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# Preliminary study on using lignin as aging inhibitor in bitumen

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**ABSTRACT:** During oxidative aging, oxygen reacts with active molecules present in bitumen producing polar compounds, principally ketones and sulfoxides, and increasing in the portion of asphaltenes. In general, oxidation reactions in bitumen yields to change its generic chemical composition and finally its colloidal structure deteriorating the physico-mechanical properties. Lignin is a natural polymer, which has been used in this study as an aging inhibitor to bitumen. Particularly, the effect of aging on the microstructure morphology, surface properties, chemical composition and rheological changes of lignin and the impact of latter as anti-oxidant in bitumen were evaluated. For the purposes of this study, Environmental Scanning Electron Microscope, Helium Pycnometer, Dynamic Vapor Sorption devices and were used to analyze the microstructure, density and specific surface area, respectively. Moreover, Fourier Transform Infrared spectroscopy was used to track the compositional changes in lignin-modified bitumen after PAV aging. Dynamic Shear Rheometer was used to analyze the rheological properties. Overall, decreasing in the carbonyl and sulfoxide compounds were tracked in lignin-modified binders confirm that lignin act as an aging inhibitor in bitumen.

## 1 INTRODUCTION

Bitumen is a complex petroleum-based material which is the most widely used binder for paving applications. However, considering the uncertainty in crude oil supply, alternative binders are encouraged to be used as a replacement of bituminous binders or performance modifiers. Especially, lignin, among others, has attracted considerable attention as a partial substitute or modifier of bitumen (Xu 2017). Lignin is the most abundant natural polymer on the Earth, with the total amount of lignin present in the biosphere to exceed 300 billion tons and increase by approximately 20 billion tons every year (Bruijninx 2016). Lignin can be found as well in co-products of timber production, or in byproducts of paper and hydrolytic industries. Thus, the utilization of lignin in binders specially designed for pavements may bring large economic benefits to sustainable development.

Nevertheless, the use of lignin is not limited only as a replacement of bitumen or modifier but it can be incorporated as an aging inhibitor as well in order to minimize the aging potential and to improve the durability of binders (Apostolidis 2017). Particularly, during oxidative aging, oxygen reacts with molecules present in bitumen producing polar compounds, principally ketones and sulfoxides, and secondary causing increase in the portion of asphaltenes. In general, oxidation reactions in bitumen yields to change its generic chemical composition and finally its colloidal structure deteriorating the physicomachanical properties. Lignin has found to retard bitumen oxidation (Sundstrom 1983, Williams & McCready 2008, Gosselink 2011, Batista 2018) mainly due to the lignin radical scavenging activity, its polyphenolic structure (Boeriu 2004,

Dizhbite 2004, Pan 2012), and the physical interaction between bitumen and lignin (Zhang 2019). However, lignin itself also has a large number of carbonyl and sulfoxide functional groups, which should be taken into account separately from the bituminous functional groups that evolve due to bitumen aging (Petersen 2009). Thus, a preliminary study was performed to evaluate the anti-aging effect of lignin in bitumen by differentiating the aging functional groups of bitumen and lignin.

## 2 MATERIALS AND METHODS

### 2.1 Material Preparation

In this study, a 70/100 pen grade bitumen with 47.5°C softening point was used. The organosolv lignin (brownish powder) was provided by Chemical Point UG (Germany), having a purity of above 87%. On the basis of previous studies (Van Vliet 2016), various contents of lignin were added into the bitumen in this study. The abbreviations Bref, BL05, BL10, BL20, BL30 stood for the added lignin by 0, 5, 10, 20 and 30% of the mass of bitumen.

The high shear mixer was used to mix lignin with bitumen. Lignin was gradually added in bitumen, the mixing temperature and rate were 163°C and 3000 rpm, respectively. The whole mixing process took about 30 minutes. Pressure Aging Vessel (PAV) was carried out to simulate the long-term aging of bitumen based on the standard testing procedure (NEN-EN 14769). To be specific, 50 ± 0.5 g bitumen was poured into a PAV pan to form a film with 3.2-mm thickness. Then, the PAV test was performed at a temperature of 100°C at 2.10 MPa for 20 hours.

## 2.2 Morphology, Density and Specific Surface Area Characterization

An Environmental Scanning Electron Microscope (ESEM) was used to observe the surface morphology of lignin at ambient temperature. The magnification was varied by  $\times 125$  and  $\times 1000$ . To ensure drying of lignin before scanning, lignin was oven-conditioned at  $80^{\circ}\text{C}$  for 24 hours. Further, approximately 20 mg of lignin was poured onto an 8-mm diameter sample holder to prepare the ESEM samples. It was important to prevent the samples from dust or other impurities before ESEM scanning.

