buildings

Article

Study on the Rheological Properties of Formic Acid Lignin Modified Asphalt

Meng Cai [1], Chao Peng [2] and Cheng Cheng [1,*]

1 School of Civil Engineering, Southwest Forestry University, Kunming 650224, China
2 Yueyang Traffic Highway Engineering Construction Co., Ltd., Yueyang 414000, China
* Correspondence: chengcheng_clx@swfu.edu.cn

Abstract: Lignin is a major waste product of biofuel and paper industries that can be used as a modifier to improve the relevant properties of asphalt. To investigate the effect of lignin and formic acid lignin wood incorporations into asphalt and the effect on asphalt binder that was unaged and aged for 85 min, 5 h, and 10 h, a series of tests were conducted, including high- and low-temperature rheological tests by a dynamic shear rheometer (DSR), followed by Fourier transform infrared spectroscopy (FTIR) tests, and finally by gel permeation chromatography (GPC). The test results show that the additions of lignin and formic acid lignin could improve the high-temperature performance and fatigue capacity of asphalt. In addition, at the glass-transition temperature, it was observed that the additions of lignin and formic acid lignin into asphalt can effectively improve cracking at low temperatures; however, the quantity of lignin and formic acid lignin should be controlled. Fourier transform infrared spectroscopy tests showed that the purity of lignin treated with formic acid decreased, and degradation and formylation of the same formic acid-treated lignin occurred, indicating that the lignin underwent chemical changes following acid treatment. The analysis of the results by gel permeation chromatography (GPC) showed that, with aging, the average molecular weight (Mw) of lignin-modified asphalt decreased. The reason was that lignin and formic acid lignin were cracked during aging, which reduced their molecular weights.

Keywords: lignin; formic acid lignin; rheological properties; infrared spectroscopy; gel chromatography

Citation: Cai, M.; Peng, C.; Cheng, C. Study on the Rheological Properties of Formic Acid Lignin Modified Asphalt. *Buildings* **2023**, *13*, 655. https://doi.org/10.3390/buildings13030655

Academic Editor: Ramadhansyah Putra Jaya

Received: 12 January 2023
Revised: 16 February 2023
Accepted: 22 February 2023
Published: 28 February 2023

1. Introduction

Asphalt is one of the most widely used types of pavement, and the rapid increase in traffic and frequency of vehicle travel, larger vehicles, and increase in axle weights, as well as the exposure to sunlight, extreme temperatures, moisture, and oxygen, can deteriorate asphalt pavements, resulting in the susceptibility of asphalt binders to deterioration [1–5]. Asphalt pavements with aged asphalt binders are not sufficiently resistant to permanent deformation, fatigue cracking, and moisture damage [6,7]. At present, researchers are mainly modifying asphalt to improve its road-performance characteristic by incorporating rubber powder [8,9], calcium carbonate [10], zinc oxide [11], SBS (styrene butadiene styrene) [12], and other modifiers for physical or chemical modifications; therefore, showing a positive modification effect by improving the high- and low-temperature performance and durability of asphalt binders, as well as asphalt mixtures. Searching for environmentally friendly and sustainable regeneration materials for road asphalt modifications, people use biomass materials, such as coffee-residue charcoal [13], oil palm shell ash [14], rice shell ash [15], and bamboo powder [16], for asphalt modifications. This has realized the improvement of asphalt performance and resource utilization of biomass waste. With the implementation of the "dual carbon" strategy, coupled with the use of oil as a non-renewable resource, a high number of resources will eventually lead to resource depletion [17], and biomass resources are important for sustainable development after oil, natural gas, coal, etc.; thus, obtaining renewable and sustainable materials to replace asphalt binders has become a top priority.

Lignin, the second most abundant biomass on Earth, is a natural polymeric material due to the presence of various reactive groups, such as phenolic hydroxyl and aromatic groups, in its molecular chain [18]. It can replace petrochemical raw materials, such as phenol [19]. More attention has been paid to the utilization of lignin, especially isolated from waste agricultural products. Since plants containing lignin absorb carbon dioxide as they grow, they reduce the amount of carbon dioxide in the atmosphere. If lignin separated from biomass is placed into roads, the carbon contained in the lignin is sequestered. The use of lignin in asphalt binders also reduces the amount of carbon dioxide produced during the transportation of petroleum-based binders to paving sites. Lignin is widely used in plastics [20] and adhesives [21]. The physical-performance test results show that with the addition of lignin, the penetration of asphalt decreases, the softening point increases, and the high-temperature stability increases [22]. The viscosity of lignin-modified asphalt is higher than that of unmodified asphalt [23]. Van Vliet et al. [24] used different types of lignin to modify asphalt and concluded that the amount and type of lignin affects the viscoelastic behavior of asphalt; the results obtained were different for different types of lignin. Zhang et al. [25] examined the effect of time and temperature on the steaming of wheat straw by formic acid with sulfuric acid as a catalyst. The results show that during the cooking process of wheat straw with formic acid, lignin in wheat straw is oxidized and cracked, which leads to the degradation of lignin's molecular weight, shifting from high-molecular-weight lignin to low-molecular-weight oligomers. Batista et al. [26] analyzed the physical and chemical properties of lignin-modified asphalt binders with the aim of applying lignin to asphalt pavements as a by-product of the pulp and paper industry. The lignin-modified asphalt binder has a lower carbonyl index, resulting in better aging resistance than conventional binders and the improved thermal stability of the binder. Pan [27] calculated the antioxidant effect of coniferyl in lignin on asphalt using the simulation calculation method, and proved the effectiveness of lignin on asphalt oxidation through X-ray photoelectron spectroscopy (XPS), and proposed that the oxidation process of lignin-modified asphalt in the air is similar to that of base asphalt; however, the oxidation rate is slower than that of base asphalt, making it a good antioxidant for asphalt. Xie [28] developed two different methods to treat lignin in order to produce high-quality asphalt-binder modifiers, a biological process based on an enzyme-mediated system and chemical process using formic acid, iron, and H_2O_2. Both the soluble fraction of biotreated lignin and insoluble fraction of chemically treated lignin can be used as high-quality asphalt-binder modifiers. Gel-permeation chromatography analysis showed that the molecular weight of the insoluble lignin fraction increased by 1.6 times compared to the molecular weight of the original sulfated lignin fraction, while the molecular weight of the soluble lignin fraction decreased significantly, in which the soluble fraction of biotreated lignin could even improve the asphalt binder's high- and low-temperature properties, providing a unique modifier. Cai [29] observed that the lignin modification showed some changes in the repetitive creep viscosity fraction Gv with increasing aging in high-temperature rheology, which may have been due to the change in the molecular weight of lignin-modified asphalt with aging. Su [30] observed that the thermal stability of lignin was slightly lower than that of asphalt, and it may decompose during the thermal oxidative aging process. The thermal oxidative aging mechanism of lignin is more of a sacrificial agent than the reason for adsorbing free radicals.

The feasibility of using lignin as a new biological modifier in roads was analyzed further, especially the industrial lignin from different sources needing to be purified during the application process. Following purification, the impact of lignin on high and low temperatures changed, especially at low temperatures. Finally, the impact of aging was analyzed. The three main objectives of this study are: (1) to compare the molecular weight and functional group changes of lignin and formic acid-treated lignin, and to analyze their change mechanisms; (2) to analyze the rheological properties of lignin and formic acid lignin before and after aging at high, mid, and low temperatures, and to analyze the change phenomenon; and (3) to use GPC to analyze the rules before and after aging, and the molecular weight is used to further analyze the reasons for the changes.

Lignin-modified asphalt is one of the important research fields. At present, scholars at home and abroad produce the same results on the improvement of lignin-modified asphalt amounts at high temperatures; however, the research conclusions for low temperatures are not uniform. Moreover, the improvement effects of lignin obtained by different treatment methods for high-temperature stability, low-temperature cracking resistance, and the aging resistance of asphalt are also different. Therefore, this experiment uses DSR to test the low-temperature rheology of modified asphalt and gel chromatography (GPC) to analyze and study this further. In addition, the pavement performance, aging performance, and micro-mechanism of lignin-modified asphalt treated with formic acid are studied to provide certain reference values for engineering practices. The specific process is shown in Figure 1.

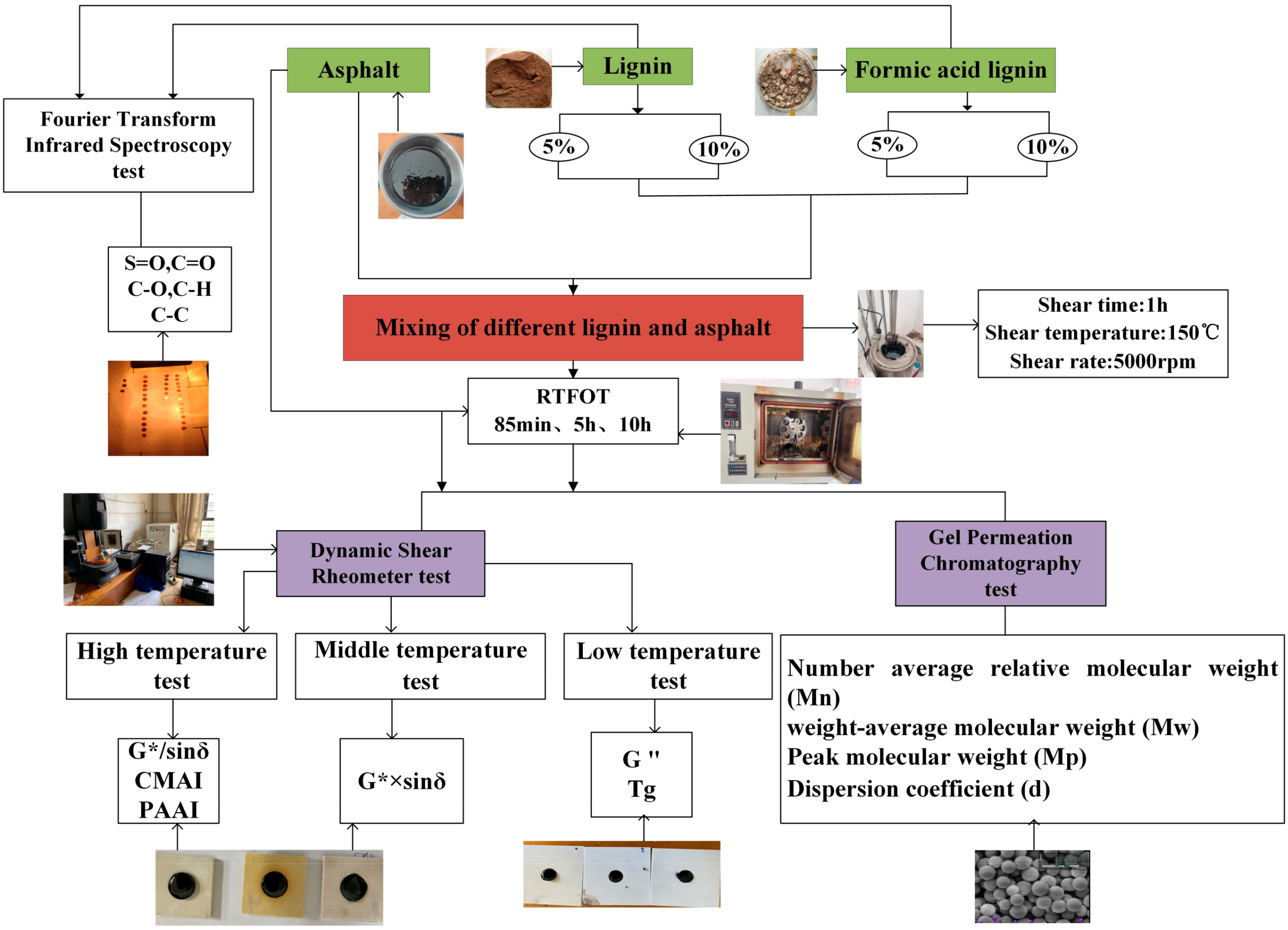

Figure 1. Experimental plan of the study.

