



Article

Laboratory Study on Influence of Blending Conditions on Chemo-Thermal Characteristics of Lignin-Modified Bitumen

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Abstract: Environmental approaches in the asphalt industry have focused on utilizing waste materials as modifiers. Lignin is a high-potential bitumen modifier due to its characteristics; however, the blending process with bitumen is critical. This study investigates the chemo-thermal characteristics of lignin-modified bitumen under two different blending protocols, including a mechanical and high-shear mixer to evaluate its performance as a modifier. According to the protocols, 5, 10, and 20% of Kraft lignin was added to a PG 58S–28 bitumen. The samples were subjected to analysis using Brookfield Rotational Viscosity (BRV), Dynamic Shear Rheometer (DSR), Fourier-Transform Infrared Spectroscopy (FTIR), Environmental Scanning Electron Microscopy (ESEM), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) tests. The BRV and DSR test results indicate a remarkable alteration in the rheological properties of lignin-modified bitumen under blending conditions. The FTIR analysis indicated that Kraft lignin did not produce new functional groups. The fibril structures of the bitumens are affected by Kraft lignin content and blending conditions due to ESEM. The Kraft lignin and blending conditions influence the thermal behavior of bitumen. The findings highlight Kraft lignin's potential as a bitumen modifier, and the fact that its characteristics are influenced by the blending protocol and Kraft lignin content.

Keywords: kraft lignin; lignin-modified bitumen; mechanical mixer; high-shear mixer; chemo-thermal characteristics; sustainable asphalt materials



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1. Introduction

The use of sustainable and environmentally friendly approaches in the asphalt industry has been a major focus of recent research studies [1]. Among these approaches, the use of waste materials from other industries as modifiers or extenders in flexible pavement has gained increasing attention. One such material is lignin, which is the second most abundant biopolymer in nature [2]. Its unique chemical and physical characteristics make it a high-potential bitumen modifier [3]. However, the blending parameters are critical factors that can significantly influence the characteristics of the resulting lignin-modified bitumen [4]. In this study, the chemo-thermal characteristics of lignin-modified bitumen samples produced under different blending conditions are investigated. The influence of two shear rates, obtained from a mechanical mixer (1000 rpm) and a high-shear mixer (5000 rpm), on the rheological properties, chemical reaction, and thermal behavior of the lignin-modified bitumen are evaluated. The results of this study provide insights into the influences of adding Kraft lignin and blending conditions on the characteristics of lignin-modified bitumen, which can be valuable for the development of sustainable and high-performance asphalt materials.

2. Background

Roads and highway networks have made the world more connected than ever before. In recent decades, increasing traffic volume has led to an undeniable demand for expanding and rehabilitating existing roads and streets. However, the road construction industry's environmental impacts cannot be ignored. Asphalt mix production has been on the rise in the United States (US) [5], and its production and application are associated with natural resource use, energy consumption, and air pollution. Reducing global greenhouse gas (GHG) emissions is crucial for preventing climate change. "To stabilize atmospheric GHG concentrations at 400 ppmv CO₂e (the carbon dioxide equivalent), industrialized countries must reduce emissions by 25–30% between 1990 and 2020 and by 85–90% between 1990 and 2050" [6]. Consequently, researchers have been investigating new additives and technologies that are more friendly from an environmental perspective. Among these approaches, the application of waste materials as a modifier or extender of bitumen in asphalt mix has gained popularity. Waste materials such as lignin, crumb rubber, used oil, crushed concrete, waste plastic bottles, recycled glass, and steel slag have all been investigated [7]. Using waste materials, coming from municipal, urban, agricultural, or forestry sources, as a bitumen modifier is a promising approach that could significantly reduce the environmental impact of road construction. Furthermore, bio-additives have shown potential for reducing the environmental impact of asphalt production with enhanced asphalt performance. These include bio-oils derived from biomass; biopolymers, such as natural fibers and starch; and natural rubber obtained from the Hevea tree; as well as waxes and nanomaterials, such as biochar and nanoclays [8]. However, due to the complex structure of bitumen and the reactions between modifiers or extenders, further research is needed for a better understanding of the characteristics of modified bitumen [9,10]. In addition, lignin is known as the second most abundant biopolymer and naturally exists in lignocellulosic plants [11]. Technical lignin refers to a form of lignin obtained from the processing of biomass. The molecular weight and structure of technical lignins can vary significantly, which influences the possible applications of lignin [12]. There are different types of technical lignins, including lignosulfonates, Kraft lignin, soda lignin, hydrolysis lignin, and Organosolv lignin [13].

2.1. Lignin-Modified Bitumen

The characteristics of lignin make it a highly promising material with potential applications in various industries. Its renewability, affordability, non-toxic nature, wide availability, and similarity in chemical structure to bitumen are key properties that make lignin a suitable modifier or alternative extender for use in the asphalt industry [14,15]. In recent years, there has been a growing interest in lignin-modified bitumen.

One area of investigation has been the rheological properties of lignin-modified bitumen. Numerous studies have been conducted to evaluate the effects of several types and concentrations of lignin additives on the viscosity, stiffness, and high- and low-temperature performance of bitumen. It has been observed that the addition of lignin can improve certain properties of bitumen, such as the high-temperature performance and resistance to fatigue. However, the use of lignin can also have drawbacks, such as increased brittleness and reduced low-temperature performance [16–19]. Al-falahat et al. (2023) conducted research to evaluate the impact of Kraft lignin as an additive at various concentrations ranging up to 30% on the rheological properties of the bitumen [20]. Their test results for Brookfield Rotational Viscosity (BRV), Dynamic Shear Rheometer (DSR), Ring-and-Ball, and Multiple Stress Creep Recovery (MSCR) showed that the addition of Kraft lignin increased the viscosity, stiffness, softening point, and high-temperature performance of the bitumen, respectively. However, this also led to a decrease in low-temperature performance, as shown by their Bending Beam Rheometer (BBR) test results [20]. Additionally, Cai et al. (2023) investigated the effect of lignin and formic acid lignin additives at concentrations of 5 and 10% [21]. Their study revealed that the inclusion of these additives could signifi-

cantly enhance the properties of the asphalt at high temperatures, while also improving its resistance to fatigue and cracking at low temperatures [21].

Chemical reactions between lignin with bitumen and the microstructure of lignin-modified bitumen are also the subjects of some studies. Zhang et al. (2019) investigated the use of lignin as an antioxidant in bitumen and evaluated its chemical and rheological properties [22]. The results of the Fourier-Transform Infrared Spectroscopy (FTIR) test on bitumen samples with 10% Organosolv lignin showed that the various functional groups of lignin did not produce new chemical functional group peaks. Moreover, the microstructures of the bitumen with and without lignin were found to be almost identical, according to the Environmental Scanning Electron Microscope (ESEM) test [22]. In another study conducted by Zhang et al. (2022), a bio-oil was used as an additive in lignin-modified bitumen [23]. FTIR spectra analysis indicated that there were no newly generated chemical functional groups in the blend of lignin, virgin bitumen, and oil. It was concluded that the blending process did not create a new chemical composition. As a result, there was either no chemical reaction or the reaction was negligible [23]. Scanning Electron Microscope (SEM) and Environmental Scanning Electron Microscope (ESEM) are important techniques for investigating lignin-modified bitumen, as they provide high-resolution images of the surface [24]. Many research studies have been conducted in this area [25–27]. For instance, Kalampokis et al. (2022) used SEM to investigate the shape and particle size distribution of lignin powder [28].

Finally, one of the noteworthy research areas of lignin-modified bitumen is the investigation of thermal properties, which are essential for its performance under high- and low-temperature conditions [29]. The thermal stability and decomposition behavior of lignin-modified bitumen can be assessed using Thermogravimetric Analysis (TGA). Numerous research studies have been conducted to investigate the thermal properties of modified bitumen [30–32]. For example, Nizamuddin et al. (2023) used TGA to investigate the effect of low-density polyethylene (LDPE) on the thermal stability of bitumen, and their results showed that blends with a higher percentage of recycled LDPE were more thermally stable and exhibited a low rate of evaporation compared to blends with low LDPE concentrations [33]. Jianfei et al. (2020) investigated the combustion properties of lignin residues using TGA. The results showed that washing processes changed the thermal characteristics of lignin samples [34]. Another important research area in the study of lignin-modified bitumen is the use of Differential Scanning Calorimetry (DSC) testing to evaluate its thermal properties, including the glass transition temperature (T_g) and degree of crystallinity [35,36]. The glass transition temperature (T_g) and degree of crystallinity are critical factors in assessing and determining the performance characteristics of bitumen [37]. Numerous research studies have employed DSC testing to investigate these properties in modified bitumen [38–40]. Wręczycki et al. (2022) investigated the potential of sulfur/organic copolymers as modifiers for bitumen binders [41]. Glass transition temperature (T_g) was one of the properties studied in their research. The incorporation of sulfur/organic copolymers was found to cause a significant decrease in T_g , by up to 4 °C, indicating that the copolymers interacted with the bitumen and altered its properties. This finding suggests that sulfur/organic copolymers have the potential to improve the low-temperature performance of bitumens [41].

2.2. Blending Protocols for Lignin-Modified Bitumen

Blending protocols play a critical role in determining the properties of lignin-modified bitumen, as they have a significant influence on the physicochemical characteristics and performances of the final product [4]. The blending conditions, such as blending temperature, time, and shear rate, can significantly affect the interaction and distribution of lignin in bitumen [42]. Numerous studies have been conducted on lignin-modified bitumen prepared with various blending protocols. Understanding the blending conditions and efficiency is crucial for ensuring the optimal performance and properties of lignin-modified

bitumen. Table 1 summarizes the variety of blending protocols used in these studies to investigate the properties of lignin-modified bitumen.

Table 1. Various blending protocols of lignin and bitumen in the literature.

Mixer (Type)	Additive (Type)	Bitumen (Type)	Blending Temp. (°C)	Blending Time (min)	Shear Rate (rpm)	Ref. (number)
High-shear mixer (HSM)	Lignin	Grade 60/70	155	30	5000	[43,44]
		Grade 70/100	163	30	3000	[23]
			160	120	3000	[45]
		Grades 50/70 and 160/220	150	60	6000	[46]
		PG 58–28	160	40	6000	[16]
		-	130	45	5000	[47]
	-	155	30	5000	[48]	
	Kraft lignin	Grade 50/70	160	60	5000	[49]
		PG 67–22	180	30 + 30	4000 + 8000	[50]
		PG 64–22	160	60	5000	[51]
	Wood lignin	Grade 70	160–168	45	1200	[15]
		Grade 70/100	163	30	3000	[22]
	Organosolv lignin	Grade 70/100	163	30	3000	[52]
	Soda lignin	Grade 60/70	155	10 + 50	4000 + 8000	[53]
	Kraft lignin and Corn stalk lignin	Grade 60/70	160	60	4000	[54]
Alkali lignin and quercetin	PG 64–22	170	45	4500	[55]	
Mechanical mixer (MM)	Kraft lignin	Grade 50/70	160	30	2000	[56]
		PG 58S–28 and PG 52S–34	170	15	1000	[20]
	Wood lignin	PG 64–22 and PG 76–22	163	30	1500	[17]
	Lignin	-	140	60	1000	[57]

In light of the growing interest in the development of sustainable and environmentally friendly approaches in the asphalt industry, the utilization of waste materials as modifiers or extenders in bitumen has emerged as a promising strategy for reducing the environmental impact. Among these waste materials, lignin, a widely available and renewable biopolymer, has garnered considerable interest due to its chemical and physical properties that make it a promising material for bitumen modification. Previous studies have investigated the rheological properties, chemical reactions, microstructure, and thermal behavior of lignin-modified bitumen, revealing both potential benefits and challenges associated with its use. However, further research is needed to elucidate the blending protocols and their influence on the performance of lignin-modified bitumen.

