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Utilization of Lignin as an Antioxidant in Asphalt Binder

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***Abstract*— The objective of this study is to investigate the viability of utilizing lignin as an antioxidant for arresting the aging of the bituminous binder. Oxidation is the primary cause of long-term aging in asphalt pavements. As a pavement oxidizes, it stiffens and can eventually crack. The use of an antioxidant as a performance enhancer in an asphalt binder could delay aging, thus increasing the life of an asphalt pavement. Lignin is highly available and well-studied antioxidant. In the present investigation, the rheological properties were characterized for bitumen binder blended with an organic lignin, 'Lignin 1', and a processed lignosulphonate, 'Lignin 2', at different percentages (5% and 7%) by weight of the base binder. Rotational Viscometer (RV) and Dynamic Shear Rheometer (DSR) tests were conducted for the rheological properties, and the Rolling Thin-Film Oven (RTFO) test and Pressurized Aging Vessel (PAV) tests were conducted for the simulation of aging. The aging index was developed for all the blends. The rheological properties of the bituminous binder in terms of their complex modulus (G*), phase angle (δ), rutting parameter (G*/sinδ) and fatigue parameter (G*×sinδ) were measured. Furthermore, the oxidation characterization was investigated through the Fourier Transform Infrared Spectroscopy (FTIR) test. Comparison of results for the unmodified binders and lignin modified binders were done, to identify the effect on aging on addition of lignin. It was concluded that lignin showed some antioxidant activity when added to asphalt binder, which was supported by FTIR results.**

***Index Terms*— Asphalt binder, FTIR, Lignin, Oxidation, Pavement aging, Rheological properties**

I. INTRODUCTION

Bitumen is widely used for the construction of highway and airport pavements, which together account for approximately 85% of the worldwide consumption of bitumen. The use of bitumen in combination with mineral aggregate to form an asphalt mixture results in a road construction material that not only has good qualities as a surfacing layer but, when correctly designed, provides the structural component layer of flexible pavement construction. The bitumen is not only an important engineering material but also a vital component in pavement engineering.

India has a road network over 4,689,842 km (in 2013), the second largest road network in the world. Roads in India are primarily bitumen – based macadamized roads. India is having 98 % flexible pavement, which is an important asset. Also, India's road network carries over 65% of its freight traffic and 85% of the passenger traffic. Large scale road infrastructure developmental projects like Bharat Nirman, National Highway Development Project (NHDP) and Pradhan Manthri Gram Sadak Yojna (PMGSY) and State Highways Improvement Programs (SHIPs), etc, are in progress.

India is a country having varied climate and excessive stress and strains on the road. The pavement deterioration is experienced due to high and low temperatures in some region. Further deterioration is due to increase in traffic density, axle loading and tyre pressure and an insufficient degree of maintenance. In order to achieve desired engineering properties, it is utmost important to modify the binders by adding additives for application of road bituminous mixes with higher performance.There is no performance enhancer in widespread use as an antioxidant, which can retard the oxidation process of bitumen. Slowing the oxidation aging of a pavement will enable the binder to maintain its elastic properties and can reduce the aging related pavement failures.

In the present study, the VG30 grade bitumen and PMB40 grade bitumen is used and different types of lignin were added, in different proportions, to both types of bitumen binder. The short – term aging and long – term aging is simulated using Rolling Thin Film Oven Test (RTFOT) and Pressure Aging Vessel (PAV) Test, respectively. The rheological properties of unaged and aged binders, in terms of their complex modulus (G*) and phase angle (δ), are characterized using Dynamic Shear Rheometer (DSR) Test. Also, the aging index is developed for all the binders. Furthermore, the oxidation characterization is investigated through the Fourier Transform Infrared Spectroscopy (FTIR) Test and the comparison of results for all the binders are done, to identify the effect on aging on addition of both antioxidants.

II. OBJECTIVES OF STUDY

The following are the objectives of the research study:-

1) To study the viability of utilizing organic lignin as an antioxidant for arresting the aging of asphalt binders.
2) To validate the oxidation characteristics using Fourier Transform Infrared (FTIR) spectroscopy investigations.

III. ASPHALT OXIDATION

Asphalt oxidation is the main cause of long-term deterioration in asphalt pavements. Oxidative aging causes the asphalt to become hard and brittle, which can finally lead to pavement failure. The asphalt binder in the mixture continues to age while the mix is being stored, transported, and eventually paved during construction. Short term aging, which takes place during mixing and laying of bituminous materials, is mainly related to oxidation and evaporation. Long term aging, which occurs during service, is mainly related to oxidation and physical hardening. Long-term oxidative aging begins immediately after a pavement is constructed. Long-term oxidation occurs at a much slower rate than the initial oxidation of asphalt during mixing and construction. Long-term aging causes a large increase in stiffness and loss of ductility. Of several mechanisms for bitumen aging, the following four are among the most important:-

1) Reaction with atmospheric oxygen.
2) Evaporation of volatiles.
3) Phase separation in connection to porous aggregates, exudation.
4) Physical hardening due to altering the molecular configuration.