2. Experiment

2.1. Raw Materials

2.1.1. Base Asphalt

The asphalt used in this paper was Maoming 70 # base asphalt. According to the relevant regulations in the Test Code for Asphalt and Asphalt Mixture of Highway Engineering (JTG E20-2011), the performance of asphalt was tested, and the test results are shown in Table 1.

Table 1. Performance index of base asphalt.

Experimental Projects	Unit	Experimental Value	Technical Requirements for Asphalt
Penetration (25 °C, 5 s, 100 g)	0.1 mm	68.5	60 to 80
Softening point	°C	50.7	>46
15 °C latency	cm	150	>100
TFOT needle penetration (25 °C)	%	76.9	>61%
Residual ductility (15 °C)	cm	132.9	>15

2.1.2. Lignin

The lignin used in this study was purchased from Jinan Yanghai Chemical Co., Ltd. It was a high-purity lignin, and its main technical indicators are shown in Table 2.

Table 2. Technical specifications for lignin.

Listings	Main Technical Indicators
Ash	1%
Lignin content	85–90%
Sugar content	1–3%
PH	7–8
Color	Brown powder

2.2. Test Methods

2.2.1. Formic Acid-Treated Lignin Preparation

The formic acid reagent with a purity of 88% produced by Guangdong Guanghua Technology Co., Ltd. (Shantou, China) and the centrifuge with a TSZ5-WS model produced by Hunan Xiangyi Laboratory Instrument Development Co., Ltd. (Changsha, China) were used to dissolve the lignin (passing 200 meshes) in formic acid at a 1:10 (g/mL) proportion, were fully stirred, the PH was adjusted to about 2–3, and then the solution was poured into a centrifuge tube and centrifuged for 10 min for 3500 r/min. After the instrument stopped, the upper-layer solution was poured into the test tube, which was the poured into the beaker; the lower-layer residue was removed; the deionized water was poured into the beaker and fully stirred; the solution was neutralized; the lignin was separated; the solution was poured into the test tube and centrifuged; the upper-layer clear solution was removed; the centrifuged lignin was retained; the deionized water was poured in, stirred, and centrifuged; the upper-layer clear solution was removed; and this was repeated until obtaining PH = 7 or close to this value. Finally, the lignin was placed in an oven at 30 °C for drying to obtain formic acid lignin. See Figure 2 for details.

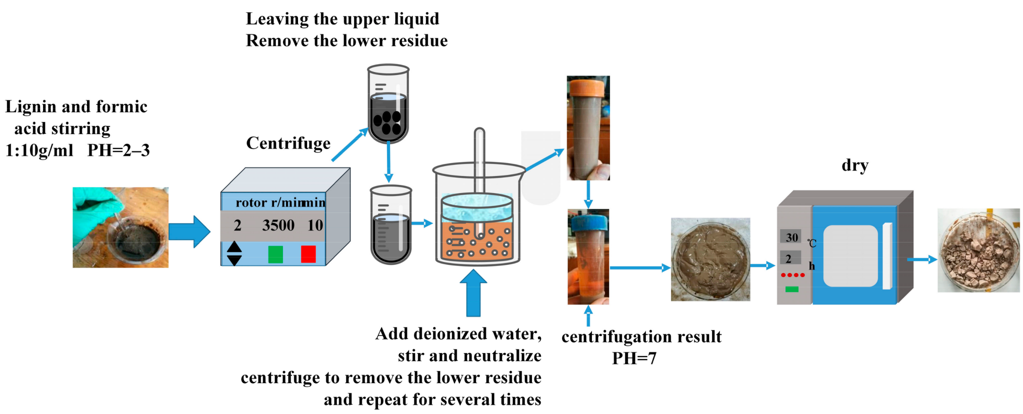

Figure 2. Extraction process of creating formic acid lignin.

2.2.2. Preparation of Modified Bitumen

The lignin and formic acid lignin were first dried in an oven at 50 °C to remove the moisture from them. Then, the lignin and formic acid lignin were passed through a 200-mesh sieve, and the lignin and formic acid lignin were obtained to be fully integrated with the bitumen. Then, a certain amount of base asphalt was heated in the flowing state in an oven, and then placed in an already-set 150 °C oil-bath pot and sheared at a 500 r/min low speed with a high-speed shearing machine. Finally, lignin and formic acid lignin were blended into the base asphalt in proportion to each other and sheared at 5000 r/min for 1 h to obtain the lignin-modified asphalt and formic acid lignin-modified asphalt. The doping amounts of lignin and formic acid lignin in this experiment were both 5% and 10%, respectively (relative to the base asphalt), and the preparation processes for lignin-modified asphalt and formic acid lignin-modified asphalt were the same. The base asphalt was labeled SK70, and the modified asphalt samples with 5% and 10% lignin contents were labeled SK70+5% L and SK70+10% L, respectively. The formic acid-modified asphalt with 5% and 10% lignin contents were labeled SK70+5% FAL and SK70+10% FAL, respectively. The specific process is shown in Figure 3.

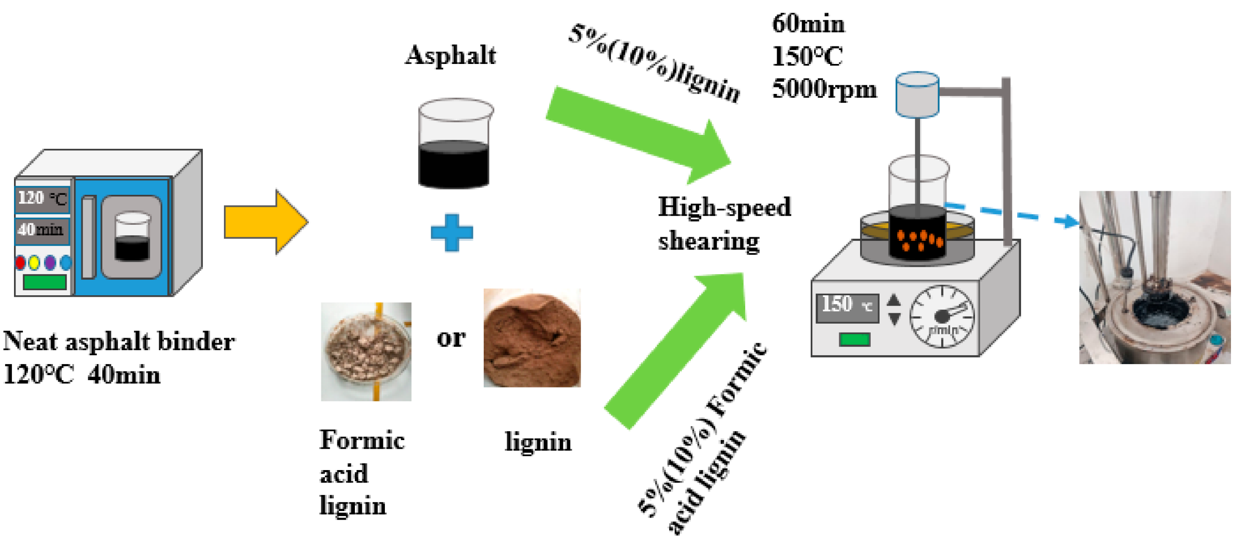

Figure 3. Preparation process of modified asphalt.

2.2.3. Preparation of Aging Specimens

In order to simulate the thermal and oxygen aging of asphalt, all asphalt specimens in this paper were used in an asphalt rotating thin-film oven (RTFOT) to simulate the actual process of the asphalt thermal and oxygen aging experiment. In this study, based on the asphalt rotating thin-film heating experiment in the JTGE 20-2011 Experimental Procedure for Highway Asphalt and Asphalt Mixture (T0610-2011), the prepared modified asphalt was poured into glass bottles (35 ± 0.5) g, placed in the rotating oven as a group of 8, and rotated at the set temperatures of 163 °C for 85 min, 5 h, and 10 h, respectively, to produce specimens at different aging times.

2.2.4. Rheological Performance Test

The DHR-1 dynamic shear rheometer manufactured by the TA Company, USA, was used to perform the temperature scan test by the strain control method with a target standard strain value of 12% and a loading frequency of 10 rad/s; the temperature scanning test was performed at a temperature range of 10~90 °C and a sampling interval of 2 °C. The low-temperature dynamic shear rheometer with an 8 mm plate was used to perform the temperature scanning of the low-temperature rheological properties of formic acid lignin-modified asphalt and lignin-modified asphalt at a temperature range of −26~10 °C.

2.2.5. Aging Index Evaluation Indicators

The analysis of the aging performance based on high-temperature rheology was evaluated using the complex shear modulus aging index (CMAI) and phase angle aging index (PAAI), respectively. According to the literature [31], the calculation equations are shown in Equations (1) and (2). The aging evaluation calculations were chosen to be performed at 30~90 °C.

$$\mathrm{CMAI} = \frac{G^*_{aged}}{G^*_{unaged}} \tag{1}$$

$$\mathrm{PAAI} = \frac{\delta_{aged}}{\delta_{unaged}} \tag{2}$$

2.2.6. Gel Chromatography Test

In this paper, we used Agilent PL-GPC50 gel chromatography with tetrahydrofuran THF as the solvent, Jordi Gel DVB as the column, tetrahydrofuran as the mobile phase, a 100 µL injection volume, 1.5 mg/mL concentration of the experimental solution, 1.0 mL/min mobile phase rate, and 45 min separation time.

