Effect of lignin-modification on the rheological properties of bitumen

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ABSTRACT: This publication presents the outcome of a study which sought to evaluate the rheological behavior of lignin-modified bitumen (bitumen 50/70 with 20% lignin) using 3 different kinds of lignin. In particular, the properties of the lignin-modified bitumen are compared with those of a conventional bitumen (50/70). As part of the present study, the chemical composition of all lignin variants was initially analyzed. In the laboratory study, the rheological properties of the bitumen were analyzed using the results of tests with the dynamic shear rheometer (DSR) and the corresponding properties were compared. The results indicated an increased stiffness of bitumen following lignin modification accompanied by a more elastic behavior, especially at high temperatures. Further lignin changes the anti-aging capacity of bitumen.

1 INTRODUCTION

Since its inception, bitumen, a by-product of petroleum refining, has been the subject of considerable attention. The applications of bitumen have gradually expanded in line with the advancement of human understanding and technological progress. To date, asphalt has become a significant raw material in a number of industries, including road construction, civil engineering and roof waterproofing. A substantial proportion of the global annual production of bitumen is consumed in the construction and maintenance of roads, thereby confirming its dominant role in the use of bitumen in the construction industry. However, the non-renewable nature of bitumen, in conjunction with the reduction in global oil reserves and the influence of external factors, has resulted in consistently elevated bitumen prices. The current situation is having a significant impact on the pavement industry, where there is an increasing demand for the construction and maintenance of asphalt pavements. Consequently, there is also an increasing demand for bitumen. The growing contradiction between supply and demand makes it imperative to look at least for a partial replacement of crude oil based bitumen that is environmentally friendly, renewable and ensures a stable supply.

The use of lignin in flexible pavements is not a new concept, Terrel (1980) presented a report related to the evaluation of wood lignin as a substitute or extender of asphalt. However, recently there has been a significant increase in interest in this topic as noted by Gaudenzi, et al. (2023). In particular, over the last decade there has been an exponential rise in research about the use of lignin in pavements. These studies explore different types of applications: as a bitumen modifier, extender or partial replacement of bitumen (Marquez 2023), and as an antioxidant additive (Ortiz 2020). The lignin has demonstrated the ability to act as a neutralizer, "hunter", stabilizer, and inhibitor of free radicals produced during oxidation processes. This antioxidant property is primarily due to the presence of phenolic groups that, given the presence of hydroxyls, have the ability to donate an electron to the free radical, affecting its reactivity and stabilizing it and thereby reducing their effects on the pavement material (Ortiz 2020). These multifunctional properties of lignin underscore its potential as a sustainable and effective practical bitumen replacement.

2 MATERIALS TESTED

In this research, a bitumen classified as 50/70 (1/10 mm) penetration grade, commonly used in asphalt pavements in Germany, was selected as the base bitumen. The 3 types of lignin employed in this research and their chemical composition are listed below (Table 1). The chemical analysis of the lignin materials was carried out at the Pontifical Catholic University of Chile. While Kraftlignin (KL) and Organosolv-Lignin (OL) have similar chemical compositions, Lignosulfonate (LL) shows high sulfur and nitrogen content as well as low carbon content. To assess the effectiveness of bitumen incorporating lignin, bitumen samples were prepared with 20 M.-

% lignin. The selected lignin percentage was chosen by prior experimental research (Marquez 2023). KL is sourced from Chile, while OL and LL are supplied from Germany.

Table 1. Main chemical components of the lignin variants.

Materials	N [%]	C [%]	H [%]	S [%]
Kraftlignin	0.20	63.6	5.7	1.40
Organosolv	0.17	63.2	5.9	0.37
Lignosulfonate	1.32	41.9	4.4	5.45