3. Laboratory Study

In this laboratory study, different amounts of a single type of lignin were added to a single type of bitumen with two different blending protocols. The lignin-modified bitumens produced were then tested to evaluate their viscosity and their viscoelastic properties before testing their chemical and thermal properties. The description of the materials, the blending protocols, and the different tests used are shown hereafter.

3.1. Materials

3.1.1. Bitumen

In this research study, an unmodified bitumen PG 58S–28 for a standard traffic level (S), obtained from Bitumar, a Canadian company, was utilized. All specifications and test results provided by the manufacturer are presented in Table 2.

Table 2. Tests and specifications of PG 58S–28 based on the manufacturer’s data sheet.

Characteristic (Unit)	Amount	Specification Limits	Standard or Test Method
Flashpoint (°C)	273	>230	ASTM D 92
Density at 25 °C (g/cm ³)	1.021	1.000–1.050	AASHTO T 228
Density at 15 °C (g/cm ³)	1.027	1.007–1.037	AASHTO T 228
Brookfield viscosity at 135 °C (mPa·s)	309	150–500	AASHTO T 316
Brookfield viscosity at 165 °C (mPa·s)	92	30–180	AASHTO T 316
Storage stability (°C)	0.3	≤2.0	LC 25-003
Ash content (%)	0.28	≤0.50	ASTM D 8078
G* /Sin(δ) at 58 °C (kPa)	1.54	≥1.00	AASHTO T 315

3.1.2. Kraft Lignin

The Kraft lignin utilized in this study is a sticky brown fine powder, derived from softwood and provided by FPInnovations (Figure 1a). Kraft lignin is a valuable and sustainable raw material produced as a byproduct of the paper industry. The main properties of this powder are presented in Table 3. The elemental analysis provided by the supplier indicated that the Kraft lignin was composed primarily of four (4) main elemental components, including carbon, hydrogen, oxygen, and sulfur, with the remaining 3% composed of other elements (Figure 1b).

Table 3. Properties of the used Kraft lignin provided by the supplier.

Property (Unit)	Value
Density (g/cm ³)	1.2–1.3
Potential Hydrogen (pH)	3–4
Molecular Weight (g/mol)	5185
Moisture Content (%)	1.3
Ash Content at 575 °C (%)	0.42
Purity (%)	95

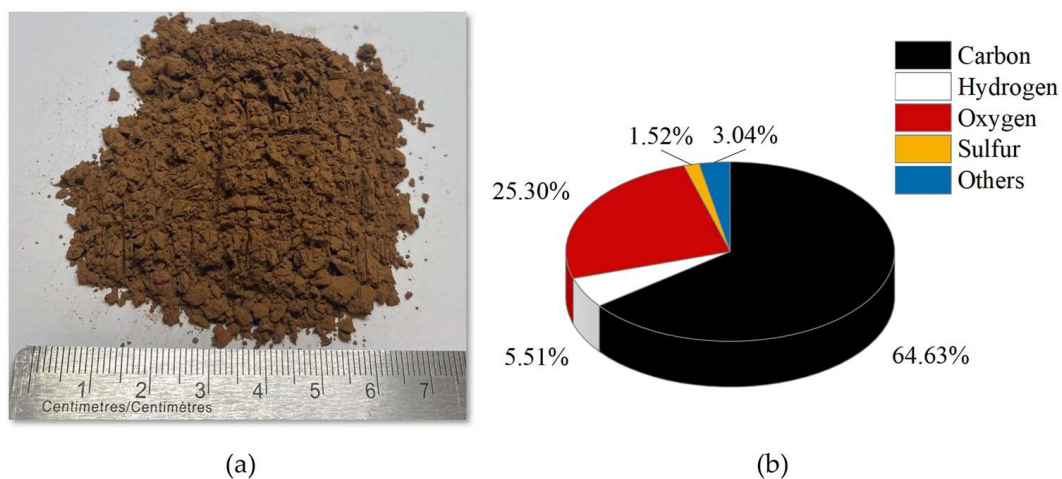


Figure 1. (a) Studied Kraft lignin powder and (b) Elemental analysis of Kraft lignin.

The particle size distribution is a critical property that can influence the performance of materials in various applications. To determine the particle size distribution of Kraft lignin, the laser diffraction technique was employed using a Mastersizer 3000 instrument equipped with a Hydro EV dispersion unit. The measurements were conducted over a range of 0.01–500 μm to ensure a comprehensive analysis of the particle size distribution. The resulting data showed that the particle size of the Kraft lignin powder fell within the range of 1 to 100 μm , with 80% of the particles between 5.47 μm (D10) and 48.7 μm (D90), as shown in Figure 2.

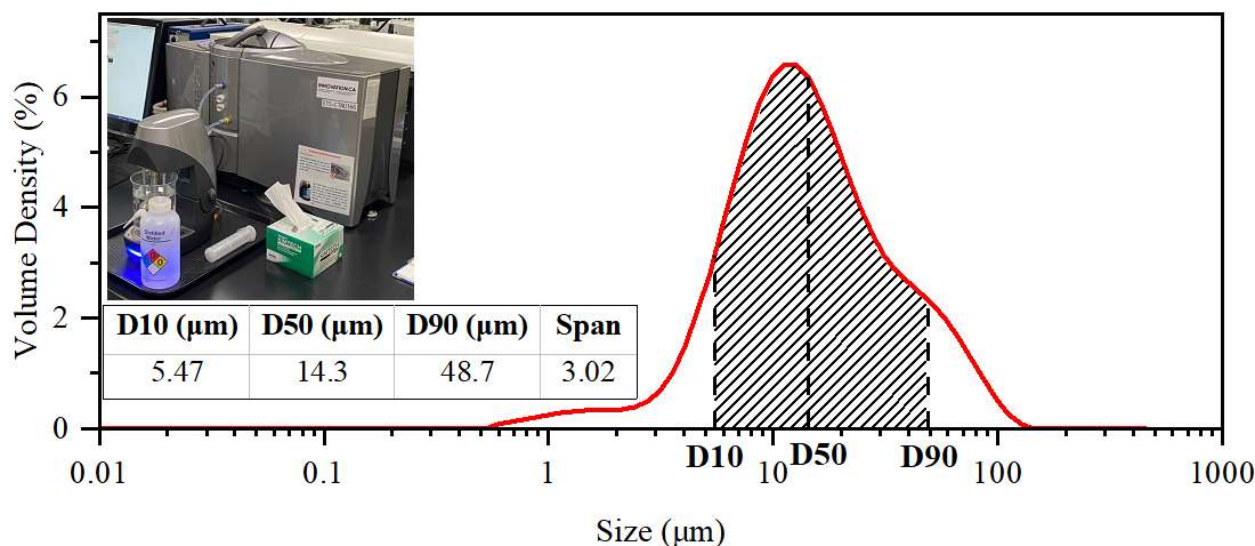


Figure 2. Particle size distribution of Kraft lignin determined by laser diffraction technique.

3.2. Sample Preparation and Blending Protocols

The main aim of this research study is to investigate the influence of Kraft lignin as a bitumen modifier on the chemo-thermal characteristics of the lignin-modified bitumen, as well as the influence of different blending conditions. To achieve this, Kraft lignin was added to the bitumen at three (3) different percentages of 5, 10, and 20% (Table 4) by weight of the lignin-modified bitumen (lignin + bitumen). According to the recently published article by our colleague, the maximum mass percentage of this specific lignin (Kraft lignin: acidic and derived from softwoods) with an unmodified bitumen (PG 58S–28 or PG 52S–34) and mixed with a mechanical mixer is 30%; otherwise, the storage stability and homogeneity of the bitumen–lignin blend are affected negatively [20]. In addition, two (2) types of mixers were utilized in this study, an IKA RW16 Basic Overhead Stirrer, with a maximum rate of 1200 rpm, referred to as the mechanical mixer (MM), and a Silverson L4RT high-shear mixer (HSM), with a maximum rate of 8000 rpm, as shown in Figure 3. This study focuses on the effect of the shear rate as the research parameter, with two (2) different rates investigated: 1000 and 5000 rpm. The blending time was fixed at 60 min, and the blending temperature was maintained at 150 ± 5 $^{\circ}\text{C}$ throughout the blending process by an oil bath. Prior to the blending process, the bitumen samples were placed in an oven at 150 $^{\circ}\text{C}$ to achieve a uniform blending temperature. Subsequently, the beaker containing the bitumen was suspended in an oil bath for 20 min to stabilize the bitumen temperature before the addition of Kraft lignin. Due to the sticky nature of Kraft lignin, the addition process of the additive was carried out gradually within 15 min, followed by 45 min of blending time, for a total of 60 min. In order to enhance the accuracy and comparability of test results, two (2) virgin bitumen specimens were processed using the same blending protocols without the addition of Kraft lignin, referred to as VB-MM for the mechanical mixer and VB-HSM for the high-shear mixer. The samples in this study were named according to Table 4.

