



Article

Investigation of the Characteristic Properties of Lignin-Modified Bitumen

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Abstract: The main objective of this study was to investigate the characteristic properties of lignin-modified bitumen with different lignin contents. The first step was the characterization of the physicochemical and thermal properties of the kraft lignin powder along with the determination of its microstructure. This was achieved by carrying out an elemental analysis, Gel Permeation Chromatography (GPC), Thermogravimetric Analysis (TGA)/Derivative Thermogravimetry (DTG), Fourier Transformation Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS) and Confocal Microscopy. After the latter tests, three (3) blends with different lignin contents (5%, 10% and 15% by weight of bitumen) were produced. Characteristic properties such as penetration, softening point, elastic recovery, force ductility, dynamic viscosity and storage stability were determined for the reference bitumen and the three lignin blends. The main conclusion was that kraft lignin powder hardens the conventional bitumen. Specifically, the addition of 15% lignin to the bitumen hardened the blend to such a degree that the bitumen changed category from 50/70 to 35/50 with respect to EN 12591.



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1. Introduction

Petroleum-based bitumen is the most commonly used binder in the pavement construction industry [1,2]. In recent years, certain researchers have pointed out the detrimental environmental impact of the petroleum industry [3]. Furthermore, due to the global scarcity and rising costs of all the products of the crude oil distillation process, new technologies and materials are being utilized in the field of road construction [4,5]. Specifically, researchers started investigating the properties of certain materials that are physically and chemically compatible with bitumen. The aim was to substitute a part or the total bitumen in the asphalt mixture.

Biomass seems like a possible solution to the above environmental and financial challenges since it has the potency to be used as a renewable source of energy (e.g., heating, electricity, transportation fuels, construction industry). Considering its widespread availability and compatibility with bitumen, many studies focused on combining these two materials to create a new bio-bitumen without compromising the physical, rheological and chemical properties of the original bitumen. The origin of biomass directly affects the chemical composition of the resulted bio-bitumen and its future in situ behavior as part of the asphalt mixture. Generally, biomass can be mixed with the bitumen in three different forms: as powder, as fibers or as bio-oil. Raouf and Williams have categorized the bitumen additives based on their replacement content of the original bitumen as (a) modifiers (<10% replacement), (b) extenders (25% to 75% replacement) or (c) direct substitutes (100% replacement) [6]. In the following paragraph, the most common biomass materials used in the bitumen will be reviewed.

Biomass can originate either from animal or plant matter. It was noticed that bio-oil deriving from waste wood decreases the viscosity of the bio-binder when unaged, but when aged it rapidly increases it due to three reasons: (a) carbonation of dicarboxylic acids, (b) polymerization and (c) volatilization of certain lightweight particles of the bio-oil [7]. The above results regarding unaged bio-binders were confirmed by Sun and Zhou who concluded that the viscosity reduction that is caused by wood waste bio-oil enhances the low temperature performance of bio-binders but compromises the performance at elevated temperatures [8]. At a molecular scale, the high carbonyl ($C=O$) and sulfoxide ($S=O$) content serve as indicators of the potential early aging of bio-binders [9,10]. The higher the carbonyl and sulfoxide indexes, the more susceptible to aging the bitumen is. According to Li et al. and Yang and You, the biomass-bitumen compatibility is higher for liquid-phase biomass modifiers (bio-oils) [11,12]. This happens due to the similar specific gravity and rheological properties between bio-oil and petroleum-based bitumen [8,13,14]. Another study indicated that all types of biomasses exhibit fluctuation with respect to their water content which could be a potential aging factor. Thus, in order to inhibit oxidative aging, a pretreatment process is required [15]. Yang et al. proved that aging can also be slowed down with the addition of polymers, such as polyethylene. Such a modification would increase the stiffness and the high critical temperature (T_c) of the bio-binder [16]. Furthermore, marine-derived bio-oil (microalgae and nanoalgae) has been investigated as a potential bitumen modifier. It was observed that the high content of resins in algae-modified bio-binders could improve the bitumen-aggregate adhesion in the asphalt mixture. On the downside, the moisture susceptibility worsened even though bio-binders have a high content of oxygen and nitrogen-based polar functional groups which strengthen the interface and obstruct the water from entering between the two materials [17,18]. Regarding animal waste, an expanding number of studies focuses on the utilization of swine manure to produce bio-binders. Like plant-based bio-binders, swine manure bio-binders act as bitumen softeners and therefore alter the viscoelastic properties of the blend [19]. Fini et al. inspected the feasibility of utilizing swine manure as a liquid modifier and concluded that this specific material can reduce the environmental and economic costs, while confirming the previous results regarding the softening impact [11].

