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ORIGINAL ARTICLE

Rheological evaluation of pg 64–22 asphalt binder modified with lignin of *pinus* and *eucalyptus* woods

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Abstract Lignin is a natural polymer and the second-most abundant material in the plant kingdom containing antioxidant properties. Research using lignin asphalt binder modifications aims to improve asphalt mixture properties, enhance aging resistance, reduce rutting, and extend fatigue lifespan. This research aims to study PG 64–22 binders with two lignin modifications, *Pinus* and *Eucalyptus,* in differing amounts. Rheological properties were studied and Fourier-transform infrared spectroscopy analysis tests for discovering chemical composition were performed. The results indicate the viability of modification by incorporating lignin into asphalt binders based on factors such as fatigue lifespan, rutting resistance, and a delayed short-term aging process.

Keywords Rheology · Asphalt · Modification · Natural polymer

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1 Introduction

Over the past few years, research has indicated that modifying asphalt binders using polymers can enhance mechanical pavement performance; these additives may be more economical for improving coating lifespan [2, 23, 25, 32, 39, 40] and enhancing anti-aging properties [1, 16, 27, 41, 44, 45]. Asphalt mixtures with polymer-modified binders demonstrate improvements in high-temperature performance, and greater fatigue and low-temperature cracking resistance, consequently decreasing their thermal susceptibility [13, 21].

This scenario involves an unknown variation of polymers; biopolymers—also known as "green polymers" [21] —are organic polymers synthesized by microorganisms, plants, trees, and other biological organisms [14]. To this extent, lignin deserves attention for being the second-most abundant biopolymer after cellulose, in addition to its presence in all vascular plants linking fibers to wood [18, 19, 26, 28, 33].

Lignin's presence in the biomass of plants can be understood as residual material primarily originating from wood, paper, biofuel industries [11] and, occasionally, agricultural processes [15]. Lignin's abundance, cementitious properties, and chemical similarity to compounds found within the binder—namely, carbides (aromatics)—containing antioxidant properties [21], draws attention to this biopolymer's particularly promising application in asphalt mixture manufacturing. Furthermore, binders incorporated with lignin prove beneficial for reducing CO_2 emissions [38] since lignin does not generate additional CO_2. Therefore, the use of lignin to manufacture asphalt mixtures can contribute to more sustainable construction and efficient production.

Lignin has gained an increased amount of attention as an additive to the asphalt binder due to its antioxidant potential to resist aging as well as to improve rheological properties [9]. According to Pan [31], lignin can be used as a binder antioxidant. However, lignin's temperature must be controlled to prevent early aging. [43] demonstrated that lignin-modified binders improve the performance of asphalt mixtures at high temperatures as well as aging resistance, although their lifespan may be reduced. Furthermore, Xie et al. [44] demonstrated that kraft lignin could be used to modify binders and improve high-temperature performance of asphalt mixtures.

Additionally, according to Batista et al. [11], lignin-modified binders significantly improve the thermal cracking resistance of asphalt mixtures at temperatures as low as 12 °C. They found that when a lignin was added to asphalt binders it caused less carbonyl and, therefore, a greater resistance to weathering compared to the conventional binder, in addition to increasing thermal stability after Rolling Thin Film Oven Procedure (RTFOT).

The physical, chemical and rheological behavior of a supplied lignin will be different from the original source, for example lignins from different plant materials have different proportions of phenylpropanoids [9]. For Santos et al. [34], various types of lignin can be obtained from a range of origins, and that industrial processes present different features depending on vegetal source, including age and species. For the oxidation process of asphalt binders, these differences are remarkable; namely, while acting as an antioxidant material, the derived units of lignin inhibit the oxidation propagation reaction by donating hydrogen, which occurs primarily in response to the presence of phenolic hydroxyl groups [30] Lignin compounds containing more phenolic hydroxyl groups and fewer aliphatic hydroxyl groups have lower molecular weight and higher antioxidant properties [39].

This research seeks to study the rheological properties of asphalt binders modified with two types of lignin, *Pinus* and *Eucalyptus*, and aims to verify the effect of this addition before and after short-term aging. This focus is also motivated to potentially decrease the cost of modified binder production for improved sustainability and to address the improper disposal of lignin into the environment.

2 Materials and methods

2.1 Materials

Table 1 presents an overview of the physical characteristics of asphalt binder.

Two types of lignin were used to modify the asphalt binder, one obtained from *Eucalyptus* wood and the other from *Pinus* wood. Both were supplied by the company Kablin (Paraná, Brazil) after the Kraft process in the form of powder passed through the #100 sieve with particle sizes below 0.15 mm. Some evaluations were made available by the donor company that show that Eucalyptus lignin has a purity of 99.79% and 96.62% of insoluble lignin and 4.08% of soluble lignin. Pinus lignin has a purity of 100.70% and 97.98% insoluble lignin and 1.80% soluble lignin.

2.2 Modification of binder with lignin

Lignin was incorporated according to research conducted by Santos et al. [34], in which pure asphalt binder was heated up to 160 °C with 200 rpm for 30 min in a mechanical mixer originating from FISATOM (São Paulo, Brazil). Both types of lignin were added to the pure binder in 3%, 6%, and 9% fractions derived from asphalt mass according to Santos et al. [34] and produced 6 types of samples, *3P* (PG 64–22 + 3% *Pinus* Lignin), *6P* (PG 64–22 + 6% *Pinus* Lignin), *9P* (PG 64–22 + 9% *Pinus* Lignin), *3E* (PG 64–22 + 3% *Eucalyptus* Lignin), *6E* ((PG 64–22 + 6% *Eucalyptus* Lignin), *9E* ((PG 64–22 + 9% *Eucalyptus* Lignin). In addition, the reference sample was also tested of pure asphalt binder which was called PG 64–22.