IV. LIGNIN

Lignin, derived from the Latin term lignum meaning wood, is an integral part of the secondary cell walls of plants. It fills the gap in the cell walls among cellulose, hemicelluloses and pectin components imparting mechanical strength to the cell wall. Lignin is the second most abundant natural substance in the world after cellulose. It is estimated that 5×10^6 metric tons of lignin are produced annually from pulp and paper industries worldwide. Lignin is a hydrocarbon and consists mainly of carbon, hydrogen, and oxygen. The chemical structure of lignin is highly aromatic in nature with many randomly attached methoxyl and hydroxyl groups. Lignin can also contain aromatic hydrogen atoms, carbonyl groups, and aliphatic double bonds.

The antioxidant effects of lignin are derived from the scavenging action of their phenolic structures on oxygen containing free radicals. Phenolic structures are benzene rings with attached hydroxyl groups. Benzene rings are six carbon structures with each carbon sharing a single and double covalent bond to another carbon. In a phenolic group, there can be one or more hydroxyl groups attached to the benzene ring. The ability of phenolic compounds to be antioxidants is the functional group’s ability to neutralize free radicals. Free radicals are known to actively break down substances by breaking apart their chemical structures. A phenol can neutralize a free radical by donating either a proton or an electron. Because of its structure, a phenol is able to do both while remaining relatively stable. Lignin contains a large amount of phenolic groups, making it an effective antioxidant.

V. REVIEW OF LITERATURE

McCready N. S. and Williams R. C. studied that oxidation is the primary cause of long-term aging in asphalt pavements. The use of an antioxidant as a performance enhancer in an asphalt binder could delay aging, thus increasing the life of an asphalt pavement. Lignin from ethanol production was used as an antioxidant in asphalt binders. A stiffening effect on the binder was caused by the addition of the lignin. The temperature ranges of the binders were widened on addition of co-products. This result suggests some antioxidant activity between the binder and the lignin. The samples with no lignin aged significantly more than the samples with lignin. Infrared spectrometry also supported the idea that lignin acts as an antioxidant by observing decreases in some oxidative aging products.

Mills – Beale J., et. al., aimed to investigate the viability of using swine waste binder to improve the rheological properties of bituminous asphalt binder. The rotational viscosity results proved that the addition of biobinder can reduce the viscosity of the asphalt binder. Further, the modified binder had lower complex moduli and phase angles compared with the base binder. Also, the BBR results indicated that biobinder had the potential to improve the thermal cracking performance of conventional asphalt binders by reducing the creep stiffness and increasing m-value. The FTIR spectra showed that addition of biobinder decreased the stiffness of the binder through the reduction in molecular carbonyl and sulphoxide bond chains at high temperature.

Lu X. and Isacsson U. studied the effect of aging on bitumen chemistry and rheology. The relationship between TFOT and RTFOT was also investigated and from this study, it was observed that aging influenced bitumen chemistry and rheology significantly. However, chemical and rheological changes were generally not consistent, and consequently, aging susceptibility of bitumens may be ranked differently when different evaluation methods are used. A strong correlation was observed between TFOT and RTFOT, and the two aging procedures show similar severity.

VI. EXPERIMENTAL METHODS

In this research, different blends are prepared by adding 'Lignin 1' and 'Lignin 2' with the asphalt binders VG30 and PMB40 in the proportion of 5% and 7% by weight of the asphalt binders. These blends were prepared using blender machine at medium speed at 150°C for 20 minutes each. The fresh or unaged binders are tested for different binder testing (penetration test and softening point test), Dynamic Shear Rheometer (determining parameters – G*, sinδ, G*/sinδ) and Rotational viscosity at 135°C. The simulation of short term aging of fresh binders is done using Rolling Thin Film Oven Test (RTFOT) for 85 minutes and at 163°C, which is as per ASTM D7175-15. These short term aged binders are then tested for binder testing (penetration test and softening point test), Dynamic Shear Rheometer (determining parameters – G*, sinδ, G*/sinδ) and Rotational viscosity at 135°C. An aging index is developed for evaluating the effect of lignin for reduction in oxidation in asphalt binder. The aging index of the blends is compared with aging index of the virgin asphalt binders. The RTFOT aged binders are simulated for long term aging using Pressure Aging Vessel (PAV) for 20 hours at 100°C at 2.1 MPa, which is as per ASTM D6521-13. Furthermore, the fresh binders, RTFOT aged binders and PAV aged binders are investigated for FTIR spectroscopy for carbonyl and sulfoxide groups in the binders.