The production of a homogeneous mixture of lignin-modified bitumen presents a number of challenges, largely due to the hydrophilic nature of lignin. It was therefore essential to exercise strict control over the mixing parameters, including temperature and rotation speed of the high shear mixer used. The optimal parameters for the mixing process were a constant mixing temperature of 135°C, a mixing rotation speed of 5,500 rpm, and a mixing duration of 60 minutes. To simulate ageing, the blends were subjected to short-term ageing in a laboratory setting, in accordance with the requirements of EN 12607-1 (2014), using a rolling thin film oven (RTFO) at 163°C for a period of 75 minutes. RTFO provides a more accurate simulation of the conditions that bitumen undergoes during mixing and placement, which are crucial for understanding the initial performance and simulates the loss of volatile compounds (such as lighter oils and solvents) during the initial heating stages. This allows for better prediction of the performance of bitumen in real-world conditions where volatiles evaporate during production, which affects the binder's consistency and long-term durability. Table 2 provides an overview of the different materials tested.

Table 2. Sample labeling.

Sample	Modification	Aging Status
B	base bitumen	unaged
B-a	base bitumen	RTFO aged
B+KL	20% Kraftlignin	unaged
B+KL-a	20% Kraftlignin	RTFO aged
B+OL	20% Organosolv	unaged
B+OL-a	20% Organosolv	RTFO aged
B+LL	20% Lignosulfonate	unaged
B+LL-a	20% Lignosulfonate	RTFO aged

3 DSR TESTS

To evaluate the rheological properties of the materials, temperature-frequency-sweeps (TFS) were conducted within a temperature range of 70°C to -40°C at 10 K intervals. The tests were performed in a strain-driven mode, adjusting the strain level to stay within the linear viscoelastic range of the materials. The frequency sweeps covered a range from 0.159 Hz to 15.92 Hz, with 10 frequencies per decade. Two samples were tested for each variant. The test parameters were selected by the authors. With the results of the TFS, master curves were employed to describe the frequency-temperature dependency of the complex shear modulus (G*) and phase angle (δ). The shift factors were determined using the Williams-Landel-Ferry (WLF) function (Dobson 1969) to produce continuous master curves. The results of the TFS were used to fit the 2S2P1D model (Di Benedetto 2007) in conjunction with the Time Temperature Superposition (TTS) principle.

4 DSR TEST RESULTS

4.1 Rheology

The outcomes of the TFS tests are illustrated in Figures 1 and 2. Firstly, the rheological data obtained from the TFS tests were employed to construct the master curves. Because smooth master curves could be constructed, all bitumen tested are thermo-rheological simple materials.

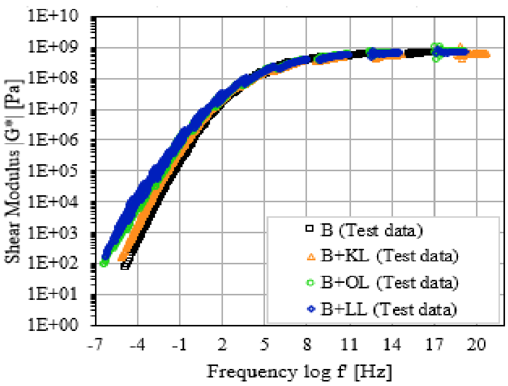

Figure 1. Master curves for the unaged materials tested (reference temperature 20°C).

The incorporation of lignin into the bitumen results in a stiffening of the binder, as evidenced by the upward shift of the functions. Figure 2 presents the Cole-Cole plots of all materials tested in RTFO-aged condition.

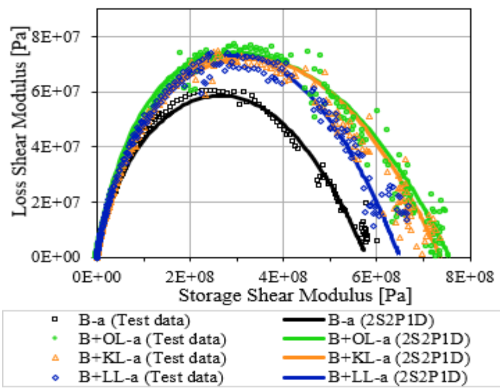

Figure 2. Cole-Cole plots of the RTFO-aged materials tested including 2S2P1D curves.