On the other hand, solid (powder and fiber) biomass modifiers present a wider variation of properties. Specifically, it has been found that Posidonia powder increases the viscosity of the bitumen and upgrades the resistance to deformation [20]. Moreover, corn stalk fibers have been proven to raise the softening point, viscosity and elastic recovery of the binder while decreasing the penetration and, consequently, the thermal susceptibility at elevated temperatures. Additionally, the increase of the complex shear modulus G^* and the decline of the phase angle δ lead to an upgrade of the rutting resistance of the asphalt binder [21]. Another study demonstrated that waste coffee grounds alter the viscoelastic behavior of bitumen, but without hindering the oxidative aging as previously believed [22]. On the contrary, grape pomace may potentially impede aging to a certain extent [23,24]. During aging, the oxygen-based functional groups react triggering the aging mechanism which causes the stiffening of the binder [9,25].

All the above show that the effect of any biomass modifier depends not only on its chemical composition, but also on its phase (liquid or solid).

Lignin can be divided into certain categories based on the chosen extraction process (e.g., kraft, organosolv, Klason, etc.) [26]. It is widely deployed as a bio-modifier due to its abundance in nature. Some studies demonstrated that lignin could delay oxidation as lignin can neutralize the free radicals which are formed during aging [27,28]. In other words, lignin is oxidized instead of bitumen. Moreover, lignin can increase the bitumen stiffness and, consequently, the resistance to deformation and rutting at high temperatures [29–32]. On the downside, high percentages of lignin may negatively influence the fatigue resistance of the bitumen [33]. Lignin originating from industrial waste can also be incorporated in bitumen and asphalt mixtures as a biopolymer [32]. Specifically, this modifier was found to upgrade the permanent deformation and cracking resistances while also reducing the

manufacturing costs when used at 20% by weight of bitumen. Furthermore, lignin can undergo chemical modification by blocking its hydroxyl groups via certain hydrophobic compounds to improve its hydrophobicity [26]. These modifiers are FGE (Phenyl glycidyl ether) and EGE (Ethylhexyl glycidyl ether).

Taking the above into account, this paper studies the effects of lignin as a modifier on the bitumen by examining the physicochemical and thermal properties of kraft lignin powder and the physical and rheological properties of lignin-modified bitumen.

2. Materials and Methods

In this study a conventional 50/70 bitumen was used as reference bitumen and was notified as RB. Blends with 5%, 10% and 15% kraft lignin powder were also produced and notified as LP-5, LP-10 and LP-15, respectively. For the reference and all blends produced, characteristic properties such as penetration, softening point, force ductility, elastic recovery, rotational viscosity and storage stability were determined. Additionally, a thorough physicochemical analysis of the kraft lignin was conducted.

2.1. Bitumen

The characteristic properties of the reference bitumen are given in Table 1.

Table 1. Characteristic properties of reference bitumen.

Property	Specification	Value
Penetration	EN1426	61
Softening point (°C)	EN1427	50.0
Elastic recovery (%)	EN13398	7
Force ductility (J/cm ²)	EN 13589 & EN 13703	0.885
Rotational viscosity (cPs)	EN 13302	Various ¹

¹ Rotational viscosity was carried out in various temperatures. All results are shown in Section 3 "Results" that follows.

2.2. Lignin Powder

The kraft lignin powder utilized in this study was examined concerning its physical, chemical, thermal and microstructural properties. Figure 1 gives a macroscopic view of the kraft lignin used.



Figure 1. Kraft lignin macroscopic view.

2.2.1. Elemental Analysis

The content of kraft lignin in C/H/O was determined by an elemental analysis carried out by the Department of Chemistry of A.U.Th (Table 2) and can be considered typical of such types of lignin. Specifically, the dominant element of lignin is carbon (C), whereas hydrogen (H) is traced in a much smaller percentage. The existence of sulfur (S) is due to the chosen method of isolation of the lignin i.e., the process of producing cellulose pulp from biomass, in which lignin is produced as a by-product (Kraft Process). Finally, a major

percentage of lignin was oxygen (O) which could potentially trigger its oxidative aging mechanism faster.

Table 2. Physicochemical properties of the kraft lignin.

Lignin Type	C (%)	H (%)	S (%)	O ¹ (%)	Ash (%)	Moisture (%)	Mw (g/mol)	Mn (g/mol)	PDI ²
Kraft	61.84	5.62	1.50	31.04	2.04	3.50	4456	856	5.2

¹ Oxygen is calculated as O (%) = 100% – C (%) – H (%) – Ash (%). ² Polydispersity Index (PDI): PDI = Mw/Mn, where Mw = weight average molecular weight & Mn = number average molecular weight.

2.2.2. Gel Permeation Chromatography (GPC)

The molecular weight of kraft lignin is considered medium to high, with an equally high polydispersity (PDI), indicating a relatively high inhomogeneity in its structure (See Table 1).