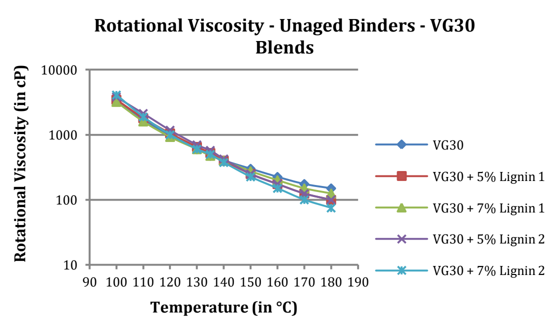
VII. RESULTS & DISCUSSION

A. Physical Properties of Bitumen

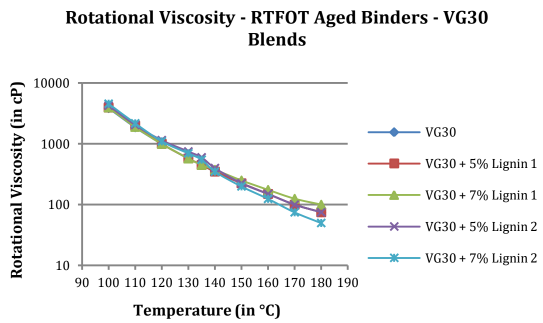
Binders were characterized by using a number of standard physical tests such as penetration test (temperature, load and time are 25ºC, 100 g and 5 sec, respectively), softening point test and viscosity test using Brookfield viscometer (temperature range from 100ºC to 180ºC, spindle No.27, and a rotating speed of 20 RPM).

With the addition of lignin content, the penetration values of VG30 and PMB40 binders decreases. This indicates that the addition of 'Lignin 1' and 'Lignin 2' to VG30 and PMB40 binder is making the binder hard. This may be happening because the addition of lignin is giving the filler effect to the binders. According to the softening point test results, with the addition of 'Lignin 1' and ;Lignin 2', the softening point of binder increases.

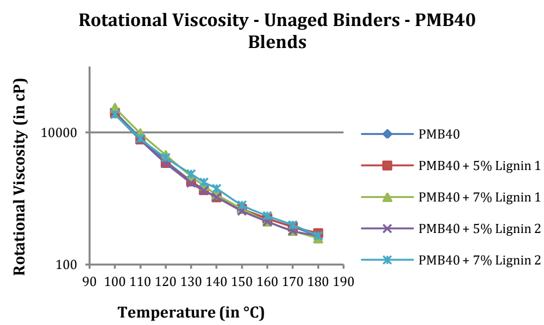
The results of rotational viscosity of unaged and RTFOT aged binders of VG30 and those of PMB40 blends are shown in Fig. 3(a), 3(b), 3(c) and 3(d), respectively.



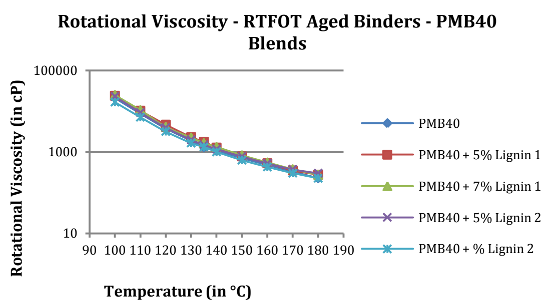
(a) Unaged binders of VG30 blends



(b) RTFOT aged binders of VG30 blends



(c) Unaged binders of PMB40 blends



(d) RTFOT aged binders for PMB40 blends

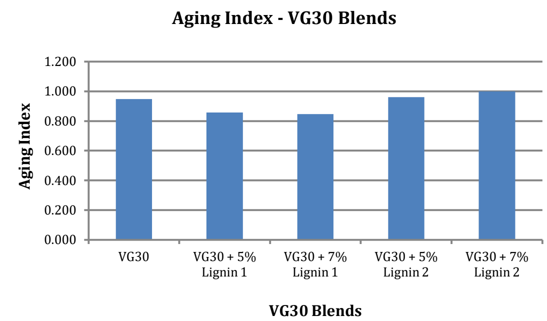
Figure 1: Rotational viscosities of binder

Fig. 1 shows that the viscosity in all the blends of VG30 and PMB40 (unmodified and modified bitumen) decrease as the temperature increase. The result shows that with the addition of lignin the viscosity of binders increases. These results are in accordance with the results of penetration test and softening point tests.

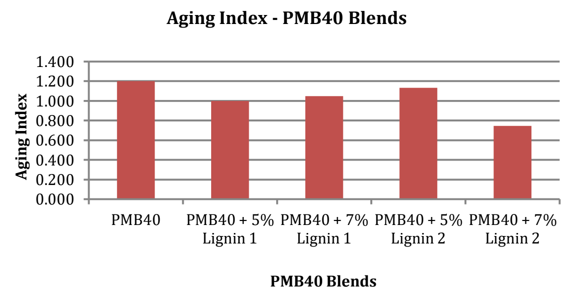
B. Aging Index

Aging Index is defined as the ratio of viscosity of RTFOT aged binder at 135°C to viscosity of unaged binder at 135°C. Aging index gives us an idea about the degree of aging induced to bitumen, for example, more is the aging index, and more will be the degree of aging in the binder.