Analyzing the values of the base bitumen and the overall shape of each curve, all lignin-modified bitumen have higher G' and G" values due to the cross linking effect of the lignin. The B+KL and B+OL show similar Cole-Cole plots and hence a similar rheological performance possibly due to the similar chemical composition of the lignin (Table 1). The high carbon content of KL and OL possibly leads to higher G_∞ values (Figure 2). The shift factors utilizing the WLF method are presented in Table 3 and the 2S2P1D model parameters are listed in Table 4.

Table 3. WLF parameters.

Materials	WLF Parameters	
	C_1 [-]	C_2 [K]
B	14	115
B-a	21	163
B+KL	14	105
B+KL-a	20	130
B+OL	20	130
B+OL-a	20	130
B+LL	20	130
B+LL-a	19	150

Table 4. 2S2P1D model parameters, β = 371, h = 0.58.

Materials	2S2P1D Parameters					
	G_∞ [MPa]	α [-]	k [-]	τ_0 [s]	R^2_{G*} [–]	R^2_δ [–]
B	640.87	2.64	0.23	2.65E-06	0.995	0.997
B-a	578.22	3.60	0.24	1.44E-05	0.995	0.994
B+KL	614.08	2.70	0.23	1.21E-05	0.998	0.986
B+KL-a	736.87	3.15	0.23	6.87E-05	0.993	0.956
B+OL	702.73	2.30	0.23	1.32E-05	0.992	0.968
B+OL-a	755.75	2.50	0.21	2.89E-05	0.992	0.968
B+LL	723.99	2.30	0.22	2.92E-05	0.992	0.986
B+LL-a	649.75	3.15	0.26	3.21E-05	0.999	0.982

The Cole-Cole plots presented in Figure 2 demonstrate the actual data and the values predicted by the 2S2P1D model. A small gap between the actual and predicted data, which is also evidenced by the R^2 values shown in Table 4, indicates that the 2S2P1D model provides a good fit for the materials tested. It can be concluded that the 2S2P1D model is capable of adequately modelling the rheological behavior of the lignin-modified bitumen tested. As a result of the aging process, the value of the parameter α increases. The G_∞ values of the aged lignin-modified bitumen are larger than that of the B-a, which indicates a higher stiffness at low temperatures. The k parameter is largest for the B+LL-a which implies a rheological different performance at low temperatures compared to the other lignin-modified bitumen.

4.2 Aging performance

The change in relevant properties of bituminous materials due to aging can be assessed using an aging index, AI:

$$AI = P_{aged}/P_{unaged} \quad (1)$$

where P_{unaged} - any physical property measured on the unaged bituminous materials, and P_{aged} - the same physical property measured under aged conditions.

To determine the AI_{G*}, the complex shear modulus at 40°C down to -10°C at a frequency of 10 Hz was employed. A material with a low AI_{G*} is less susceptible to the effects of aging, and therefore exhibits fewer changes in comparison to unaged materials. Figure 3 illustrates the AI_{G*} for all materials.

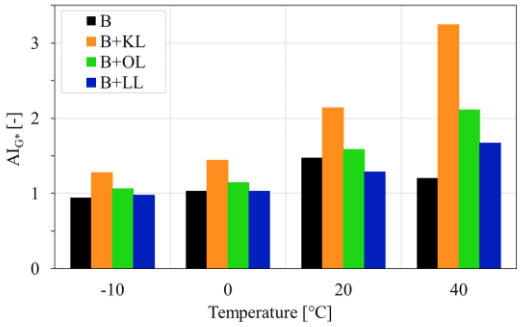

Figure 3: AI_{G*} at 10 Hz for the materials tested.

The findings indicate that the base bitumen B and the B+LL exhibits reduced sensitivity to aging effects in comparison to the lignin-modified bitumen B+KL and B+OL. Among the lignin-modified bitumen, the B+KL demonstrates the highest degree of aging susceptibility.

4.3 Modification Index

To present the lignin modification effects on the bitumen, the modification index (MI) was first calculated for the complex shear modulus at different temperatures at a frequency of 10 Hz (Figure 4). The formula used is as follows:

$$MI = M/B \quad (2)$$

where M – the modified bitumen property and B – the corresponding base bitumen property. In general, the modification of lignin results in an increase in stiffness, in unaged and aged state.

