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ASSESSMENT OF LIGNIN AS A POTENTIAL BIO-MODIFIER FOR CONVENTIONAL BITUMEN

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Abstract

The main objective of this study was the investigation of the characteristic properties of lignin-modified bitumen with different lignin contents. Three (3) blends with different lignin contents (5%, 10% and 15% by weight of bitumen) were produced. Characteristic properties such as penetration, ring & ball, elastic recovery, force ductility, dynamic viscosity and storage stability were determined for the reference bitumen and the three lignin blends. Furthermore, the results of the tests were utilized to calculate the Penetration Index (PI), Activation Energy (E_a), Viscosity-Temperature Susceptibility (VTS) Index and Mixing Temperature (T_{mixing}) along with their respective Pearson's Correlation Coefficient (PCC), R^2 and p-values. 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. Additionally, a strong linear statistical correlation was observed between E_a and VTS Index suggesting that these values should be taken into consideration when characterizing the temperature susceptibility of bio-modified bitumen.

Keywords: bitumen, bio-binder, lignin, lignin-modified bitumen, flexible pavements

1 Introduction

Petroleum-based bitumen is the binding agent that keeps aggregates together at a flexible pavement. The origin of the crude oil directly affects the properties of the produced bitumen. However, the rising costs of petroleum-derived products and the significant environmental impact that that they have had led researchers around the globe to investigate alternative materials from a different source [1]. One of these materials is biomass. Specifically, bio-based products, called bio-modifiers, have been used to alter (modify) the characteristics of conventional bitumen. The origin and the form of the biomass utilized can have a major influence on the newly produced bio-bitumen. Such examples are algae, rice husk, olive waste, spent coffee grounds and corn stalk [2-6]. All biomasses consist of three different components at different percentages regardless of their nature: cellulose, hemicellulose and lignin. The properness and applicability of a modifier depend on how the modifier affects the on-field performance of the bitumen and the pavement in general. The modifiers under consideration need to not only maintain but also improve the performance of the pavement under various traffic loads and environmental conditions (temperature, UV radiation, moisture etc.). Taking into consideration that lignin exists in abundance in all plant-based organisms, the present study revolves around the utilization of lignin as a potential bio-modifier for the conventional bitumen. Specifically, the characteristic properties of Kraft lignin-modified bitumen were examined. Afterwards, a correlation statistical analysis was performed to locate if and how the various properties of lignin-modified bio-bitumen relate with each other.

2 Materials and methods

2.1 Bitumen

A conventional 50/70 penetration grade bitumen was used as a reference and a basis for the production of the lignin-modified blends. The characteristic properties of the reference bitumen are displayed in Table 1:

Table 1 Characteristic properties of reference bitumen

Property	**Specification**	**Value**
Penetration [dmm]	EN 1426	61
Softening point [°C]	EN 1427	50.0
Elastic recovery [%]	EN 13398	7
Force ductility [J/cm²]	EN 13589 & EN 13703	0.885
Dynamic viscosity fPa.s]	EN 13302	Various[1]

[1]Dynamic viscosity tests were conducted in a wide range of temperatures. The relevant results are displayed in the "Results" section.

2.2 Kraft lignin

The lignin under investigation is a by-product of the Kraft process (Kraft lignin) and has a dark brown colour. A thorough physicochemical, thermal and microstructural characterization of the lignin can be found in the authors' previous research [7].

2.3 Mixing Conditions

The mixing of bitumen with lignin took place at 160 °C for 30 minutes using a high shear mixer at 3,000 rpm. Kraft lignin was mixed into bitumen at 5%, 10% and 15% content by weight of bitumen. Consequently, the blends were denoted as LP-5, LP-10 and LP-15, respectively, whereas the reference unmodified bitumen was denoted as RB.

3 Results

3.1 Penetration test

The penetration test evaluates the consistency of bitumen. The addition of lignin brought about a gradual decrease of the penetration values (Table 2). Specifically, lignin hardened bitumen to such an extent that a change of bitumen category was observed from 50/70 to 35/50 with respect to EN 12591 when incorporating lignin at 15% by weight of bitumen.