The tests performed were: Fourier-transform infrared spectroscopy–FTIR [8], Rotational viscosity [5], Linear amplitude sweep–LAS [4], Performance grade–PG [7], Multiple stress creep recovery–MSCR [6] e Master curve.

Table 1 Physical characteristics of asphalt binders

Test		Standard	Specification	Values
Penetration (0,1 mm)		ASTM D5	50–70	56.40
Softening point (°C)		ASTM D36	> 46	50.20
Rotational viscosity (cP)	135 °C, SP, 21, 20 rpm	ASTM D4402	> 274	413.50
	150 °C, SP, 21, 50 rpm	–	> 122	214.00
	177 °C, SP, 21 100 rpm	–	57 a 285	83.00
Thermal susceptibility index		–	(− 1,5) a (+ 0,7)	− 0.86
Softening point addition (°C)		ASTM D36	< 8	7.90
Retained penetration (%)		ASTM D5	> 55	47.0

2.3 Fourier transform infrared spectroscopy–FTIR

FTIR was performed according to the standard [8]. A beam of infrared light with wavelengths ranging from 500 to 4000 cm^{-1} was provided, so that the organic chemical compounds present in the samples absorbed them in certain ranges of wavelengths and, consequently, detected from their transmittance. Based on these intensities and positioning of the wavelengths, it was possible to analyze the level of molecular interaction and chemical bonds of the ligands under analysis. FTIR analysis was performed on aged by the RTFO process and non-aged. They were used for each type of asphalt and content studied.

2.4 Rheological property testing

The first rheological test to be carried out was the rotational viscosity following the one determined by norm [5]. In this test, eight grams of the asphalt binder were placed inside a cylinder with a spindle. The binder was heated at temperatures established by the standard [5] of 135, 150 and 177 °C. For each temperature a torque was made with a rod connected to the cylinder at the following speeds: 20, 50 and 100 rpm, respectively. This procedure was done before and after the aging process in the short term and two samples of each content were used. Then the average was taken to obtain the final value.

Another test performed before and after the short-term aging process was Performance Grade following the standard [7]. Limitations to the limitation of the equipment it was not possible to obtain the lowest temperature. The test is based on the temperature variation at 46 °C with steps of 6 °C and for each step the parameter G*/senδ must be analyzed, which should not have values lower than 1.00 kPa for the binders before the short-term aging process and 2.20 kPa for those after that procedure. Upon reaching these limits the test was completed. The samples were also used to analyze the Aging Index (AI) using the G*/senδ parameter ratio after and before the RTFO to assess the behavior of the ligand as it ages. In this test two samples were used for each binder and content studied and the average was taken to obtain its values.

The MSCR assay was also carried out following the standard [6]. The samples used were obtained after the short-term aging procedure. The execution temperature was selected by means of the PG temperatures of each binder and content before and after the RTFO. From the determined PGs the values between each content were compared before and after aging, the lowest temperature between the PGs was chosen as the test temperature for the MSCR. Two samples were also used for each binder and content analyzed and the average was taken to obtain its final value.

The LAS was performed following the standard [4] which determines that the samples used must be aged. To perform the test, the geometry of the rheometer had to be heated to 56°C to ensure adherence of the sample to the geometries that would eventually apply the test loads. After this process it was necessary for the samples to be cooled to a temperature of 25 °C. This was determined based on studies that used PG classification ligands similar to the present study [20, 25]. Two samples were used for each binder and content analyzed and the average was taken to obtain its final value.

The last rheological test performed was Master Curve which measures the variation of the dynamic modulo (G*) and phase angle (δ) as a function of the given frequency. For this, a frequency scan (between 3.96×10^{-6} Hz and 0.08 Hz) was performed for temperatures of 46, 52, 58, 64, 70, 76 and 82 °C and, subsequently, the data of the curves for each temperature were shifted on the time scale to obtain a single smoothed function curve for the reference temperature, which was 25 °C. In this test, two samples were made for each binder and content analyzed.

Pure and modified rheological parameters were verified using a dynamic shear rheometer (DSR)—specifically, a Discovery Series Hybrid Rheometer (DHR-1) provided by the Federal University of Campina Grande (UFCG)'s Pavement Engineering Laboratory (LEP). For FTIR analysis, an FT-IR VERTEX 70 spectrometer was used.

3 Results and discussion

3.1 Fourier-transform infrared spectroscopy–FTIR

Pure and modified binders using two types of lignin were submitted for FTIR testing to analyze functional groupings of their structure. Figures 1 and 2 show the results of the pure and modified binder, respectively, for this test before the short-term aging process.

According to these results, the FTIR spectrum of pure and modified binders before RTFO antes do RTFO had the following characteristic bands: a doublet at 2920 cm^{-1} and 2850 cm^{-1} indicating vibrations of symmetrical and asymmetric axial stretches of groups CH_2 and CH_3 (aliphatic); the bands at 1458 cm^{-1} and 1375 cm^{-1} are related to the angular deformations of the groups, CH_2 and CH_3; the band at 870 and 810 cm^{-1} indicate folding of groups = CH in aromatic rings, and band at 720 cm^{-1} indicating "rocking" deformation for $(CH_2)_n$ com $n \geq 4$.

According to Santos et al. [34] the aging process caused by the oxidation of the asphalt binder generates changes in the matrix of the asphalts verified in the absorption spectrum in the infrared by increasing the transmittance in the 1730 cm^{-1} band of the carbonyl group (C = O), indicating the presence of compounds formed by the oxidation process such as carboxylic acids, aldehydes and ketones, and also, increased transmittance in the 1030 cm^{-1} band, referring to the sulfoxide group.

Figures 3 and 4 shows the FTIR spectrum after the short-term aging process.