2.2.7. Infrared Spectroscopy Tests

The functional group properties of lignin and formic acid lignin were analyzed, respectively, by the Fourier infrared spectroscopy experiment using VERTEX 80 manufactured by BRUKER, with 400–4000 cm^{-1} as the acquisition interval, 32 scans, and a 4 cm^{-1} resolution. The different lignin samples were added to the appropriate amount of potassium bromide (KBr) and were completely dissolved in petroleum ether in KBr crystals (spectral purity) at a ratio of 1:100 (mass ratio) when fully ground in agate mortar. Then, the solvent was evaporated, mixed well under dry conditions, and then ground and pressed.

3. Results and Discussion

3.1. Mechanistic Analysis of Lignin and Formic Acid Treatment of Lignin

To distinguish the changes between lignin and lignin treated with formic acid, the characteristics of lignin hanging energy groups and molecular weight changes were investigated for lignin and formic acid lignin, respectively, and the results are shown in Figure 4.

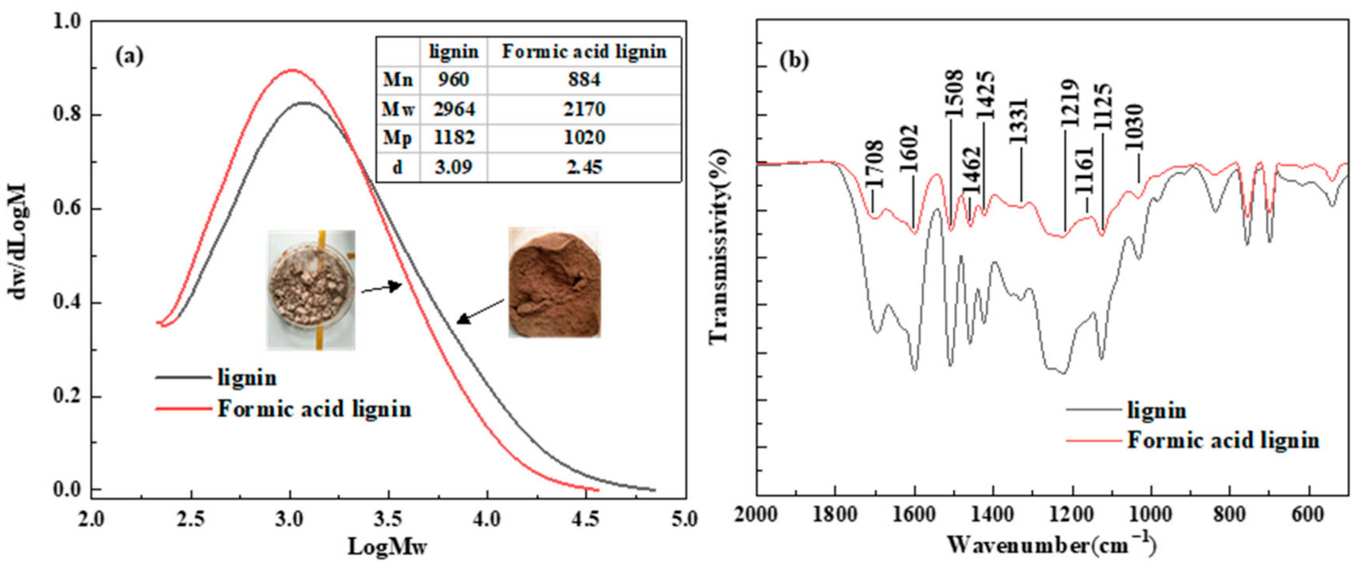

Figure 4. Infrared spectra of lignin and formic acid lignin with molecular weight distributions. (**a**) GPC; (**b**) FTIR.

In Figure 4a, for the lignin and formic acid lignin molecular weight distributions, the horizontal coordinate represents the logarithmic value of the heavy mean molecular weight and the vertical coordinate is the relative lignin content; it can be observed that the molecular weight of formic acid-treated lignin decreases and both Mn (the number average molecular weight) and Mw (the weight average molecular weight) decrease. The reason for this is that under strong-acid conditions, lignin dissolves in the formic acid solution, its molecular chains break, and some small molecules are generated, causing formic acid changes in the relative molecular mass distribution of lignin. The specific values are shown in Figure 4a, where Mn, Mw, and Mp (the peak molecular weight) of lignin are reduced from 960, 2964, and 1182 before formic acid treatment to 884, 2170, and 1022, respectively, resulting in some changes in lignin properties.

Different types of raw materials and separation methods can lead to differences in the structural characteristics of the isolated lignin. In order to gain further insight into the changes in the chemical compositions of lignin and formic acid-treated lignin during the deterioration process, the structural characteristics of lignin isolated by the formic acid method were investigated by applying infrared spectroscopy (FTIR) experiments to characterize its functional groups. Figure 4b shows the infrared spectral results, in which the skeletal structure of formic acid-treated lignin remains unchanged and still retains the lignin FT-IR characteristics absorption peaks at 1602, 1508, 1425, 1462, and 1331 cm^{-1}. The absorption at 1602, 1508, and 1425 cm^{-1} was weaker than that of the untreated lignin, suggesting that the formic acid-treated lignin was less pure and that the benzene ring structure was not destroyed by formic acid treatment [32]. At 1708 cm^{-1}, the non-conjugated carbonyl C=O stretching vibration in the ester group had a stronger peak due to the formylation of lignin caused by formic acid treatment [33]. At the same time, the absorption of the non-conjugated carbonyl C–O stretching vibration of lignin at 1708 cm^{-1} was enhanced and the carbonyl content significantly increased. The absorption peak at 1708 cm^{-1} was attributed to the C=O stretching vibration and the characteristic absorption peak of the aromatic skeleton vibration at 1611 cm^{-1} was attributed to syringyl (S), 1508 and 1219 cm^{-1} to guaiacol (G), and 1462 cm^{-1} to p-hydroxyphenyl (H). According to the FT-IR analysis results, lignin is a typical SGH lignin [34]. The comparison of the characteristic peaks revealed changes in lignin and formic acid-treated lignin, where the intensity of absorption peaks characterizing the benzene ring structure of formic acid lignin at 1602, 1508, and 1462 cm^{-1} were significantly weaker, indicating that the degradation of formic acid lignin occurred, and its content was significantly reduced. In addition, the decrease in the intensity of the absorption peaks at 1425 cm^{-1} (bending vibration in the C–H plane of lignin) and 1331 cm^{-1} (stretching vibration of lignin C–O) were further evidence of the degradation of formic acid lignin [35]. This indicates that lignin undergoes chemical changes after formic acid treatment and formylation modification helps in the development of lignin for functional bio-based materials. This result is also consistent with the gel permeation chromatography (GPC) results.

3.2. Rheological Performance Analysis

3.2.1. Analysis of High-Temperature Rheological Properties

Figure 5 shows the results of temperature scans of different modified asphalts, demonstrating the variation patterns of complex modulus G* and phase angle δ with temperature for different lignin and formic acid lignin-modified asphalts. As the temperature increases, complex modulus G* gradually decreases because the asphalt properties gradually change from an elastic to a viscous flow state with the increase in temperature, and the asphalt then becomes softer, which shows the decrease in complex modulus G*. Both for lignin-modified asphalt and formic acid lignin-modified asphalt, complex modulus G* increased with the increase in lignin incorporation, indicating that the incorporation of a modifier can improve the deformation resistance of asphalt. The temperature scan curves of formic acid lignin-modified asphalt (10% lignin content) and lignin-modified asphalt(5% lignin content) largely overlapped, indicating that both had the same effect on the high-temperature resistance of the asphalt. The complex modulus G* of lignin-modified asphalt was greater than that of formic acid lignin-modified asphalt G* at the same dose, indicating that the resistance to deformation of asphalt by lignin was greater than that of formic acid lignin. The phase angle δ increased with the increase in lignin incorporation, indicating that the incorporation of lignin and formic acid lignin improved the elastic property of the asphalt and had a good effect on the high-temperature resistance of the asphalt. The phase angle δ of lignin not treated with formic acid was significantly smaller than the phase angle of formic acid-treated lignin asphalt, indicating that the lignin-modified asphalt was stronger than the formic acid lignin-modified asphalt at a temperature range of 30–90°, giving it a stronger resistance to high-temperature deformation. The improvement of lignin-modified asphalt was greater than that of formic acid lignin-modified asphalt; such an observation was probably due to the grater molecular weight of lignin compared to that of formic acid lignin, and the incorporation of base asphalt improved the molecular weight of the asphalt. In Figure 5c, it can be observed that the complex modulus of the lignin-modified asphalt is the greatest when aged for about 5 h, while the complex modulus of the formic acid lignin-modified asphalt is the smallest, and the same pattern of the phase angle can be observed. In Figure 5d, it can be observed that the complex modulus of both lignin-modified asphalt and formic acid lignin-modified asphalt increase with increasing the admixture at 10 h. The gap of the complex modulus increased, indicating that the molecular weight of lignin and formic acid lignin may have changed with aging.