Table 2 Penetration test results

Blend	**Penetration** [dmm]
RB	61
LP-5	57
LP-10	51
LP-15	42

3.2 Ring and ball test

The ring & ball test examines the softening point of bitumen. The softening point of the binders followed the opposite trend of the penetration values thus confirming the hardening effect noticed in the previous test. According to Table 3, the largest increase of the softening point was at 15% lignin content where the softening point reached its highest value at 54 °C.

Table 3 Ring and ball test results.

Blend	Penetration index
RB	-0.73
LP-5	-0.55
LP-10	-0.44
LP-15	-0.65

3.3 Penetration index (PI)

Penetration Index is a number that characterizes the temperature susceptibility of conventional petroleum-based binders. It is associated with the penetration and ring & ball test results. However, the applicability and validity of this index for bio-modified bitumen has not been established yet. Therefore, an assessment of this index is necessary to fully comprehend the performance of bio-modified bitumen in both high and low temperature domains. In general, a higher PI indicates a binder with less temperature susceptibility and thus a less temperature-dependent behavior. Table 4 demonstrates that the addition of lignin increased the PI value which reached its peak at -0.44 for LP-10. Consequently, lignin made the performance of bitumen more consistent by reducing its temperature sensitivity.

Table 4 Penetration Index results

Blend	Penetration index
RB	-0.73
LP-5	-0.55
LP-10	-0.44
LP-15	-0.65

3.4 Elastic recovery test

This test evaluates the elastic recovery of bitumen. The impact of lignin powder was trivial on the elastic recovery of bitumen (Table 5). Specifically, none of the blends under assessment exceeded 10% of elastic recovery.

Table 5 Elastic recovery test results

Blend	**Elastic recovery** [%]
RB	7
LP-5	10
LP-10	9
LP-15	9

3.5 Force ductility test

The cohesion of bitumen was assessed via the force ductility test at 15 °C. According to Table 6, the maximum force and total energy demonstrated an increase after the lignin bio-modification reaching a peak at 10% lignin content at 24.3 N and 1.72 J/cm², respectively.

Table 6 Force ductility test results

Blend	**Maximum force** [N]	**Total energy** [J/cm²]
RB	15.2	0.89
LP-5	16.9	1.30
LP-10	24.3	1.72
LP-15	22.3	1.53

3.6 Dynamic viscosity test

The dynamic viscosity of bitumen was measured with a Brookfield viscometer using a No.27 spindle at 20 rpm for temperatures between 130 °C and 180 °C in order to cover all pumping and use-phase temperatures. In most cases, an increase of the lignin content content led to higher dynamic viscosity values (Table 7). As expected, the dynamic viscosity became lower at higher temperatures. The differences between the blends under investigation became less pronounced at temperatures above 160 °C.

Table 7 Dynamic viscosity test results (Pa.s)

Blend	**130 °C**	**140 °C**	**150 °C**	**160 °C**	**170 °C**	**180 °C**
RB	0.875	0.375	0.250	0.175	0.125	0.100
LP-5	0.925	0.375	0.250	0.200	0.150	0.100
LP-10	0.875	0.425	0.300	0.200	0.175	0.125
LP-15	0.900	0.500	0.325	0.225	0.175	0.150

3.7 Mixing temperature (T_{mixing})

According to previous research, the mixing temperature is the temperature where the dynamic viscosity of bitumen is equal to 0.2 Pa.s [8]. Table 8 demonstrates that lignin powder caused an increase of the mixing temperature up to 166 °C for the LP-15 blend. The increments for the rest of the bio-modified blends were trivial (1-2 °C).