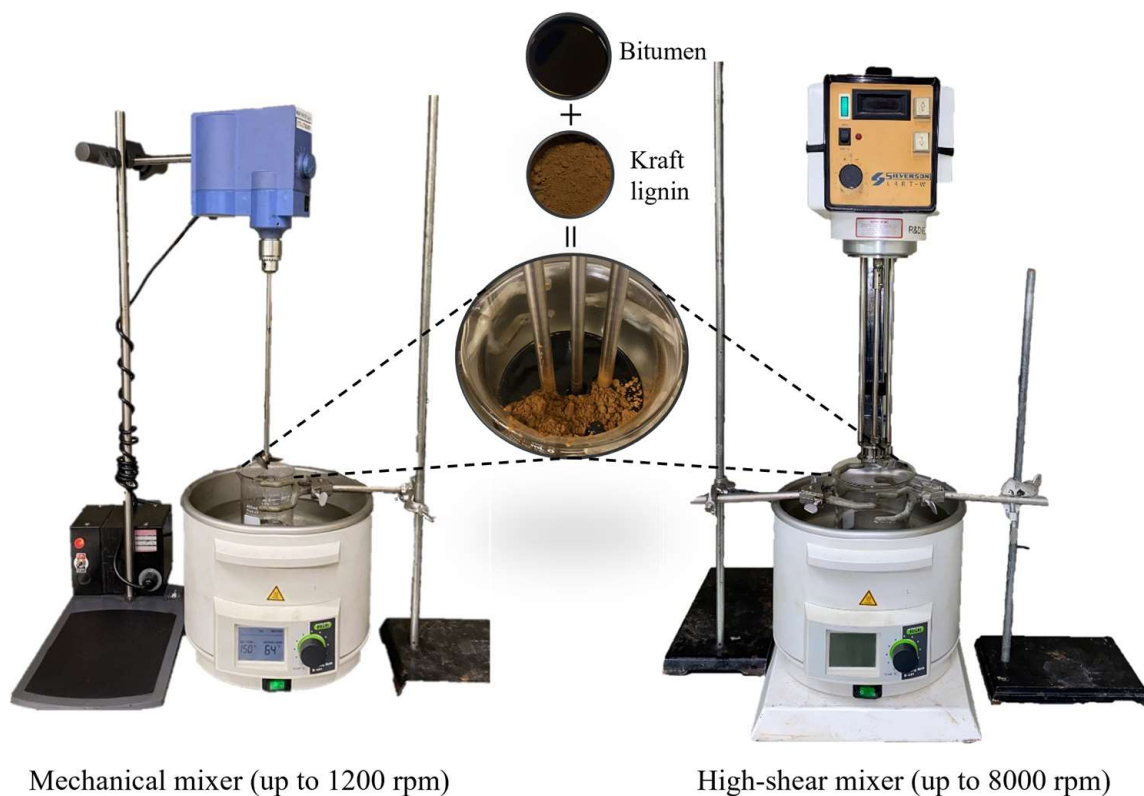


Figure 3. Blending Kraft lignin and bitumen using Mechanical Mixer (MM) and High-Shear Mixer (HSM) in the oil bath.

Table 4. Details of specimens tested in the study.

Sample Details	Kraft Lignin (wt %) ¹	Blending Protocol	Code
Virgin Bitumen (VB)	0	---	VB
		MM	VB-MM
		HSM	VB-HSM
Bitumen with added Kraft lignin (L)	5	MM	5L-MM
		HSM	5L-HSM
	10	MM	10L-MM
		HSM	10L-HSM
	20	MM	20L-MM
		HSM	20L-HSM

¹ The lignin content is a percentage of the total weight of the lignin-modified bitumen (lignin + bitumen).

3.3. Testing

3.3.1. Brookfield Rotational Viscosity (BRV) Test

In this study, the influence of Kraft lignin, as an additive, on the viscosity of bitumen was evaluated, as the fine powder nature of lignin can significantly modify this property of bitumen.

The viscosity of bitumen samples was determined using a Brookfield Rotational Viscometer (BRV) device, which characterizes the bitumen for workability during pumping, mixing with aggregate, and compaction of hot mix asphalt. To perform the BRV test, a cylindrical spindle was rotated inside a container filled with bitumen at a specified speed. To determine the viscosity of bitumen, the torque needed to maintain a constant rotational speed of the spindle was measured. A Brookfield DV2T viscometer produced by Ametek-Brookfield was used in this study. The BRV test was conducted following the

test procedures described in the LC 25-007 Quebec test method, at 135 and 165 °C for all samples. The bitumen samples were poured into a cylindrical container and placed in the device at a temperature of 135 followed by 165 °C with a conditioning time of 15 min for each temperature. At each temperature, nine (9) readings of viscosity were recorded at 1 min intervals.

3.3.2. Dynamic Shear Rheometer (DSR) Test

In this laboratory study, the Dynamic Shear Rheometer (DSR) test was conducted to evaluate the linear viscoelastic (LVE) properties of unaged bitumen samples. The DSR test was carried out according to the AASHTO T315 standard, using a Kinexus DSR produced by Malvern. A sinusoidal shear load with a loading frequency of 10 rad/s was applied on a 25 mm diameter plate with a sample thickness of 1 mm. The test was conducted at 58, 64, and 70 °C. Rheological parameters, such as the norm of the complex shear modulus ($|G^*|$) and phase angle (δ), were determined. Additionally, $|G^*|/\sin(\delta)$ values were calculated to evaluate, to some extent, the rutting resistance of the bitumen samples.

3.3.3. Fourier-Transform Infrared Spectroscopy (FTIR) Test

The chemical composition of bitumen is complex and multifaceted due to the diverse origins of crude oil resources. The addition of modifiers to enhance the mechanical properties of bitumen results in further complexity in its chemical characteristics.

Fourier-transform infrared spectroscopy (FTIR) is a commonly used and appropriate analytical technique for detecting chemical compounds and obtaining information on the chemical composition of materials at the molecular level. It has the potential to yield both qualitative and quantitative outcomes, which could be valuable for research studies. This study investigates the chemical interactions between bitumen and Kraft lignin. When two materials are in contact, their molecular vibrations can change due to chemical interactions. These changes can be detected by comparing the FTIR spectra of the individual materials with the FTIR spectra of the mixture. In this study, attenuated total reflectance ATR-FTIR was used to gather spectral information from Kraft lignin and bitumen samples. The Spectrum Two™ FTIR Perkin Elmer, which incorporates a Diamond crystal, was employed to obtain data within the wavenumber range of 4000 to 400 cm^{-1} at a 4 cm^{-1} resolution. Twenty (20) scans were recorded for each spectrum. Prior to each test, the ATR crystal was cleansed using limonene and isopropanol, and a background spectrum was captured.

3.3.4. Environmental Scanning Electron Microscope (ESEM) Test

The intricate behavior of bitumen is influenced by both its chemical composition and microstructure. This fact motivates researchers to investigate bitumen structures at the micro and nano scales, using various technologies to establish the relationship between microstructure and physical properties.

Environmental Scanning Electron Microscopy (ESEM) is a type of electron microscopy that enables the imaging of oily materials, such as bitumen, in their natural state. This technique eliminates the need for bitumen conductive coating processes and ultra-high vacuum typically required for conventional Scanning Electron Microscopy (SEM) [24]. ESEM can be used to investigate the morphology and dispersion of modifiers within the bitumen matrix, aiding in a better understanding of its behavior. In this study, the protocol developed by Mikhailenko et al. (2017) was followed [58]. The bitumen samples were softened at 150 °C for 30 min. Approximately 0.5 to 1 g of bitumen was poured into 8 mm diameter and 2 mm height stainless steel molds using a spatula. The sample then was flattened by placing the mold on a hotplate to ensure a flat surface. Observations were conducted at room temperature using a FEI Quanta 250 FEG ESEM. The test parameters were set up with an acceleration voltage of 20 keV, a chamber pressure of 0.8 mbar in low vacuum mode, and a magnification of $\times 1000$ in secondary electron (SE) mode.

3.3.5. Thermogravimetric Analysis (TGA) Test

Thermogravimetric Analysis (TGA) is one of the methods to study the thermal properties of materials. The sample weight change is measured at a given temperature and time while the temperature is rising under a constant heating rate. The sample could lose weight due to the decomposition and debonding of the structural components or gain weight due to an instant gas reaction. Thermograms of TG and derivatives thermogravimetric (DTG) provide valuable information. DTG curves are the first differential of TG curves, which is an indicator of the degradation rate at a given temperature. Different interpretations and multifunctional analyses can be made from this information to investigate thermal characteristics of the material. The thermal and oxidative stability, durability of material against temperature, determining the multi-component material according to degradation stages, kinetic reaction, amount of volatile component, and moisture, are the most crucial parameters that could be identified. In this laboratory study, the TGA test was conducted with the STA8000 PerkinElmer's device under air atmosphere for Kraft lignin powder and bitumen samples. The testing temperature range was considered from room temperature to 1000 °C, with a heating rate of 10 °C/min and a gas flow of 50 mL/min.

3.3.6. Differential Scanning Calorimetry (DSC) Test

Another technique commonly used to investigate the thermal behavior of materials is Differential Scanning Calorimetry (DSC). This technique provides valuable information about the physical, chemical, and thermal properties of materials by measuring the heat absorbed or released during a controlled heating or cooling process. DSC works on the principle of differential heat flow measurement, where a sample and a reference material are subjected to the same controlled temperature program. Any difference in heat flow between the sample and reference is measured and plotted as a function of temperature. The DSC test was performed on 5–10 mg of material in an aluminum hermetic pan. A nitrogen (N₂) atmosphere with a flow rate of 50 mL/min was maintained throughout the test using the DSC2500 instrument from TA Instruments. The samples were prepared by cutting them into small pieces and placed in a pan. The pan and the pierced lid were crimped using a press.

The samples were subjected to four (4) temperature cycles, ranging from −80 to 160 °C, to accurately characterize their thermal properties (Figure 4). The 1st cycle aimed to facilitate proper contact between the bitumen sample and the pan by softening the bitumen. To achieve this objective, the samples were subjected to a temperature increase from room temperature to 130 °C, with a heating rate of 20 °C/min. The 2nd cycle involved a temperature decrease to −80 °C, with a rate of 10 °C/min, followed by an increase to 160 °C. This cycle aimed to eliminate any thermal history in the samples. In the 3rd cycle, the temperature again dropped to −80 °C to eliminate the cold crystallization effect. The last and 4th cycle had a slightly different setup from the others. As reported in the Apostolidis et al. (2021) research, their study showed that Temperature Modulation-DSC (TM-DSC) is a more accurate technique than Temperature Linear-DSC (TL-DSC) for analyzing bitumen [59]. They also found that TM-DSC can detect the glass transition (T_g) region in bitumen with high precision. As a result, for the 4th cycle, the TM-DSC protocol was set up with a heating rate of 5 °C/min, with ±0.5 °C modulation every 80 s.

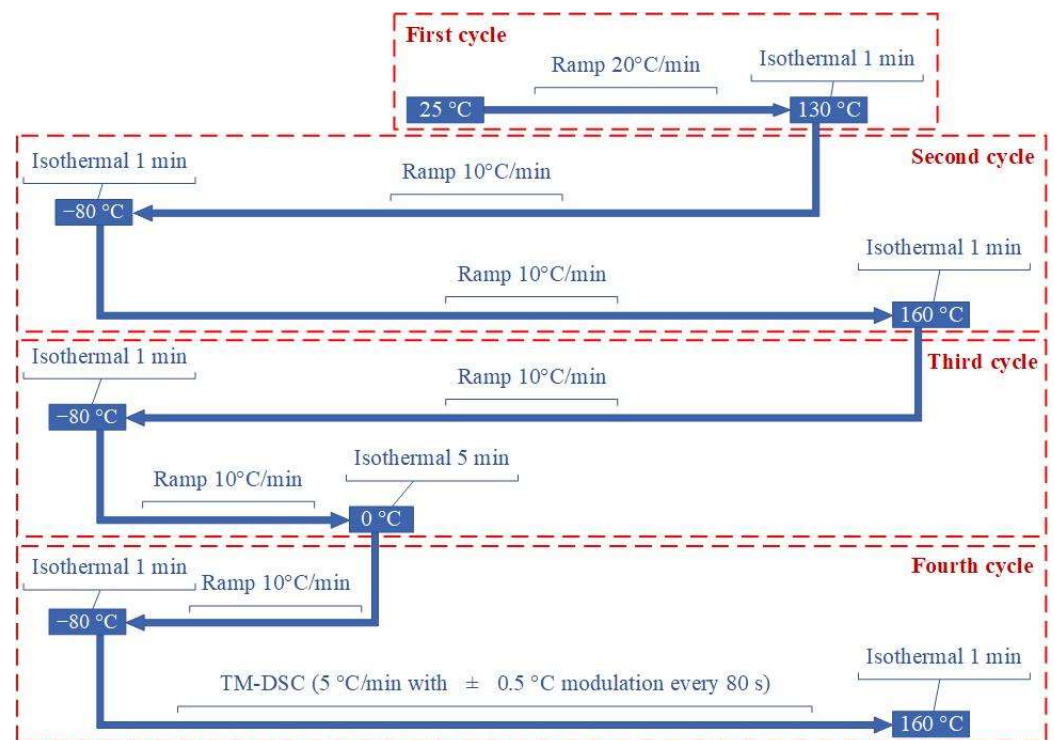


Figure 4. DSC methodology for samples.