Density measurements of lignin particles were conducted in a Helium Pycnometer (HP). A high precision electronic scale was used to weigh a small amount of sample. Helium was gradually filled in the chambers containing the lignin when the equilibrium was reached, the pressure of the chamber was measured. Then, expansion valve opened automatically and the gas flowed into the expansion chamber. Once the equilibrium was reached, the pressure of the current condition was measured. By comparing twice equilibrium pressures and volume of chamber, the volume of lignin calculated and density was determined.

The specific surface area was calculated by Braunauer-Emmett-Teller (BET) method after conducting surface measurements in a Dynamic Vapor Sorption (DVS) device. The amount of lignin was about 50 mg necessary due to the high uptakes of vapors on the high surface area. The ambient temperature  $25^{\circ}\text{C}$  was selected, and a 100-sccm flow rate was used in the test. The typical partial pressure range for BET experiments was 0.05 to 0.30% ( $P/P_0$ ). It was therefore ideal to collect an isotherm between these limits using 5%  $P/P_0$  steps. The BET method assumed a physical adsorption mechanism in monolayer coverage was obtained, followed by multilayer adsorption, it could be applied to any adsorption system. The total surface area and the specific surface area were determined.

## 2.3 Chemical Characterization

FTIR spectroscopy of a single-point Attenuated Total Reflectance (ATR) fixture was used to collect spectra data of lignin and bitumen samples and to track chemical compositional changes. The wavenumber ranged from 600 to  $4000\text{ cm}^{-1}$  with a resolution of  $4\text{ cm}^{-1}$ . Nine replications for each sample were analyzed. Different functional groups have a different light-absorption spectrum. The functional group aging index (AI) was used for the main absorption bands of lignin to compare the changes of functional groups with the changes of spectra. The range of chemical functional groups of lignin and bitumen were calculated and considered has been summarized in (Zhang 2019).

The aging effect of lignin itself is not obvious or even negligible but still contains the aging functional

groups. In order to eliminate the effect of lignin itself, the increase ratio index (IRI) was calculated by the changes in the aging index under different aged conditions and the proportion of bitumen in the mix. The equation is listed below.

$$IRI = \frac{AI_{Aged} - AI_{Fresh}}{W} \quad (1)$$

where  $AI_{Aged}$  is the aging index of samples in aged condition;  $AI_{Fresh}$  is the aging index of samples in unaged condition;  $W$  is the mass fraction of bitumen in the mix,  $W = m_{bitumen} / m_{total}$ .

## 2.4 Rheological Characterization

To characterize the rheological properties, complex shear modulus ( $G^*$ ) of bitumen over a wide range of temperatures and frequencies were performed by the Dynamic Shear Rheometer (DSR). In this study, the parallel-plates geometry with an 8-mm diameter and 2-mm gap were used at the range of temperature from  $-10$  to  $30^{\circ}\text{C}$  with  $10^{\circ}\text{C}$  increment, and for relatively elevated temperature range from  $30$  to  $60^{\circ}\text{C}$  with  $10^{\circ}\text{C}$  increments used the 25-mm diameter plates and 1-mm gap. The samples were tested with a frequency sweep from 100 to 0.1 rad/s at each temperature. The master curves were generated by the results at a reference temperature of  $20^{\circ}\text{C}$ . The effect of the different content of lignin and aged conditions were depicted by master-curves.

# 3 RESULTS AND DISCUSSION

## 3.1 Microstructural Morphology

The microstructure of lignin particles in different magnification ( $\times 125$  and  $\times 1000$ ) was shown in Fig. 1.  $10\text{-}200\text{ }\mu\text{m}$  was the range of the size of lignin particles, smaller fractions of particles that seem to be crushed from larger ones. The lignin particles were observed some angularities in fresh condition. There was an agglomeration phenomenon after aging, the agglomeration phenomenon was confirmed as the density of aged particles increased. And the surface of the particles became smoother and color appearance was darker.

The density of the lignin was  $1.3774\text{ g/cm}^3$ , which was measured by HP. The specific surface area was  $147.0593\text{ m}^2/\text{g}$ , which was calculated by the BET method in DVS. The physical properties of lignin were measured after aging as well. The overall color of lignin particles became darker, the density increased to  $1.5029\text{ g/cm}^3$  and the specific surface area decreased to  $65.0475\text{ m}^2/\text{g}$ . The specific surface area of fresh (unaged) lignin was two times more than that of aged lignin. The larger the powder area, the greater the friction between the particles. After aging, the density of lignin increased and its specific surface area decreased. In addition, its surface be-

came smoother, possibly because it was in contact with oxygen during aging.