2.2.3. Thermogravimetric Analysis—Derivative Thermogravimetry

The Thermogravimetric Analysis (TGA)/Derivative Thermogravimetry (DTG) curves depict the profile of the thermal decomposition of lignin and characterize its thermal stability. Figure 2 shows the TGA/DTG curves for the kraft lignin used in this study.

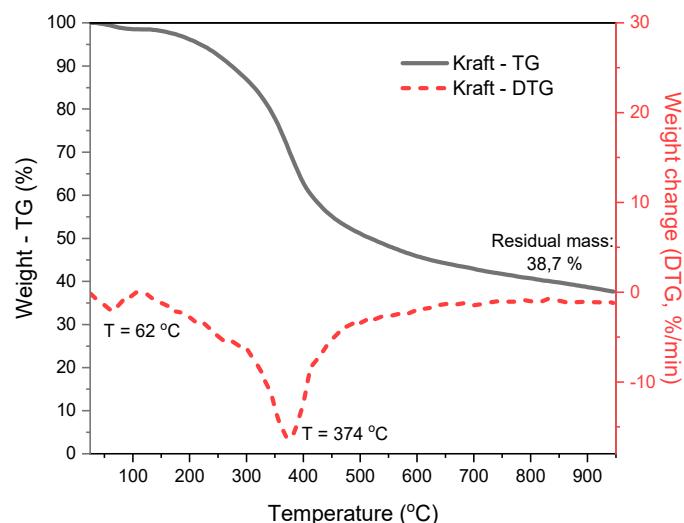


Figure 2. Kraft lignin Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) curves.

As Figure 2 shows, lignin is decomposed in three stages. The first stage occurs from 60–100 °C due to the evaporation of the moisture of lignin. As the moisture content was relatively small, i.e., ~3.5% (Table 2), the mass loss of this stage was insignificant (almost 3%). The second stage, representing the main lignin degradation stage, was observed from 170 °C until 600 °C [34] and was expected to be wide (in terms of temperature range), because lignin decomposes over a wide range of temperatures due to its complex structure, contrary to other biomass components such as cellulose and hemicellulose. A mass loss of almost 55% was observed and was caused by the decomposition of the molecular structure of lignin via breaking of ether and C-C bonds followed by decomposition of the initially produced phenolic and oxygenated aromatics [35]. The intensity of this stage was further proven by the sharp DTG peak centered at 374 °C. The last stage of weight loss was displayed above 600 °C due to the slow pyrolysis and gasification of the remaining phenolic and aromatic lignin oligomers. Regarding the residual mass observed at 950 °C, it is within expected ranges, since heating of lignin under inert atmosphere (N_2) is known to result in the formation of residual char of about 30–45 wt.% [34]. The above results indicate that lignin will not be decomposed during mixing and compaction of asphalts, which require much lower temperatures.

2.2.4. Fourier Transformation Infrared Spectroscopy

Fourier Transformation Infrared Spectroscopy (FTIR) is used to obtain the infrared spectrum of absorption or emission of a solid, liquid or gas and can reveal the chemical functional groups within them. Figure 3 shows the infrared spectrum for the kraft lignin used in this study.

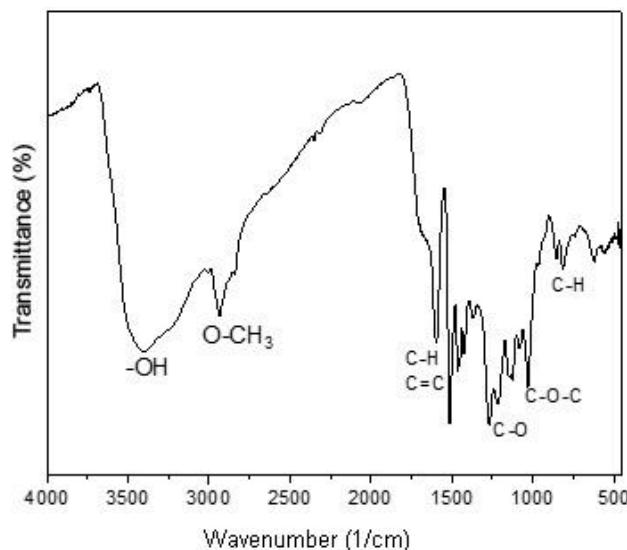


Figure 3. Kraft lignin IR spectrum.

The absorbance peaks at 2937 cm^{-1} and 2833 cm^{-1} are related to the methoxy $-\text{OCH}_3$ group. The peaks around $1500\text{--}1650\text{ cm}^{-1}$ correspond to the vibration of C-H and C=C bonds within the phenol compounds, whereas the range $1218\text{--}1268\text{ cm}^{-1}$ reflects the existence of C-O bonds. Additionally, the absorbance at $1030\text{--}1080\text{ cm}^{-1}$ is correlated to the vibrations of ether intermolecular C-O-C bonds. In conclusion, no absorbance peaks were located for carbonyl (1700 cm^{-1}) and sulfoxide (1040 cm^{-1}) groups, which are believed to be possible indicators of future early aging of lignin-modified bitumen [9,10].