Through the FTIR spectra after the aging process, there was a low variation in the intensity of transmittance in the pure and modified asphalts in the bands 1730 cm^{-1} of the carbonyl group (C = O) and 1030 cm^{-1} of the group of sulfoxides that are linked to the oxidation process between the spectra of pure and modified binders, before and after short-term aging. There was also no increase in peaks in the bands mentioned in samples modified with lignin from both plant species. Thus, asphalts modified with lignin have a tendency to reduce susceptibility to the aging process in the short term when compared to the conventional asphalt.

3.2 Rotational viscosity

The results of pure and modified binders before and after RTFOT aging rotational viscosity are presented in Fig. 5.

After analyzing binder viscosity values before and after short-term aging, it was observed that the aging process caused an increase in viscosities, as expected. Some studies have studied the physical–chemical properties of the asphalt binder and changes in the chemical structure, caused by the addition of additives, reaching the conclusion that thermal oxidation causes changes in the behavior of aliphatic and aromatic structures, forming carbonyl groups.

The variation in both lignin types can be understood according to the differences in chemical compositions between conifers (*Pinus*) and leafy (*Eucalyptus*) species. According to Silveira & Milagres [35], lignin originating from *Eucalyptus* presents a greater amount of carbon groups related to *Pinus* lignin. This may indicate a better mixture of the asphalt binder with material from the *Pinus* species because this lignin also has phenolic hydroxyl groups in its chemical composition that causes the stabilization of free radicals responsible for the oxidation process [11].

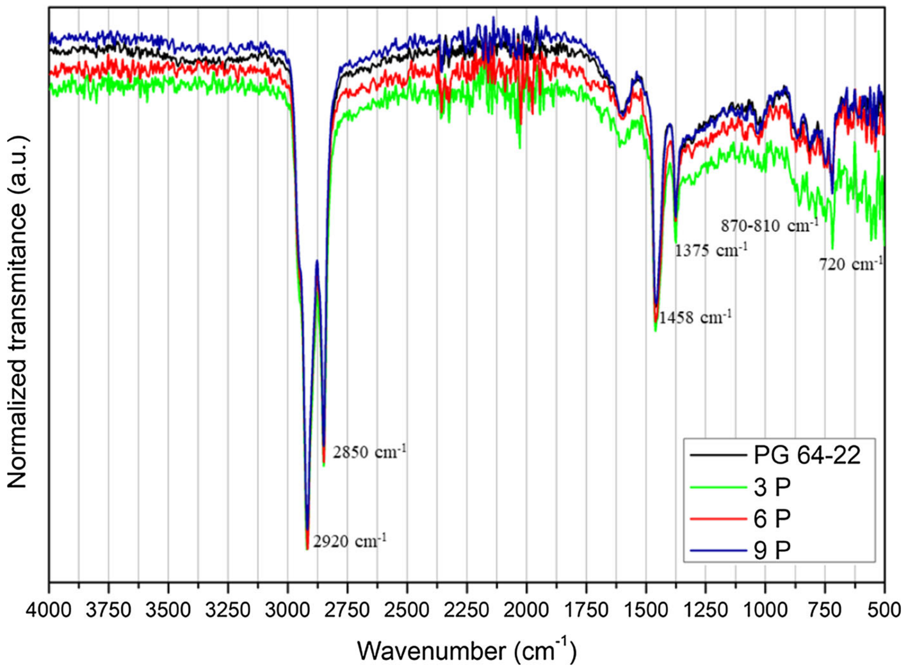


Fig. 1 FTIR of pure and modified *Pinus* lignin binders

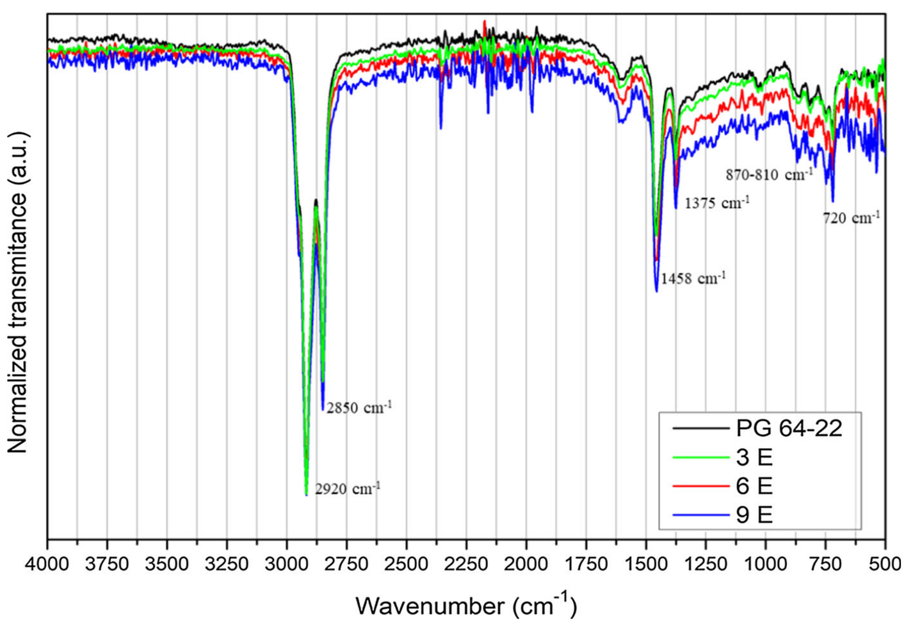


Fig. 2 FTIR of pure and modified *Eucalyptus* lignin binders

3.3 Performance grade

Figure 6 presents PG temperatures of evaluated binders.