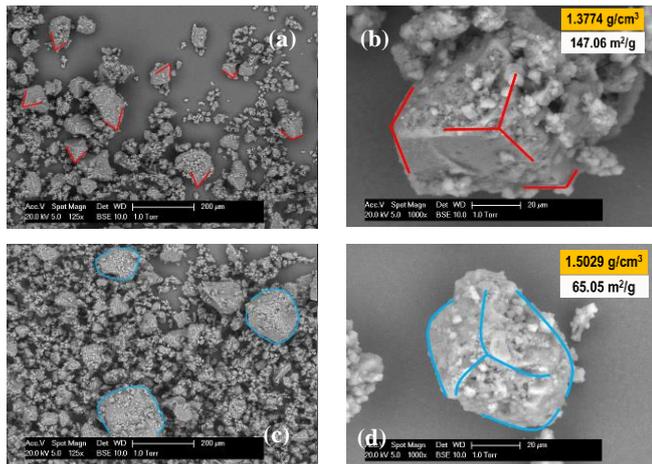


Fig. 1. ESEM images; Magnification  $\times 125$  of (a) fresh, (c) aged lignin; Magnification  $\times 1000$  of (b) fresh and (d) aged lignin.

### 3.2 Chemical Compositional Changes

IR spectra results of various lignin modified bitumen are shown in Fig. 2. Each IR spectra was the average result of the nine replications. The peaks of certain functional groups could be found in both base materials. They corresponded one by one, it showed that the lignin added in bitumen did not produce new chemical functional group peaks. This figure illustrated that lignin itself contains carbonyl and sulfoxide functional groups. The absorbance indices of fresh and aged conditions are shown in Fig. 3. The values of indices were also the average of the nine measurements.

Fig. 3 gives an overview of the aging indicators for different materials at fresh and aged conditions. The aging indices of various samples at the fresh state increased with the increase of lignin content. Aging indices of samples with 5% content of lignin in bitumen were relatively small, so the increase was very slight. Obviously, all aging indices increased with aging. To evaluate the anti-aging effect of different lignin modified binders, the aging indices were used to calculate the IRI described by Eq. 1. The results are shown in Fig. 4.

IRI had eliminated the effect of lignin. The higher the IRI value is, the faster the aging functional groups increase at the same aging process, vice versa. Apparently, the addition of lignin declined the growth rate of both carbonyl and sulfoxide compounds comparing to neat bitumen (Bref). It showed that lignin shows to an anti-aging effect since it reduced the production of related functional groups. The changes in the two functional groups with the content of lignin were different. The increase rate of the carbonyl group decreased first and then increased with the content of lignin increasing. IRI reached the lowest when the content of lignin was 10%. However, the increase rate of sulfoxide basically did not change with lignin content. The IRI of sulfoxide was slightly different from each other

compared with that of the carbonyl. Compared to neat bitumen (Bref), it was still significantly lower.

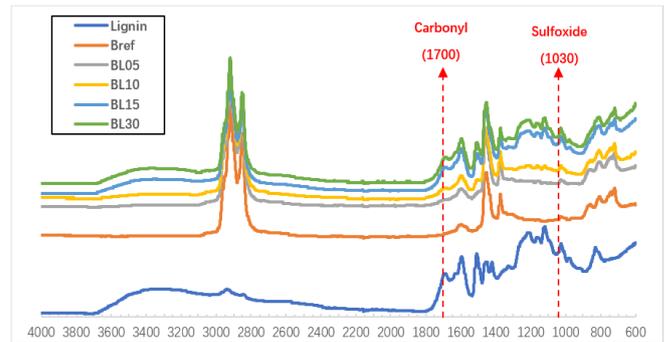


Fig. 2. IR spectra of lignin-modified bitumen.

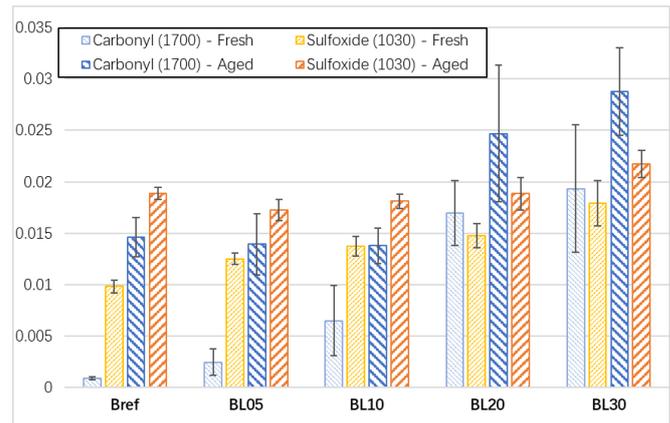


Fig. 3. Carbonyl and sulfoxide indices of lignin-modified bitumen.