The aging index of VG30 blends and PMB40 blends are as follows:-



(a) VG30 blends



(b) PMB40 blends

Figure 2: Comparison of aging index

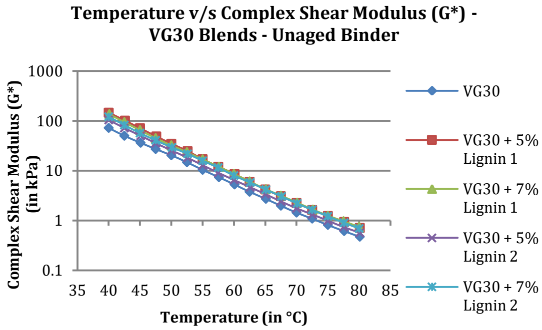
Results plotted in Fig. 2(a) and Fig. 2(b), indicated that the addition of 'Lignin 1' and 'Lignin 2' does not affect the aging index of VG30 significantly, whereas, in case of PMB40 binder the aging index reduces significantly after the addition of 'Lignin 1' and 'Lignin 2'.

C. Rheological Test Results

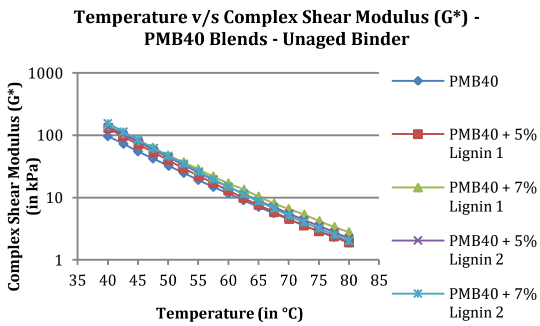
Dynamic Shear Rheometer test was conducted by using a temperature sweep starting from 40ºC to 80ºC, while the frequency was fixed at 10 rad/s. Parallel plates with diameter of 25 mm and 1 mm gap were used for unaged binders and RTFOT aged binders, and for PAV aged binders, plates with diameter 8 mm and 2 mm gap was used.

D. Effect of Temperature and Lignin Content on Complex Shear Modulus

Temperature sweep test was run on unaged, RTFOT aged and PAV aged binders, for VG30 and PMB40 binders, complex modulus was obtained and plotted against temperature as illustrated in Fig. 3, Fig. 4 and Fig. 5.

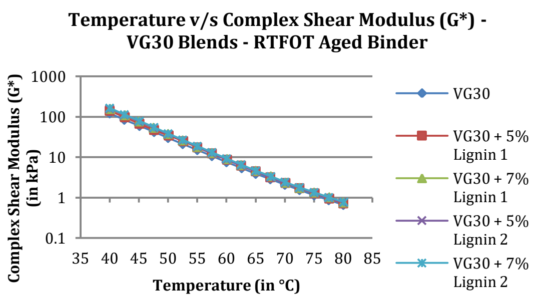


(a) VG30 blends

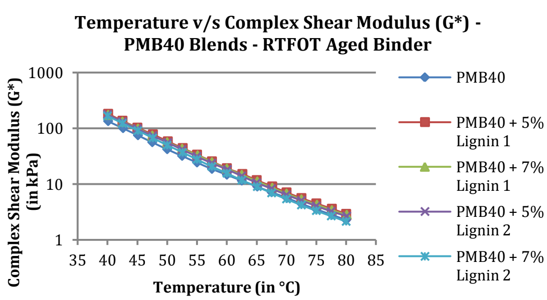


(b) PMB40 blends

Figure 3: Temperature v/s complex shear modulus (G*) for unaged binders

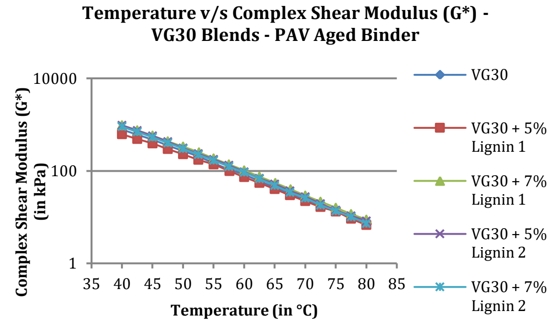


(a) VG30 blends

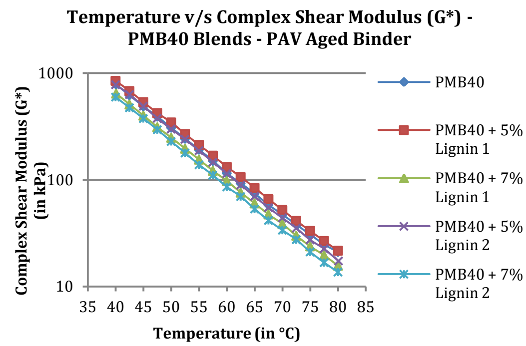


(b) PMB40 blends

Figure 4: Temperature v/s complex shear modulus (G*) for RTFOT aged binders



(a) VG30 blends



(b) PMB40 blends

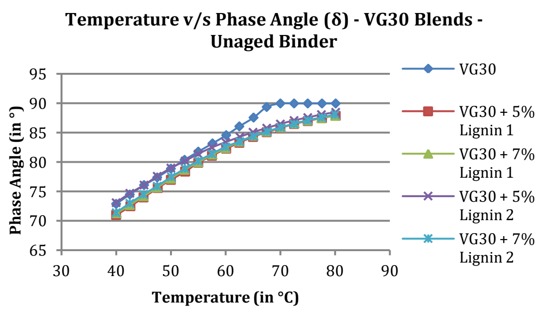
Figure 5: Temperature v/s complex shear modulus (G*) for PAV aged binders