4. Results and Discussion

4.1. BRV Results

The BRV test results for all bitumen samples at 135 and 165 °C are shown in Figure 5. The results show the influences of Kraft lignin with different percentages and blending conditions on the rotational viscosity of the bitumen samples. More precisely, the measured viscosities allow quantifying the influence of Kraft lignin, as an additive, on the stiffness of bitumen, specifically at a high percentage of additive.

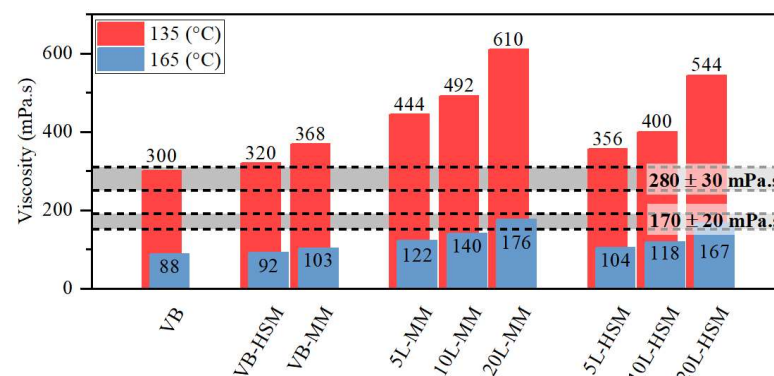


Figure 5. The viscosity of bitumen samples at 135 and 165 °C.

Generally, adding Kraft lignin increases the viscosity of the virgin bitumen at 135 and 165 °C and enhances the high-temperature stability. As seen in Figure 5, the viscosity of virgin bitumen at 135 °C is 300 mPa·s, which is similar to what the manufacturer measured (value of 309 mPa·s: Table 2). The addition of 5, 10, and 20% of Kraft lignin using a high-shear mixer (HSM) increase the viscosity to 356, 400, and 544 mPa·s, respectively. Likewise, samples prepared using a mechanical mixer (MM) exhibit a similar trend (444, 492, and 610 mPa·s for 5, 10, and 20% of Kraft lignin, respectively).

The mechanisms behind the observed increase in viscosity may relate to the molecular weight of Kraft lignin and bitumen. According to the producer's data sheet, the molecular weight of Kraft lignin is 5185 g/mol. Bitumen has a wide range of molecular weights, depending on the crude oil source and composition, but it seems that bitumen has a lower molecular weight than Kraft lignin. This increase in molecular weight may lead to higher viscosity. In addition, the polarity of Kraft lignin may be a potential factor influencing the rheological properties of the modified bitumen. As bitumen is known to possess a relatively high polarity, the presence of Kraft lignin may further contribute to the increase in viscosity. Moreover, Kraft lignin is a powder, so it contains solid particles, which increases the viscosity.

The influence of the shear rate on viscosity is significant. Samples prepared by a high-shear mixer (HSM) show a lower viscosity compared to the mechanical mixer (MM) samples. Figure 5 illustrates the impact of the shear rate on virgin bitumen. Processing virgin bitumen (VB) using a high-shear mixer (HSM) results in a 7% increase in viscosity, whereas using a mechanical mixer (MM) increases it by 23%. The difference in viscosity could be attributed to a greater loss of volatiles from the virgin bitumen (VB) processed by the MM. When blending Kraft lignin with bitumen using a MM, which has a three-bladed head, the rotational motion of the mixer creates a centrifugal force that pushes the bitumen outward, resulting in a non-flat surface with a funnel shape (Figure 6a). This shape increases the surface area of the bitumen in contact with air, leading to higher oxidation. However, HSM has a different head design that creates a flat surface on the bitumen during blending (Figure 6b). This flat surface reduces the contact area of the bitumen with air, thus reducing the possibility of oxidation. Further, the selection of an appropriate head for a high-shear mixer (HSM) may influence the properties of the final product. Among the various heads available, the widely used head for powder materials was used. An HSM could lead to reduced stiffness and oxidation during the blending process compared to a MM.

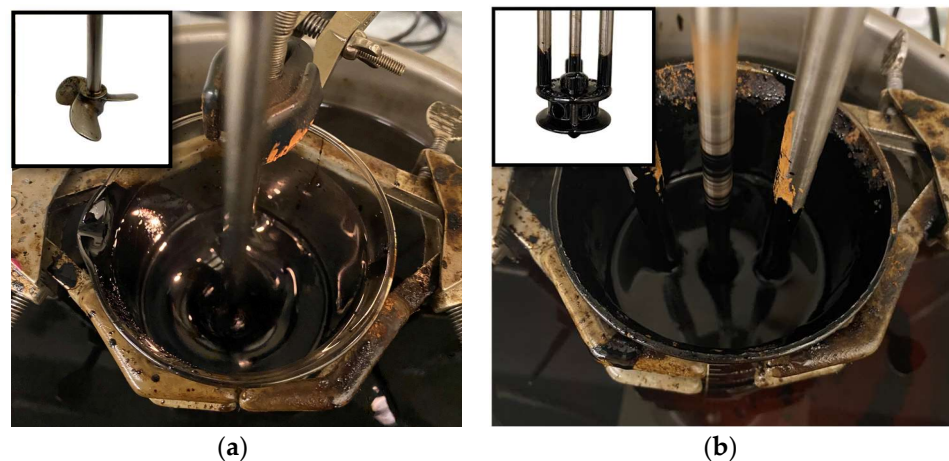


Figure 6. Comparison between (a) the mechanical mixer (MM) and (b) the high-shear mixer (HSM) during blending process.

In general, according to the test results, all samples that were processed in either mixer have higher viscosity. According to the LC 25-007 test method, the required viscosity for mixing and compaction is 170 ± 20 mPa·s and 280 ± 30 mPa·s, respectively, for binder used for hot mix asphalt (HMA) (limits presented in Figure 5). To achieve these target values, it is necessary to increase the mixing and compaction temperature. Due to its higher viscosity, bitumen requires higher temperatures to become sufficiently fluid for mixing and compaction, resulting in higher energy consumption. It is noteworthy that the viscosity of both virgin and modified bitumens does not exceed the prescribed limit of 3000 mPa·s at 135 °C, as specified by AASHTO M320.

4.2. DSR Results

Figures 7 and 8 depict the results of the dynamic shear rheometer (DSR) test conducted on unaged bitumen samples. The DSR test results indicate a remarkable modification in the rheological properties of lignin-modified bitumen under different blending conditions.

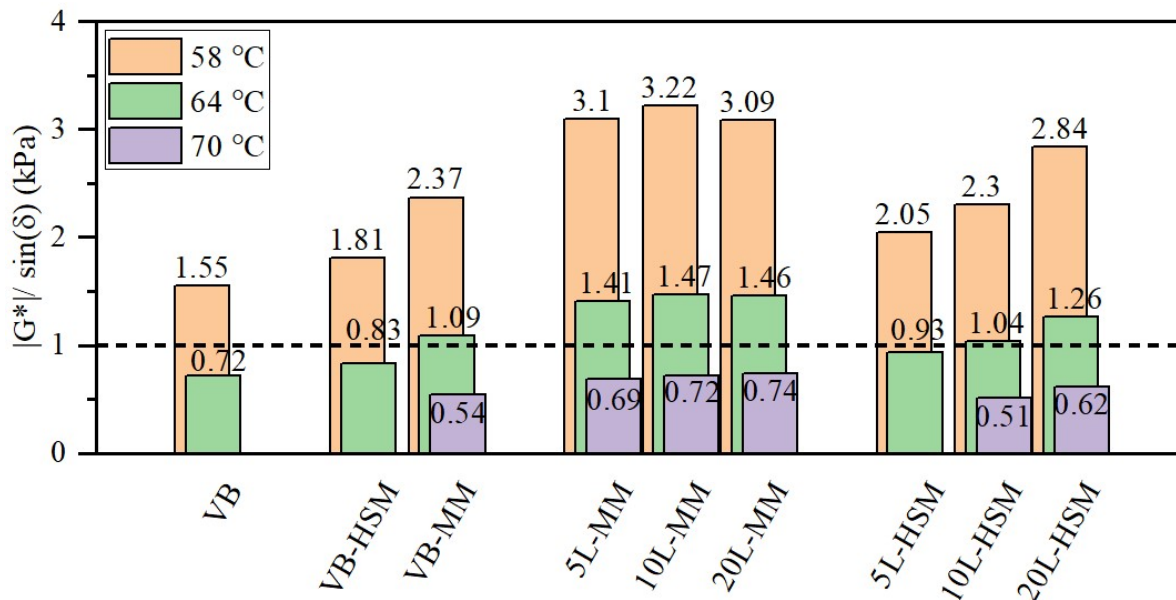


Figure 7. Impact of Kraft lignin on the $|G^*|/\sin(\delta)$ of bitumen under two blending conditions (dotted line: minimum value to be obtained at 58 °C).

The variation of $|G^*|/\sin(\delta)$ with temperature for bitumen with different Kraft lignin contents (0, 5, 10, and 20%) in different blending conditions is shown in Figure 7. The $|G^*|/\sin(\delta)$ parameter is, to some extent, an indicator of the rutting resistance of an asphalt binder. Furthermore, it is essential to note that the value of $|G^*|/\sin(\delta)$ in the DSR test should surpass 1.00 kPa for unaged asphalt binders, as specified by the Performance Grade (PG) standards for bitumen (*Ministère des Transports du Québec*: 4101 standard). The results indicate an increasing trend in the value of $|G^*|/\sin(\delta)$ for all bitumen samples, compared to the VB sample. The samples without Kraft lignin show a significant increase in stiffness ($|G^*|$ value increasing) and in elastic behavior (δ value reducing) during the blending process, which is noteworthy, with a rise, for the $|G^*|/\sin(\delta)$ parameter, from 1.55 kPa for VB to 1.81 and 2.37 kPa for VB-HSM and VB-MM, respectively, at 58 °C. As the addition of Kraft lignin results in an upward shift in $|G^*|/\sin(\delta)$, it indicates an increase, to a certain extent, in the rutting resistance. This increment is more prominent in MM samples than in HSM samples, which suggests that in the MM blending process, as previously discussed, more volatile and light components were lost and exhibited more stiffness ($|G^*|$) and less viscous behavior (δ) in general. Therefore, it can be concluded that the addition of Kraft lignin significantly enhances, to some extent, the rutting resistance of bitumen, and the blending process also affects the $|G^*|$ and δ . For more information on the effect of lignin on rutting resistance, refer to Al-falahat et al. (2023) [20]. For instance, the HSM samples exhibit increases of 32, 48, and 83% for the 5L-HSM, 10L-HSM, and 20L-HSM samples, respectively, for the $|G^*|/\sin(\delta)$ parameter, which is an indicator for rutting resistance.

