.70**	**-4.22**	**-3.95**	**-4.22**	**-4.53**	**-4.62**

Table C7.50. Viscosity Temperature Susceptibility for Blend 4

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.80	0.65	0.65	0.65	0.65				
2.82	0.60	0.60	0.60	0.60	0.60	0.59		
2.83	0.54	0.56	0.55	0.55	0.55	0.55	0.54	0.54
2.84	0.52	0.52	0.52	0.51	0.51	0.50	0.50	0.49
2.85	0.48	0.45	0.45	0.45	0.45	0.45	0.44	0.44
2.86		0.42	0.41	0.41	0.42	0.41	0.41	0.40
2.87		0.42	0.38	0.39	0.39	0.38	0.38	0.37
2.88		0.38	0.32	0.36	0.35	0.35	0.34	0.34
2.89			0.32	0.32	0.32	0.32	0.32	0.31
"VTS" Values	**-3.74**	**-3.48**	**-3.90**	**-3.67**	**-3.58**	**-3.58**	**-3.49**	**-3.53**

Table C7.51. Viscosity Temperature Susceptibility for Blend 5

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.80	0.63	0.62	0.62	0.61	0.61	0.61		
2.82	0.58	0.56	0.56	0.56	0.56	0.56	0.55	
2.83	0.53	0.53	0.53	0.53	0.53	0.52	0.52	0.52
2.84	0.43	0.46	0.46	0.46	0.46	0.46	0.46	0.45
2.85	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.42
2.86		0.43	0.41	0.41	0.41	0.40	0.39	0.39
2.87		0.38	0.41	0.41	0.41	0.40	0.39	0.37
2.88			0.32	0.32	0.35	0.35	0.35	0.34
2.89			0.32	0.32	0.35	0.34	0.35	0.33
"VTS" Values	**-4.67**	**-3.43**	**-3.29**	**-3.27**	**-2.94**	**-3.00**	**-2.80**	**-2.70**

Table C7.52. Viscosity Temperature Susceptibility for Blend 6

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.63	0.63	0.62	0.62	0.61	0.61		
2.80	0.58	0.57	0.57	0.57	0.56	0.56	0.56	
2.82	0.52	0.51	0.51	0.51	0.51	0.50	0.50	0.50
2.83	0.48	0.48	0.48	0.47	0.46	0.46	0.45	0.45
2.84	0.43	0.43	0.43	0.43	0.42	0.42	0.42	0.41
2.85		0.38	0.32	0.32	0.34	0.34	0.35	0.35
2.86		0.43	0.41	0.40	0.39	0.32	0.32	0.31
2.87				0.26	0.30	0.29	0.29	0.29
"VTS" Values	**-4.20**	**-3.24**	**-3.71**	**-4.13**	**-3.75**	**-4.10**	**-4.05**	**-3.98**

Table C7.53. Viscosity Temperature Susceptibility for Blend 7

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.64	0.63	0.63	0.62	0.62	0.62		
2.80	0.58	0.57	0.57	0.57	0.56	0.56	0.56	
2.82	0.52	0.51	0.51	0.52	0.51	0.51	0.51	0.51
2.83	0.48	0.48	0.49	0.49	0.49	0.48	0.48	0.47
2.84	0.43	0.46	0.48	0.48	0.47	0.46	0.45	0.45
2.85	0.43	0.43	0.38	0.38	0.38	0.38	0.37	0.37
2.86			0.32	0.32	0.32	0.31	0.31	0.31
2.87				0.26	0.27	0.27	0.27	0.27
"VTS" Values	**-3.66**	**-3.35**	**-4.08**	**-4.36**	**-4.20**	**-4.25**	**-4.28**	**-4.44**

Table C7.54. Viscosity Temperature Susceptibility for Blend 8

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.60	0.60	0.60	0.59	0.59	0.58		
2.80	0.62	0.57	0.57	0.58	0.56	0.55	0.54	
2.82	0.57	0.56	0.54	0.52	0.51	0.51	0.50	
2.83	0.50	0.50	0.49	0.49	0.48	0.47	0.46	0.45
2.84	0.50	0.48	0.46	0.45	0.44	0.43	0.42	0.41
2.85	0.48	0.46	0.46	0.45	0.44	0.42	0.41	0.39
2.86	0.61	0.58	0.55	0.53	0.48	0.45	0.44	0.36
"VTS" Values	**-2.46**	**-2.58**	**-2.62**	**-2.70**	**-2.77**	**-2.92**	**-2.96**	**-2.63**

Table C7.55 Viscosity Temperature Susceptibility for Blend 9

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.62	0.61	0.61	0.60	0.59	0.59		
2.80	0.59	0.58	0.57	0.57	0.56	0.55	0.55	
2.82	0.54	0.53	0.53	0.52	0.51	0.50	0.50	
2.83	0.50	0.49	0.49	0.48	0.47	0.46	0.45	0.45
2.84	0.43	0.43	0.41	0.41	0.42	0.42	0.41	0.40
2.85		0.38	0.38	0.38	0.39	0.38	0.38	0.38
2.86		0.38	0.38	0.36	0.36	0.35	0.35	0.34
"VTS" Values	**-3.80**	**-3.69**	**-3.63**	**-3.65**	**-3.48**	**-3.53**	**-3.44**	**-3.16**

Table C7.56. Viscosity Temperature Susceptibility for Blend 10

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.65	0.64	0.64	0.64	0.64			
2.80	0.62	0.62	0.61	0.61	0.61	0.60		
2.82	0.59	0.57	0.57	0.56	0.55	0.55	0.55	
2.83	0.48	0.50	0.50	0.50	0.49	0.49	0.48	0.48
2.84	0.48	0.48	0.48	0.48	0.47	0.46	0.46	0.45
2.85		0.45	0.45	0.45	0.44	0.43	0.43	0.42
2.86			0.38	0.38	0.38	0.39	0.39	0.38
"VTS" Values	**-4.07**	**-3.58**	**-3.68**	**-3.63**	**-3.64**	**-3.57**	**-3.33**	**-2.93**

Table C7.57. Viscosity Temperature Susceptibility for Blend 11

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.76	0.64	0.63	0.63	0.63	0.62			
2.78	0.61	0.60	0.58	0.58	0.58	0.58		
2.79	0.55	0.54	0.54	0.54	0.53	0.53	0.52	0.52
2.80	0.53	0.52	0.51	0.50	0.49	0.48	0.47	0.47
2.82	0.48	0.48	0.48	0.48	0.47	0.46	0.45	0.44
2.83	0.43	0.43	0.43	0.41	0.39	0.38	0.37	0.37
2.84			0.32	0.32	0.32	0.32	0.32	0.31
2.85				0.26	0.26	0.26	0.26	0.26
2.86					0.23	0.23	0.23	0.23
2.87					0.23	0.23	0.22	0.20
"VTS" Values	**-3.40**	**-3.19**	**-3.74**	**-4.18**	**-4.05**	**-4.07**	**-4.10**	**-4.11**

Table C7.58. Viscosity Temperature Susceptibility for Blend 12

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.76	0.66	0.66	0.65	0.65				
2.78	0.64	0.63	0.62	0.59	0.59	0.59		
2.79	0.60	0.58	0.56	0.56	0.55	0.54	0.54	
2.80	0.56	0.54	0.53	0.53	0.51	0.50	0.50	0.50
2.82	0.56	0.54	0.52	0.51	0.50	0.47	0.46	0.45
2.83	0.55	0.53	0.51	0.49	0.47	0.46	0.43	0.42
2.84	0.43	0.38	0.38	0.36	0.35	0.35	0.34	0.33
2.85		0.38	0.32	0.32	0.32	0.31	0.30	0.30
2.86		0.38	0.32	0.32	0.27	0.27	0.27	0.26
2.87			0.32	0.32	0.27	0.27	0.27	0.25
"VTS" Values	**-2.65**	**-3.16**	**-3.44**	**-3.34**	**-3.75**	**-3.70**	**-3.75**	**-3.90**

Table C7.59. Viscosity Temperature Susceptibility for Blend 13

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.76	0.68	0.67	0.67	0.67				
2.78	0.64	0.63	0.63	0.62	0.62			
2.79	0.62	0.61	0.60	0.58	0.57	0.56	0.56	
2.80	0.58	0.57	0.56	0.55	0.52	0.51	0.51	0.50
2.82	0.57	0.55	0.53	0.53	0.49	0.48	0.47	0.46
2.83	0.52	0.52	0.50	0.49	0.47	0.45	0.43	0.42
2.84	0.48	0.48	0.38	0.38	0.37	0.36	0.36	0.35
2.85			0.32	0.32	0.32	0.32	0.32	0.32
2.86				0.30	0.30	0.29	0.29	0.28
2.87					0.23	0.23	0.23	0.23
"VTS" Values	**-2.58**	**-2.57**	**-3.91**	**-3.89**	**-4.07**	**-4.14**	**-4.01**	**-4.01**

Table C7.60. Viscosity Temperature Susceptibility for Blend 14

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.76	0.66	0.65	0.65	0.65				
2.78	0.62	0.62	0.61	0.61	0.60			
2.79	0.57	0.56	0.55	0.55	0.54	0.54	0.53	
2.80	0.51	0.51	0.50	0.49	0.48	0.48	0.48	0.48
2.82	0.48	0.46	0.45	0.45	0.44	0.44	0.43	0.43
2.83	0.48	0.46	0.45	0.43	0.42	0.42	0.40	0.39
2.84	0.43	0.43	0.43	0.40	0.38	0.34	0.33	0.33
2.85			0.32	0.30	0.29	0.29	0.29	0.28
2.86				0.26	0.23	0.23	0.23	0.23
2.87				0.26	0.22	0.22	0.22	0.22
"VTS" Values	**-3.09**	**-3.18**	**-3.50**	**-3.86**	**-4.16**	**-4.12**	**-4.05**	**-4.05**

Table C7.61. Viscosity Temperature Susceptibility for Blend 15

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.75	0.67	0.66	0.66	0.65				
2.76	0.64	0.63	0.61	0.60	0.59	0.59		
2.78	0.56	0.55	0.55	0.55	0.54	0.54	0.54	
2.79	0.52	0.51	0.50	0.50	0.50	0.50	0.50	0.49
2.80	0.48	0.46	0.46	0.45	0.45	0.45	0.45	0.44
2.82	0.43	0.41	0.41	0.41	0.41	0.40	0.40	0.39
2.83		0.38	0.38	0.36	0.36	0.36	0.35	0.35
2.84			0.32	0.32	0.32	0.31	0.31	0.31
2.85				0.27	0.27	0.27	0.27	0.27
"VTS" Values	**-3.81**	**-3.86**	**-3.78**	**-3.81**	**-3.74**	**-3.74**	**-3.82**	**-3.81**