Fig. 3(a) showed that the complex shear modulus (G*) is lowest for the unmodified bitumen as compared to lignin modified bitumen. From the results it is observed that, with the increase in 'Lignin 1' content, G* value decreases, whereas, with the increase in 'Lignin 2' content, G* value increases. After short term aging, Fig. 4(a), with the increase in 'Lignin 1' and 'Lignin 2' content, G* value increased and after long term aging, Fig. 5(a), with the increase in 'Lignin 1' content, an increase in G* value is observed, whereas, an opposite trend is observed with increase in 'Lignin 2' content. The results indicate that addition of lignin to VG30 binder will improve its performance.

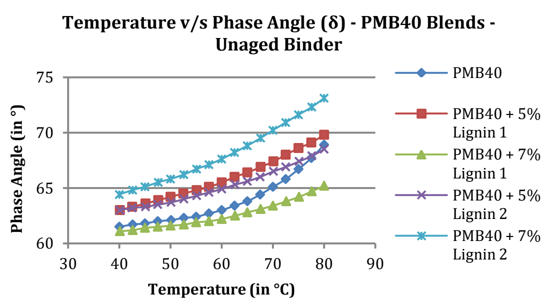
Fig. 3(b) showed that the complex shear modulus (G*) is lowest for the unmodified bitumen as compared to lignin modified bitumen. From the results it is observed that, with the increase in 'Lignin 1' and 'Lignin 2' content, G* value increases. After short term aging, Fig. 4(b) with the increase in 'Lignin 1' and 'Lignin 2' content, G* value decreased and after long term aging, Fig. 5(b), with the increase in ‘Lignin 1’ content, an increase in G* value is observed, and a same trend is observed with increase in ‘Lignin 2’ content. It was also observed that at high temperatures, that is, beyond 65°C all binders behaved similar.

D. Effect of Temperature and Lignin Content on Phase Angle

Temperature sweep test was run on unaged, RTFOT aged and PAV aged binders, for VG30 and PMB40 binders, phase angle was obtained and plotted against temperature as illustrated in **Fig. 6, Fig. 7** and **Fig. 8**.