Figure 8 illustrates the norm of the complex shear modulus ($|G^*|$) and the phase angle (δ) of all samples, indicating a significant modification for the HSM and MM samples in different ways. An increase in the $|G^*|$ value indicates that the lignin-modified bitumen samples are becoming stiffer. A decrease in δ values suggests that the samples are becoming more elastic and less viscous, as they are able to respond more quickly to the applied stress.

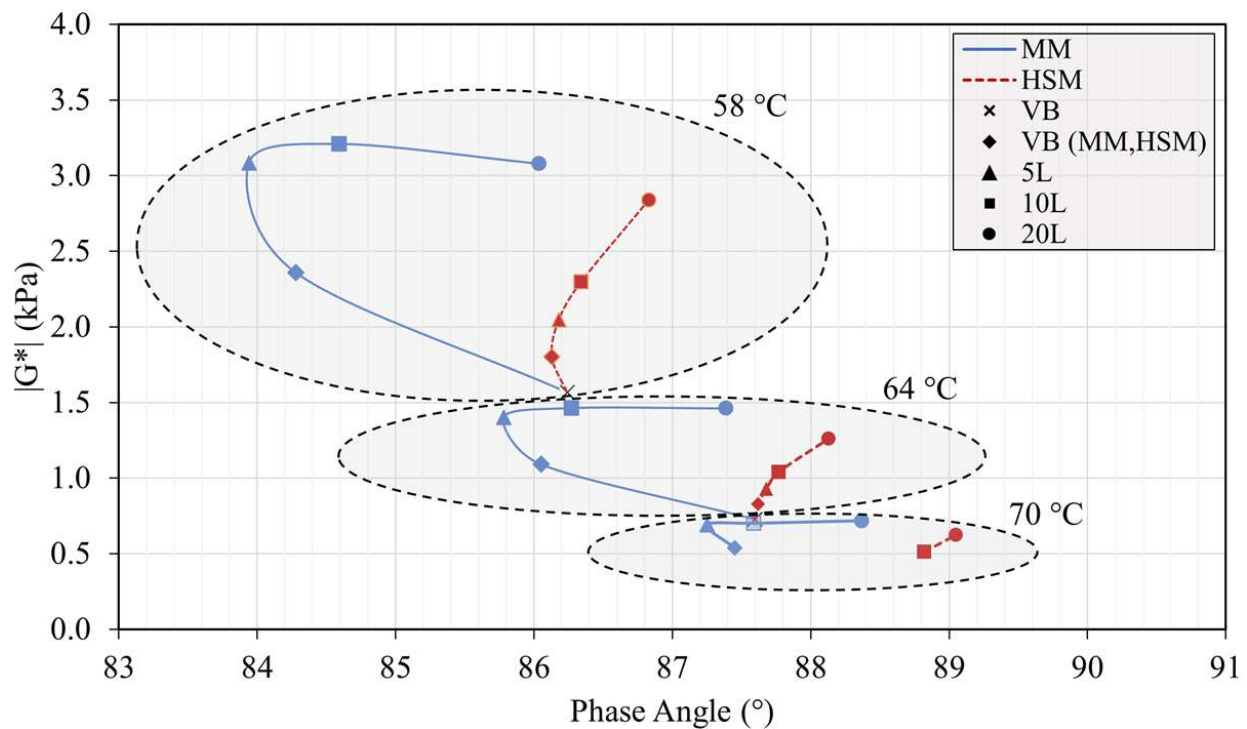


Figure 8. Norm of complex shear modulus $|G^*|$ and phase angle (δ) of specimens using DSR test.

Regarding the impact of Kraft lignin as an additive, the results show that adding Kraft lignin in the HSM samples leads to a significant increase in stiffness ($|G^*|$), but does not have a significant effect on the viscous behavior (a small change in the δ value) (Figure 8). Conversely, the MM samples exhibit less alteration in $|G^*|$ (stiffness), but remarkable changes in the δ (viscous behavior). For instance, in HSM samples at 58 °C, the δ value changes by -0.07 , 0.12 , and 0.68% (less than 1%) for 5, 10, and 20% of Kraft lignin, respectively. All changes suggest that the addition of Kraft lignin using HSM does not have a remarkable impact on δ . However, the changes in $|G^*|$ are remarkable. The HSM blending process itself leads to an increase in $|G^*|$ by 15% at 58 °C. Furthermore, the addition of 5, 10, and 20% of Kraft lignin results in a significant increase in $|G^*|$ by 31, 47, and 81%, respectively, at 58 °C. For MM samples at 58 °C, the blending process increases the $|G^*|$ by 51%. Meanwhile, by increasing the Kraft lignin percentage, $|G^*|$ increases by 97, 105, and 97% for the 5L-MM, 10L-MM, and 20L-MM samples, respectively.

Lastly, in terms of blending conditions, samples prepared with a MM exhibited higher $|G^*|$ and lower δ values compared to those prepared with HSM (Figure 8). These findings indicate that the MM samples have greater stiffness and elasticity than the HSM samples. It is important to note that the HSM samples exhibit a distinctly different behavior compared to the MM samples. These findings highlight the significant impact of blending conditions on the rheological behavior of modified bitumen with Kraft lignin. Further, it can be concluded that the MM samples undergo more extensive oxidation and aging. These observations align with the results obtained from the BRV tests.

4.3. FTIR Results

The FTIR spectroscopy analysis was performed to investigate the influence of Kraft lignin addition on the chemical structure of bitumen under different blending conditions. Figure 9 shows the FTIR spectral results of VB and HSM samples. The FTIR spectrum presented in this study was obtained as an average of three (3) replicates. To ensure consistency and comparability, all spectra were normalized to the band with the highest intensity in the bitumen spectrum using a min–max normalization approach [60].

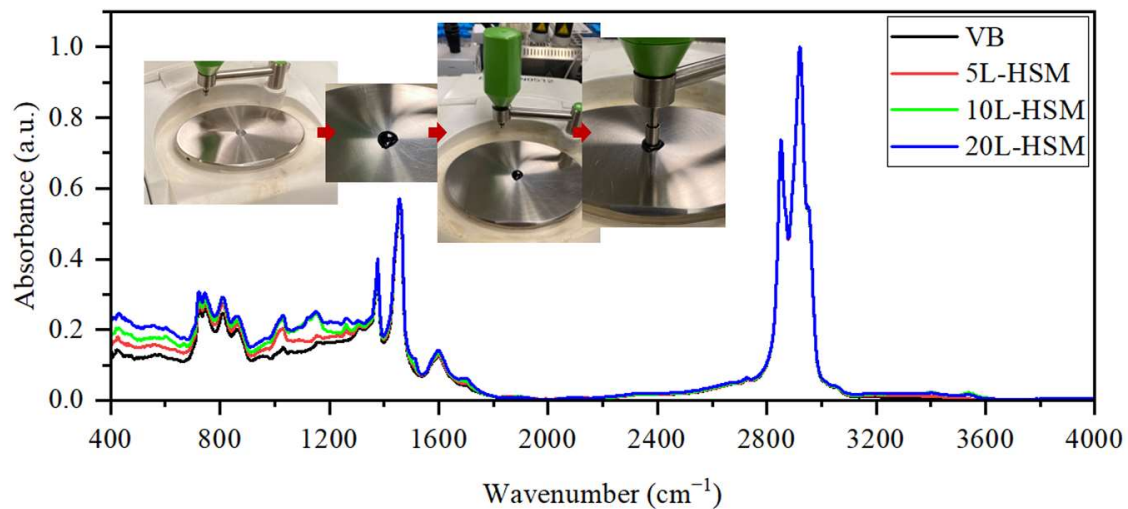


Figure 9. FTIR spectra of VB, 5L-HSM, 10L-HSM, and 20L-HSM binders (wavenumber of 400 to 4000 cm^{-1}) (average of three replicates per sample type).

As shown in Figure 9, significant changes observed are between 2000 to 400 cm^{-1} , which are typically referred to as the “fingerprint region” [61]. This region contains a unique pattern of absorption peaks that can identify specific functional groups present in the modified bitumen sample.

From a chemical reaction point of view, the FTIR spectra of Kraft lignin and modified bitumen with 5, 10, and 20% of Kraft lignin for HSM samples in the fingerprint region are shown in Figure 10. A shift to higher wavenumbers (2000 to 400 cm^{-1}) in an FTIR spectrum can indicate a change in chemical structure and an increase in bond strength, but does not necessarily mean a chemical reaction has occurred [62,63]. The shift in peak position (y -axis) can also be due to changes in intermolecular interactions.

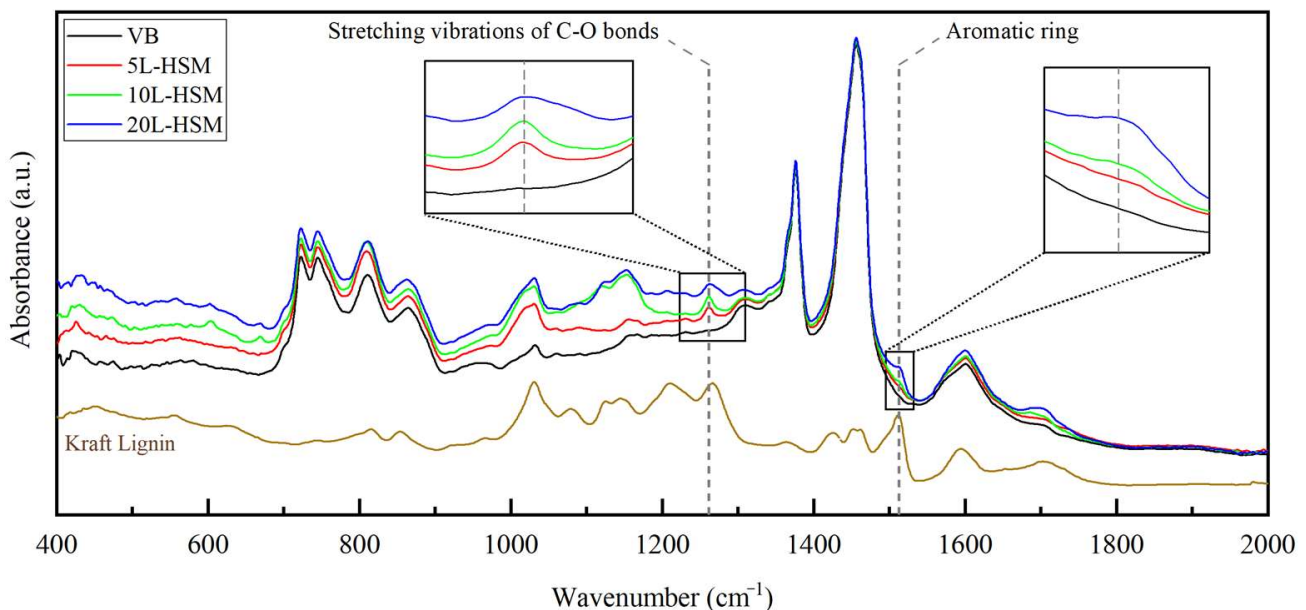


Figure 10. FTIR spectra of Kraft lignin, VB, 5L-HSM, 10L-HSM, and 20L-HSM samples (wavenumber of 400 to 2000 cm^{-1}).

