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Research on the optimal dosage of Bio-Oil/Lignin composite modified asphalt based on rheological and Anti-Aging properties

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ABSTRACT

With the increasing awareness of environmental protection and attention to resource reuse, the development of high-performance and degradable green biomass pavement materials attracts a lot of interest. Lignin and bio-oil effectively combined to play a synergistic role can improve various properties of asphalt and partially replace petroleum-based asphalt. Therefore, this paper aims to study the rheological and aging properties of bio-oil/lignin composite modified asphalt (OLMA) and determine the optimal dosage by Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), and Fourier transforms infrared spectroscopy (FTIR) tests. From the DSR tests, it can be seen that OLMA can improve the high-temperature, fatigue, cracking, and relaxation performance of asphalt. BBR test obtained that OLMA can improve the asphalt's low-temperature performance and critical temperature. The method for evaluating the aging degree of composite modified asphalt was proposed. FTIR test results revealed that OLMA could reduce the increased rate of the aging index. The optimum dosage of 10% bio-oil and 20% lignin composite modified asphalt was determined. It proved that lignin and bio-oil are promising asphalt additives, modifiers, and replacements.

1. Introduction

Petroleum-based asphalt is an indispensable material in pavement construction [1]. However, as a product of petroleum crude oil refining, asphalt is a non-renewable resource formed by the remains of animals and plants in the long geological evolution [2]. As a result, asphalt reserves are decreasing, and prices are increasing [3]. At the same time, the asphalt production process will consume a lot of energy, generate greenhouse gases and cause the greenhouse effect. Therefore, using green resources to replace or modify petroleum-based asphalt is an inevitable trend in future developmentYang et al. [4]. Biomass is an essential green resource with large reserves, wide distribution, renewable and degradable properties. The total amount of 550 gigatons of carbon (Gt C) of biomass is distributed among the biosphere, and plant-based biomass is approximately 450 Gt C [5]. Therefore, it has recently attracted much attention as a modifier [6–8] or replacement for asphalt [9,10].

Lignin is the second most abundant natural polymer, which follows cellulose. The total amount of lignin currently on Earth is assessed at over 300 billion tons, with a growth of approximately 20 billion tons per year [11]. Furthermore, lignin ("Black Liquor"), as a by-product of the paper and pulp industry, has a worldwide production of 130 billion tons [12], but only 2% has been effectively used [13], and it is seriously polluting the environment and ecology. However, it is possible to extract high-purity lignin with little or no polluted water discharge through the organic solvent pulping method (OSPM), as shown in Fig. 1. In the preparation process of OSPM, lignin will participate less in chemical reactions, which can protect the original molecular structure and functional groups of lignin. Compared with other types of lignin (such as lignosulfonate, alkali lignin, etc.), it has the characteristics of a high proportion of active reactive groups, easy separation and purification from solvents, and fewer sulfur-containing impurities.

Lignin, known as "the ideal substitute for inexhaustible non-renewable materials," has attracted increasing attention as an asphalt substitute, modifier, and antioxidant. Van Vliet incorporated various lignin into asphalts and demonstrated that when 25 % lignin was added to the asphalt, it exhibited performance characteristics similar to polymers. In addition, lignin can improve its viscoelastic properties [10]. Arafat proved the feasibility of replacing 6 % petroleum-based asphalt binder with lignin in a hot mix asphalt mixture. The effect is better in a warm asphalt mixture with a lower construction temperature [14].