2.2.5. Scanning Electron Microscopy/Dynamic Light Scattering

Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS) were used to acquire information about the shape and particle distribution of the kraft lignin, respectively. Figure 4 shows the shape of the lignin particles under SEM. As it can be seen from Figure 4, the kraft lignin consists of spherical and irregularly shaped particles.

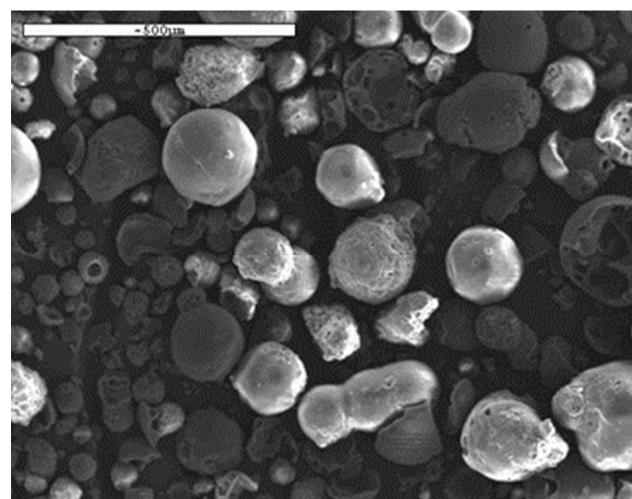


Figure 4. Lignin particles under SEM.

Figure 5 shows the results of the DLS analysis. As can be seen from Figure 5, the lignin particles have a particle size within the range of 50–200 μm . The majority of lignin particles have a size of almost 76 μm .

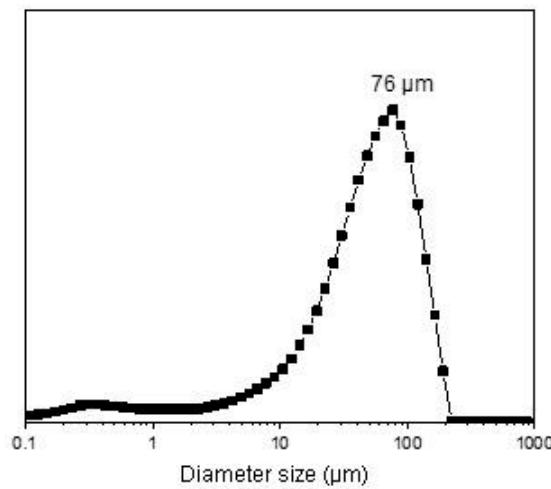


Figure 5. Kraft lignin particle size distribution.

2.2.6. Confocal Microscopy

In addition to the Scanning Electron Microscopy, Confocal Microscopy was also used. Figure 6 shows the microstructure of lignin powder as observed at the confocal microscope. As can be seen, the images confirm the particle size distribution of the DLS technique (50–200 μm). Furthermore, it validates the spherical and irregular shape of the lignin particles which was observed in Figure 4 (SEM analysis). The topographical layers of lignin are displayed in Figures 7 and 8. Lignin demonstrates significant height differences and irregularities which could imply a high porosity and thus potential high absorption of bitumen.