Table C7.62. Viscosity Temperature Susceptibility for Blend 16

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.66	0.66	0.66	0.66				
2.80	0.63	0.62	0.62	0.62	0.62			
2.82	0.60	0.59	0.59	0.58	0.58	0.57		
2.83	0.55	0.54	0.54	0.53	0.53	0.52	0.52	0.52
2.84	0.52	0.50	0.50	0.50	0.50	0.50	0.49	0.49
2.85	0.48	0.46	0.46	0.46	0.45	0.45	0.44	0.44
2.86	0.43	0.43	0.43	0.43	0.44	0.43	0.43	0.42
2.87	0.43	0.43	0.43	0.43	0.42	0.42	0.40	0.39
"VTS" Values	**-3.09**	**-3.11**	**-3.07**	**-3.03**	**-2.92**	**-2.83**	**-2.73**	**-2.92**

Table C7.63. Viscosity Temperature Susceptibility for Blend 17

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.63	0.61	0.61	0.59	0.59	0.58		
2.80	0.58	0.57	0.56	0.55	0.54	0.54	0.53	
2.82	0.56	0.55	0.54	0.53	0.52	0.51	0.50	0.49
2.83	0.48	0.48	0.48	0.47	0.46	0.45	0.44	0.43
2.84	0.43	0.43	0.43	0.43	0.42	0.42	0.40	0.39
2.85		0.38	0.38	0.38	0.37	0.37	0.36	0.35
2.86			0.34	0.34	0.34	0.34	0.33	0.32
2.87				0.32	0.30	0.30	0.29	0.29
"VTS" Values	**-4.17**	**-3.99**	**-3.95**	**-3.58**	**-3.62**	**-3.56**	**-3.62**	**-3.55**

Table C7.64. Viscosity Temperature Susceptibility for Blend 18

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.67	0.66	0.66	0.66				
2.80	0.64	0.63	0.62	0.61	0.61			
2.82	0.58	0.58	0.58	0.57	0.57	0.57	0.57	
2.83	0.54	0.55	0.54	0.54	0.53	0.53	0.52	0.52
2.84	0.50	0.50	0.50	0.50	0.49	0.48	0.48	0.48
2.85		0.48	0.48	0.47	0.47	0.46	0.46	0.45
2.86			0.43	0.43	0.43	0.43	0.42	0.41
2.87				0.41	0.40	0.39	0.39	0.38
"VTS" Values	**-3.68**	**-3.24**	**-3.20**	**-3.11**	**-3.06**	**-3.00**	**-3.13**	**-3.12**

Table C7.65. Viscosity Temperature Susceptibility for Blend 19

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.68	0.68	0.68	0.68				
2.80	0.67	0.66	0.66	0.66				
2.82	0.64	0.64	0.63	0.62	0.62			
2.83	0.60	0.60	0.59	0.59	0.59	0.58		
2.84	0.56	0.56	0.55	0.55	0.55	0.54	0.54	
2.85	0.52	0.52	0.51	0.51	0.51	0.50	0.50	0.49
2.86	0.48	0.48	0.48	0.48	0.47	0.46	0.46	0.46
2.87	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.42
2.88		0.38	0.38	0.38	0.38	0.38	0.38	0.38
"VTS" Values	**-3.25**	**-3.18**	**-3.15**	**-3.11**	**-3.42**	**-3.46**	**-3.35**	**-3.30**

Table C7.66. Viscosity Temperature Susceptibility for Blend 20

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.67	0.66	0.65	0.65				
2.80	0.62	0.62	0.61	0.61	0.61	0.61		
2.82	0.57	0.57	0.56	0.55	0.55	0.55	0.55	
2.83	0.52	0.52	0.52	0.52	0.51	0.51	0.50	0.50
2.84	0.48	0.48	0.48	0.48	0.48	0.47	0.47	0.46
2.85	0.43	0.43	0.43	0.43	0.43	0.42	0.42	0.41
2.86		0.38	0.38	0.38	0.38	0.38	0.38	0.37
2.87		0.38	0.38	0.38	0.35	0.35	0.35	0.34
"VTS" Values	**-4.03**	**-3.74**	**-3.66**	**-3.59**	**-3.75**	**-3.75**	**-3.60**	**-3.71**

Table C7.67. Viscosity Temperature Susceptibility for Blend 21

Log Temperature (°Rankine)	Log Log(Viscosity)/ Shear Rate							
	0.5	**1**	**2**	**4**	**10**	**20**	**50**	**100**
2.79	0.61	0.60	0.60	0.59	0.59	0.58		
2.80	0.56	0.55	0.54	0.54	0.53	0.53	0.53	
2.82	0.50	0.49	0.49	0.49	0.49	0.48	0.48	0.48
2.83	0.46	0.46	0.46	0.46	0.46	0.45	0.45	0.44
2.84		0.43	0.43	0.43	0.43	0.43	0.43	0.42
2.85		0.38	0.36	0.36	0.35	0.34	0.34	0.33
2.86				0.30	0.30	0.30	0.30	0.30
2.87						0.30	0.29	0.29
"VTS" Values	**-4.21**	**-3.66**	**-3.75**	**-3.99**	**-3.91**	**-3.68**	**-3.68**	**-3.69**