Generally, the results of all samples indicate that the addition of lignin resulted in growth at failure temperature, which also occurred after short-term aging and suggests that the addition had enhanced the

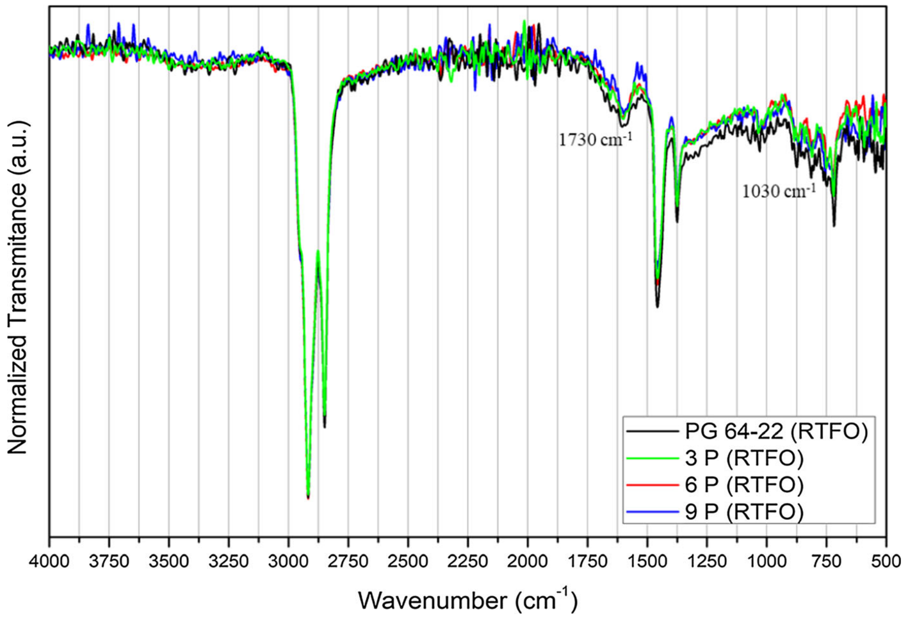


Fig. 3 FTIR of pure and modified Pinus lignin binders after RTFO

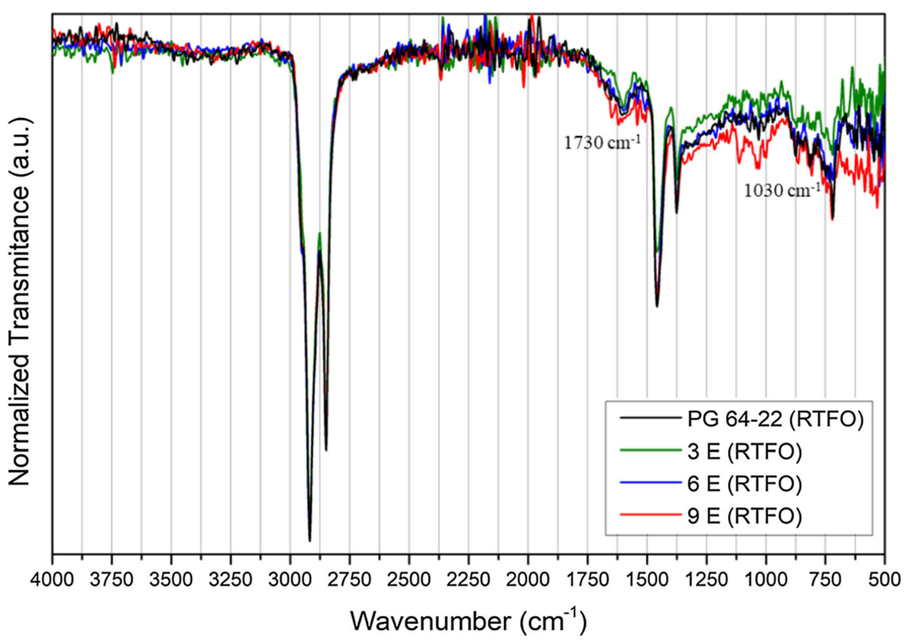


Fig. 4 FTIR of pure and modified Eucalyptus lignin binders after RFTO

aging resistance of the materials. After analyzing both types of lignin, their differences were insignificant.

Figure 7 presents aging index (AI) values obtained from the binder's dynamic module and phase angle before and after RTFOT short-term aging process.

The addition of lignin reduced the oxidation and volatilization of the binder's chemical components. As identified in Fig. 7, the modified ligands have lower AI values when compared to the reference ligand. This result suggests that the addition of lignin reduced the oxidation and the aging tendency of the binder, thus