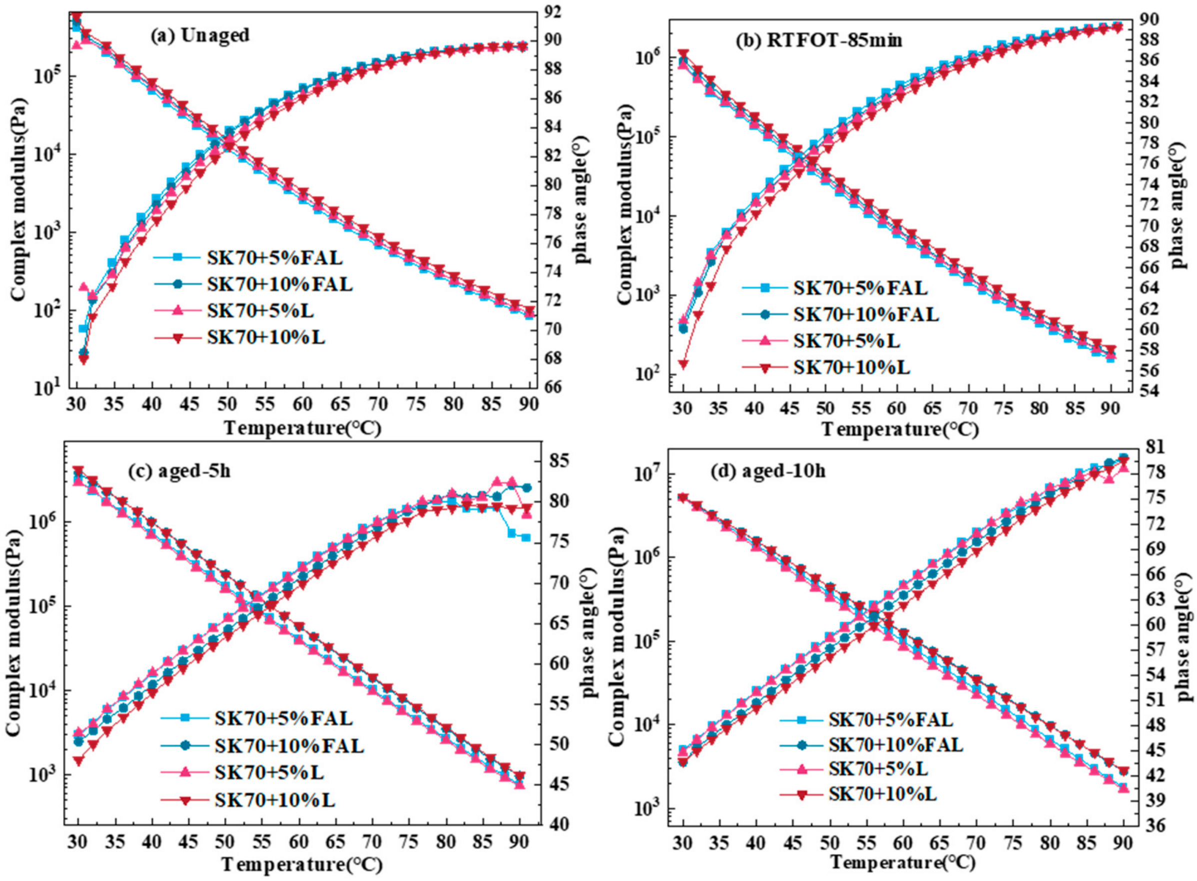

Figure 5. Variation curves of complex modulus G* and phase angle δ with temperatures for each asphalt specimen in different aging states.

To investigate the deformation resistance of the modified asphalt further, rutting factor analysis was performed. The higher the rutting factor value, the better the elasticity of the asphalt material and the stronger its resistance to deformation [36]. In Figure 6, it can be observed that the rutting factor of different types of asphalt under different aging conditions is consistent, in which the rutting factor of lignin-modified asphalt is the greatest, followed by formic acid lignin-modified asphalt, where the higher the dose, the stronger the rutting resistance. For the short-term aging condition of 5 h, the rutting/deformation resistance of formic acid lignin-modified asphalt is the lowest and the deformation resistance of lignin-modified asphalt is the best, probably because the internal molecules of formic acid lignin appeared to be cleaved, while the lignin molecules had not yet reached the cleavage temperature. For the short-term aging conditions of 10 h, with both lignin-modified asphalt and formic acid lignin-modified asphalt, the lower the lignin dose, the lower the asphalt's resistance to deformation, and the gap between their rutting factors increased. At the same time, it was observed that the rutting resistance of SK70+5% FAL was better than that of SK70+5 L, because lignin molecules had cracking reactions with the increasing aging time at high temperatures.

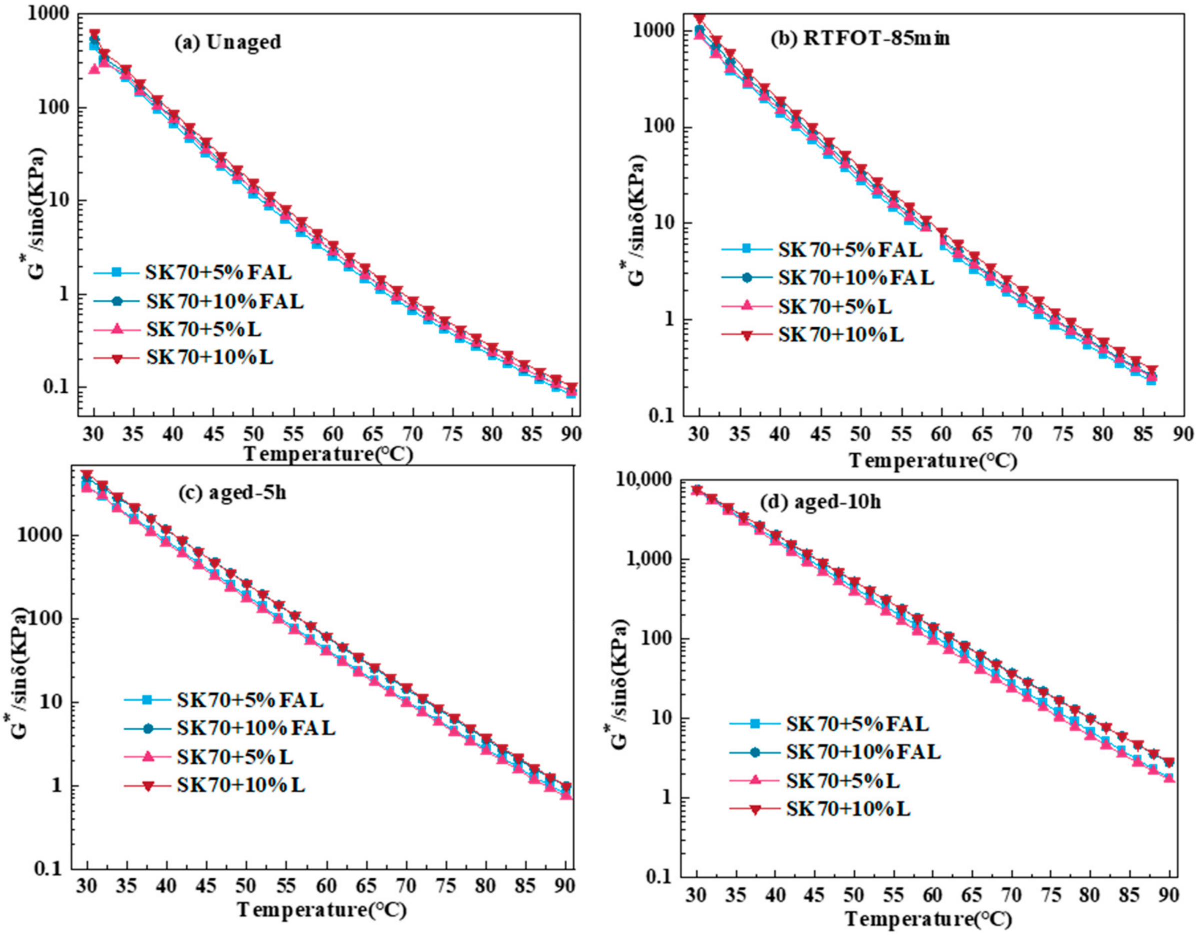

Figure 6. Curves of rutting factor (G*/sinδ) with temperatures for each asphalt specimen during different aging states.

To analyze the high-temperature performance further, the complex modulus aging index (CMAI) and phase angle aging index (PAAI) were derived using Equations (1) and (2). As shown in Figure 7a, the aging index increases and then decreases with the increase in temperature in a parabolic pattern. SK70+5% L-modified asphalt has the best aging resistance under the short-term aging condition of 85 min, and SK70+5% FAL with the same amount of admixture has the worst aging resistance, which indicates that the aging resistance of lignin-modified asphalt is better than that of formic acid lignin-modified asphalt. From the PAAI, as shown in the analysis presented in Figure 7b, by comparing the two modified asphalts, SK70+5% L and SK70+5% FAL were observed to present a better anti-aging effect when the admixture content was 5%.

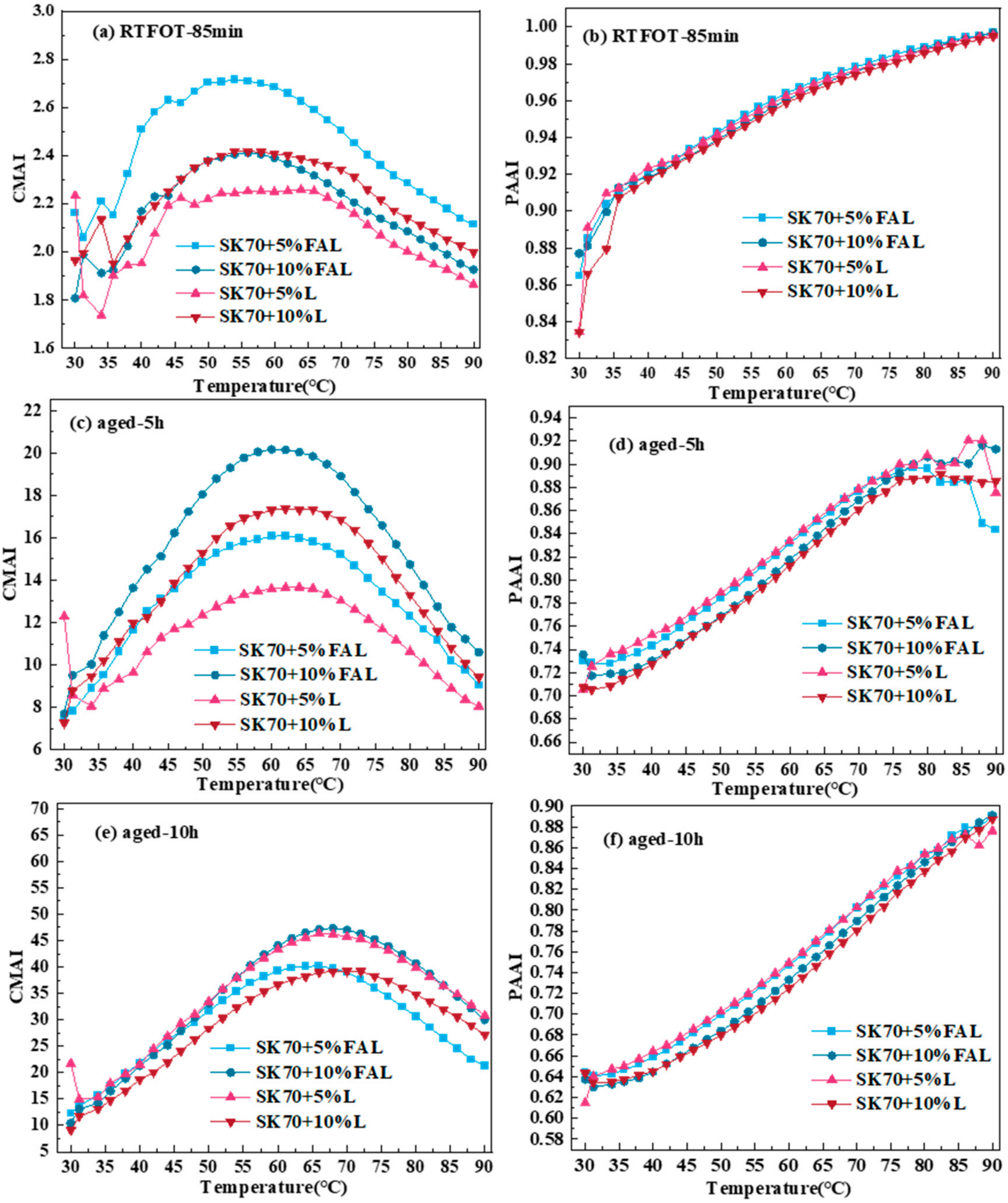

Figure 7. Curves of complex modulus aging and phase angle aging indexes with temperatures for each asphalt specimen during different aging states.