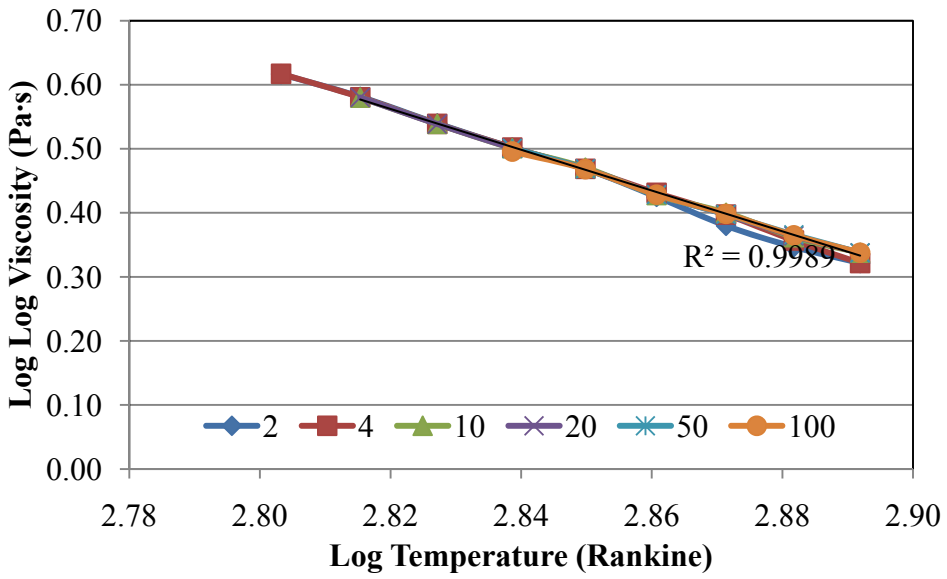

Figure C7.15. Log Log Viscosity versus Log Temperature for AAD

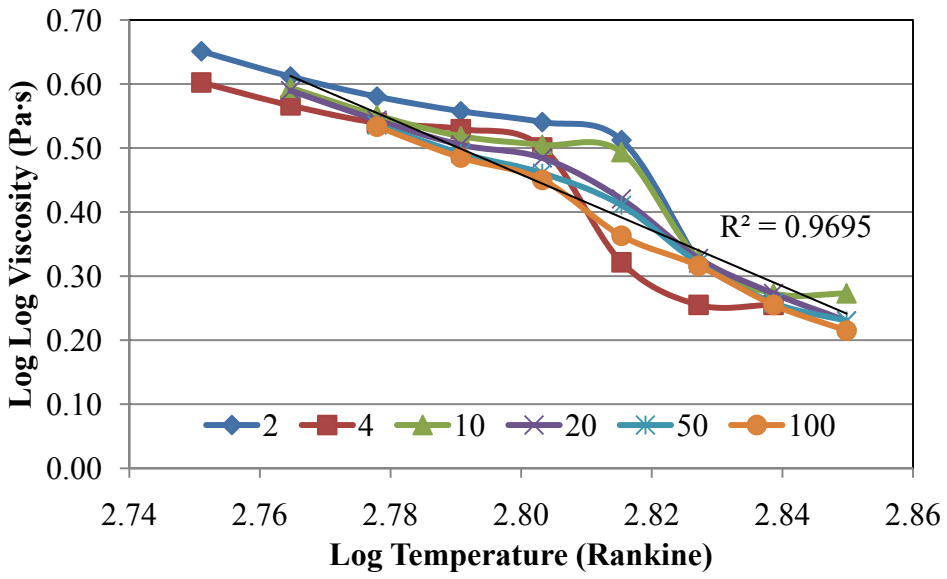

Figure C7.16. Log Log Viscosity versus Log Temperature for Blend 3

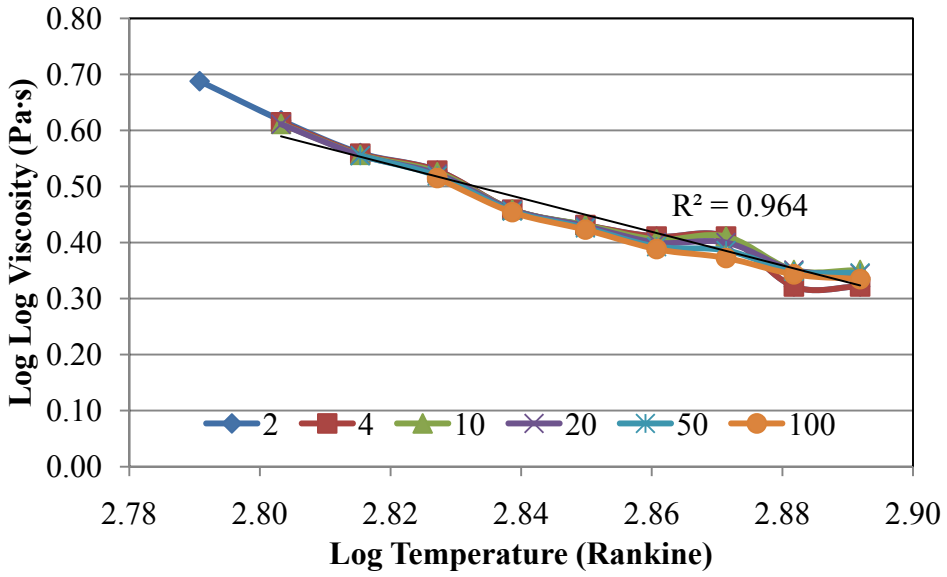

Figure C7.17. Log Log Viscosity versus Log Temperature for Blend 5

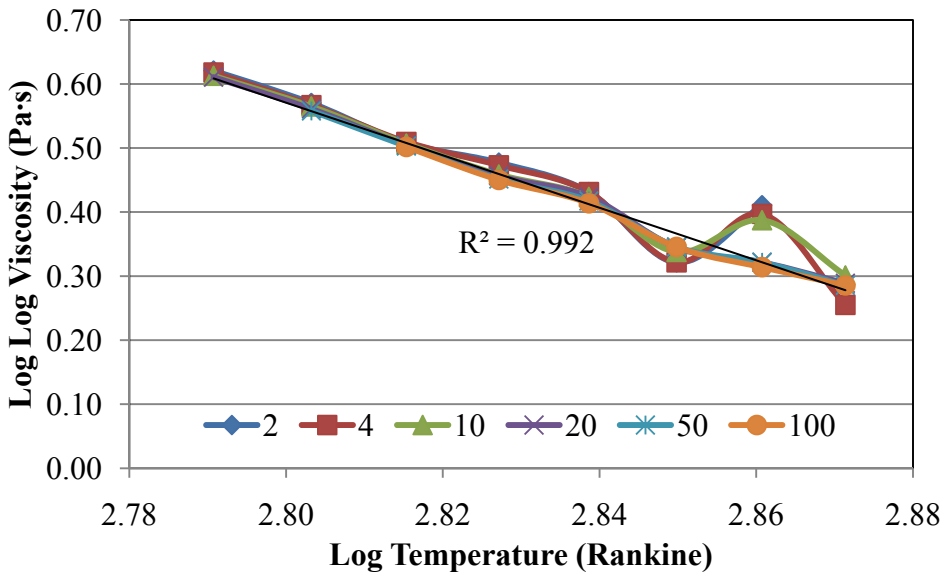

Figure C7.18. Log Log Viscosity versus Log Temperature for Blend 6

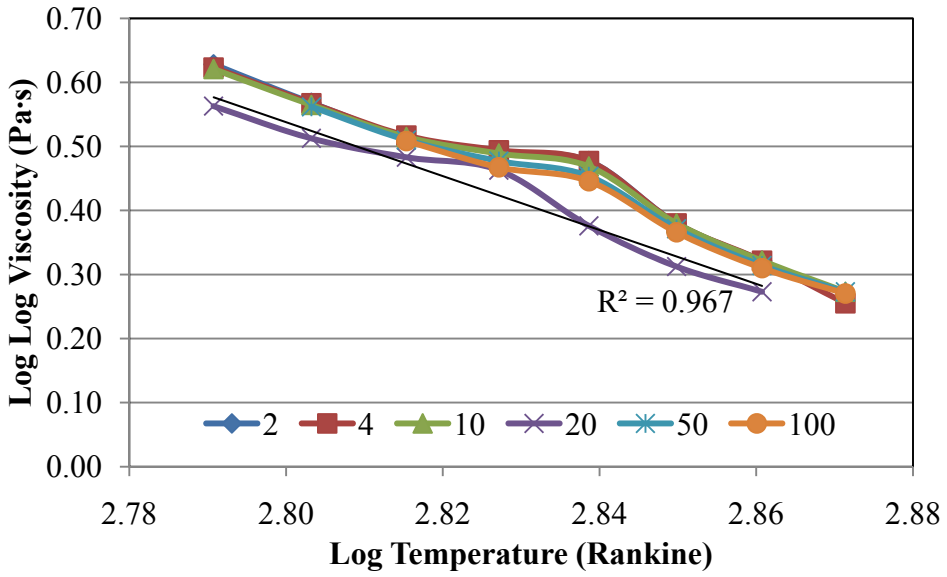

Figure C7.19. Log Log Viscosity versus Log Temperature for Blend 7

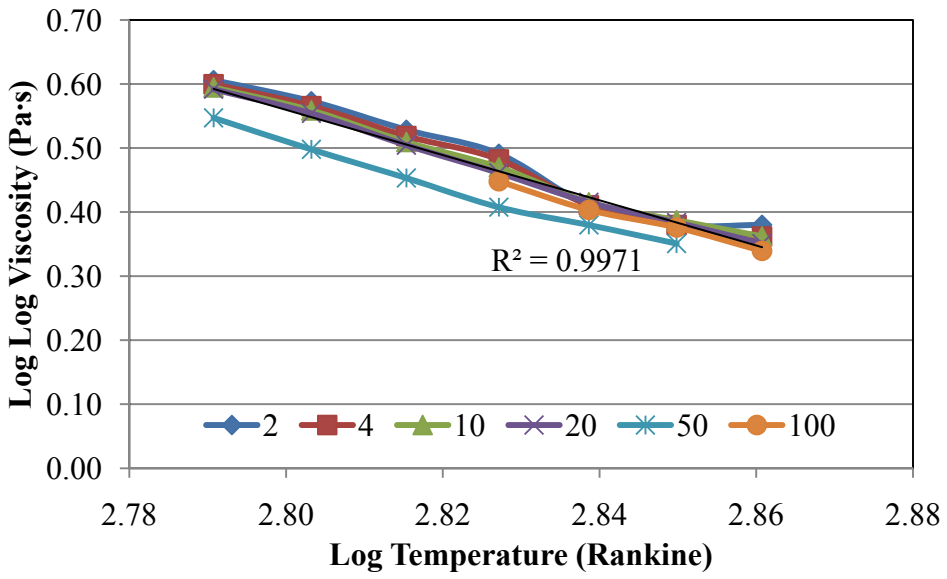