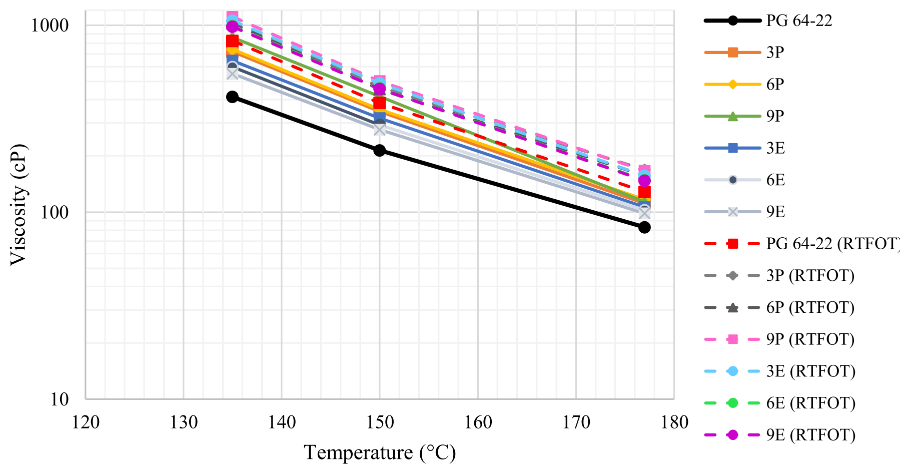


Fig. 5 Rotational viscosity before and after RTFOT aging

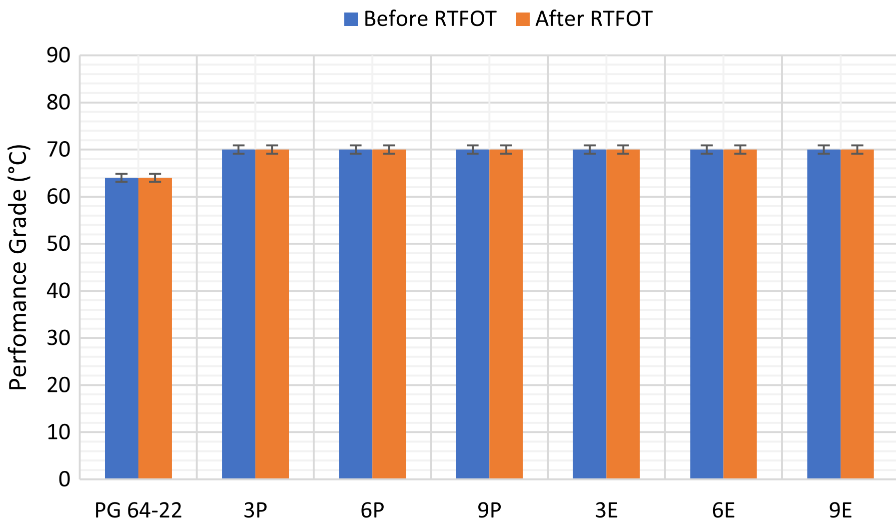


Fig. 6 Performance Grade (PG)

reflecting lower maintenance costs and longer life of the final asphalt mixture. According to Azadfar [10], this occurs because lignin acts as an antioxidant; this means that lignin undergoes oxidation in place of the binder by donating hydrogen which reacts with the binder's free radicals, thus allowing it to avoid oxidation.

3.4 Multiple stress creep recovery–MSCR

3.4.1 Non-recoverable compliance–Jnr

The results of non-recoverable compliance parameters are presented in Fig. 8.

The MSCR test was performed with the PG temperature of each sample, which can be seen in Fig. 6. The analysis of Fig. 8 verified that modified binders presented a smaller reduction in non-recoverable compliance when compared to the pure binder. Despite this low reduction, this is considered a positive outcome supporting the use of lignin modification. To evaluate the bearing capacity of road traffic volume, [3] suggests a rating based on Jnr values at 3200 Pa.

All modified content incorporating lignin binders, including the pure binder, were classified as standard traffic. This can be verified by testing for maximum PG temperatures, which demonstrates the most disadvantageous situation in which the material becomes unable to easily detect elastic return as a result of the

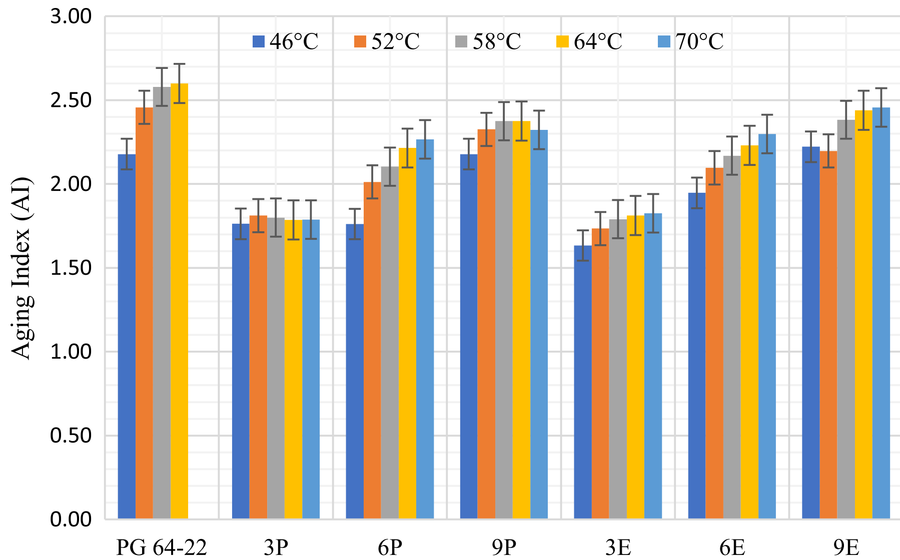


Fig. 7 Aging Index (AI)

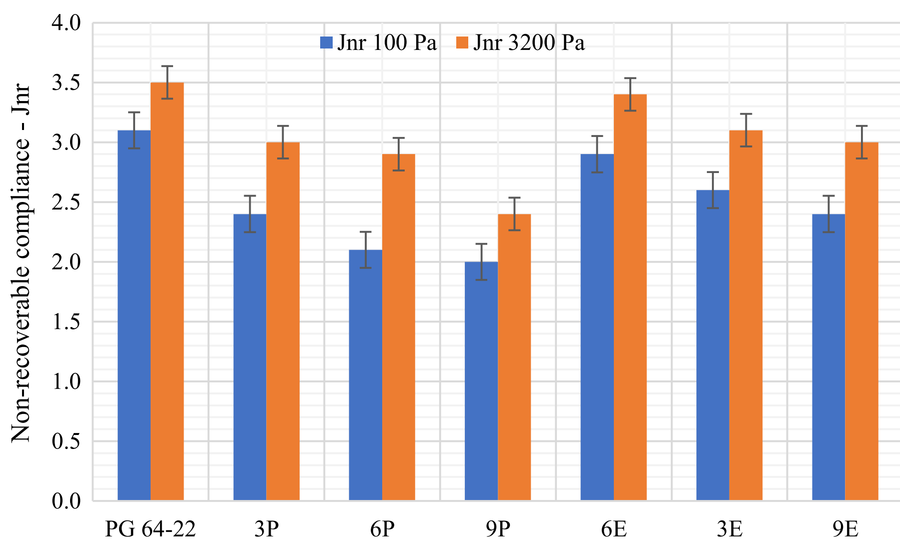


Fig. 8 Non-recoverable compliance at 100 and 3200 Pa

binder's fluidity of features while under this condition [42]. Thus, modified binders obtained higher temperatures regarding the pure binder. Therefore, this test was performed using all samples with pure binder temperatures of 64°C. Figure 9 shows the results of this condition.