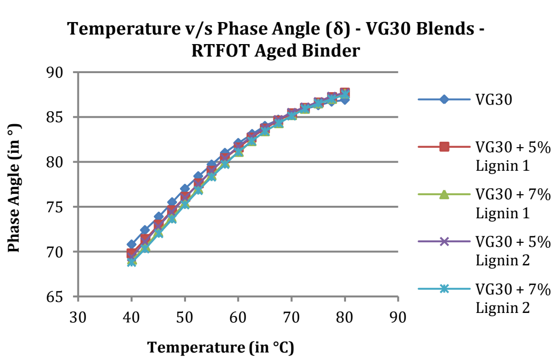


(a) VG30 blends

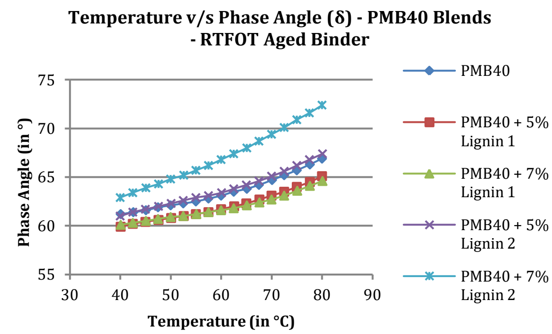


(b) PMB40 blends

Figure 6: Temperature v/s phase angle (δ) for unaged binders

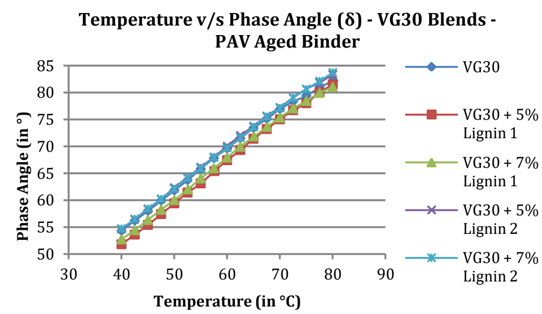


(a) VG30 blends

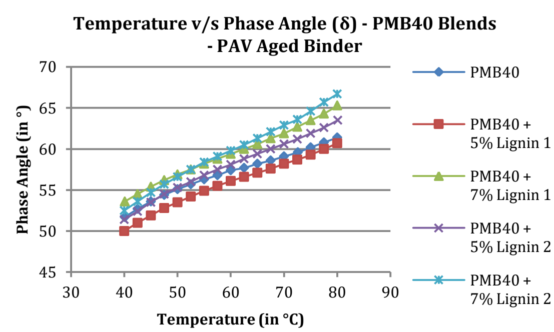


(b) PMB40 blends

Figure 7: Temperature v/s phase angle (δ) for RTFOT aged binders



(a) VG30 blends



(b) PMB40 blends

Figure 8: Temperature v/s phase angle (δ) for PAV aged binders

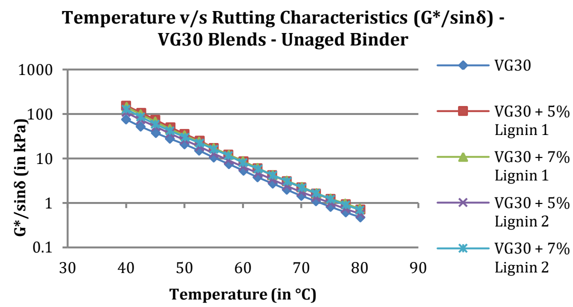
From Fig. 6(a), it is observed that at lower temperatures, the addition of ‘Lignin 1’ and ‘Lignin 2’ made the binder more elastic than viscous. The unaged binders of VG30 blends will recover to their original condition without dissipating energy. Also, at higher temperatures (T > 55°C), lesser phase angle is desirable since this reduces permanent deformation. Here, with the increase in ‘Lignin 1’ and ‘Lignin 2’ content, a slight increase in phase angle is observed. This indicates that less content of

'Lignin 1' and 'Lignin 2' are preferable. From Fig. 7(a), it appears that when the binders are short term aged, which is, aging during storage, transportation and application, at lower temperatures, with the increase in 'Lignin 1' and 'Lignin 2' content, the elasticity in binder increases. But, at higher temperature, with the increase in 'Lignin 1' and 'Lignin 2' content, the elasticity in binder reduces slightly. When the binders are aged for long term, Fig. 8(a), which is, long – term field oxidative aging, at lower temperatures, with the increase in 'Lignin 1' and 'Lignin 2' content, elasticity reduces, whereas, at higher temperatures, with the increase in 'Lignin 1' and 'Lignin 2' content, phase angle decreases and increases, respectively. This indicates that with the increase in 'Lignin 1' and 'Lignin 2' content, reduction in permanent deformations in pavement are observed in 'Lignin 1' modified blends of VG30.

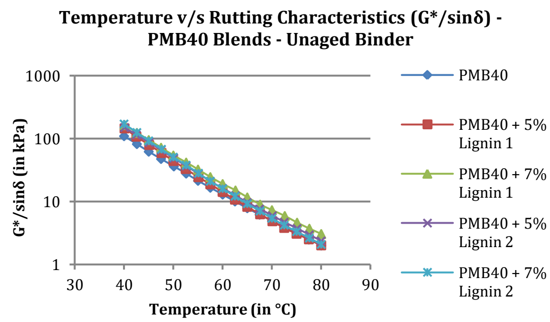
From Fig. 6(b), it is observed that at lower temperatures, the addition of 'Lignin 1' and 'Lignin 2' made the binder more viscous than elastic. Here, with the increase in 'Lignin 1' and 'Lignin 2' content, a slight decrease and increase in phase angle, respectively, is observed. This indicates that less content of 'Lignin 1' and more content of 'Lignin 2' are preferable. From Fig. 7(b), it appears that when the binders are short term aged, at lower temperatures, with the increase in 'Lignin 1' and 'Lignin 2' content, the elasticity in binder decreases. But, at higher temperature, with the increase in 'Lignin 1' content, elasticity increases and with the increase in 'Lignin 2' content, the elasticity in binder reduces slightly. When the binders are aged for long term, Fig. 8(b), at lower temperatures, with the increase in 'Lignin 1' and 'Lignin 2' content, elasticity reduces, whereas, at higher temperatures, with the increase in 'Lignin 1' and 'Lignin 2' content, phase angle increases. This indicates that with the increase in 'Lignin 1' and 'Lignin 2' content, reduction in permanent deformations in pavement are observed in 'Lignin 1' modified blends of PMB40.

E. Effect of Temperature and Lignin Content on Rutting Characteristics

Temperature sweep test was run on unaged and RTFOT aged binders, for VG30 and PMB40 binders, rutting parameter (G*/sinδ) was obtained and plotted against temperature as illustrated in Fig. 9 and Fig.10.