Figure C7.20. Log Log Viscosity versus Log Temperature for Blend 9

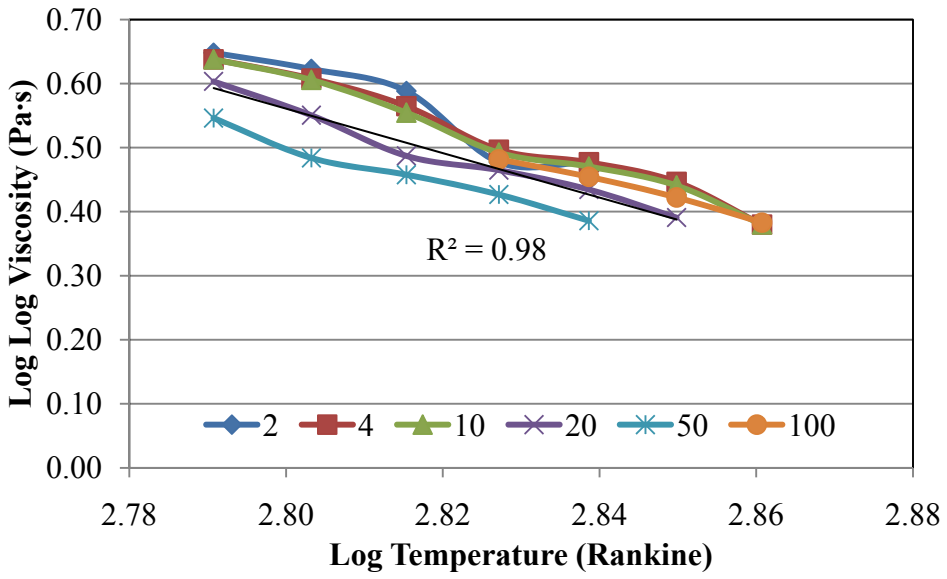

Figure C7.21. Log Log Viscosity versus Log Temperature for Blend 10

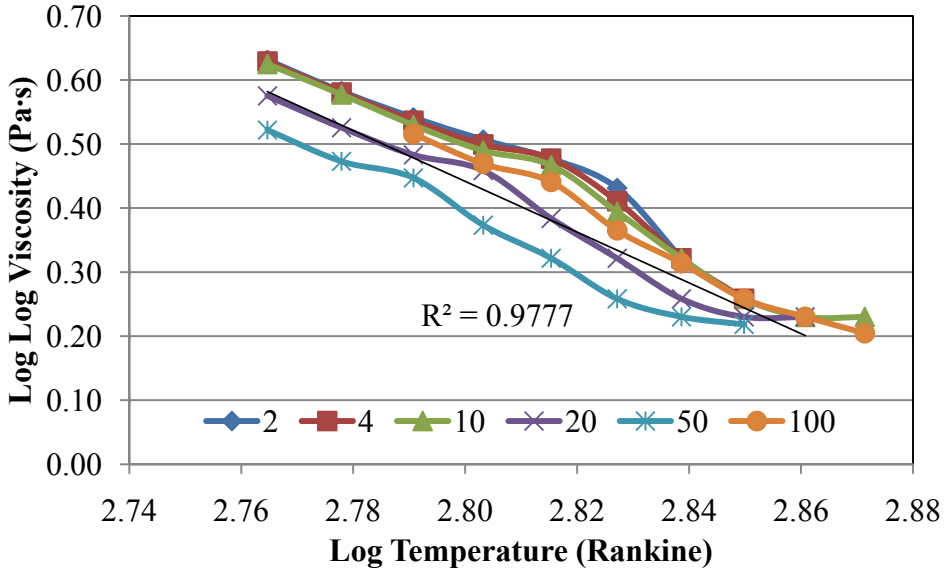

Figure C7.22. Log Log Viscosity versus Log Temperature for Blend 11

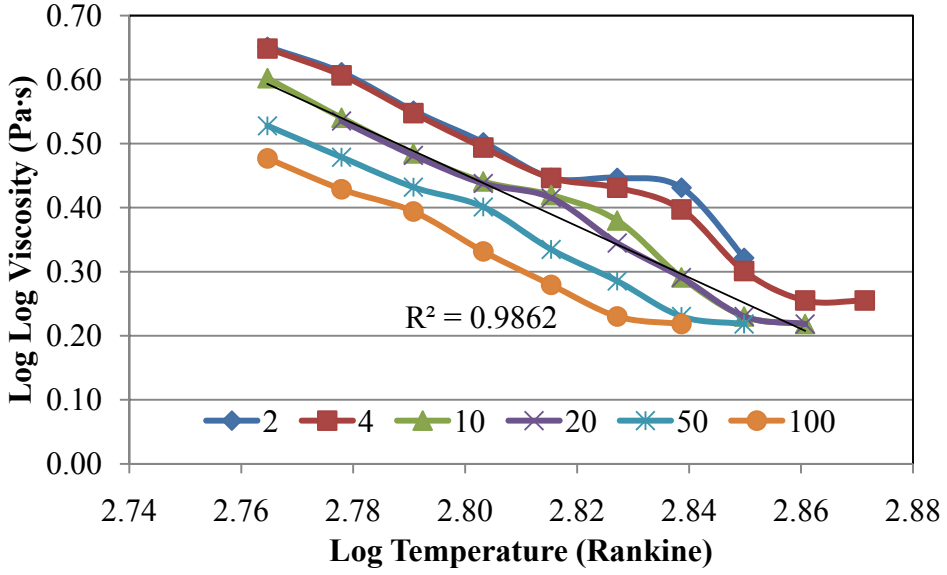

Figure C7.23. Log Log Viscosity versus Log Temperature for Blend 14

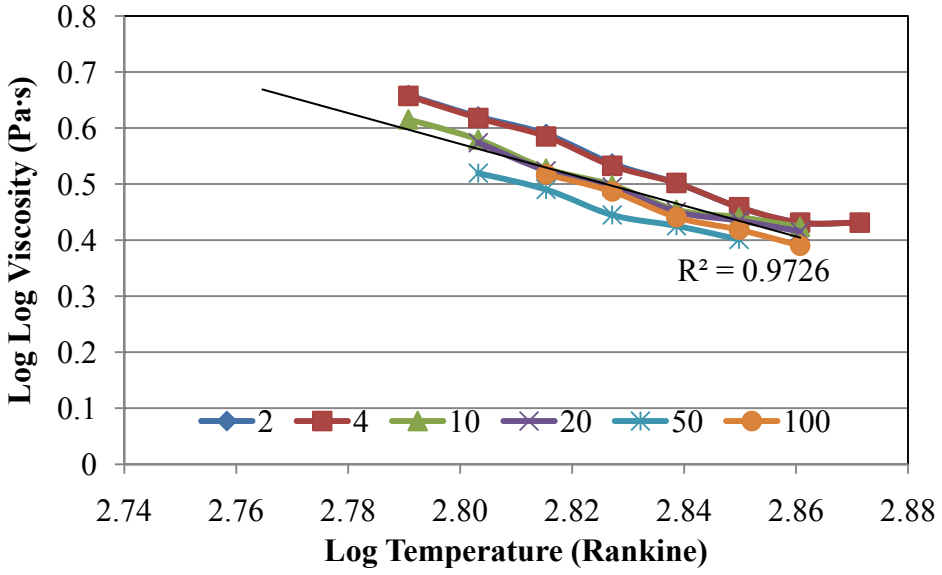

Figure C7.24. Log Log Viscosity versus Log Temperature for Blend 16

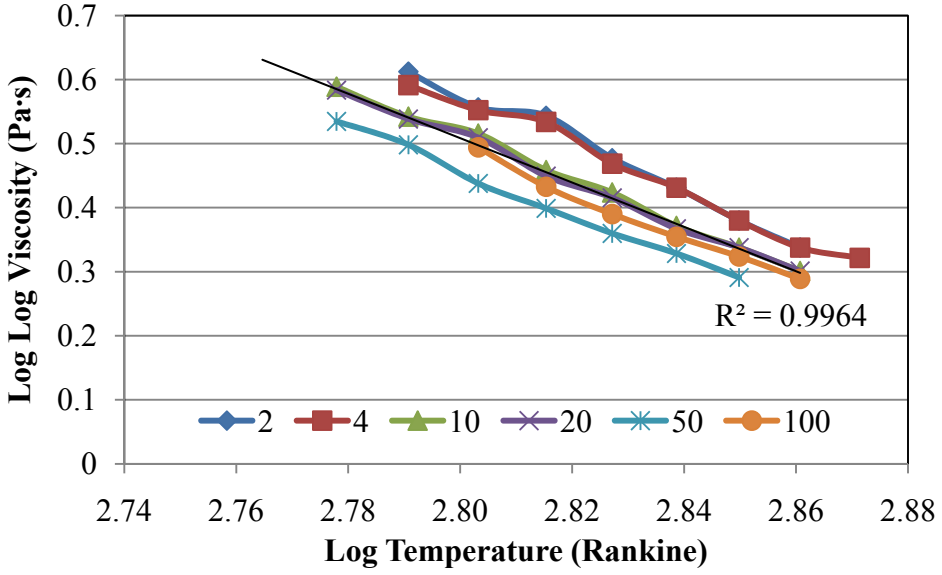

Figure C7.25. Log Log Viscosity versus Log Temperature for Blend 17