Using this test condition, it was verified that all contents excluding 9% *Pinus* had Jnr between 1,0 and 2,0 kPa^{-1}, which was classified for bearing heavy traffic (S), while the 9% *Pinus* sample was classified for very heavy traffic (V).

3.5 Linear amplitude sweep–LAS

Figure 10 presents a correlation between *A* and *B* parameters.

Since parameter A is related to the change in the integrity of the material caused by the accumulated damage, higher values of A mean that the sample maintained its initial integrity. Results indicate the binder with 3% *Pinus* lignin had presented a significantly higher *A* parameter when compared to the pure binder, generating a 158% increase. Other *Pinus* lignin

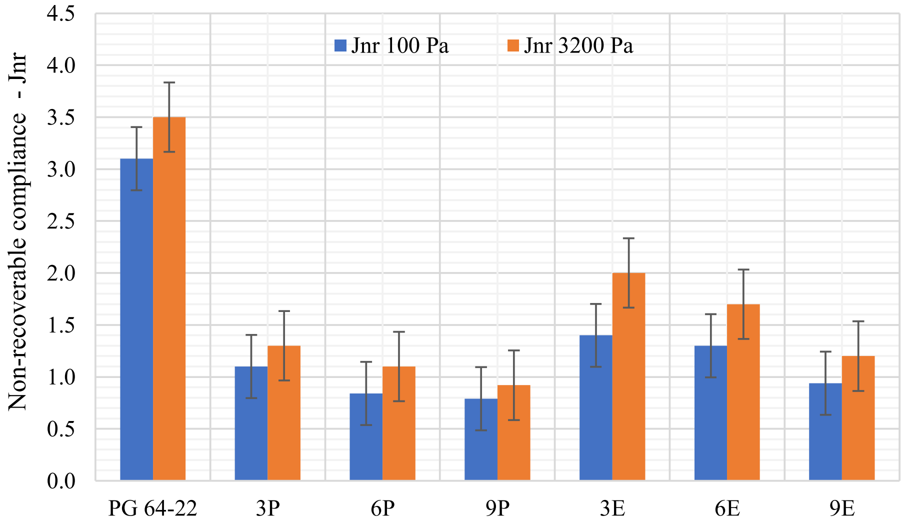
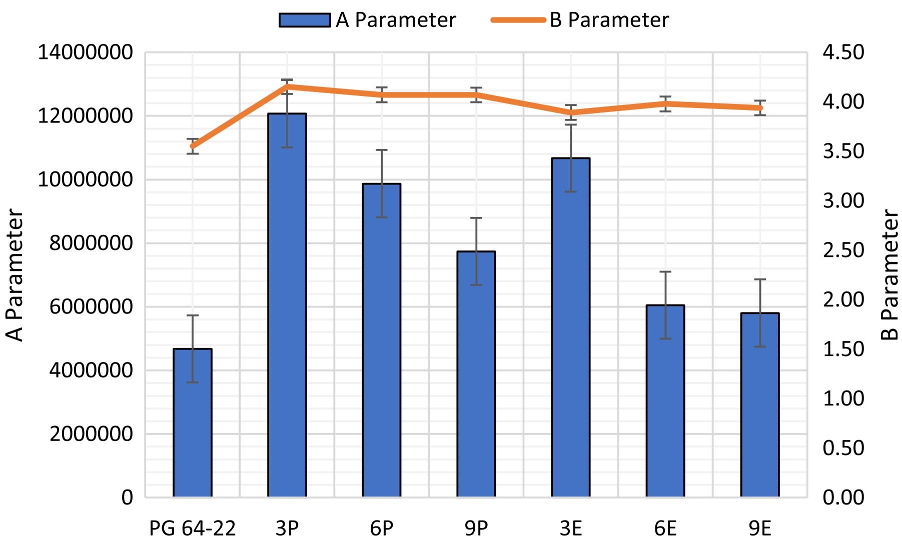


Fig. 9 Non-recoverable compliance at 100 and 3200 Pa (64 °C)

Fig. 10 Ratio between *A* and *B* values



contents also obtained growth results: around 111% and 66% per additional 6% and 9%, respectively. After analyzing both lignin types, values for the addition of *Eucalyptus* presented a significant reduction when compared to *Pinus*. However, obtained representative growth relating to the pure binder was around 128%, 29%, and 24% per additional 3%, 6%, and 9%.

Parameter B is related to the sensitivity of the asphalt binder to the variation in the level of deformation. For Kodrat et al. [24], higher absolute values of the *B* parameter indicate that the material lifespan decreases at a higher rate while the deformation amplitude increases. Also, according to the author, the increase in this parameter can also indicate a greater susceptibility to deformation under temperature variations. According to this parameter, binder modification with lignin increased sensitivity to variation in the level of deformation, despite ensuring higher damage resistance; this therefore presents a disadvantage of the binder, indicating a higher strain susceptibility under variations in temperature.

Figure 11 presents chart demonstrating stress versus strain obtained from LAS test under controlled deformation.