It can be observed from Figure 7c,d that, compared to the short-term aging index (CMAI), the lower the addition of lignin, the more obvious the aging-resistance effect. At the same time, it was observed that SK70+5% L-modified asphalt had the best effect, which is consistent with the short-term aging index, indicating that the additions of formic acid lignin and lignin can delay the aging of asphalt, and non-acid-treated lignin had the best effect. With the increase in the addition of lignin and formic acid lignin, the CMAI aging index also increased, and the CMAI aging index of SK70+10% FAL-modified asphalt was the lowest, indicating that its anti-aging effect was the worst.

From Figure 7e,f, it can be observed that with the increase in the aging process, the addition of lignin and formic acid lignin made the anti-aging effect of asphalt more obvious.

At the same time, the higher the lignin content, the better the anti-aging effect. Our research results are similar to those of Arafat [37] et al., and verify the fact that lignin increases the aging resistance of an asphalt binder under high-temperature conditions. Secondly, the 85 min and 5 h aging index patterns of formic acid lignin-modified asphalt are different, indicating that aging leads to internal changes in lignin. The phase angle at an 85 min aging index compared to a 5 h aging index, with an increase in the temperature, the changes in the curve tended to become more consistent, indicating that the higher the temperature, the greater the long-term aging resistance of the asphalt.

3.2.2. Medium Temperature-Variation Performance Analysis

The mid-temperature failure temperature was divided according to the formula G* × sinδ equal to 5000 kPa [38]; the complex modulus versus phase angle for the mid-temperature is shown in Figure 8.

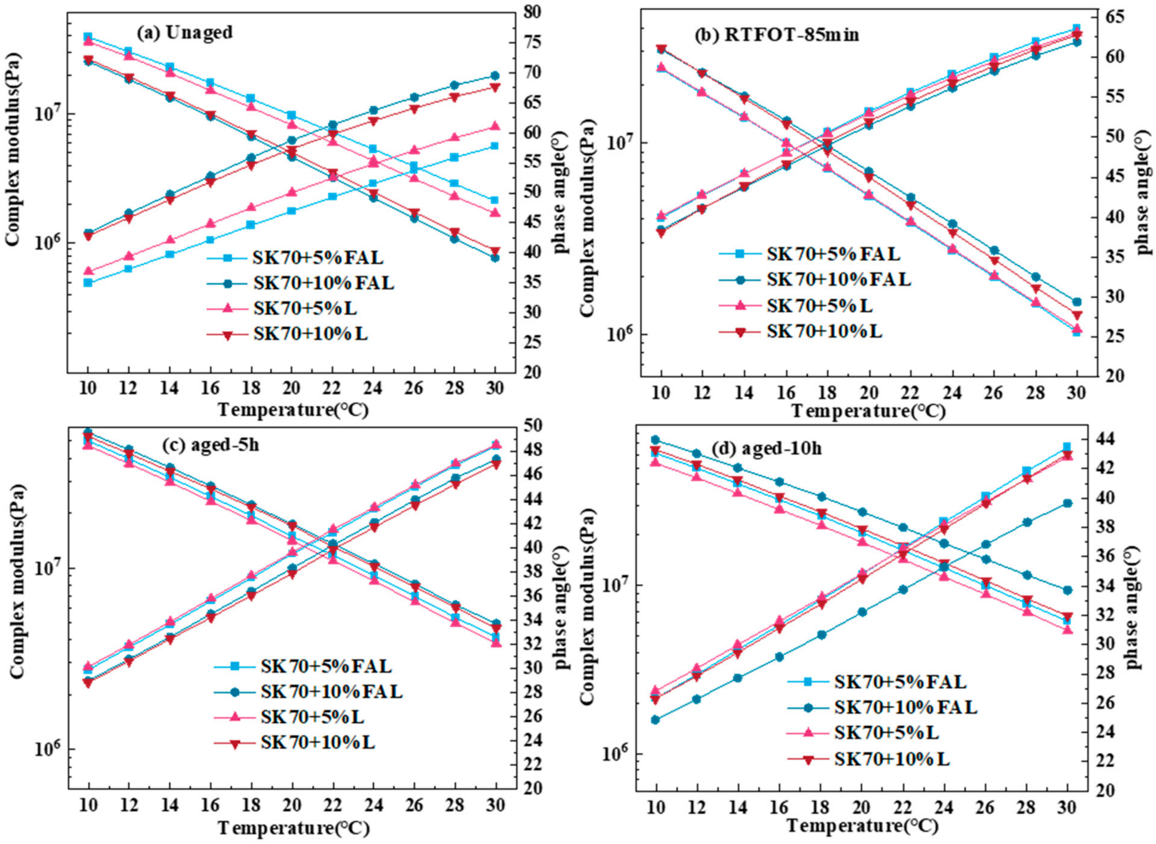

Figure 8. Variation curves of complex modulus and phase angle with temperatures for each asphalt specimen at different aging states.

In Figure 8a, it can be observed that the complex modulus of unaged SK70+5% FAL is observed to be the greatest, followed by SK70+5% L. However, SK70+10%L and SK70+10% FAL have smaller complex moduli. The phase angles present the same pattern. It can be observed from Figure 8b–d that the complex modulus of SK70+10% FAL is the greatest after 85 min of aging, followed by SK70+10% L, and it was also observed that the deformation resistance of asphalt was poor when the content was small. The anti-deformation behavior of aging for 5 h was the same as that of 85 min; however, it was observed that the anti-deformation effect of formic acid lignin -modified asphalt was better than that of lignin-modified asphalt with the same amount of lignin and formic acid lignin after aging for 10 h; this is contrary to the law of complex moduli at high temperatures. The reason for this may be due to the high susceptibility of lignin to crack under high temperatures.

To explore the rheological properties at mid-temperatures further, the fatigue factor curve results are plotted in Figure 9. The lower the value of the fatigue factor, the better the fatigue resistance [39]. According to the results presented in Figure 9a, the fatigue resistance values of SK70+10% L and SK70+10% FAL are almost the same. However, the fatigue performance of the asphalt was observed to be slightly worse with a less-modifier dose. Additionally, the fatigue resistance was observed to be better with a less-modified admixture for 85 min of aging, as shown in Figure 9b, while the fatigue resistance was observed to be almost the same for formic acid lignin and lignin with the same admixture contents. In Figure 9c, 5 h aged SK70+5% L has the best fatigue resistance, followed by SK70+5% FAL, and the worst is SK70+10% FAL. It was observed that aging for 10 h had the same pattern as that of aging for 5 h, as shown in Figure 9d; however, it was also observed that the gap of each modified asphalt increased after aging for 10 h, indicating that lignin and lignin molecules treated with formic acid may have changed with aging.

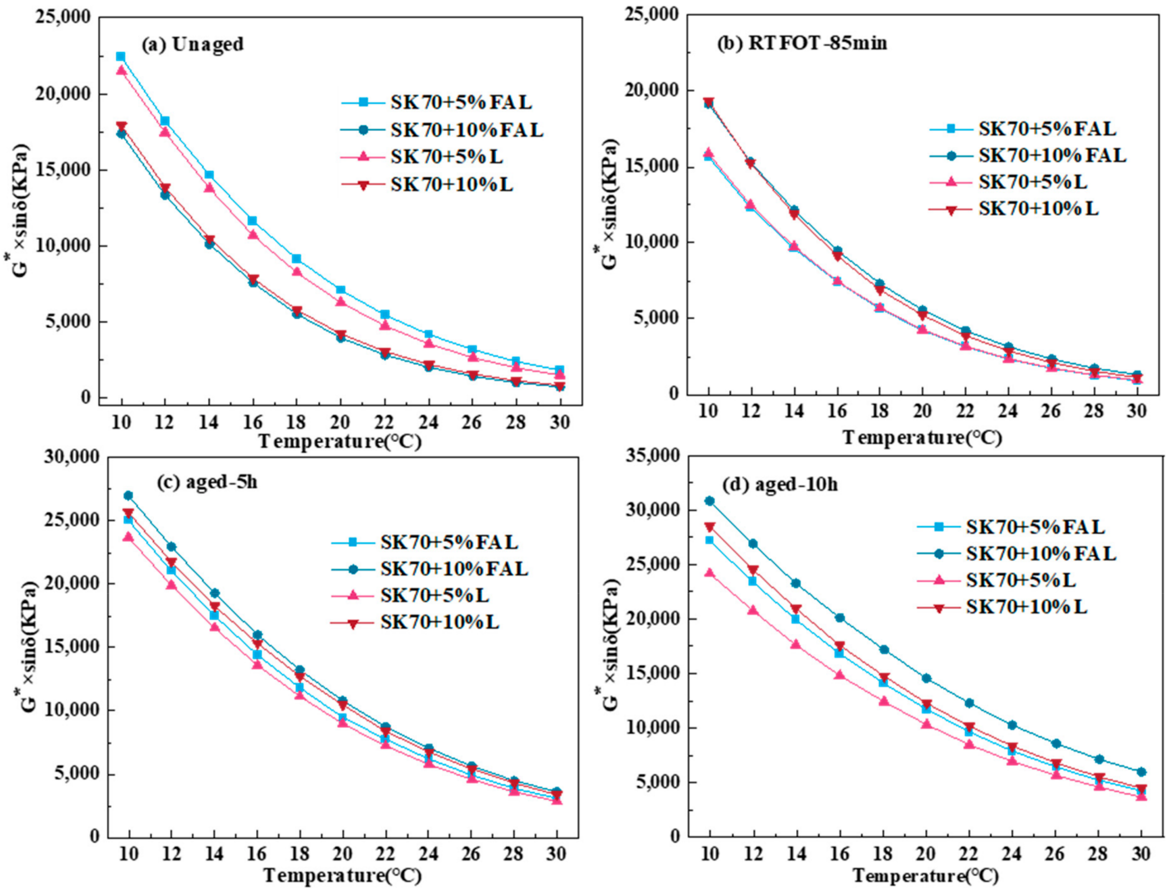

Figure 9. Curves of fatigue factor with temperatures for each asphalt specimen in different states.