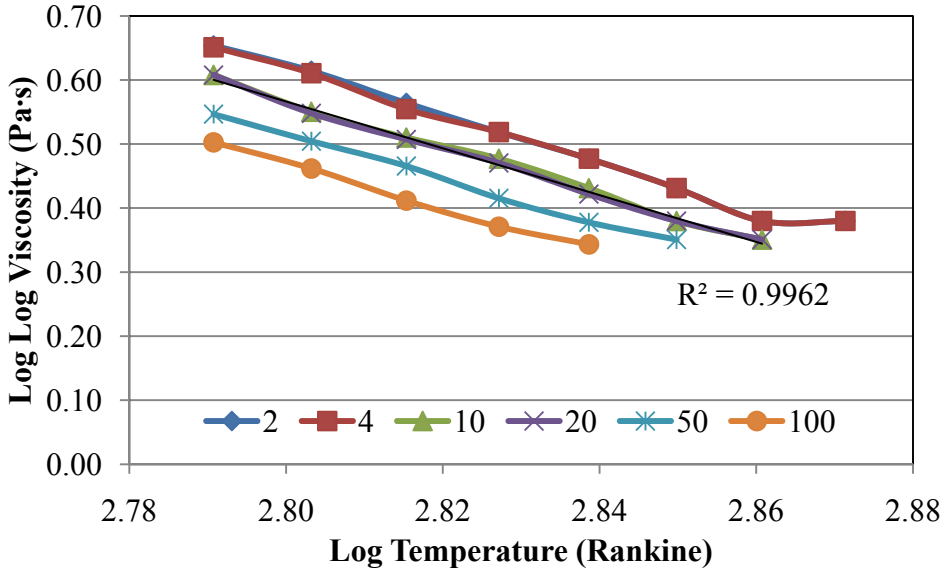

Figure C7.26. Log Log Viscosity versus Log Temperature for Blend 20

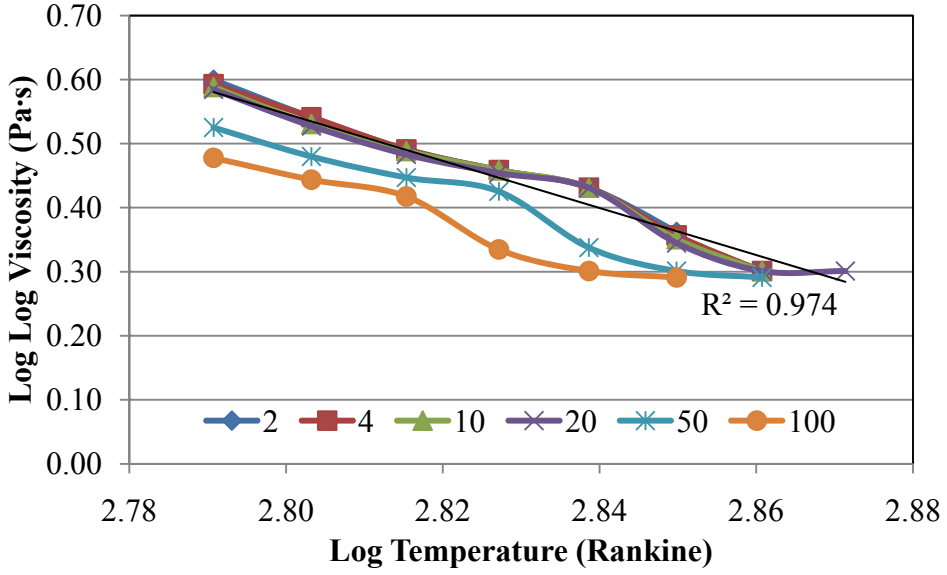

Figure C7.27. Log Log Viscosity versus Log Temperature for Blend 21

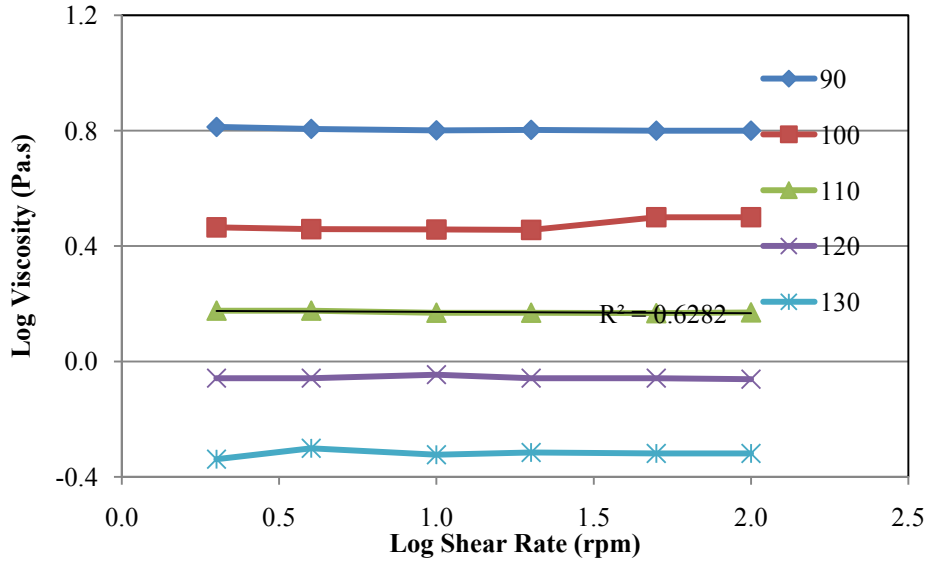

Figure C7.28. Power-law Model for AAD Blend

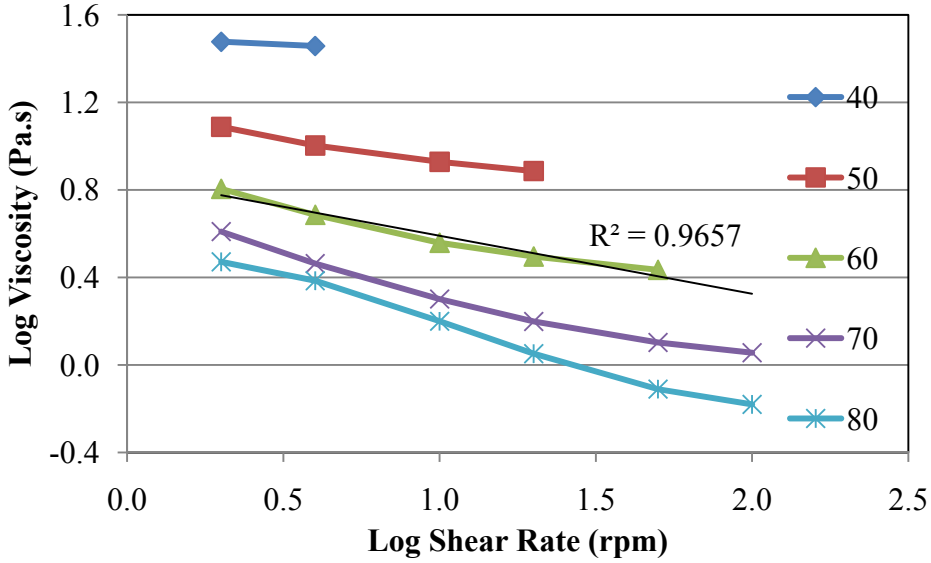

Figure C7.29. Power-law Relationship for Blend 3

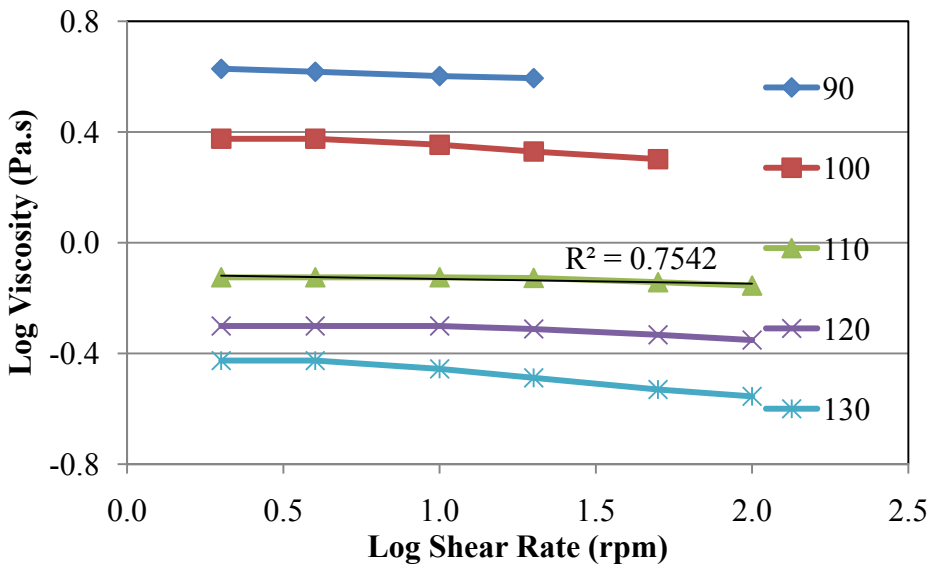

Figure C7.30. Power-law Relationship for Blend 5

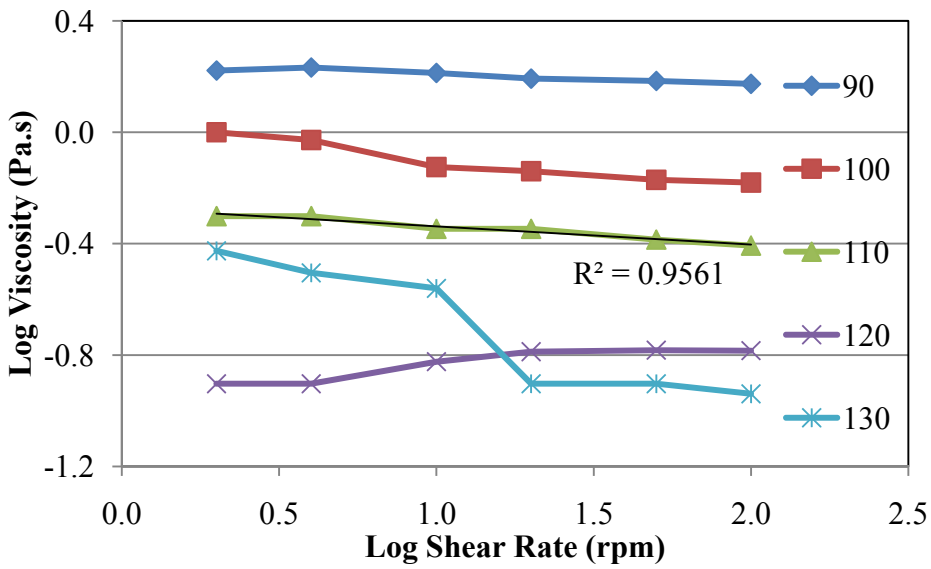

Figure C7.31. Power-law Relationship for Blend 6

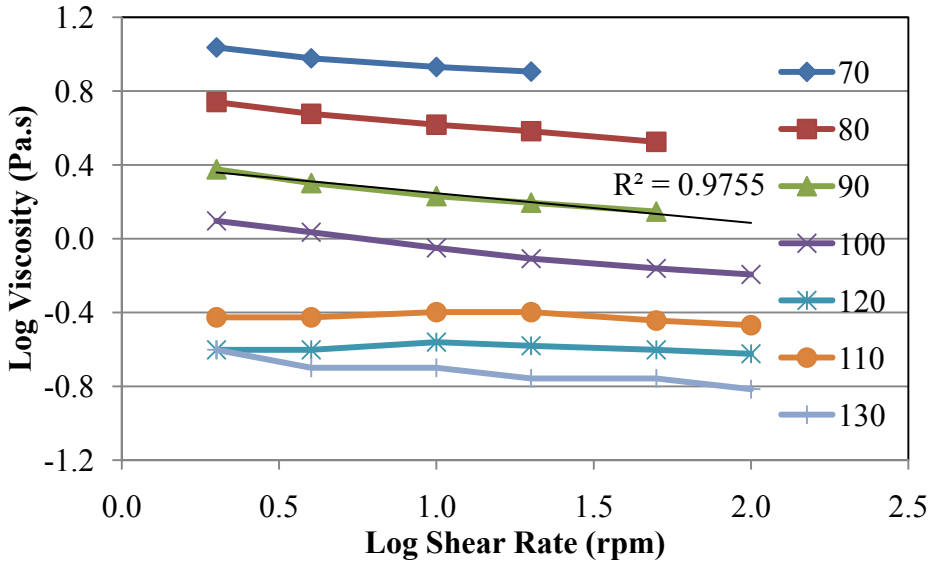