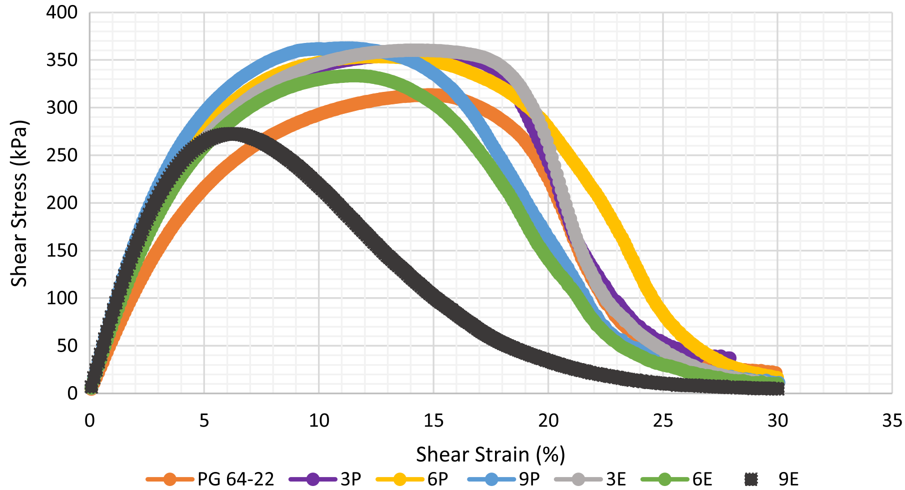


Fig. 11 Stress x Strain curves of pure and modified binders

Curves in Fig. 11 indicate that all lignin-modified binders related to the pure binder bore higher shear stress and presented amplitudes between 25 and 30% with a similar stress/strain pattern. For *Pinus* lignin, it was possible to observe higher stress-bearing capacity at an amplitude of 15–20%. Meanwhile, the stress peak for *Eucalyptus* lignin was found between 10 and 15%. It is worth noting that the 9E sample presents a different behavior from the others, where the peak was around 5% converging to stress 0 under 30% deformations, indicating a lower capacity of stress capacities.

The damage occurs to the extent that the binder's response to applied stresses decreases. If no damage occurs, the response to material damage remains constant for any induced deformation [22], as can be seen for the low levels of deformation in Fig. 11. Then, the asphalt associated with lignins, with the exception of 9E, endured greater deformations with residual stresses, which gives them better behavior when applying stresses and deformations.

A model derived from the relation between applied load and binder fatigue lifespan was determined using the principle of viscoelastic continuum damage (VECD). Figure 12 presents this model for analyzing binder fatigue obtained from the LAS test at 25 °C using Nf parameter (relating lifespan to number of cycles before failure) at different levels of strain [37].

Pamplona et al. [29] observed that binder fatigue resistance relates to levels of stress. When subjected to lower stress levels, increased binder stiffness correlates with longer lifespan. However, in regard to higher stress levels, increased binder stiffness results in a shorter lifespan. Therefore, results presented in Fig. 12 under all strain amplitudes demonstrate the superior curves of 3% binder contents when compared to that of the pure binder.

Other contents presented with a lifespan estimation inferior to the pure binder, but the modified asphalt binder with 9% Eucalyptus lignin deserves to be highlighted, which showed lower values for Nf. This behavior was already expected, since this same content provided the least integrity to the material for different levels of deformation, in which parameter A corresponds to the deformation amplitude value of 1%.

Lastly, the analysis of binder damage resistance through the viscoelastic continuum damage (VECD) principle demonstrated a strong correlation between binder fatigue resistance and strain levels [36].

3.6 Master curve

For the binders analyzed, Fig. 13 shows the dynamic shear modulus master curves within the reduced frequency domain before short-term aging using the reference temperature of 25 °C.

In reference to these charts, the superior trend in curves containing the addition of lignin related to the pure binder can be observed. After analyzing sample results, an increase of the |G*| parameter (representing material stiffness) was verified by frequency sweeps executed for all contents when compared to the pure binder. These findings highlight the *Pinus* type,