3.2.3. Low-Temperature Rheological Performance Analysis

Asphalt is a temperature-sensitive material expected to present certain characteristics, such as viscosity, flexibility, and less or no fracture at low temperatures, and the transition temperature of asphalt from rubber to glass states characterizes the low-temperature performance of asphalt. The phase angle δ represents the ratio of elasticity and viscosity; the larger δ is, the more viscous asphalt is and the stronger its fluidity and resistance to low temperatures. Figure 10 illustrates the results of complex modulus versus phase angle for different asphalts at low temperatures.

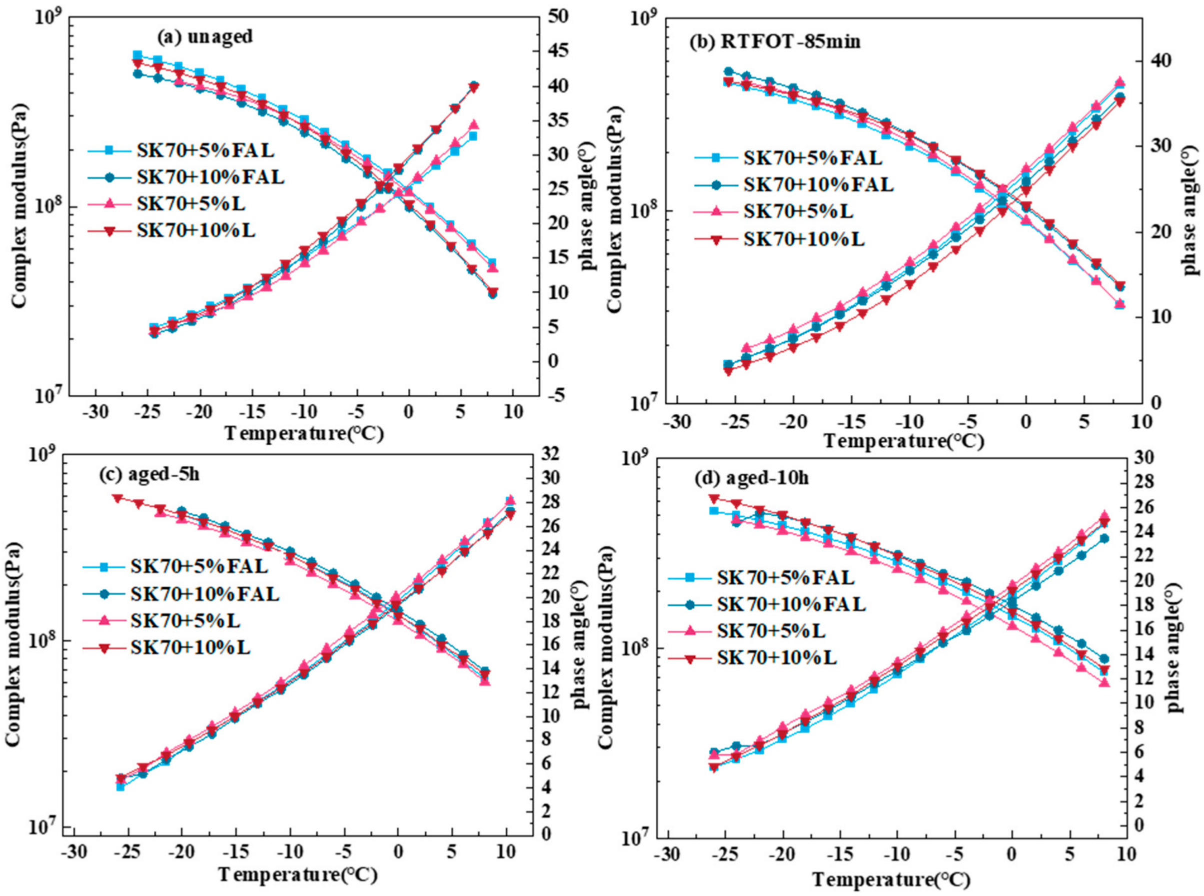

Figure 10. Curves of complex shear modulus G* and phase angle δ with temperatures for each asphalt specimen during different aging states.

As shown in Figure 10, when unaged, there is little difference in the complex modulus at low temperatures, and difference becomes significant as the temperature increases, and, in contrast, the greater the admixture content, the poorer the resistance to deformation. From the phase angle, there is little difference in the resistance to cracking of asphalt at sub-zero temperatures. In Figure 10b, it can be observed that the greater the admixture content at 85 min of aging, the stronger the resistance to deformation, and the pattern continues for 5 h of aging. Additionally, as shown in Figure 10d, it is observable that the 5 h of aging presents the same behavior; however, the gap between the modified bitumen increases, indicating that the lignin and formic acid lignin molecules may change during aging.

In order to observe the low-temperature performance more intuitively, knowing that the loss modulus G″ and low-temperature crack resistance of asphalt are proportional, the greater the loss modulus, the greater the energy used to resist low-temperature flows, the better the resistance to low-temperature fractures, the peak value was usually used as the glass-transition temperature Tg; to calculate the glass-transition temperature Tg, extract the Tg value of different modified asphalts in each aging stage, and the lower the temperature, the better the result [40]. The related details are shown in Figures 10 and 11.

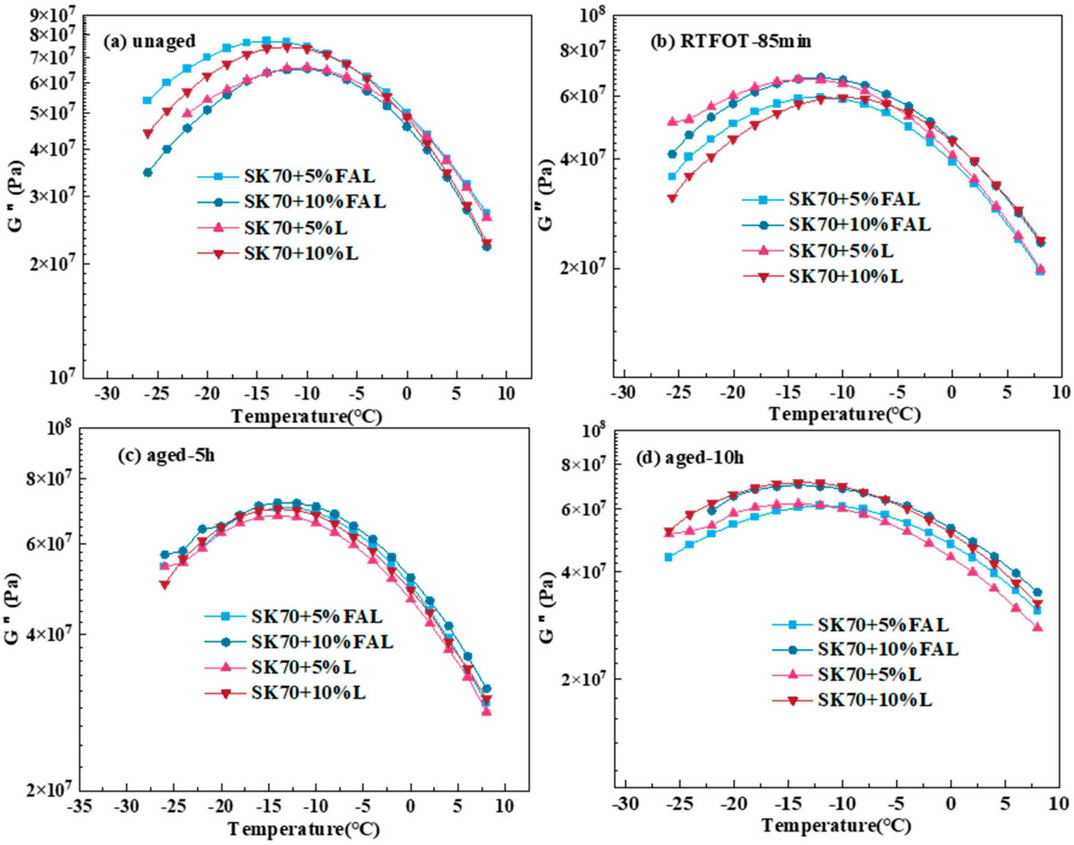

Figure 11. Curve of loss modulus G" with temperatures for each asphalt specimen at different states.

From Figure 11, it can be observed that the loss modulus of modified bitumen increases with the temperature and decreases with the increase in temperature after reaching a maximum value at a certain temperature. In Figure 11a, it can be observed that the loss modulus of lignin-modified bitumen is greater than that of formic acid lignin-modified bitumen at temperatures higher than −6 °C and decreases with the increase in the amount of modifier incorporated. The formic acid lignin-modified asphalt (with 5% lignin content) gradually increased at temperatures lower than −6 °C. When observed, the peak value of formic acid lignin-modified asphalt (with 5% lignin content) was around −14 °C, and the rest of the modified asphalt was around −12 °C, indicating that the addition of formic acid lignin improved the low-temperature crack resistance of the asphalt.

It can be observed from Figure 11b that when the temperature is higher than −6 °C for 85 min of aging, the higher the admixture content, the better the resistance to cracking. When the temperature was lower than −6 °C, SK70+5% L had the best anti-cracking effect, followed by SK70+10% FAL, and the least fortunate was SK70+10% L. In Figure 11c, it can be observed that as aging occurs, the gap of the loss modulus is not as significant as short-term aging-modified bitumen; on the contrary, the SK70+10% FAL loss modulus is the largest and the most resistant to cracking. The pattern of the loss modulus in Figure 11d is very obvious, with SK70+10% L- and SK70+10% FAL-modified bitumen having a higher resistance to cracking, where the modifier dose is slightly lower in resistance to cracking. With aging, the molecules of lignin and formic lignin may undergo cleavage and the large molecular weight becomes small, and the greater the admixture quantity, the better the resistance to cracking.

From the Tg results, as shown in Figure 12, for SK70+5% specimens, with aging, Tg decreases, showing good anti-cracking behavior, while in SK70+10% L, it can be observed that, with aging, Tg changes without obvious patterns, indicating that lignin can effectively improve the low-temperature cracking performance; however, the amount of admixture is not recommended to be too high. For the SK70+5% FAL specimens, it was observed that with aging, it did not prevent low-temperature cracking, whereas for SK70+10% FAL specimens, it was observed that with aging, it could effectively prevent low-temperature cracking, indicating that formic acid lignin could effectively modify the cracking performance; however, the quantity of admixture is not recommended to be too low.