Figure C7.32. Power-law Relationship for Blend 9

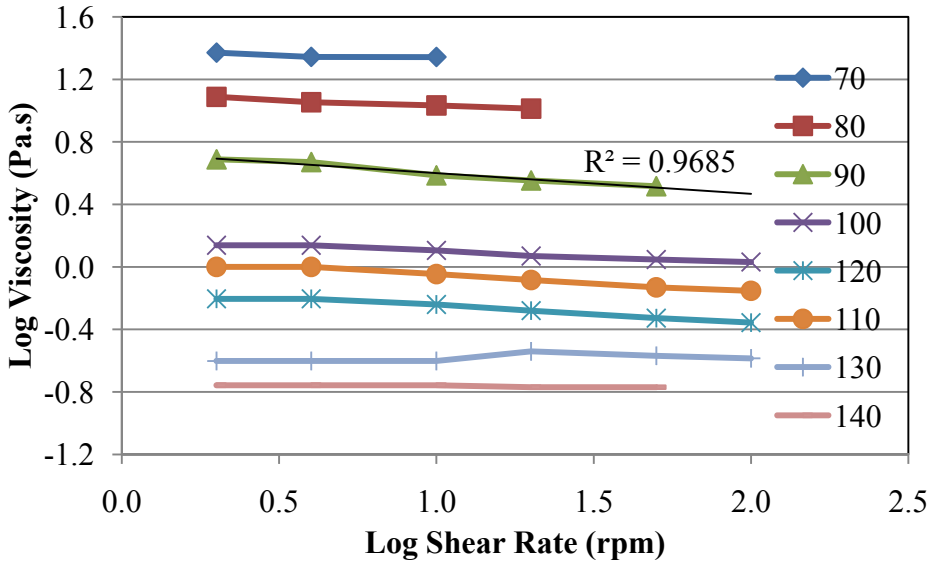

Figure C7.33. Power-law Relationship for Blend 10

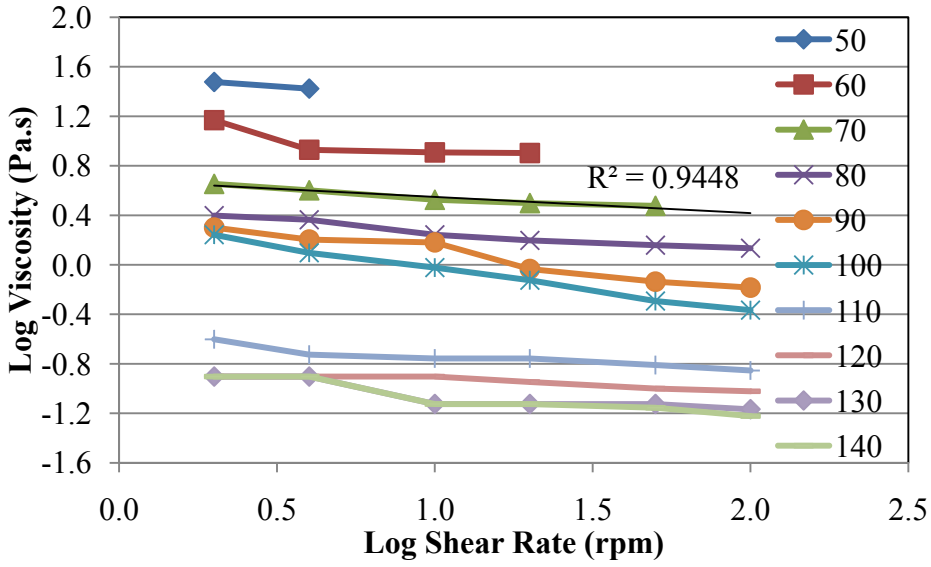

Figure C7.34. Power-law Relationship for Blend 12

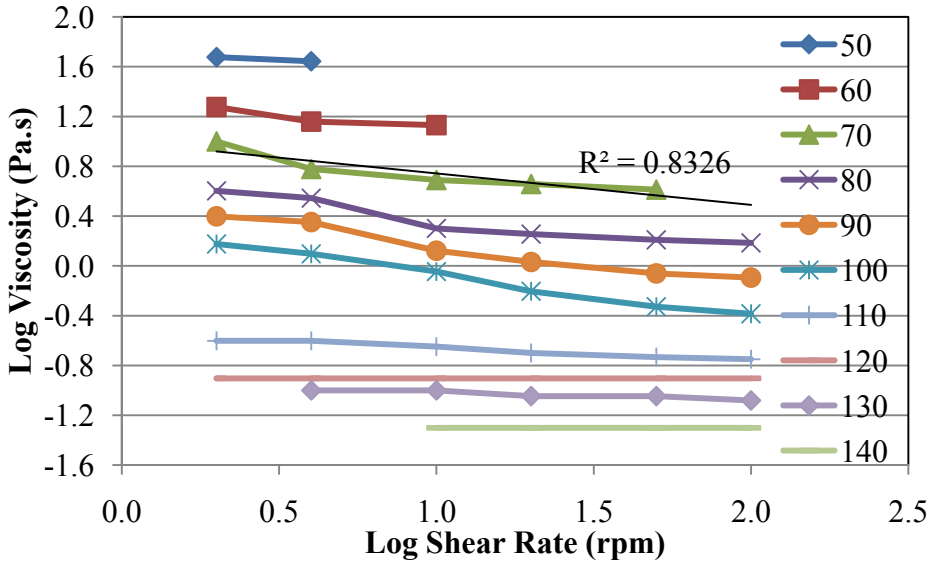

Figure C7.35. Power-law Relationship for Blend 13

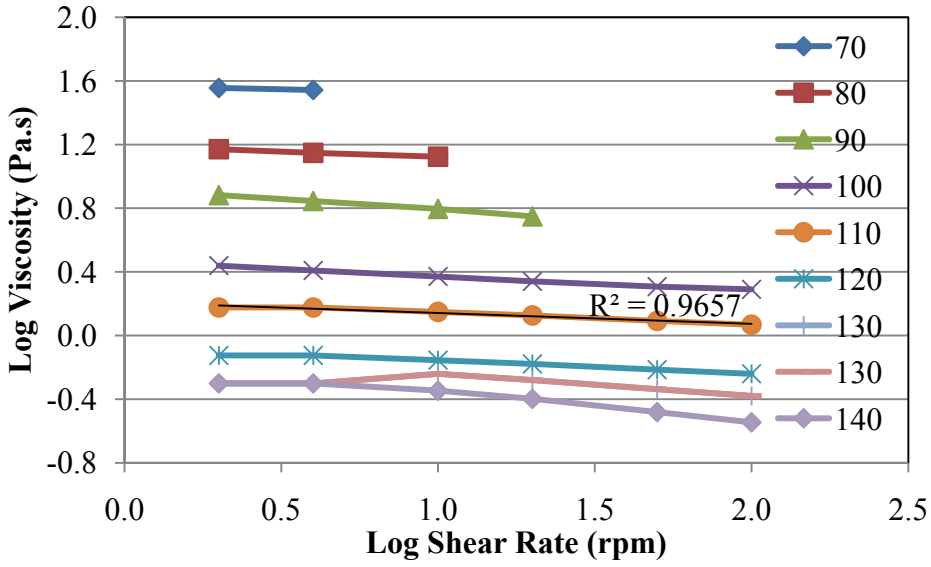

Figure C7.36. Power-law Relationship for Blend 16

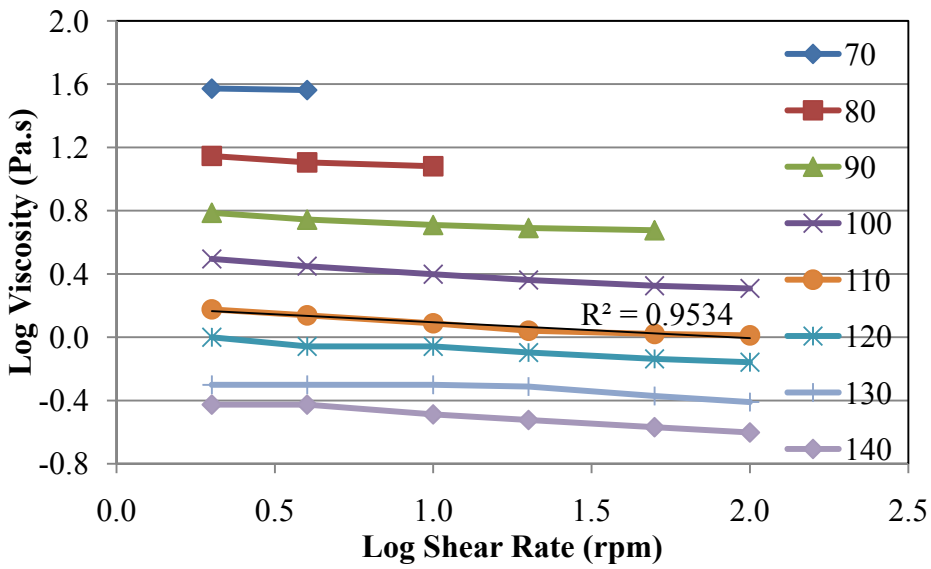

Figure C7.37. Power-law Relationship for Blend 18

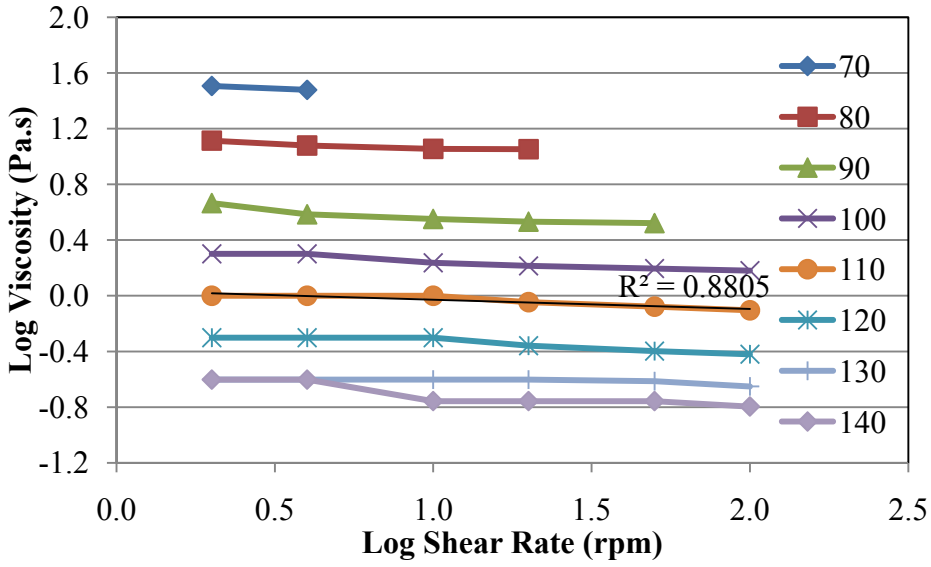

Figure C7.38. Power-law Relationship for Blend 20