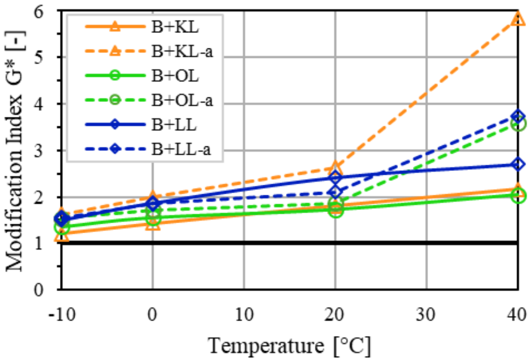

Figure 4. MI of complex shear modulus at 10 Hz for the materials tested.

In the aged state, the highest rise in stiffness is observed for B+KL. Similar stiffening effects of comparable magnitude were observed in mastic samples (Rochlani 2021), suggesting that lignin may also act as a filler.

In order to provide a concise overview and evaluation of the findings related to the rheology of the aged lignin-modified bitumen in comparison to the base bitumen, a spider diagram, was developed (Figure 5) for the MI on the basis of the following parameters: phase angle at 10 Hz and 20°C (representing the rheology at medium temperatures), Glass shear modulus (represents the response at low temperatures), complex shear modulus at 20°C and 10 Hz (representing the stiffness at medium temperature range), AI_{G^*} and AI_{δ} at 20°C and 10 Hz (representing the aging at medium temperature range).

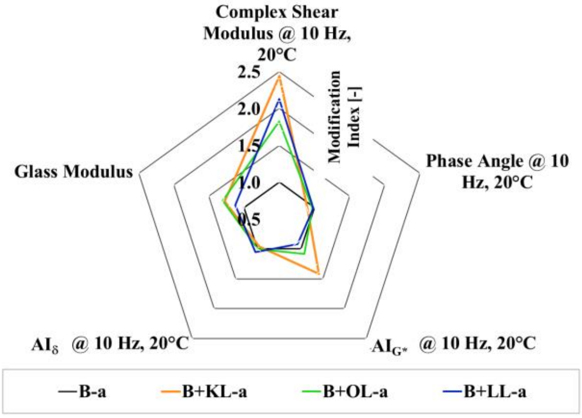

Figure 5. Performance diagram.

The most significant effects of lignin modification are manifested in terms of a considerable increase in G* and a slight increase in G_{∞}. In the case of B+KL, a significantly higher degree of aging susceptibility can be observed.

5 CONCLUSIONS

This article examines the impact of three different lignins on the performance of a bitumen, pen grade 50/70, at a representative quantity of 20 M.-%. The analysis was focused on rheological characterization with the objective of evaluating the potential antioxidant effect of lignin. The rheological performance was evaluated through a TFS test, which was employed to assess the viscoelastic properties. In light of the findings, the following conclusion can be drawn.

- The modification with lignin significantly impacts the bitumen performance.
- The chemical composition of lignin affects the rheological properties of lignin-modified bitumen. In the unaged and RTFO aged condition, there is an increase (1.5 to 2.5 times depending on the temperature and type of lignin) in stiffness due to crosslinking effects between lignin and bitumen. The high carbon content of KL and OL possibly leads to even higher viscosity and hence to higher G_{∞} values compared to the OL.
- The results show that lignin has similar stiffening effect compared to a mineral filler.
- Furthermore, the KL modified bitumen displays a heightened susceptibility to aging, manifested in stiffness, in comparison to the base bitumen. The LL-modified bitumen shows less sensitivity to aging at temperatures > 20°C than the base bitumen possibly due to the higher sulfur content. That supports the hypothesis that lignin could enhance the aging resistance of bitumen under certain conditions.

It is essential to emphasize that the objective of this research was to analyze a limited number of lignin samples and only one percentage of lignin in short term aging condition. The bitumen should also be tested in long term aging conditions. The results are therefore preliminary. In order to evaluate the effect of lignin-modified bitumen on the asphalt mixture level, further performance tests on asphalt samples should be undertaken.

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