Table 8 Mixing temperature results

Blend	**Tmixing** [°C]
RB	161
LP-5	162
LP-10	163
LP-15	166

3.8 Activation energy (E_a)

Activation energy is the energy barrier that molecules need to surpass in order to start flowing. Its calculation method is based on the Arrhenius Equation as described in the relative literature [9]. Lower activation energy values result in a lower temperature sensitivity. As the lignin content increased, a reduction of the E_a values was observed indicating a more stable and less temperature-dependent performance (Table 9).

Table 9 Activation energy results

Blend	**Ea** [kJ/mol]
RB	63.30
LP-5	61.50
LP-10	55.85
LP-15	54.47

3.9 VTS index

The last index that has been under assessment as a possible temperature susceptibility index for bitumen is the VTS Index. An in-detail calculation methodology is described in the relative literature [10]. Higher VTS Indexes are related to higher temperature sensitivity for any given petroleum-based bitumen. Table 10 shows that the addition of lignin made bitumen less sensitive to temperature changes which verifies and comes in agreement with the Penetration Index and activation energy results.

Table 10 VTS Index results

Blend	**VTS Index**
RB	1.004
LP-5	1.004
LP-10	0.899
LP-15	0.857

3.10 Statistical analysis

In order to statistically evaluate the credibility of the aforementioned indexes and find if any correlations exist between them, the Pearson's Correlation Coefficient was calculated along with the respective R^2 and p-values (Tables 11-13). A strong correlation was found between the activation energy and the VTS Index (PCC = 0.98, R^2 = 0.96). The significance of this correlation is further validated by the p-value which is equal 0.019 and thus much lower than the threshold level of 0.05 based on a confidence level of 95%. Finally, although PI is considered to be a consistent method of quantifying the temperature susceptibility of petroleum-based bitumen, it cannot be applied for bio-modified bitumen as the PCC values with activation energy and VTS Index are too low (-0.45 and -0.28, respectively).

Table 11 Pearson's Correlation Coefficient statistical results

	PI	T_{mixing}	E_a	VTS Index
PI	N.A.	0.02	-0.45	-0.28
T_{mixing}	0.02	N.A.	-0.84	-0.86
E_a	-0.45	-0.84	N.A.	0.98
VTS Index	-0.28	-0.86	0.98	Not applicable

Table 12 R^2 statistical results.

	PI	T_{mixing}	E_a	VTS Index
PI	N.A.	0.00	0.20	0.08
T_{mixing}	0.00	N.A.	0.70	0.74
E_a	0.20	0.70	N.A.	0.96
VTS Index	0.08	0.74	0.96	Not applicable

Table 13 P-values statistical results.

	PI	T_{mixing}	E_a	VTS Index
PI	N.A.	0.979	0.553	0.721
T_{mixing}	0.979	N.A.	0.162	0.140
E_a	0.553	0.162	N.A.	0.019
VTS Index	0.721	0.140	0.019	Not applicable

3.11 Storage stability test

The storage stability test assesses the stability of modified bitumen when stored at elevated temperatures for extended periods of time. From Table 14 it can be seen that all lignin-modified blends presented a softening point difference close to 0.5 °C between the bottom and top parts of the aluminium tube. Therefore, the lignin-modified blends could be characterized as sufficiently homogeneous as no major segregation took place during the test.

Table 14 Storage stability test results.

Blend	**Temperature difference** [°C]
LP-5	0.4
LP-10	0.6
LP-15	0.4

4 Conclusions

- Lignin had a hardening effect on bitumen as demonstrated by the reduced penetration and increased softening point and dynamic viscosity values.
- The force ductility test displayed a reinforcement of the elastic phase of bitumen after the lignin bio-modification.
- The elastic recovery of bitumen was not extensively affected by lignin.
- Lignin did not cause segregation phenomena during the storage stability test regardless of its content (%).
- Lignin brought about a slight increment of the mixing temperature.
- The temperature susceptibility of bitumen was decreased with the incorporation of lignin into bitumen according to the PI, E_a and VTS Index results.
- A strong statistical correlation between E_a and VTS Index was observed suggesting that these values are credible as temperature sensitivity indexes not only for conventional petroleum-based binders, but also for bio-modified ones.

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