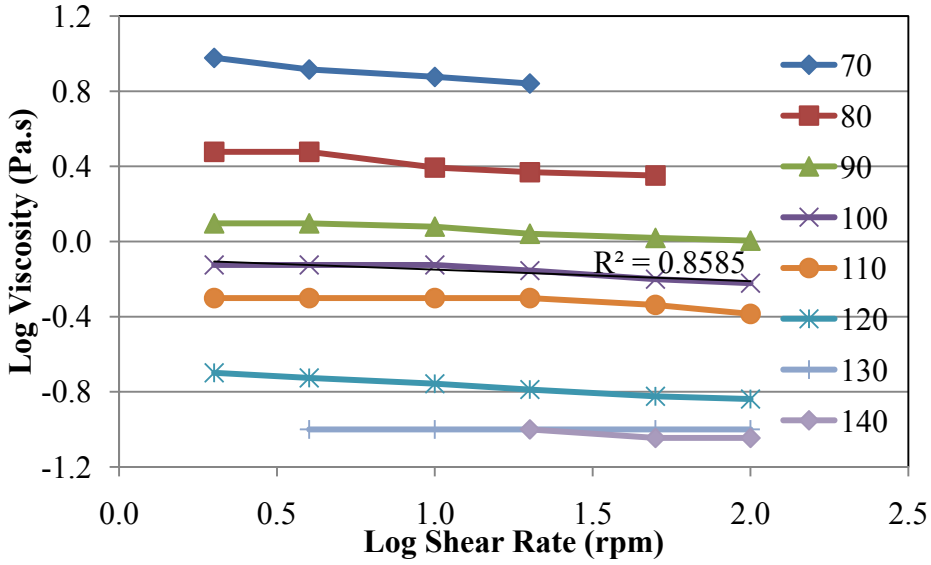

Figure C7.39. Power-law Relationship for Blend 21

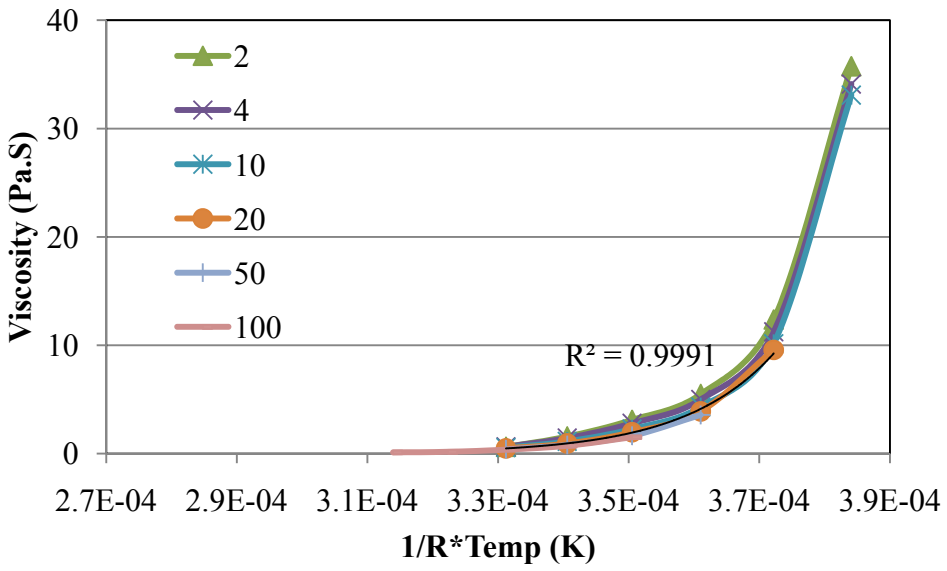

Figure C7.40. Arrhenius –type Model for Blend 2

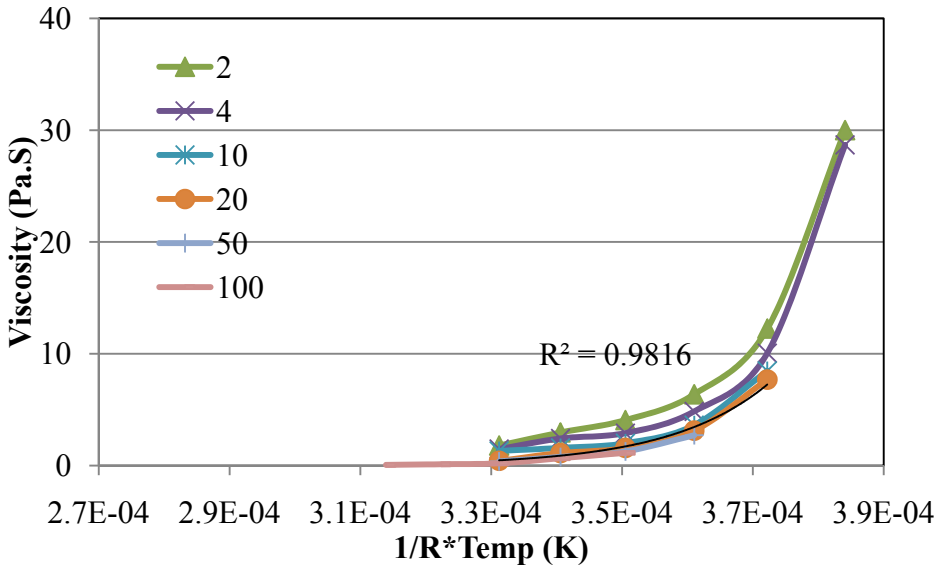

Figure C7.41. Arrhenius –type Model for Blend 3

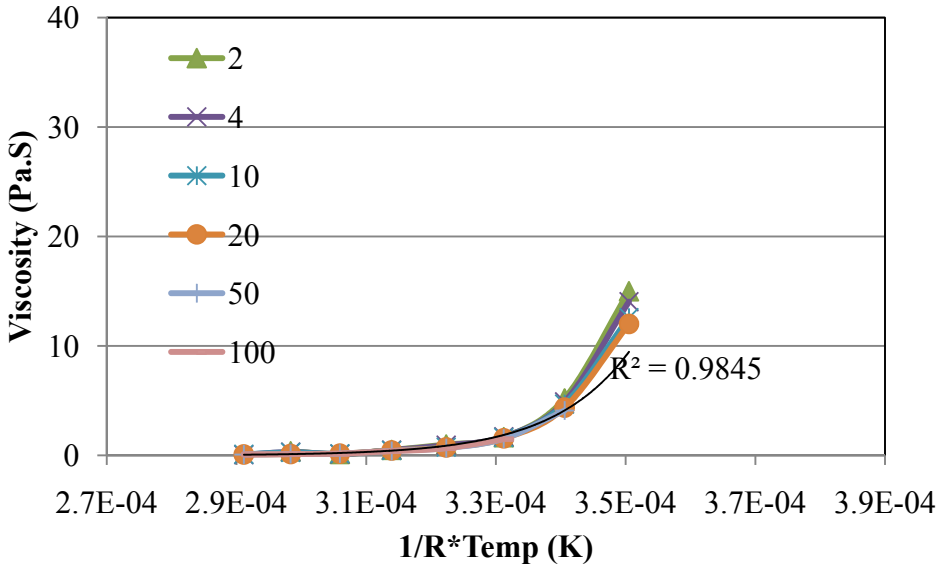

Figure C7.42. Arrhenius –type Model for Blend 6

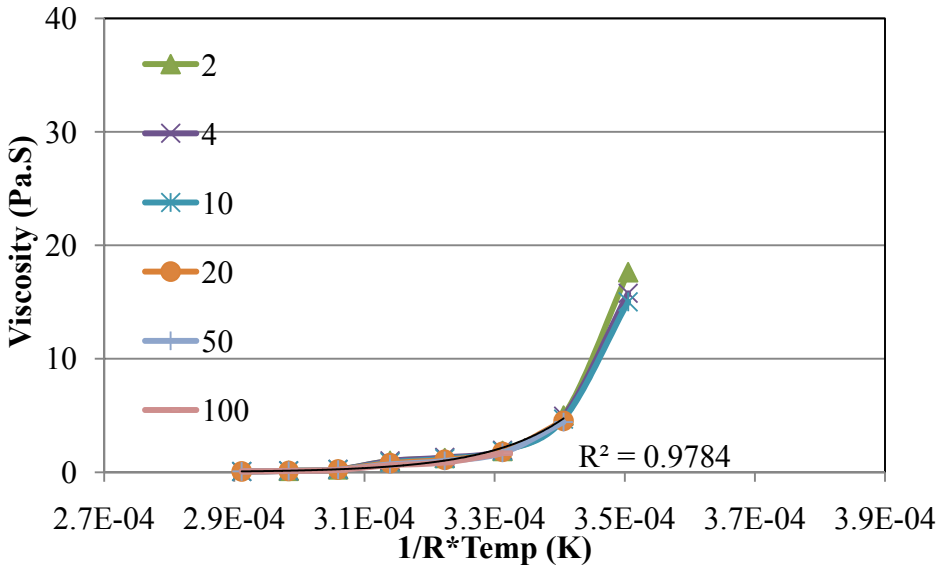

Figure C7.43. Arrhenius –type Model for Blend 7

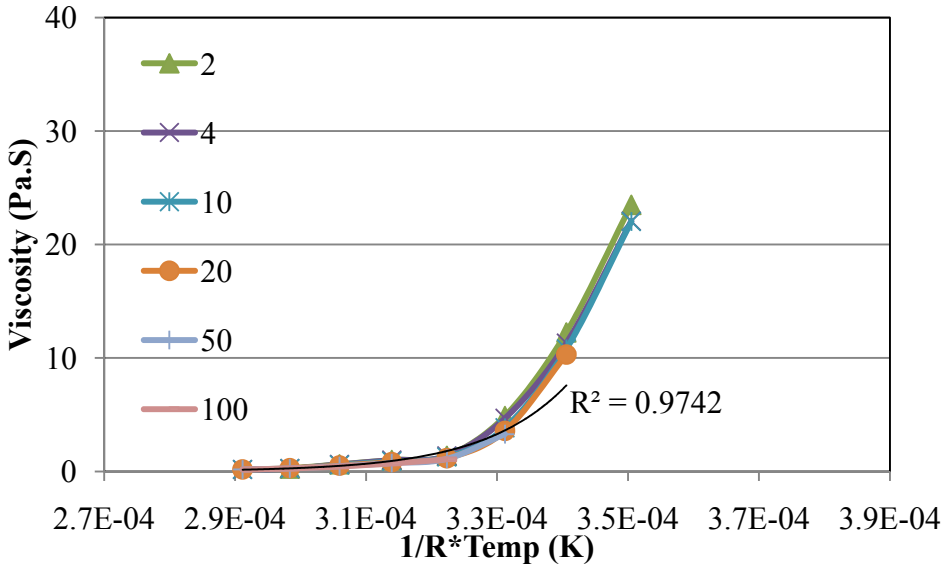

Figure C7.44. Arrhenius –type Model for Blend 10

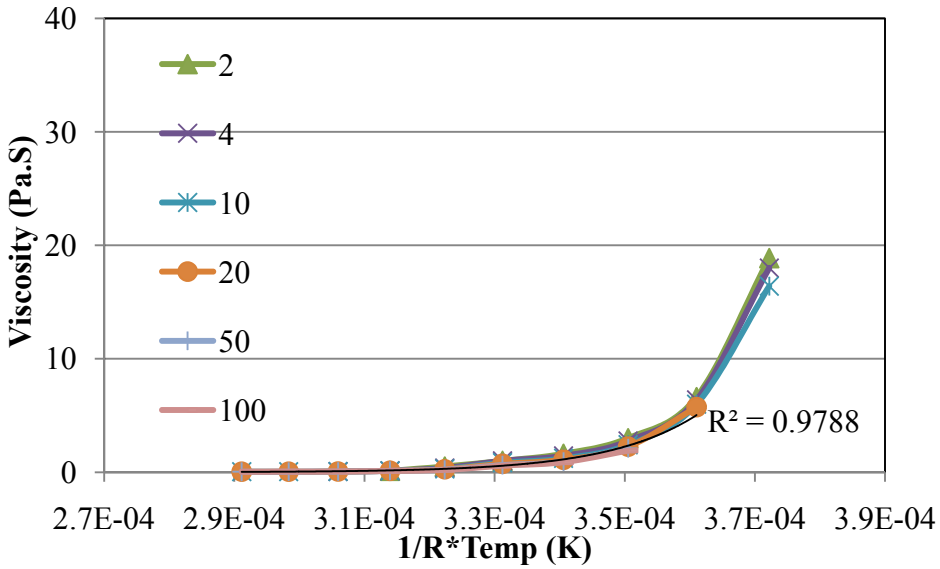