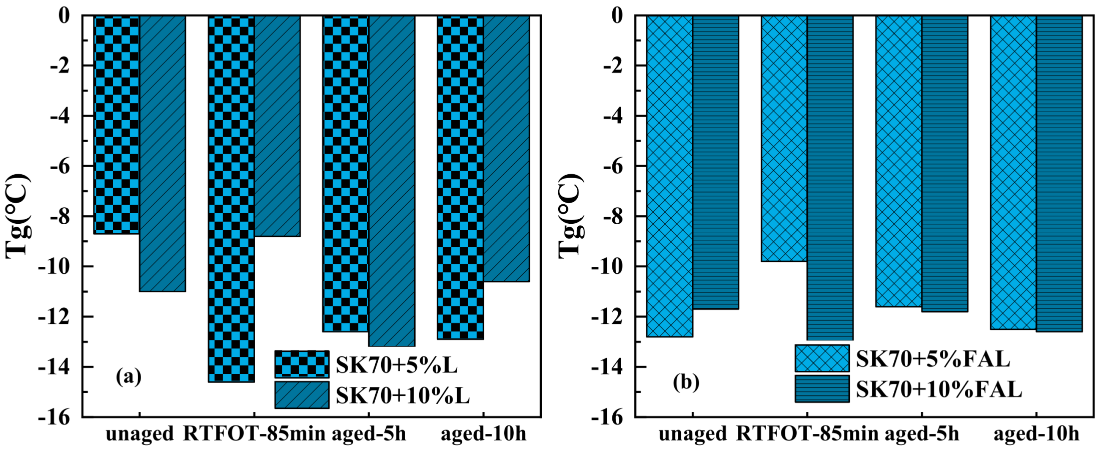

Figure 12. Glass-transition temperature Tg value/°C. (**a**) Lignin modified asphalt: (**b**) Formic acid lignin modified asphalt.

3.3. Gel-Permeation Chromatography (GPC) Analysis

In addition to the reason for capturing free radicals, the mechanism of lignin thermo-oxidation aging is more of a "sacrificial agent" [30]. Therefore, the influence of aging on the molecular weight and distribution of lignin-modified asphalt and formic acid lignin-modified asphalt was investigated, and samples with a 5% content were selected for testing. Samples before and after aging were, respectively, dissolved in tetrahydrofuran, and their molecular weights were tested using GPC. The results are shown in Figure 13.

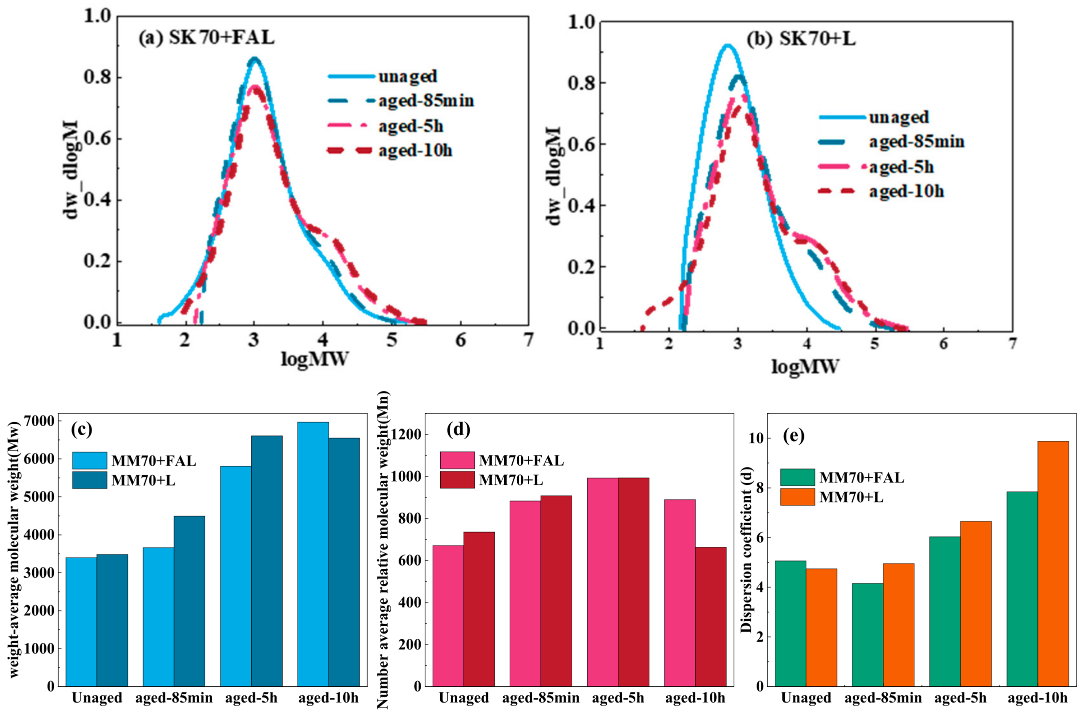

Figure 13. Gel chromatography of different modified asphalts with methyl lignin and different aging times. ((**a**) SK70+FAL: (**b**) SK70+L: (**c**) Weight average molecular weight: (**d**) Number average molecular weight: (**e**) Dispersion coefficient).

Figure 13a,b shows that the molecular weights of lignin-modified asphalt and formic acid lignin-modified asphalt move in the direction of larger molecules after different aging times, reflecting the change in the molecular weight of modified asphalt before and after aging. The molecular weight of the modified asphalt before and after aging was mainly between 10^2–10^5. With the increase in the aging time, the modified asphalt moved towards a high molecular weight. A small part of the molecules of formic acid lignin-modified asphalt decomposed after 85 min of aging, while a large part of small molecules decomposed after 5 h of aging; the small molecules of formic acid lignin-modified asphalt further decomposed after aging for 10 h; however, the minimum molecular weight did not exceed that before aging. A comparison between lignin-modified asphalt and formic acid lignin-modified asphalt before and after aging showed that the molecular weight of formic acid lignin-modified asphalt dramatically changed and presented a large deviation. When aged for 85 min, many molecules did not crack as when they were aged for 5 h, while lignin-modified asphalt decomposed a high number of small molecules when aged for 10 h, and the minimum molecular weight exceeded that before aging. From the degree of change in the molecular weight before and after aging, SK70+FAL-modified asphalt had better heat-aging resistance than SK70+L-modified asphalt.

In order to investigate the combined effect of different aging levels on the base and modified asphalt, in this paper, Mw, Mn, and d before and after the aging of lignin-modified asphalt and formic acid lignin-modified asphalt were derived using Agilent PL-GPC50 gel chromatography, and the results are shown in Figure 13c–e.

From Figure 13c–e, it can be observed that the patterns of Mn of lignin-modified bitumen and formic acid lignin-modified bitumen are the same, increasing and then decreasing with aging, and decreasing at 10 h of aging, and the longer the aging time, Mn decreases, indicating that the decomposition of small molecules of polymers and large molecules simultaneously exist during the aging process. From the weight average molecular weight Mw, it can be observed that the lignin-modified asphalt Mw increases and then decreases with aging, while the formic acid lignin-modified asphalt continues to increase with aging. The dispersion coefficients d of lignin-modified bitumen and formic acid lignin-modified bitumen increase with aging, indicating that the molecular weight at a certain concentration decreases. The dispersion coefficient increases with the increase in aging time, and the increase indicates that there are many components with molecular weights at a certain range, and the range of the phase change of molecular weight is consistent with the temperature range of transition of aggregate components of asphalt; therefore, the heat-absorption capacity of asphalt must increase, which shows that the overall change is intense and the temperature sensitivity is enhanced. The addition of lignin and formic acid lignin can improve the high-temperature stability of asphalt after aging.

Compared to different aging times and before aging, the Mw of lignin-modified asphalt increased by 1.29, 1.9, and 1.88 times, and the Mw of formic acid lignin-modified asphalt increased by 1.08, 1.7, and 2.05 times, respectively, and from these ratios, it can be observed that the molecular weight of lignin-modified asphalt began to show a decrease at 10 h. Although formic acid lignin-modified asphalt did not decrease, the growth rate began to decrease; and from the values of the Mw, the values of lignin-modified asphalt and formic acid lignin-modified asphalt were much lower than before aging after 5 h, probably because the lignin was cleaved during the aging process, which reduced the Mw values and also explained the problems that occurred in the rheological properties. While Murugan et al. [41] studied the pyrolytic behavior of lignin in wood, it was observed that lignin was dominated by a series of small-molecule cleavage products at 162 °C to 246 °C. The temperature at aging was 163 °C, but the actual temperature in the asphalt was much higher than 163 °C, which indicated lignin cleavage in the modified asphalt during aging.

4. Conclusions

In this study, dynamic shear rheometer (DSR), Fourier transform infrared spectroscopy (FT-IT), and gel permeation chromatography (GPC) were used to characterize the effects of lignin and formic acid lignin on asphalt. Through the abovementioned research, the following conclusions can be drawn:

(1) In terms of color, lignin changes from brown to light-white after being purified by formic acid. Fourier transform infrared spectroscopy shows that the purity of lignin treated with formic acid is reduced, and the infrared spectra of lignin and formic acid lignin are similar. However, the lignin treated with formic acid is degraded and formylated, indicating that the lignin presents chemical changes after acid treatment.
(2) Based on the analysis of the DSR results, it is observed that lignin-modified asphalt is stronger than formic acid-treated lignin-modified asphalt at high and mid-temperatures, and has stronger resistance to high-temperature deformation, fatigue, and aging.
(3) From the glass-transition temperature, it is observable that at low temperatures, lignin and formic acid lignin can effectively improve the low-temperature cracking; however, the content of lignin is not recommended to be too high, and the content of formic acid lignin is not recommended to be too low.
(4) According to the results of the gel permeation chromatography (GPC), from the increased magnification Mw value, the ratio of lignin-modified asphalt and formic acid lignin-modified asphalt decreases, because lignin and formic acid lignin are cracked during aging, which reduces their molecular weights.

To summarize, lignin, as a sustainable asphalt extender, has environmental benefits and provides a baseline for future research. To evaluate the modification effect from a broader perspective, in addition, relevant mixing and field tests should also be conducted to check the actual performance and potential, and we suggest paying attention to the impact of molecular weight on its performance in the future, establishing a relationship model between the molecular weight of lignin or its chemical structure and rheological properties and anti-aging, and finally studying the life cycle assessment and implementation of this technology at the industrial level.