According to the test results, new peaks are generated at 2 wavenumbers of 1260 and 1510 cm^{-1} , which intensified with increasing Kraft lignin percentage. The wavenumber of 1260 cm^{-1} is associated with the stretching vibration of C-O bonds in aliphatic and aromatic

ethers, while the wavenumber of 1510 cm^{-1} is commonly attributed to the stretching vibration of aromatic ring structures [64]. Meanwhile, Kraft lignin has peaks in the same wavenumbers, indicating the presence of Kraft lignin in the bitumen, not a new chemical reaction. On the other hand, the peak values of the curves for other wavenumbers are slightly different, but the peak positions of the curves are basically the same, indicating that the Kraft lignin does not produce new functional groups, but intensifies the existing peaks. It can be speculated that the physical interaction between the two components leads to the observed changes in the FTIR spectra, and no chemical reaction occurs. It is important to note that the FTIR results for the MM samples are consistent with those of the HSM samples, indicating that the blending conditions do not significantly affect the chemical composition of the modified bitumen. Based on these findings, it can be concluded that the addition of Kraft lignin to modified bitumen can alter the chemical structure of the bitumen without causing any chemical reaction between the two components. The results suggest an increase in the strength of certain chemical bonds due to the presence of Kraft lignin. These findings have important consequences for the use of Kraft lignin as a sustainable modifier for bitumen.

4.4. ESEM Results

Environmental Scanning Electron Microscopy (ESEM) was used to investigate the morphology of the Kraft lignin, virgin bitumen, and lignin-modified bitumen samples. To analyze the images, ImageJ software (version 1.52a) was used. The ESEM images provide valuable information about the microstructure, surface topography, and elemental composition of the samples.

Figure 11a shows a representative ESEM image of the Kraft lignin. The Kraft lignin particle sizes were analyzed using ESEM, and the results show that the particle sizes ranged from 2 to $50\text{ }\mu\text{m}$. The particle size of Kraft lignin powder is a crucial factor that can influence the properties of lignin-modified bitumen. Smaller particle sizes promote uniform dispersion within the bitumen matrix, resulting in a homogeneous mixture. Additionally, smaller particles provide a larger interfacial area between lignin and bitumen, facilitating interaction and bonding. These findings are consistent with the observations from the laser granulometry test (Section 3.1.2 and Figure 2), indicating the reliability of the measurement methods employed. Moreover, the ESEM image reveals that the Kraft lignin particles exhibit angularity and rough surface characteristics. These features can be attributed to the inherent properties of Kraft lignin.

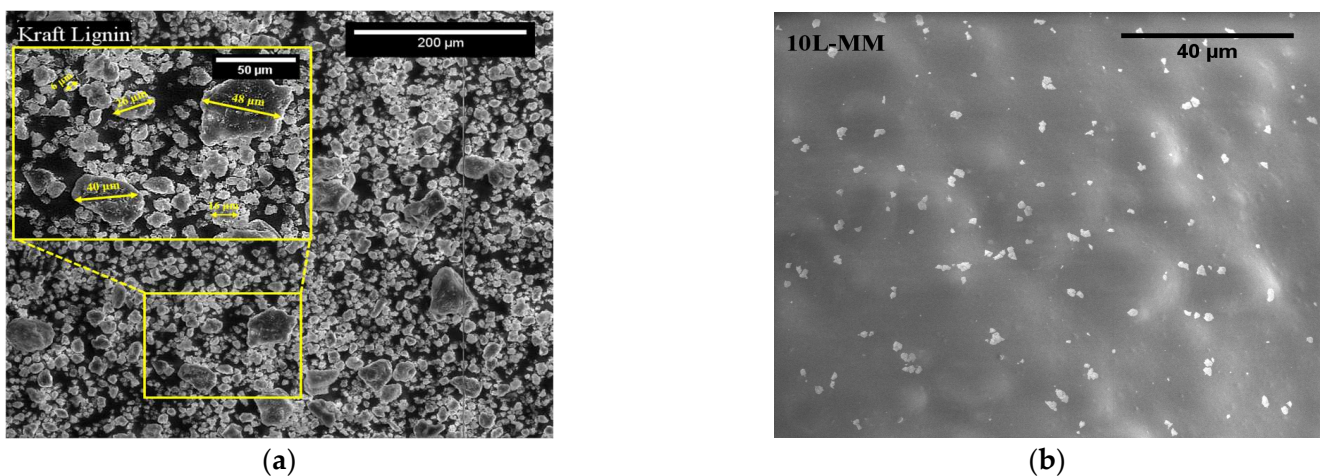


Figure 11. ESEM image of: (a) Kraft lignin and (b) 10L-MM sample (magnification of $\times 1000$).

Figure 11b shows the ESEM image of the Kraft lignin in bitumen for a 10L-MM sample. The visual observation of the sample reveals that there is a good dispersion of Kraft lignin in the bitumen, and there is no aggregation of Kraft lignin particles. The dispersion of Kraft

lignin particles in bitumen is a crucial factor that can significantly affect the properties of the lignin-modified bitumen. A well-dispersed Kraft lignin powder can lead to improved performance properties. On the other hand, poor dispersion can lead to several negative effects, including reduced effectiveness of Kraft lignin, decreased homogeneity, and reduced mechanical properties of modified bitumen [10]. The analysis of particle sizes shows that the visible particle sizes ranged $2 \pm 1 \mu\text{m}$. Interestingly, the measurement of the area shows that only 2.5% of Kraft lignin is visible in the modified bitumen 10L-MM, suggesting that the remaining Kraft lignin (5.7%) might have absorbed or dissolved in the bitumen (91.8%)—here, percentage by volume, not by weight. To determine the percentage of visible Kraft lignin particles in the 10L-MM sample, a representative area was randomly selected for analysis. Individual particle areas were measured using ImageJ software.

Figure 12 shows nine ESEM images revealing the fibril (worm-shaped) structure of bitumen samples with three different percentages of Kraft lignin and two blending conditions. Upon examination of the images, it can be observed that the fibril structure of the bitumen samples is affected by both the Kraft lignin content and the blending conditions. Specifically, increasing the amount of Kraft lignin in the samples results in the more widespread distribution of visible Kraft lignin particles within the fibril structure, as shown in images c, d, e, g, h, and i (Figure 12). Furthermore, the blending process used during sample preparation also plays a crucial role in determining the fibril structure. Image b, which depicts virgin bitumen processed in a mechanical mixer (VB-MM), exhibits a thinner diameter and more voids or pores in comparison to image f, showing virgin bitumen processed in a high-shear mixer (VB-HSM). Based on the quantitative measurements, the average diameter of the fibril structure of the MM sample and HSM sample are 9.5 and 13.4 μm , respectively. The increased oxidation during blending using MM may have led to the thinner fibril structure observed. Based on the findings presented in this study, it can be concluded that both the Kraft lignin content and the blending conditions significantly affect the fibril structure of bitumen samples.

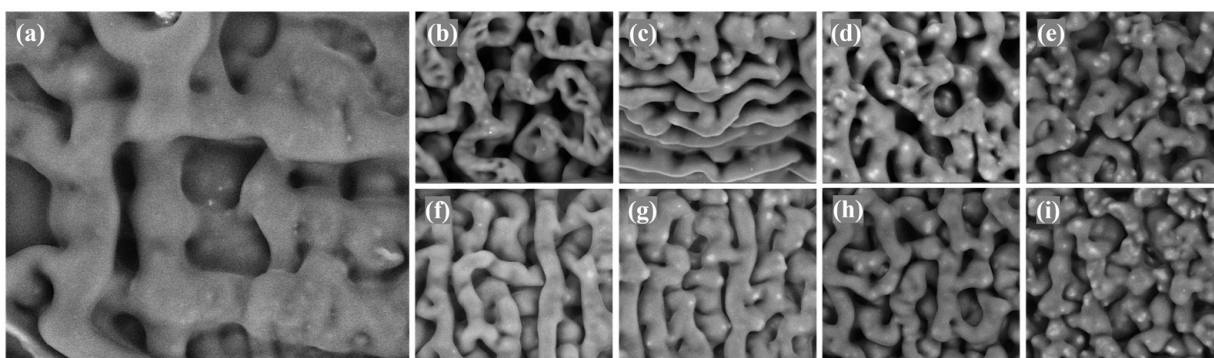


Figure 12. ESEM images for: (a) VB, (b) VB-MM, (c) 5L-MM, (d) 10L-MM, (e) 20L-MM, (f) VB-HSM, (g) 5L-HSM, (h) 10L-HSM, and (i) 20L-HSM.

4.5. TGA Results

The thermal behavior of Kraft lignin and lignin-modified bitumen samples was studied using thermogravimetric analysis (TGA). This study aimed at evaluating the thermal characterization of Kraft lignin under combustion (thermal-oxidative) conditions and assessing the impact of Kraft lignin addition on the thermal behavior of bitumen within the operational temperature of the bitumen and hot mix asphalt. The TGA analysis was also carried out to evaluate the effect of blending conditions on the thermal behavior of the modified bitumen samples. The TG/DTG thermogram of Kraft lignin is shown in Figure 13.