Figure C7.45. Arrhenius –type Model for Blend 11

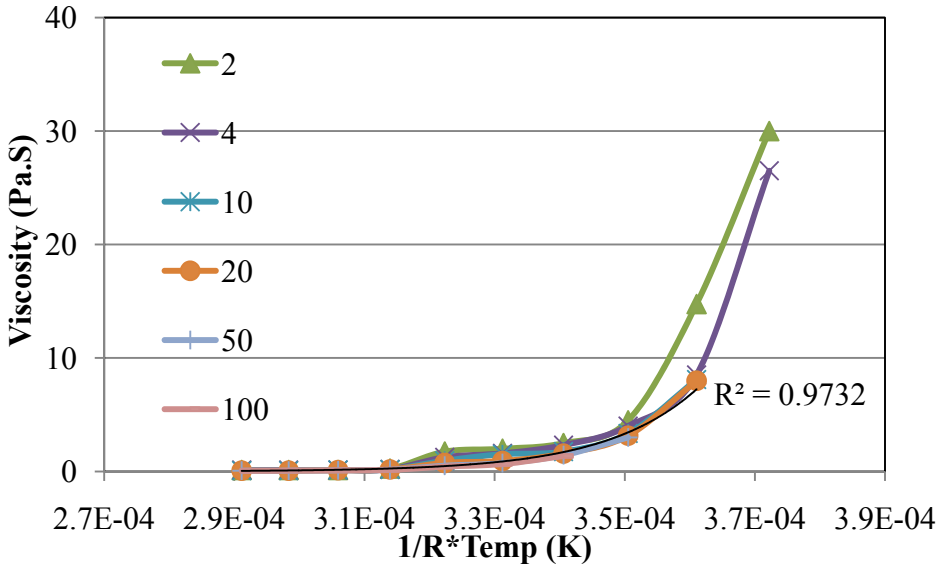

Figure C7.46. Arrhenius –type Model for Blend 12

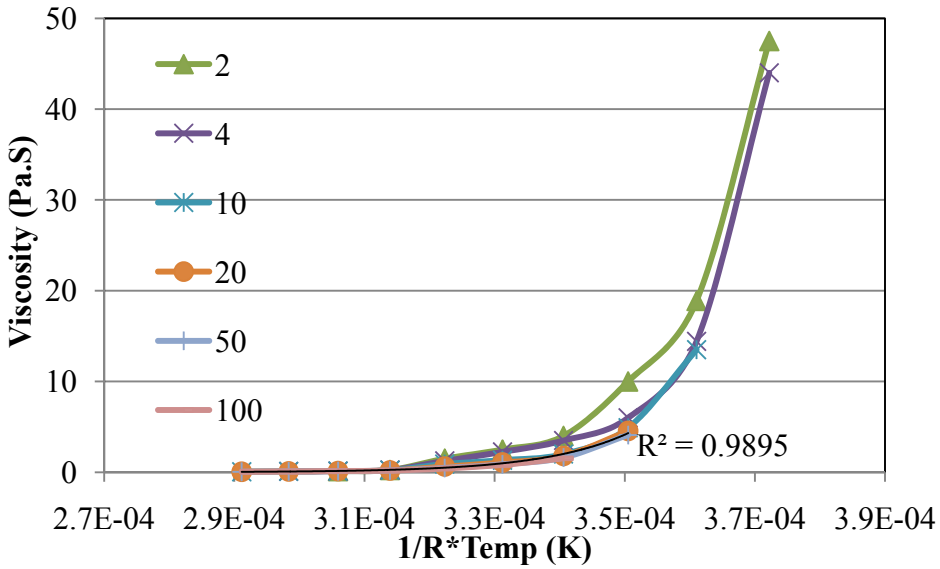

Figure C7.47. Arrhenius –type Model for Blend 13

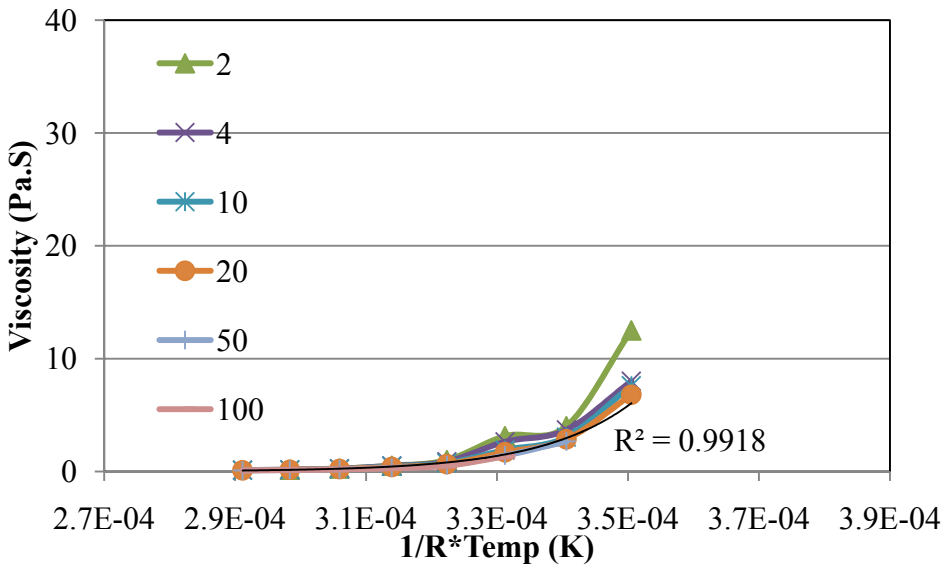

Figure C7.48. Arrhenius –type Model for Blend 17

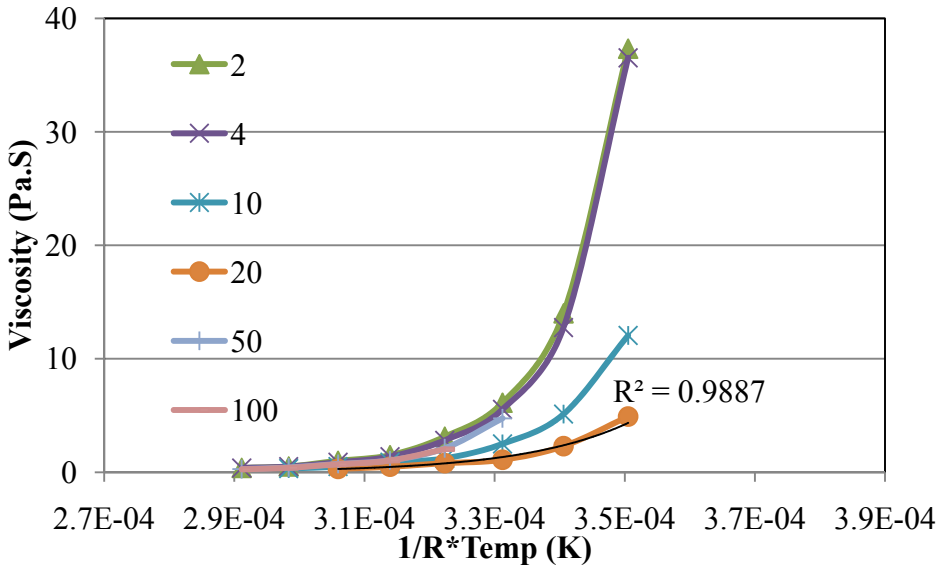

Figure C7.49. Arrhenius –type Model for Blend 18

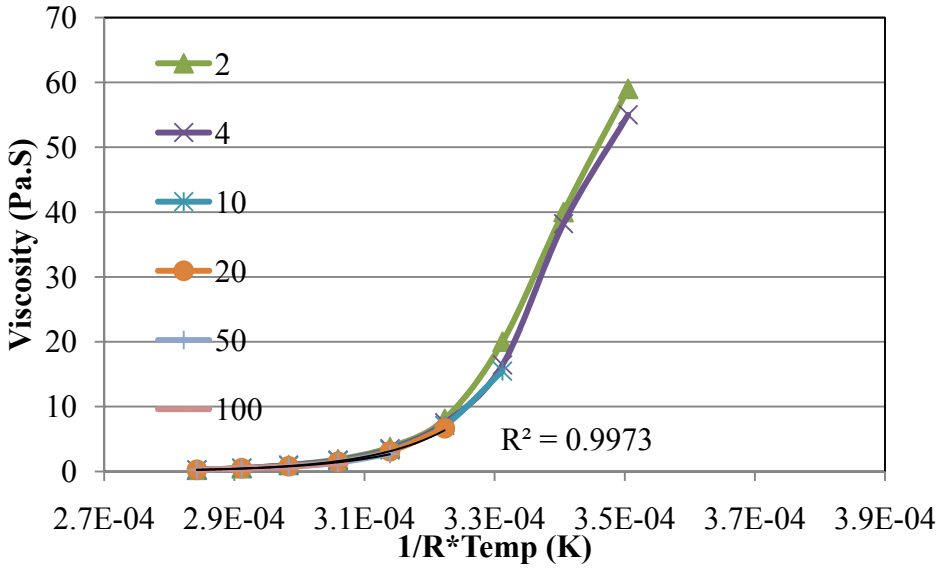

Figure C7.50. Arrhenius –type Model for Blend 19

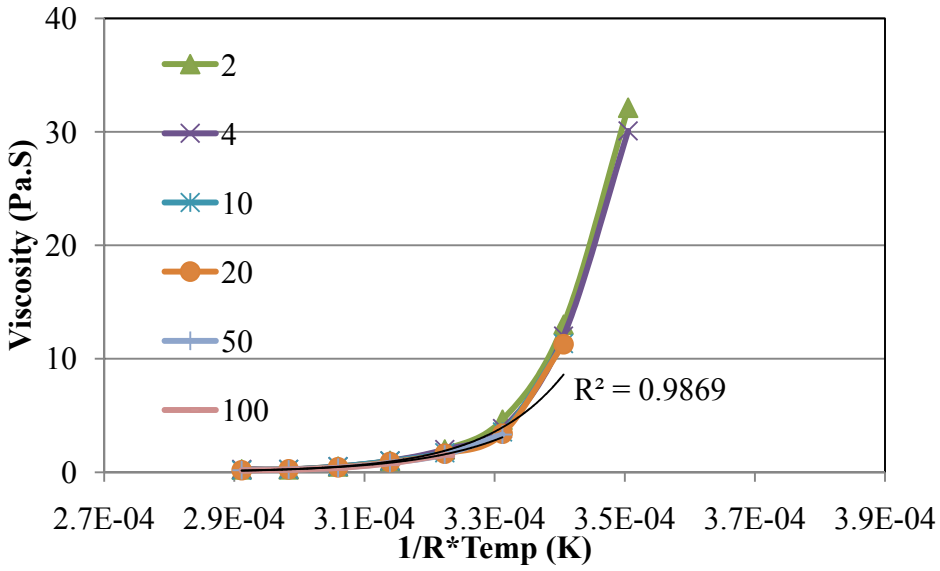

Figure C7.51. Arrhenius –type Model for Blend 20