Author Contributions: M.C.; writing—original draft preparation and review and editing, literature review and methodology, C.P.; experimental work and testing, C.P.; investigation and writing—original draft preparation, C.C.; supervision and funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science and Technology Planning Project of Yunnan Science and Technology Department (Joint Agricultural Project), grant number 202101BD070001-060; Science and Technology Project of Gui Zhou Highway Bureau, grant number 2021QLM06; Scientific Research Fund of Yunnan Provincial Department of Education, grant number 2020J0420.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Polo-Mendoza, R.; Martinez-Arguelles, G.; Walubita, L.F.; Moreno-Navarro, F.; Giustozzi, F.; Fuentes, L.; Navarro-Donado, T. Ultraviolet ageing of bituminous materials: A comprehensive literature review from 2011 to 2022. *Constr. Build. Mater.* **2022**, *350*, 128889. [CrossRef]
2. Walubita, L.F.; Ling, M.; Pianeta, L.M.R.; Fuentes, L.; Komba, J.J.; Mabrouk, G.M. Correlating the asphalt-binder MSCR test results to the HMA HWTT and field rutting performance. *J. Transp. Eng. Part B Pavements* **2022**, *148*, 04022047. [CrossRef]
3. Mousavinezhad, S.; Shafabakhsh, G.; Ani, O.J. Nano-clay and styrene-butadiene-styrene modified bitumen for improvement of rutting performance in asphalt mixtures containing steel slag aggregates. *Constr. Build. Mater.* **2019**, *226*, 793–801. [CrossRef]
4. Cheraghian, G.; Wistuba, M.P. Ultraviolet aging study on bitumen modified by a composite of clay and fumed silica nanoparticles. *Sci. Rep.* **2020**, *10*, 11216. [CrossRef] [PubMed]
5. Sandoval, C.H.H.; Amaya, X.V.C.; Molano, E.A.S. Effect of aging on the properties of asphalt and asphalt mixtures. *Ing. Univ.* **2015**, *19*, 335–349. [CrossRef]

6. Thives, L.P.; Ghisi, E. Asphalt mixtures emission and energy consumption: A review. *Renew. Sustain. Energy Rev.* **2017**, *72*, 473–484. [CrossRef]
7. Zhu, J.; Birgisson, B.; Kringos, N. Review article: Polymer modification of bitumen: Advances and challenges. *Eur. Polym. J.* **2014**, *54*, 18–38. [CrossRef]
8. Poovaneshvaran, S.; Hasan, M.R.M.; Jaya, R.P. Impacts of recycled crumb rubber powder and natural rubber latex on the modified asphalt rheological behaviour, bonding, and resistance to shear. *Constr. Build. Mater.* **2020**, *234*, 117357. [CrossRef]
9. Dong, D.; Huang, X.; Li, X.; Zhang, L. Swelling process of rubber in asphalt and its effect on the structure and properties of rubber and asphalt. *Constr. Build. Mater.* **2012**, *29*, 316–322. [CrossRef]
10. Shen, C.; Li, R.; Pei, J.; Cai, J.; Liu, T.; Li, Y. Preparation and the Effect of Surface-Functionalized Calcium Carbonate Nanoparticles on Asphalt Binder. *Appl. Sci.* **2019**, *10*, 91. [CrossRef]
11. Peng, X.; Li, X.-F. Research on the Performance and Mechanism of Nanometer ZnO/SBS Modified Asphalt. *J. Highw. Transp. Res. Dev.* **2007**, *6*, 16–20.
12. Zhang, W.; Zou, L.; Wang, Y.; Liu, J.; Yang, C.; Di, J.; Hu, H.; Yang, Z. Influence of High Viscosity Petroleum Resin (HV-PR) on the Intermediate and High Temperature Performances of Styrene–Butadiene–Styrene Block Copolymer (SBS) Modified Bitumen. *Arab. J. Sci. Eng.* **2022**, *47*, 12521–12533. [CrossRef]
13. Ji, C.; Zhao, S.; Peng, C. Analysis of Anti-aging Performance of Coffee Ground Charcoal Modified Asphalt Based on Rheological Parameters. *For. Eng.* **2020**, *36*, 118.
14. Calabi-Floody, A.; Thenoux, G. Controlling asphalt aging by inclusion of byproducts from red wine industry. *Constr. Build. Mater.* **2012**, *28*, 616–623. [CrossRef]
15. Rusbintardjo, G.; Hainin, M.R.; Yusoff, N.I. Fundamental and rheological properties of oil palm fruit ash modified bitumen. *Constr. Build. Mater.* **2013**, *49*, 702–711. [CrossRef]
16. Zhao, T.; Gao, M.L.; Zhang, G.M.; Zhu, S.L. Study on High Temperature Rheological Properties of Bamboo Powder Modified Asphalt. *For. Eng.* **2022**, *38*, 143–152. [CrossRef]
17. Cheng, Z.S. *Demand for Oil Will Exceed Supply After 2007*; China Petroleum & Chemical Corporation: Beijing, China, 2005; p. 53.
18. Jiang, Y.; Zhang, B.Q.; Li, G.J. Structure and Application of Lignin. *Liaoning Chem. Ind.* **2022**, *51*, 655–661. [CrossRef]
19. Singh, S.; Verma, J.P.; de Araujo Pereira, A.P.; Sivakumar, N. Book review: Production of biofuels and chemicals from lignin. *J. Clean. Prod.* **2018**, *203*, e966–e967. [CrossRef]
20. Yang, J.; Lv, X.J.; Wang, D.Z. Lignin Applied in Plastics. *Chin. Polym. Bull.* **2002**, *4*, 53–59.
21. Sun, Q.N.; Qin, T.F.; Li, G.Y. Progress on Activation and Application to Wood Adhesives of Lignin. *Chin. Polym. Bull.* **2008**, *9*, 55–60.
22. Terrel, R.L.; Rimsritong, S. *Wood Lignins Used as Extenders for Asphalt in Bituminous Pavements (with Discussion)*; Association of Asphalt Paving Technologists Proceedings: San Antonio, TX, USA, 1979; p. 48.
23. Sundstrom, D.W.; Klei, H.E.; Daubenspeck, T.H. Use of byproduct lignins as extenders in asphalt. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 496–500. [CrossRef]
24. van Vliet, D.; Slaghek, T.; Giezen, C.; Haaksman, I. Lignin as a green alternative for bitumen. In Proceedings of the 6th Euroasphalt & Eurobitume Congress, Prague, Czech, 1–3 June 2016; pp. 1–3. [CrossRef]
25. Zhang, J.; Deng, H.; Lin, L.; Sun, Y.; Pan, C.; Liu, S. Isolation and characterization of wheat straw lignin with a formic acid process. *Bioresour. Technol.* **2010**, *101*, 2311–2316. [CrossRef]
26. Batista, K.B.; Padilha, R.P.L.; Castro, T.O.; Pasa, V.M.D.; Lins, V.F.C.; Silva, C.F.S.C.; Leite, L.F.M.; Araújo, M.F.A.S. High-temperature, low-temperature andweathering aging performance of lignin modified asphalt binders. *Ind. Crop. Prod.* **2018**, *111*, 107–116. [CrossRef]
27. Pan, T. A first-principles based chemophysical environment for studying lignins as an asphalt antioxidant. *Constr. Build. Mater.* **2012**, *36*, 654–664. [CrossRef]
28. Xie, S.; Li, Q.; Karki, P.; Zhou, F.; Yuan, J.S. Lignin as renewable and superior asphalt binder modifier. *ACS Sustain. Chem. Eng.* **2017**, *5*, 2817–2823. [CrossRef]
29. Cai, M.; Zhao, X.; Han, X.; Du, P.; Su, Y.; Cheng, C. Effect of Thermal Oxygen Aging Mode on Rheological Properties and Compatibility of Lignin-Modified Asphalt Binder by Dynamic Shear Rheometer. *Polymers* **2022**, *14*, 3572. [CrossRef]
30. Su, Y.; Tang, S.; Cai, M.; Nie, Y.; Hu, B.; Wu, S.; Cheng, C. Thermal oxidative aging mechanism of lignin modified bitumen. *Constr. Build. Mater.* **2023**, *363*, 129863. [CrossRef]
31. Wu, J.; Liu, Q.; Wang, C.; Wu, W.; Han, W. Investigation of lignin as an alternative extender of bitumen for asphalt pavements. *J. Clean. Prod.* **2021**, *283*, 124663. [CrossRef]
32. Wu, X.; Chen, L.; Hui, Q.I. Effect of cobalt-60 gamma-ray irradiation on separation of components from corncob by formic acid. *J. Radiat. Res. Radiat. Process* **2018**, *36*, 1–8.
33. Zhu, S.; Wang, Z.; Yu, H.; Liu, Y. Fractionation of lignin and cellulose from *Pterocarpus macarocarpus* Kurz using formic acid. *J. Beijing Univ. Chem. Technol.* **2019**, *46*, 57.
34. Zhang, Y.; Qin, M.; Xu, W.; Fu, Y.; Wang, Z.; Li, Z.; Willför, S.; Xu, C.; Hou, Q. Structural changes of bamboo-derived lignin in an integrated process of autohydrolysis and formic acid inducing rapid delignification. *Ind. Crops Prod.* **2018**, *115*, 194–201. [CrossRef]

35. Wang, X.Q.; Ren, H.Q.; Zhao, R.J. FTIR and XPS Spectroscopic Studies of Photodegradation of Moso Bamboo (Phyllostachys Pubescens Mazel). *Spectrosc. Spectr. Anal.* **2009**, *29*, 1864–1867. [CrossRef]
36. Mills-Beale, J.; You, Z.; Fini, E.; Zada, B.; Lee, C.H.; Yap, Y.K. Aging influence on rheology properties of petroleum-based asphalt modified with bio-binder. *J. Mater. Civ. Eng.* **2012**, *26*, 121010200100007. [CrossRef]
37. Arafat, S.; Kumar, N.; Wasiuddin, N.M.; Owhe, E.O.; Lynam, J.G. Sustainable lignin to enhance asphalt binder ox-idative aging properties and mix properties. *J. Clean. Prod.* **2019**, *217*, 456–468. [CrossRef]
38. Zhuo, Z.G.; He, W.L.; Li, H.J. Evaluation of the asphalt anti-aging performance based on the failure temperature dynamic equations. *J. Transp. Sci. Eng.* **2019**, *35*, 1–8. [CrossRef]
39. Wang, G. Fatigue Performance Evaluation of Asphalt Binders Based on Linear Amplitude Sweep Test. *Pet. Asph.* **2018**, *32*, 45–50. [CrossRef]
40. Cao, L.P.; Tan, Y.Q.; Dong, Z.J.; Sun, L.J. Evaluation for Low Temperature Performance of SBS Modified Asphalt Using Glass Transition Temperature. *China J. Highw. Transp.* **2006**, *2*, 1–6. [CrossRef]
41. Murugan, P.; Mahinpey, N.; Johnson, K.E.; Wilson, M. Kinetics of the Pyrolysis of Lignin Using Thermogravimetric and Differential Scanning Calorimetry Methods. *Energy Fuels* **2008**, *22*, 2720–2724. [CrossRef]