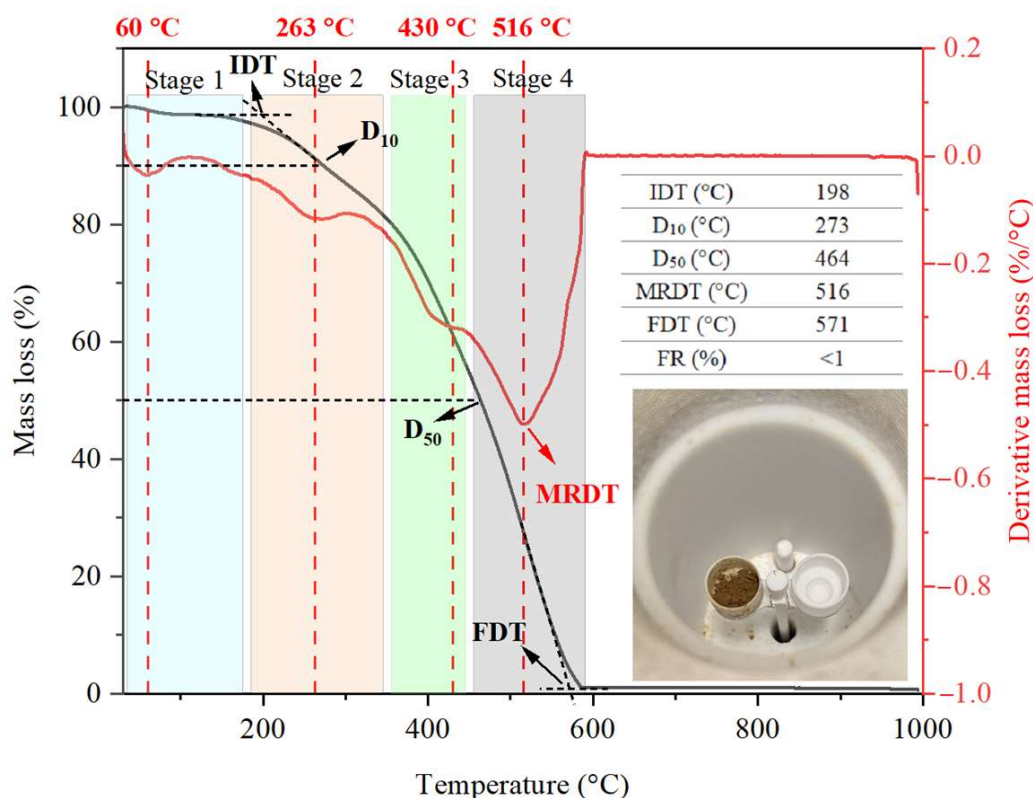


Figure 13. TG/DTG thermograms of Kraft lignin.

The results show that Kraft lignin has an initial decomposition temperature (IDT) of 198 °C and a final decomposition temperature (FDT) of 571 °C. The D_{10} value, indicating 10% decomposition of Kraft lignin, is 273 °C, while the D_{50} value, representing 50% decomposition, is 464 °C. The weight loss process of Kraft lignin is divided into four (4) stages with respect to initial mass.

The 1st weight loss stage occurs at a temperature range between room temperature and 180 °C, caused by the dehydration drying process. This is due to the moisture that exists in the Kraft lignin. From room temperature to 100 °C, the weight loss is due to evaporation of free water. At 60 °C, the maximum weight loss rate is recorded. As the temperature rises, chemisorbed water begins to be removed [34,65]. The weight loss for free and chemisorbed water is 1.3 and 2.6%, respectively.

The 2nd weight loss stage takes place from 180 to 350 °C, where 16.4% weight loss is observed due to thermal decomposition carbonization. During this stage, the polysaccharides and a small number of hydroxyl (-OH) and ether bonds (-C-O-C-) break down [34].

During the 3rd stage, which occurs within the temperature range of 350 to 450 °C, a weight loss of 26.3% is observed. This stage involves the late phases of thermal decomposition and carbonization processes.

In the 4th stage, which takes place between 450 and 590 °C, a significant weight loss of 53.8% is observed. This stage is characterized by the combustion of carbonized Kraft lignin. The release of these gases suggests that Kraft lignin is undergoing significant thermal degradation. The maximum rate of decomposition temperature (MRDT) of Kraft lignin is found at a temperature of 516 °C, which indicates the temperature range where the maximum component in the material is decomposing. The final residue (FR) of Kraft lignin is determined to be less than 1%. The analysis of the TGA and DTG curves provides a clear understanding of the thermal behavior of Kraft lignin.

Thermal stability is an important property of bitumen, as it can affect its performance and durability. In this study, the thermal stability of the bitumen samples is evaluated. To quantify the thermal stability of the samples, the D_1 parameter is defined, which is the

temperature at which 1% of the sample decomposes. The D_1 values for all samples are determined from the TGA test results. The D_1 values provide valuable information on the thermal stability of the samples. A higher D_1 value indicates that the material is more thermally stable, as it can withstand higher temperatures before decomposing. Therefore, by comparing the D_1 values of the samples, the effectiveness of any modification processes on the thermal stability of the material can be evaluated.

As shown in Figure 14, the blending processes increase the D_1 value of the virgin bitumen (VB) from 242 to 265 °C for mechanical mixing (MM) and from 242 to 259 °C for high-shear mixing (HSM). The increase in the D_1 value of the VB-MM and VB-HSM suggests that the blending process may have improved the thermal stability of the material. The higher D_1 value indicates that the processed bitumen sample can withstand higher temperatures before decomposing, compared to the VB sample. VB-MM has a higher D_1 value in comparison to VB-HSM. The increase in the D_1 value could be attributed to the removal of volatile components and increased oxidation levels in the MM sample during the blending process, which can increase the molecular weight and stiffness and enhance resistance to thermal changes. Further investigation is required to fully understand the underlying mechanisms contributing to this observation.

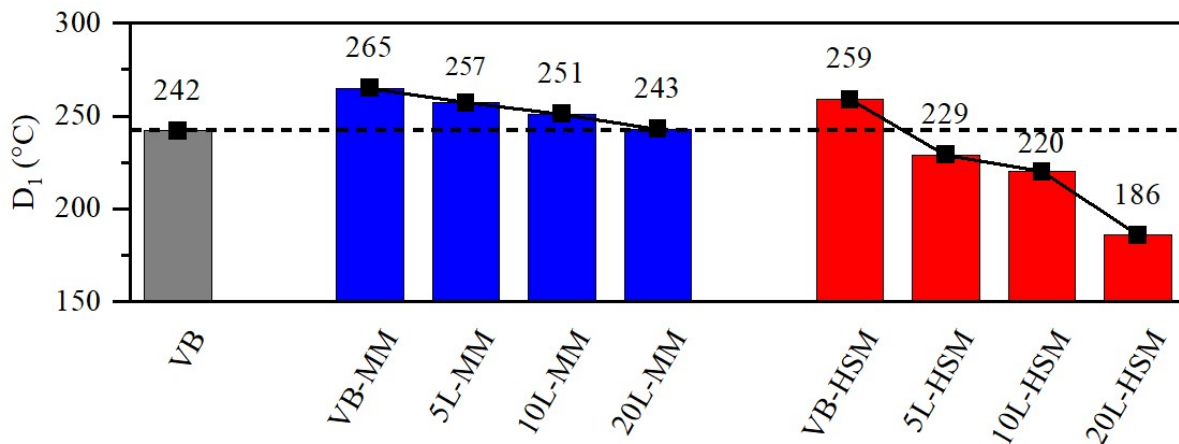


Figure 14. D_1 value of bitumen samples.

The D_1 values for MM are 257 °C, 251 °C, and 243 °C for 5, 10, and 20% of Kraft lignin, respectively. One of the reasons for the decrement in the D_1 value can be attributed to the lower thermal stability of Kraft lignin compared to bitumen. Moreover, the use of HSM results in a further decrease in thermal stability. The D_1 values for HSM samples are 229, 220, and 186 °C for 5, 10, and 20% of Kraft lignin, respectively. Possible reasons for the lower thermal stability in lignin-modified bitumen samples include alterations to the chemical composition and microstructure of the bitumen, as well as the introduction of impurities or degradation during the Kraft lignin modification process. FTIR test results (Section 4.3) show no significant changes in functional groups, suggesting that chemical modifications to the bitumen are not the primary reason for the lower D_1 value. It is likely that multiple factors are contributing to the lower thermal stability of lignin-modified bitumen samples. Further investigation is required to determine the exact mechanisms involved.

The effect of different percentages of Kraft lignin on the operational temperature of the hot mix asphalt (<200 °C) was investigated by thermogravimetric analysis (TGA). The TG and DTG thermograms of the Kraft lignin, VB, and HSM samples are presented in Figure 15.

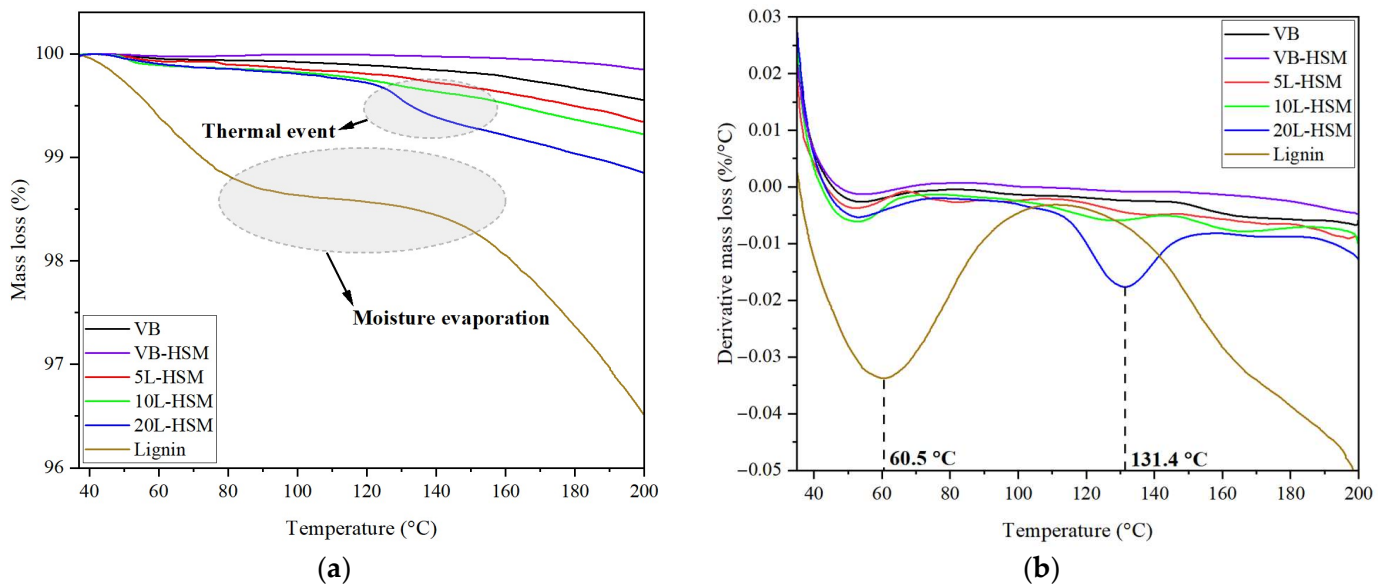


Figure 15. (a) TG and (b) DTG thermograms of VB, VB-HSM, 5L-HSM, 10L-HSM, and 20L-HSM samples on the operational temperature of the asphalt mix.

The VB sample has more mass loss compared to the VB-HSM sample in the temperature range of 100–200 °C. This indicates that the blending process caused the loss of volatile components from the bitumen. The lignin-modified bitumen samples showed more mass loss than the VB and VB-HSM samples, and the mass loss increased with increasing Kraft lignin percentage. This result suggests that the presence of Kraft lignin in the bitumen affects its thermal behavior, which can be attributed to the thermal decomposition of Kraft lignin. Interestingly, a thermal event was observed at 131 °C in the 20L-HSM sample, which is not present in other samples. The reason for this thermal event is unclear, and further investigation is needed to understand the underlying mechanism. One possible explanation is that it could be related to the interaction between Kraft lignin and bitumen with a higher amount of Kraft lignin, leading to a new phase formation. Overall, the results prove that the addition of Kraft lignin to bitumen affects its thermal behavior, and the Kraft lignin percentage in the modified bitumen plays a significant role in determining the mass loss curve.