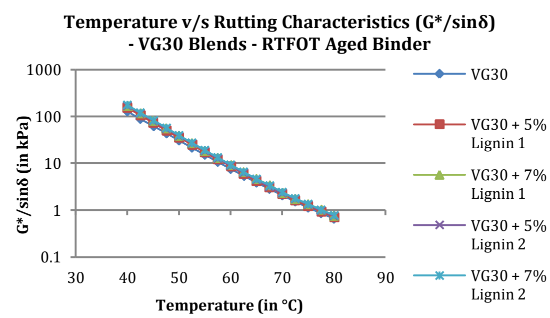


(a) VG30 blends

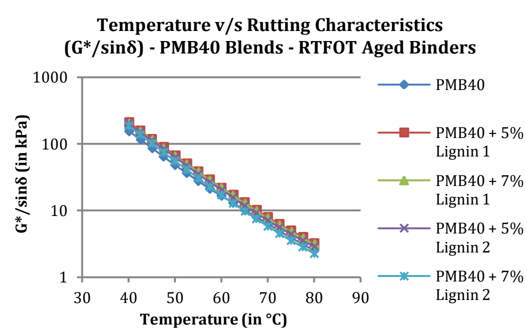


(b) PMB40 blends

Figure 9: Temperature v/s rutting parameter (G*/sinδ) for unaged binders



(a) VG30 blends



(b) PMB40 blends

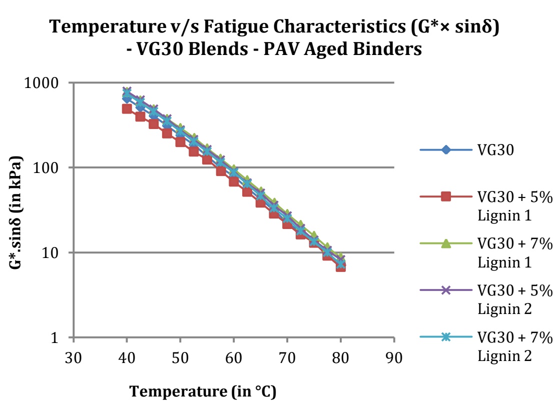
Figure 10: Temperature v/s rutting parameter (G*/sinδ) for RTFOT aged binders

Results revealed that the maximum temperature for a good viscoelastic performance of modified binders, increased with the increase in content of 'Lignin 1' and 'Lignin 2' in VG30 blends & increased with increase in content of 'Lignin 1' and decreased with increase in content of 'Lignin 2' in PMB40 blends, compared to original bitumen. Hence, 'Lignin 1' modified binders of VG30 and PMB40 blends will exhibit higher resistance to rutting compared to unmodified bitumen. 'Lignin 2' modified binders of VG30 blends and PMB40 blends will exhibit higher and lower resistance to rutting. Also, results indicated that maximum temperature of the pavement is adequate to prevent pavement from severe deterioration during service.

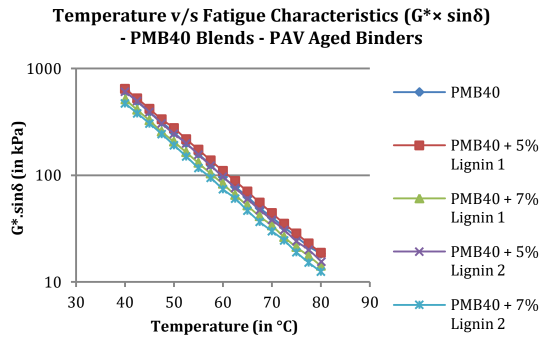
From Fig. 9(a), it is observed that, at lower and higher temperatures, with the increase in 'Lignin 1' and 'Lignin 2' content, the G*/sinδ value increased. A similar trend is followed when the binders were short term aged, Fig. 10(a). When the binder was modified with lignin, initially, with the increase in 'Lignin 1' and 'Lignin 2' content, at lower and higher temperatures, the G*/sinδ value increased, Fig. 9(a). But, when the binders were short term aged, Fig. 10(b), at lower and higher temperature, the G*/sinδ value increased. This indicates that with the long term use of lignin modified bitumen, more content of 'Lignin 1' and 'Lignin 2' will result in more rutting.

F. Effect of Temperature and Lignin Content on Fatigue Characteristics

Temperature sweep test was run on PAV aged binders, for VG30 and PMB40 binders, fatigue parameter was obtained and plotted against temperature as illustrated in Fig. 11.



(a) VG30 blends



(b) PMB40 blends

Figure 11: Temperature v/s fatigue parameter (G*× sinδ) for PAV aged binders

When the binders were long term aged, Fig. 11(a), at lower and higher temperatures, with the increase in 'Lignin 1' content, G*/sinδ value increased, whereas, with the increase in 'Lignin 2' content, G*/sinδ value decreased. Hence, it appears that with long term use of lignin modified bitumen, more content of 'Lignin 1' will show a better fatigue resistance than that of 'Lignin 2'.

For long term aged Fig. 11(b), at lower and higher temperature, the G*/sinδ value increased. This indicates that with the long term use of lignin modified bitumen, more content of 'Lignin 1' and 'Lignin 2' will result in more fatigue.

G. Fourier Transform Infrared (FTIR) Spectroscopy Test Results

Fig. 12 and **Fig. 13** represent the graphs of comparison of carbonyl content and sulphoxide content in VG30 blends. **Fig. 14** and **Fig. 15** represent the graphs of comparison of carbonyl content and sulphoxide content in PMB40 blends.