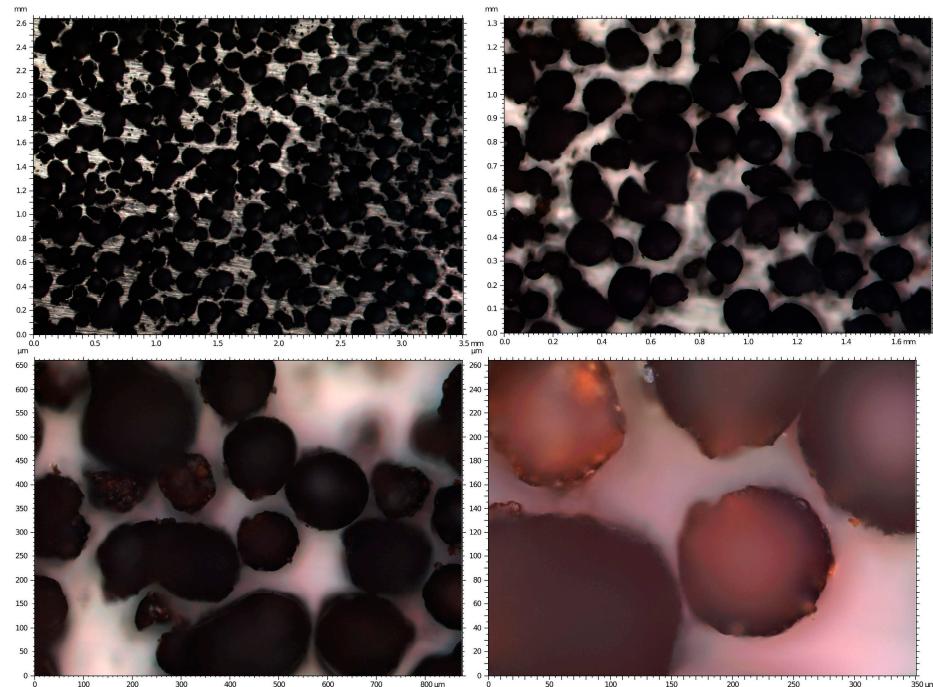


Figure 6. Lignin powder under the confocal microscope: $\times 5$ (**top left**), $\times 10$ (**top right**), $\times 20$ (**bottom left**), $\times 50$ (**bottom right**).

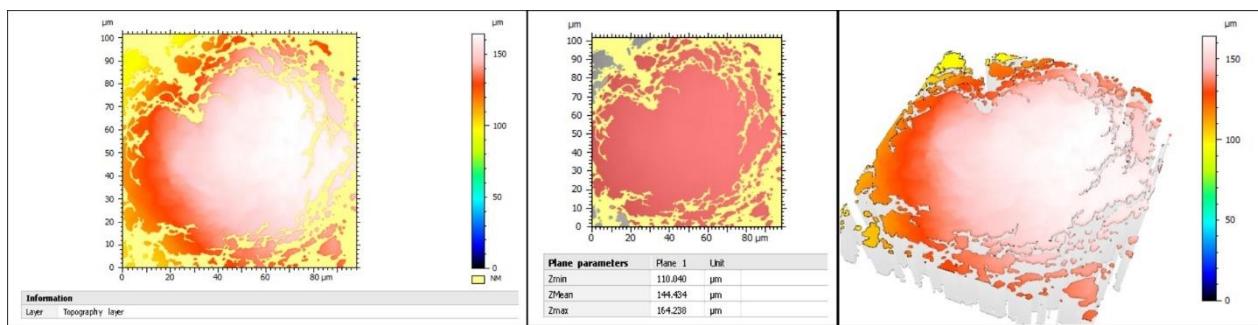


Figure 7. Topography of the peaks and valleys of lignin powder ($\times 100$).

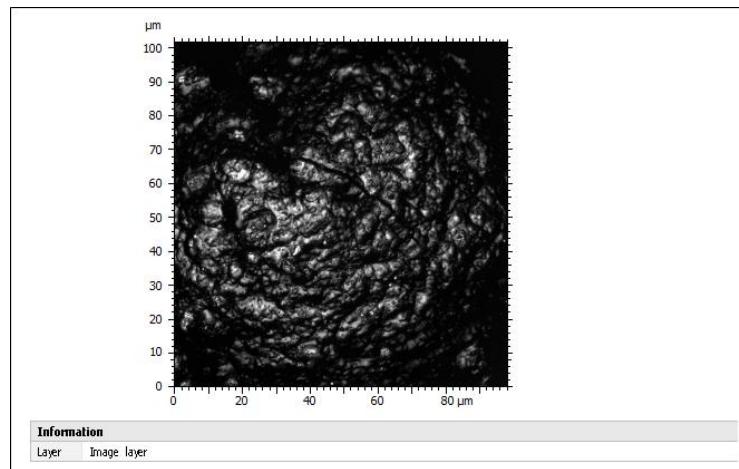


Figure 8. Lignin particle under the confocal microscope ($\times 100$).

2.2.7. Mixing Conditions

In order to decide the mixing conditions for the lignin blends, the relevant literature was considered. Table 3 shows the results of the literature review. According to Table 3, there is quite a variation among researchers about the mixing conditions of lignin with bitumen.

Table 3. Mixing conditions of bitumen with lignin by literature review.

No. Reference	Mixing Temperature (°C)	Rotational Speed (rpm)	Mixing Time (min)	Mixer Type
[2]	163	3000	30	High shear mixer
[28]	160	5000	60	Mechanical stirrer
[29]	160	6000	40	Shear mixer
[30]	180	4000/8000	30/30	High speed shear mixer
[31]	164	1200	45	High speed shear mixer
[36]	170	N.M. ¹	10	N.M. ¹
[37]	163	3000	30	High shear mixer
[38]	120	N.M. ¹	7	N.M. ¹
[39]	160	4800	N.M. ¹	High shear mixer
[40]	160	300	60	Low shear mixer
[41]	150	6000	60	High shear mixer

¹ N.M. = Not mentioned.

The mixing conditions considered for the current study, with respect to Table 3 and the available equipment at the Highway Engineering Laboratory of A.U.Th. were: mixing temperature 160 °C and mixing time 30 min, using a high shear mixer at a rotational speed of 3000 rpm. As mentioned before, apart from the reference bitumen (RB) three lignin-RB blends were produced: (i) blend LP-5 (5% lignin by weight of bitumen), (ii) blend LP-10 (10% lignin by weight of bitumen) and (iii) blend LP-15 (15% lignin by weight of bitumen).