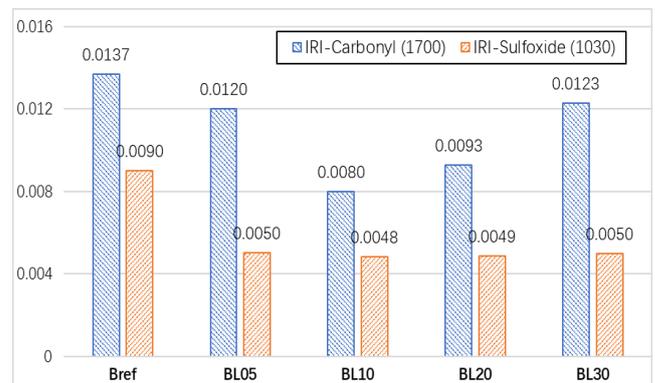


Fig. 4. IRI of carbonyl and sulfoxide indices.

The top surface of bitumen which is exposed to oxygen, ages first. As time proceeds, the internal species of bitumen starts to be oxidized due to the diffusion of oxygen into the bitumen. In the case of bitumen with organosolv lignin particles, the diffusion of oxygen is potentially prohibited to flow and react with the sensitivity carbon and sulfur species of bitumen and to produce carbonyl and sulfoxide compounds. In other words, it would take a longer time for the oxygen to diffuse and react with these bituminous species. Here, on the basis of spectroscopic results, not new reaction products are observed with the addition of lignin in bitumen, and thus it is believed that lignin possibly is able to inactivate oxidation promoters and oxygen receptors that might be in bitumen. The mechanism of inhibition of oxidation is thus based on prohibiting the susceptible to oxygen species to be transformed to carbonyl or

sulfoxide compounds and thus decelerating the overall oxidation process of bitumen.

### 3.3 Rheological Changes

The master-curves of complex modulus of different materials are shown in Fig. 5. High modulus of the material indicated increase resistance to deformation. Each tested material had three replicates. Obviously, the modulus increased with the increase of (fresh or aged) lignin content in bitumen and over different aging time periods. Over the range of high frequencies, the properties between all samples were very close. Although modulus increase improved the resistance to deformation, it may be prone to brittle fracture, which affected the low-temperature performance. However, the effect of lignin on bitumen mainly reflected at high temperatures showing improved high resistance to deformation.

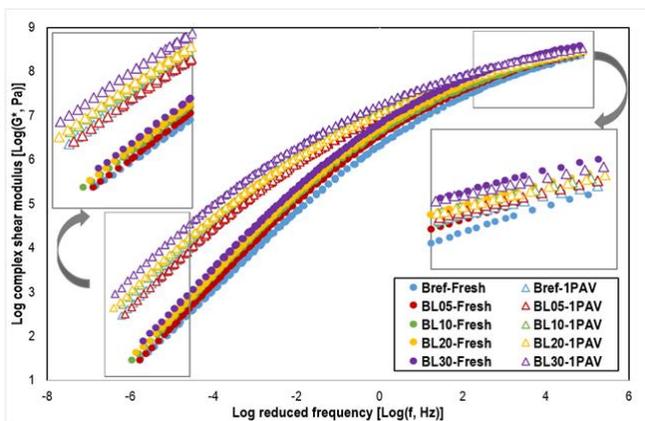


Fig. 5. Master curves of complex shear modulus

## 4 CONCLUSION

The research presented in this paper has shown the preliminary conclusions on the use of lignin as an aging inhibitor in bitumen. After aging, the lignin particles agglomerated, the density of lignin increased and its specific surface area decreased. In addition, its surface became smoother, the color of appearance became darker. Moreover, the IRI of aging functional groups was designed to accurately evaluate the anti-aging performance of lignin. The addition of lignin in bitumen reduced production and inhibited the formation rate of carbonyl and sulfoxide compounds. The changes in IRI in these two compounds were different possibly due to their different chemical properties. Finally, the master-curves of complex modulus have demonstrated that lignin in bitumen improved high-temperature resistance to deformation and potentially led to the enhancement of brittle fracture at low temperatures.

## 5 ACKNOWLEDGMENTS

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