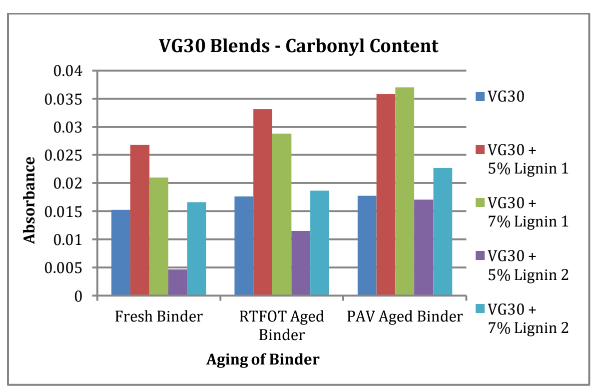


Figure 12: Comparison of carbonyl content for VG30 blends

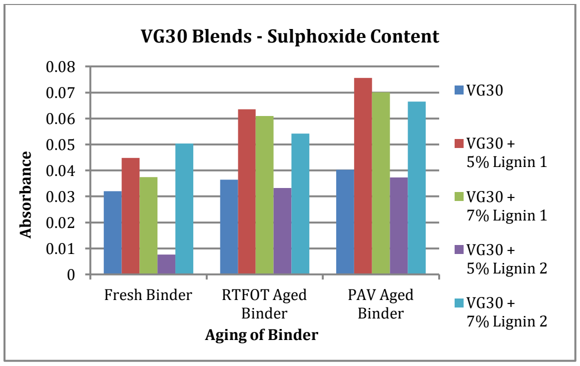


Figure 13: Comparison of sulphoxide content for VG30 blends

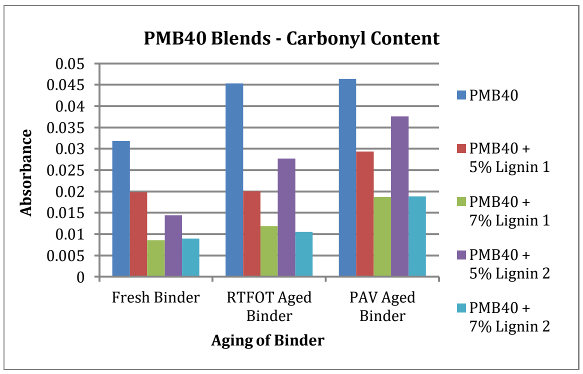


Figure 14: Comparison of carbonyl content for PMB40 blends

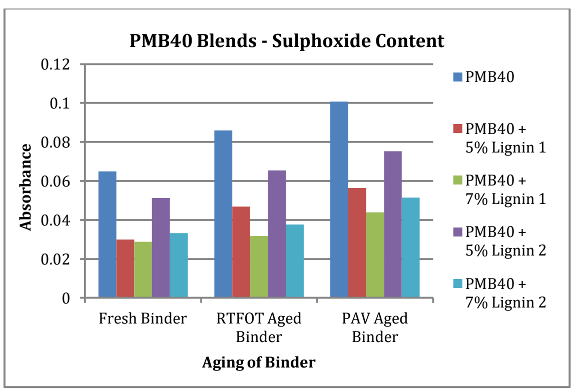


Figure 15: Comparison of sulphoxide content for PMB40 blends

The FTIR results suggest that there is some antioxidant activity of lignin when added to asphalt binder. It was observed from results that the effect of lignin as an antioxidant is binder specific. The addition of organic lignin, that is, 'Lignin 1' into VG30 bitumen caused an increase in the carbonyl content and sulphoxide contents, whereas, when 'Lignin 1' was added to PMB40 it showed a decrease in carbonyl and sulphoxide contents. Similar trend was observed for 'Lignin 2' with PMB40 binder, the lignin possibly acted as an antioxidant and caused a decrease in carbonyl and sulphoxide contents. Whereas with VG30, an increase in carbonyl and sulphoxide content was observed, it may be happening due to the cellulose and hemicellulosic materials present in lignins which may have caused the binders to accelerate aging or they acted as fillers.

VIII. CONCLUSION

According to this research, following conclusions can be drawn:-

1) The addition of 'Lignin 1' (that is, organic lignin) and 'Lignin 2' (that is, processed lignosulfonate) to asphalt binder caused significant rheological changes depending upon the type of the binder and type of Lignin.
2) Stiffening effect was observed in VG30 and PMB40 binder after the addition of both types of lignin, on the basis of reduced penetration values and increased softening point values.
3) On the basis of viscosity values and aging indices, it can be concluded that Lignin shows some antioxidant activity when added to asphalt binder. FTIR results also support their results.
4) Addition of lower dosages of Lignin, that is, 5% – 7%, is favorable for better performance of the asphalt binder in terms of G*, G*/sinδ and G*× sinδ. Higher dosages of Lignin may negate the effect of Lignin.
5) The addition of higher dosages of lignin containing products results in a greater increase in the stiffening effect. An increased stiffening effect can affect the low temperature properties of asphalt binder which can lead to early cracking in – service.

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