3. Results

3.1. Needle Penetration Test

The needle penetration test was carried out at 25 °C with respect to the EN 1425 specification. Figure 9 shows the bitumen samples tested for RB and LP-15. Lignin particles are clearly detected inside the LP-15 blend under the influence of light.



Figure 9. Penetration test samples of RB (left) and LP-15 (right).

Figure 10 shows the penetration results for the RB and the LP blends. As it can be seen from Figure 10 the addition of lignin in bitumen has a stiffening effect. As the lignin content increases, penetration values are reduced. It is worth noting that for 15% lignin the RB changes bitumen category and from an original category of 50/70 bumps to the category of 35/50, with respect to the bitumen categories specified in EN 12591. The latter could be beneficial in areas with an absence of hard bitumens or in areas where softer bitumens are commonly used and harder bitumens may be needed for specific uses (Scandinavian countries or regions of the arctic circle).

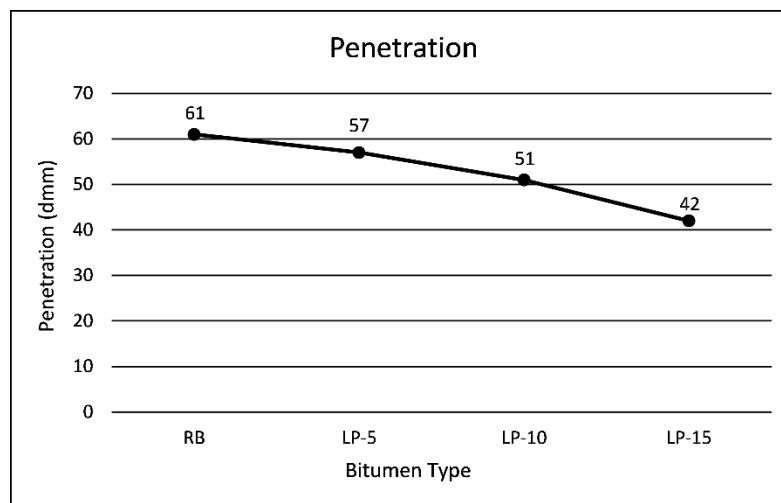


Figure 10. Penetration results.

Figure 11 shows the penetration results in terms of % value change, with respect to the RB value. As it can be seen from Figure 11, as the lignin content increases the change in penetration value increases. All the above results are in agreement with the results of previous studies which concluded that the addition of lignin hardens the reference bitumen.

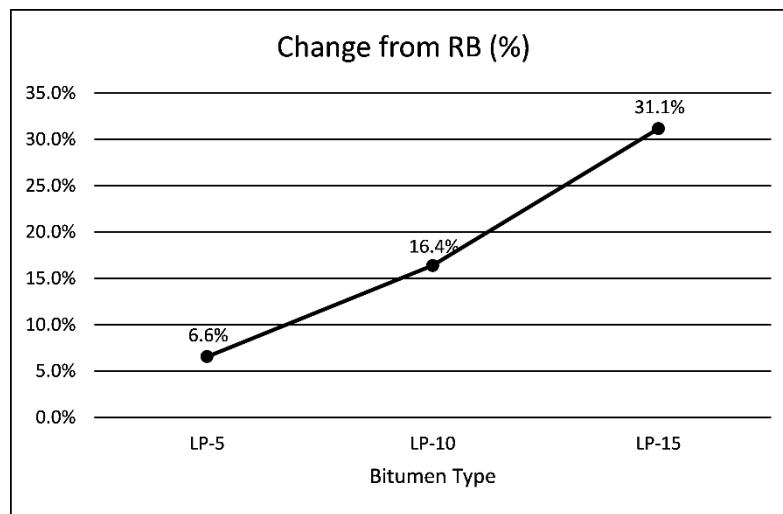


Figure 11. Change in penetration with respect to reference bitumen.

3.2. Softening Point Test

The softening point test was carried out with respect to the EN 1426 specification. Figure 12 shows the results of the softening point test.

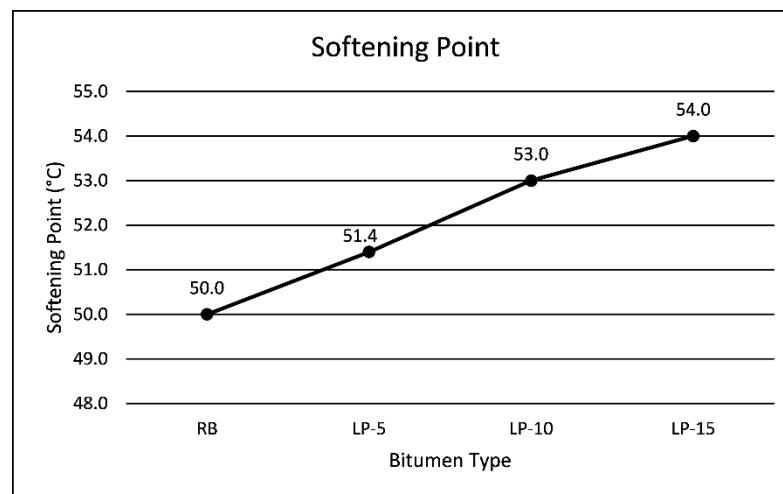


Figure 12. Softening point results.