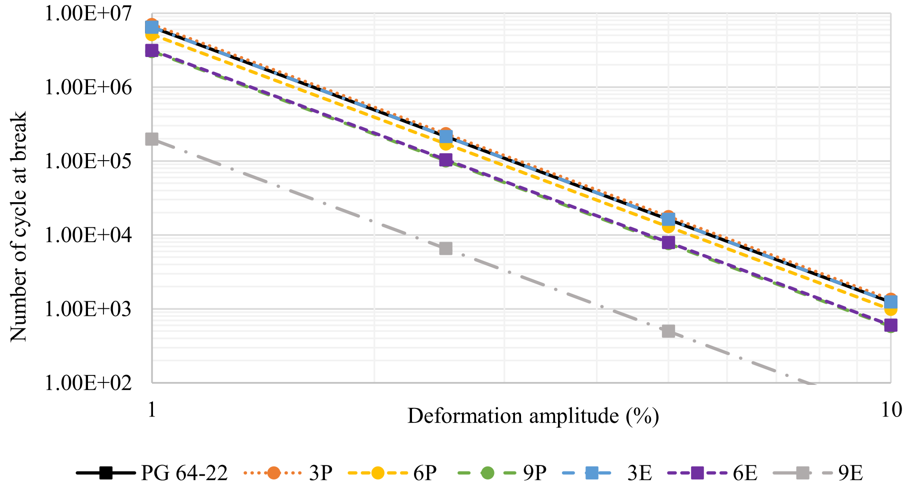


Fig. 12 Estimation of fatigue lifespan

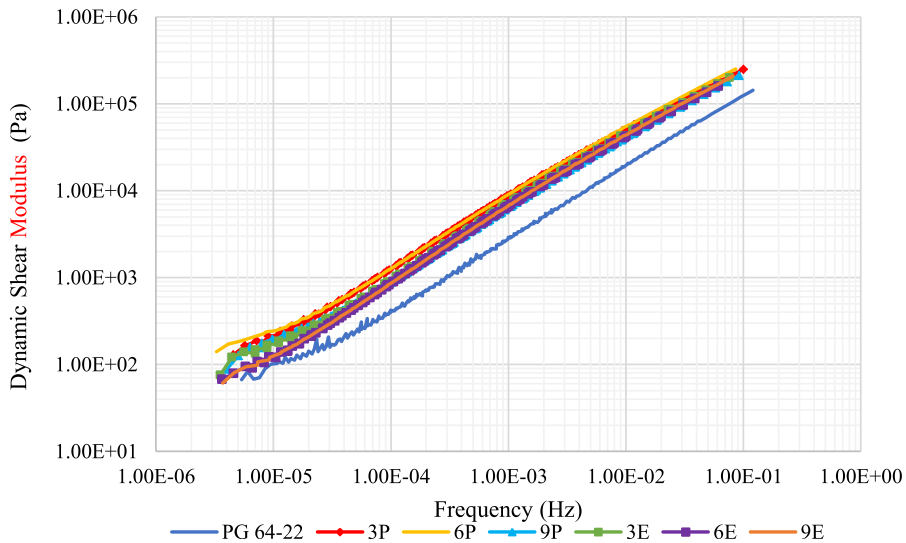


Fig. 13 Master curves of binders before RTFOT

indicating its ability to improve properties related to resistance across all tested temperatures.

For low frequencies representing higher temperatures, this tendency is desirable since the material demonstrates increased fluidity in locations where plastic deformations may occur. For high frequencies/ low temperatures, stiffness is also considered a desirable feature to the extent that the material does not become fragile or brittle, but retains the capacity to bear stress while subjected to various conditions [17].

It was verified that low frequencies (10^{-5} Hz to 10^{-4} Hz) did not result in pure binder curves demonstrating defined properties. The appearance of ripples is a result of data-reading interferences within this frequency range, and may also indicate sample damage. In particular, loadings become increasingly harmful the more slowly they are applied within this frequency range. Figure 14 presents phase angles for pure and modified binders prior to short-term aging.

It was verified that the addition of different lignin contents correlated positively with growth in binder elasticity; notably, the modified binders demonstrated a reduction in the phase angle of all analyzed frequencies without presenting a significant difference between both lignin types involved in this research. Pamplona et al. [29] described how phase angle reductions represent the binder's elasticity growth, demonstrating an advantage in durability.

This analysis makes it possible to verify that the addition of lignin performs positively with the

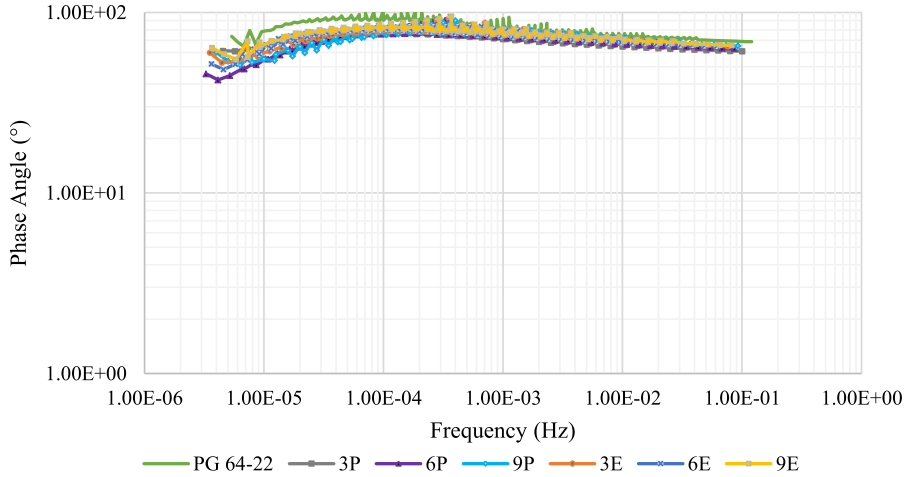


Fig. 14 Binders phase angles before RTFOT

increase of stiffness (highlighted by parameter |G*|), as well as phase angle δ reduction, thus suggesting a tendency of the binder has greater resistance to rutting, fatigue, and thermal cracking. However, to truly conclude these results, more specific tests are needed. This trend was also seen with the other tests, especially LAS, where the modifying binders showed better responses to fatigue cracking.

4 Conclusions

The rheology of modified binders indicated that the addition of lignin increased the binder's viscosity. During a performance grade test, these binders reached higher failure temperatures in which changes occurred after the RTFO aging process, which confirms lignin's antioxidant features. Prior to the research results, the modification of pure binder using lignin proved beneficial in its ability to delay the short-term aging and stiffening of materials. Further, as observed during MSCR and LAS tests, there was an improvement in rutting and fatigue resistance.

The differentiated FTIR spectra that the asphalts modified with both lignins have a tendency to reduce susceptibility to the aging process in the short term. In this way, lignins tend to act as oxidizing materials.

Therefore, pure binder modification containing variable amounts of different types of lignin provided benefits such as the reduction of rutting, increased fatigue lifespan, and lower susceptibility to short-term aging. For a better veracity of these conclusions, it is recommended to carry out more specific tests, with a more in-depth analysis of rheology.

However, it is possible to verify that besides lignin's viability as an alternative from a rheological perspective, it may also prove environmentally significant by addressing the incorrect disposal of residue generated by the paper and cellulose industry, which may also may also add value beyond an economic perspective.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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