4.6. DSC Results

The glass transition temperature (T_g) and crystallinity are two (2) important parameters that can be determined from differential scanning calorimetry (DSC) test results of bitumen samples. T_g is the temperature at which the bitumen transitions from a glassy state to a rubbery state, and it can be determined from the onset of the slope change in the heat flow curve that occurs during heating. Crystallinity, on the other hand, is the measure of the degree of crystalline fraction in bitumen, and it can be determined by comparing the measured heat of fusion to the theoretical heat of fusion. These parameters are crucial for understanding the thermal properties of bitumen, which in turn can affect the performance of asphalt pavement. The effects of Kraft lignin modification and blending conditions on the thermal properties of bitumen are discussed by comparing the T_g and crystallinity values of all samples (Figure 16).

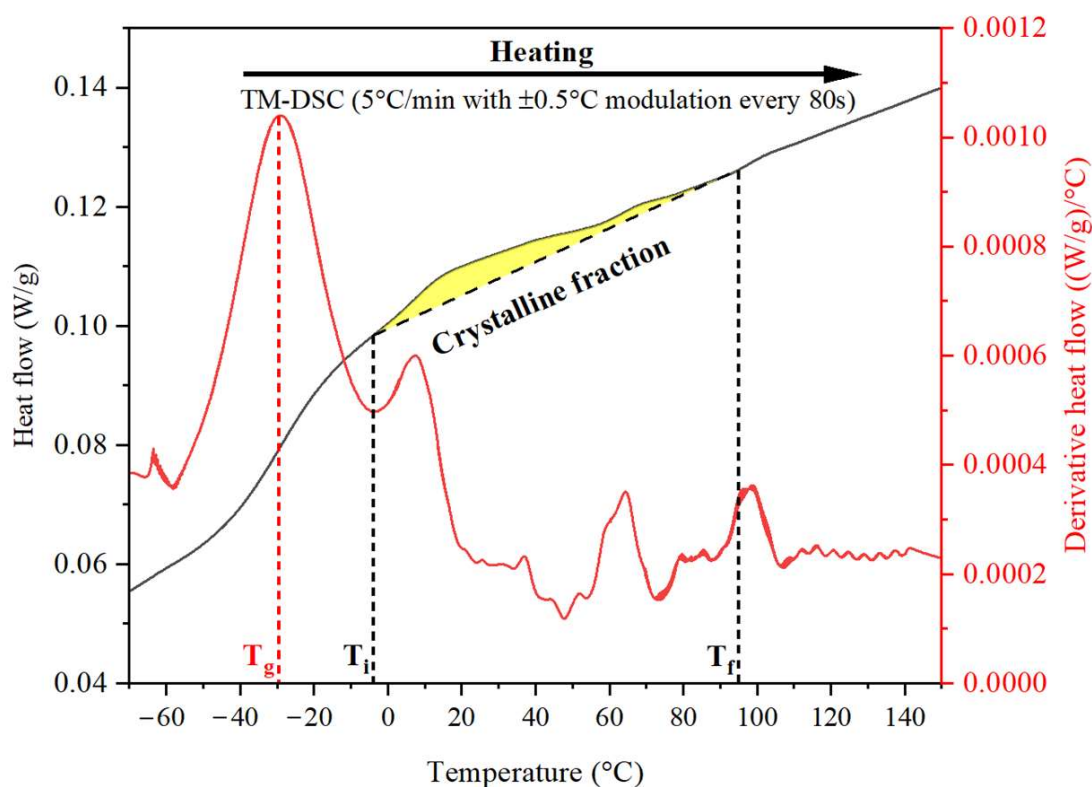


Figure 16. Glass transition temperature (T_g) and crystallization fraction of virgin bitumen using TM-DSC technique (T_i and T_f represent the initial and final temperatures, respectively, used to calculate the crystalline fraction).

As shown in Figure 17, the T_g values of the bitumen samples are obtained from the DSC analysis.

In terms of blending conditions, it is observed that the T_g of the VB-HSM and VB-MM samples is -29.3 , and -29.9 °C, respectively, which is lower than the VB sample (-29.2 °C). This suggests that the blending conditions have a small impact on the physical properties of bitumen.

In terms of the Kraft lignin effect, it is observed that the T_g of the HSM samples decreases as the Kraft lignin percentage increases, whereas the T_g of the MM samples remains relatively constant with increasing Kraft lignin content. This suggests that the effect of Kraft lignin on the T_g of bitumen is dependent on the blending conditions. The decrease in T_g with increasing Kraft lignin content in the HSM samples can be attributed to the increased interaction between the Kraft lignin and bitumen molecules due to the high shear rate. It is important to note that from the FTIR test results (Section 4.3), even if there is no chemical reaction between Kraft lignin and bitumen in HSM samples, the two components may still exhibit some degree of miscibility or compatibility with each other, which can also affect the T_g of the modified bitumen. It is important to acknowledge that the observed differences in T_g values among the samples are relatively small, within 1 °C. While these differences may not be as pronounced as in other studies [66,67], they still provide valuable insights into the low-temperature behavior of modified bitumen.

In conclusion, the DSC analysis of the bitumen samples shows that the blending conditions and Kraft lignin content have a small, but positive impact on the glass transition temperature (T_g) of bitumen (lower values than VB). These results suggest that the incorporation of Kraft lignin in bitumen can be an effective method to modify the physical properties of bitumen, but the blending conditions must be carefully controlled to achieve the desired effect.

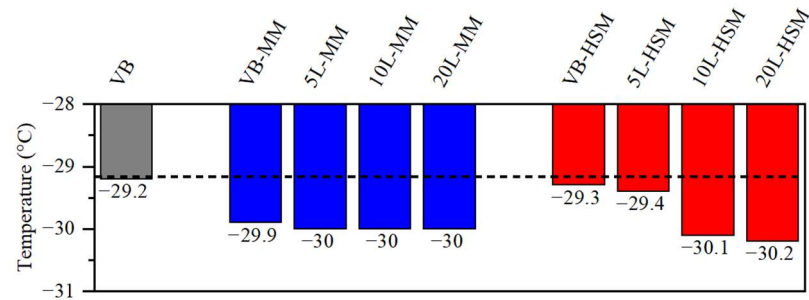


Figure 17. Glass transition temperature (T_g) of bitumen samples.

The calculation of the crystallizable fraction (%) is performed to determine the content of the crystalline fraction in the VB and lignin-modified bitumen samples. Table 5 shows that there is not a significant change in the crystallizable fraction with the addition of Kraft lignin and blending conditions. A higher crystallizable fraction (yellow zone in Figure 16) indicates a greater degree of crystalline structure within the bitumen. In this study, despite the Kraft lignin modification, the crystallizable fraction remains relatively constant across the lignin-modified bitumen samples. This suggests that the addition of Kraft lignin does not have a substantial impact on the formation or content of the crystalline fraction within the bitumen. It is important to note that while the crystallizable fraction does not show significant changes, other thermal properties, such as the glass transition temperature (T_g), are influenced by the Kraft lignin addition and blending conditions, as discussed earlier. Further analysis and characterization techniques may be necessary to investigate the detailed effects of Kraft lignin modification on the crystalline structure of bitumen and its potential implications for the performance of asphalt pavement.

Table 5. Content of crystallizable fraction of samples.

Code	VB	VB-HSM	5L-HSM	10L-HSM	20L-HSM	VB-MM	5L-MM	10L-MM	20L-MM
Content of crystallizable fraction (%)	1.4	1.7	1.5	1.5	1.4	1.6	1.5	1.4	1.2

5. Conclusions

In this study, the chemo-thermal characteristics of lignin-modified bitumen were investigated with different percentages (5, 10, and 20%) of Kraft lignin under 2 blending protocols, including mechanical mixer (MM) and high-shear mixer (HSM). The results obtained from various tests, including Brookfield Rotational Viscosity (BRV), Dynamic Shear Rheometer (DSR), Fourier-Transform Infrared Spectroscopy (FTIR), Environmental Scanning Electron Microscopy (ESEM), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC), provided valuable insights into the effect of blending conditions and properties of lignin-modified bitumen. The findings of the study are as follows. In terms of the influence of blending conditions:

- The MM-produced samples result in higher viscosity and $|G^*|/\sin(\delta)$ values compared to the HSM samples. Additionally, HSM samples exhibit distinctly different $|G^*|$ and δ values compared to the MM samples (Sections 4.1 and 4.2);
- The blending conditions do not significantly affect the chemical composition of the modified bitumen (Section 4.3); meanwhile, it affects the fibril structure of bitumen (Section 4.4);
- The thermal stability decreases more when using a HSM (Section 4.5);
- The T_g of HSM samples decreases with increasing Kraft lignin percentage, indicating an interaction between Kraft lignin and bitumen due to the high shear rate (Section 4.6).
- In terms of the Kraft lignin effect:

- The addition of Kraft lignin increases the viscosity, stiffness, high-temperature stability, and $|G^*|/\sin(\delta)$ value of bitumen (Sections 4.1 and 4.2);
- The addition of Kraft lignin alters the chemical structure of the modified bitumen without causing chemical reactions (Section 4.3). Moreover, increasing the amount of Kraft lignin in the samples leads to a more widespread distribution of Kraft lignin particles within the fibril structure, with no aggregation of Kraft lignin particles, here, for mass contents up to 20% (Section 4.4);
- The addition of Kraft lignin to bitumen decreases the thermal stability. A thermal event observed at 131 °C in the 20L-HSM sample suggests a possible interaction between Kraft lignin and bitumen at higher Kraft lignin content (20%), leading to the formation of a new phase (Section 4.5);
- The miscibility or compatibility between Kraft lignin and bitumen, even without chemical reaction, may slightly influence the T_g of modified bitumen, whereas the crystallizable fraction remains relatively constant across the lignin-modified bitumen samples (Section 4.6).

Finally, this study highlights the potential of Kraft lignin as a bitumen modifier and emphasizes the influence of blending protocols and Kraft lignin content on the performance and properties of lignin-modified bitumen. The choice of the mixer can have a significant impact on the quality and characteristics of the lignin-modified bitumen in terms of blending Kraft lignin with bitumen. While a mechanical mixer may be sufficient for some additives, a high-shear mixer can provide more consistent and higher-quality results for Kraft lignin. The findings contribute to the development of environmentally friendly approaches in the asphalt industry by utilizing waste materials as modifiers. Further research is required to optimize the blending process.

Further improvements can be made in the study of lignin-modified bitumen. It is essential to investigate TGA-FTIR, which provides a more comprehensive understanding of the chemical changes occurring during the thermal degradation process. To enhance future research in this area, considering additional analytical techniques are recommended, such as the determination of carbonyl and sulfoxide indices using FTIR, and the kinematic effect of lignin-modified bitumen through TGA. The results of this study are part of an ongoing effort and larger project to investigate the feasibility and performance of incorporating lignin into modified and unmodified bitumens, and cold, warm, and hot mix asphalts, and future publications will cover these aspects.

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