Based on the results displayed at Figure 12, as the lignin content increases, the softening point also increases. The latter verifies the stiffening effect of the lignin addition to the RB. Figure 13 demonstrates the change in softening point with respect to the RB softening point value. The maximum change was 8% for the LP-15 blend.

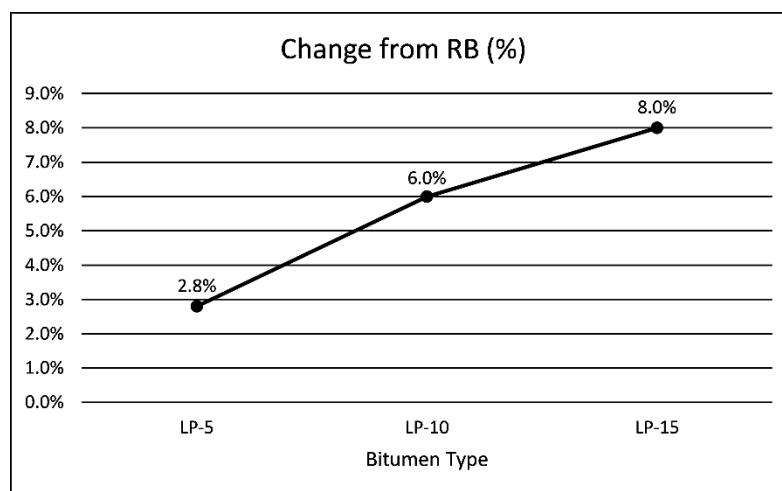


Figure 13. Change of softening point with respect to reference bitumen.

3.3. Elastic Recovery Test

The elastic recovery test was carried out at 25 °C, with respect to EN 13398. The test was performed in order to detect potential significant change in the elastic recovery of the RB, with the addition of kraft lignin powder. The relevant results are given in Table 4. As it can be seen from Table 4, no significant change in the elastic recovery has been achieved with the addition of up to 15% of lignin powder.

Table 4. Elastic recovery results.

Bitumen/Blend	Elastic Recovery (%)
RB	7
LP-5	10
LP-10	9
LP-15	9

3.4. Force Ductility Test

The force ductility test is used to characterize the cohesion of modified bitumen and bituminous binders. According to EN 13589 and EN 13703, the proposed initiating testing temperature of the test is 5 °C. In this study, the reference bitumen and all lignin blends have resulted in premature cracking at 5 °C and 10 °C, before the completion of the test. However, results were obtained for 15 °C testing temperature. The relevant results are given in Table 5.

Table 5. Force ductility results at 15 °C.

Bitumen/Blend	Maximum Force (N)	Deformation Energy (J/cm ²)
RB	15.2	0.89
LP-5	16.9	1.30
LP-10	24.3	1.72
LP-15	22.3	1.53

According to EN 14023 and with respect to the force ductility test, modified bitumens are categorized by their deformation energy. Deformation energy occurs from the plot force vs. displacement, which is the graphical representation of the test results. In the case of the RB and blends of Table 5, all tested samples are categorized as $\geq 0.5 \text{ J/cm}^2$ (category 9 of Table 1 of EN 14023). Figure 14 shows the force vs. displacement plot for the RB and lignin blends. As it can be observed from Figure 14 and the values of Table 5, the force ductility curves of the lignin blends, show an increase in the maximum force, elastic phase

and the total area under the curve which indicate an increase in stiffness of the binder. The latter interpretation of the force ductility plots was based on the research of Mturi and Nkapele [42].

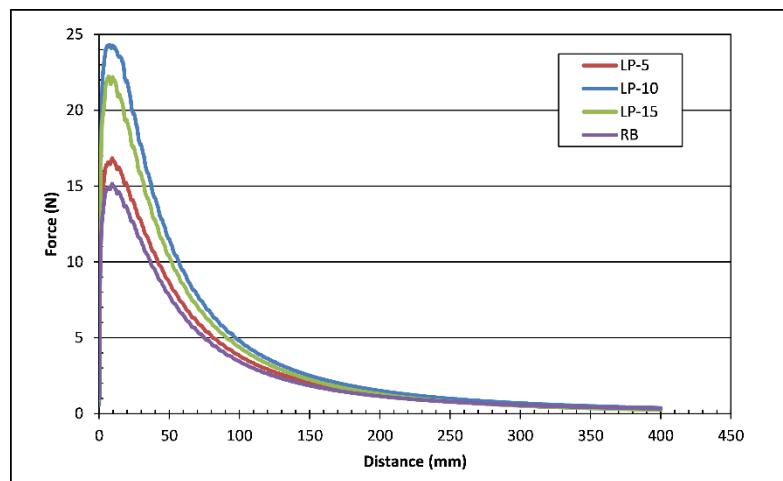


Figure 14. Force vs. distance plot results of force ductility test.

3.5. Dynamic Viscosity Test

The dynamic viscosity of the RB and lignin blends was measured in accordance with EN 13302 using a rotating spindle viscometer. The testing temperature was from 130 °C to 180 °C in steps of 10 °C, so to cover all pumping and use-phase temperatures of the RB and LP blends. The results of the total testing temperature range are given in Figure 15. Figure 15 suggests that the addition of lignin has raised the viscosity of the RB. The LP-15 blend showed the highest viscosity values for temperatures ranging from 140 °C to 180 °C.

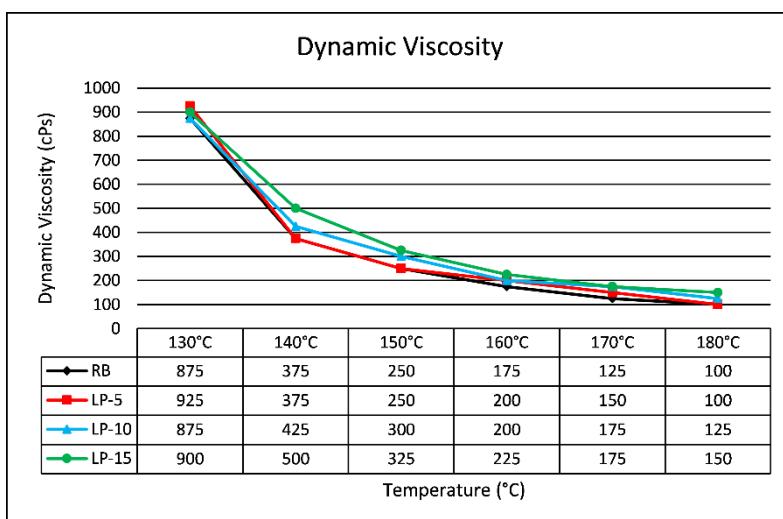


Figure 15. Dynamic viscosity values of the four blends at different temperatures.

3.6. Storage Stability Test

The storage stability test was carried out in accordance with EN 13399 for the lignin blends. The results were expressed in difference in softening point and are given in Table 6. The very small difference in softening point for all lignin blends indicates no separation of the lignin into the bitumen under prolonged storage at elevated temperature. The latter verifies the proper choice of mixing conditions that were used in the current study. It is also noted that the results of Table 6, are contradictory to other previous studies which concluded that lignin is usually segregated from the bitumen during prolonged storage at

high temperatures [33,43]. This contradiction of results can be attributed to the different mixing conditions of the lignin blends.

Table 6. Storage stability results.

Bitumen/Blend	Difference in Softening Point (°C)
LP-5	0.4
LP-10	0.6
LP-15	0.4

4. Conclusions

Based on the results obtained in this study the following conclusions can be drawn.

1. Kraft lignin can be characterized as thermally stable for the mixing and compaction temperatures of asphalt mixtures.
2. Mixing conditions for lignin-bitumen blends vary among researchers.
3. The addition of kraft lignin had a stiffening impact on the reference 50/70 bitumen as noticed by the decline of penetration values and the increase of the softening point. The addition of 15% lignin hardened the bitumen to such a degree that the bitumen changed category from 50/70 to 35/50 with respect to EN 12591.
4. The addition of kraft lignin to the RB had no noticeable changes in terms of the elastic recovery results.
5. The force ductility test showed that the addition of kraft lignin resulted in an increase in the maximum tensile force and the total area under the force/displacement plot, which indicates an increase in stiffness of the RB.
6. Kraft lignin-modified blends did not show separation between the binder and the lignin under prolonged storage at a high temperature.
7. Conclusion No. 6 verifies the proper selection of mixing conditions in the current study.

Considering all the conclusions above, it could be said that kraft lignin powder seems to be a promising modifier especially for soft bitumens.

5. Future Work

The continuation of the current research includes further investigation of the chemical and rheological properties (using a Dynamic Shear Rheometer) of kraft lignin-modified bitumen. The performance after short- and long-term aging procedures will also be investigated. Additionally, LCA and LCCA analyses need to be conducted to assess the environmental and financial feasibility of using kraft lignin in the pavement construction industry.

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Conflicts of Interest: The authors declare no conflict of interest.

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