Lignin can play a modifying effect to improve various properties of asphalt. Norgbey pointed out that lignin can enhance the cohesion and adhesion of asphalt, which will reduce the asphalt's fluidity at high and

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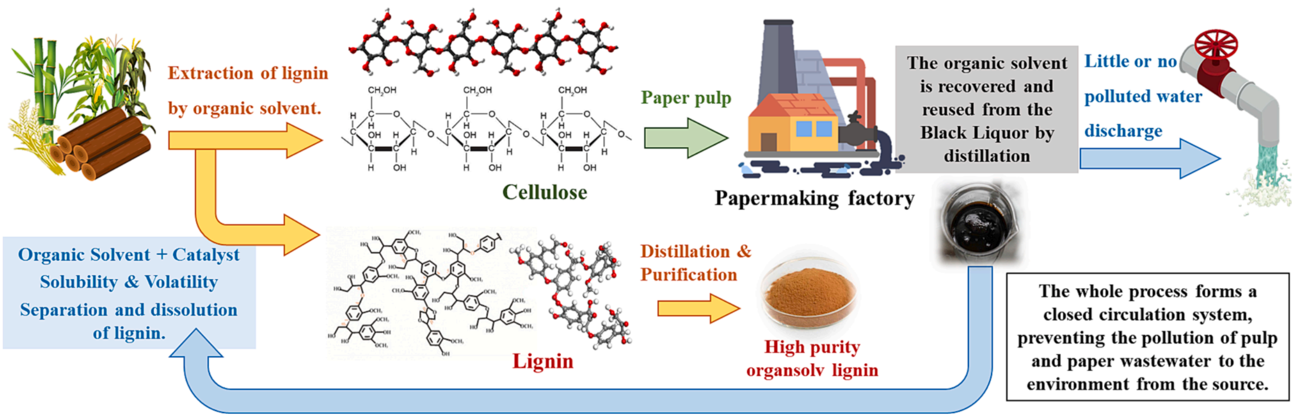


Fig. 1. Schematic diagram of the organic solvent pulping method.

low temperatures, and improve the recovery performance at high temperatures, reduce fatigue life [15]. By analyzing the physical and chemical properties of lignin-modified asphalt (LMA), Batista proved that lignin could enhance the resistance to permanent deformation, cracking, and photodegradation of asphalt [16]. Xu revealed that lignin could improve the rutting resistance and high-temperature stability of asphalt, and it negatively impacted its durability. In addition, lignin was found to increase the risk of cracking at low temperatures through the BBR test [6]. Gao found that lignin increases the viscosity and elastic components of asphalt binder, delays the oxidation reaction, and improves the resistance to deformation at high temperatures. In contrast, lignin reduces the fatigue life of asphalt [8]. The gap here is that most of the studies only point out, but limited studies have addressed, the deterioration of low temperature and fatigue performance of LMA.

The studies revealed that lignin could effectively delay the oxidation of asphalt and act as an antioxidant role in reducing the effect of aging on the durability of binders and mixtures. Xu calculated the functional group indexes of LMA under different aging states by FTIR and demonstrated that lignin could reduce the formation of aging functional groups such as carbonyl and sulfoxide during short-term and long-term aging [6]. Williams also characterized the aging states by quantifying the functional groups supplementing with PG tests to evaluate the effect of lignin on critical temperature. It was shown that the chemical reaction between asphalt and lignin promotes the inhibition of oxidative aging reaction Williams and McCready [17]. Boeriu used principal component and multi-factor analysis to establish the relationship between chemical composition and antioxidant capacity based on the fingerprint region of the lignin infrared spectrum [18]. Dizhbite used DPPH to measure and analyze the natural antioxidant effect of lignin from a chemical view, attributed the antioxidant effect to lignin's particular chemical structure, and the factors that affect the free radical scavenging ability were obtained [19]. However, the antioxidant mechanism of lignin remains to be further determined.

Bio-oil is mainly obtained through the fast pyrolysis process of biomass, including crop straw, grain husk, bark branches, bamboo bagasse, waste cooking oil, and livestock manure [21,20]. The pyrolysis temperature dramatically influences the yield and composition of bio-oil. The properties of bio-oil often affect the compatibility with asphalt, which further affects the road performance of modified asphalt. Zhang found that the bio-oil obtained from the waste wood chips was acidic and had a density similar to asphalt [22]. The study manifested that bio-oil and petroleum asphalt are mainly composed of four elements, C, H, O, and N, which have good compatibilityYang et al. [23]. Pütün proved that bio-oil obtained from rice straw, as a new green resource, has great potential value and prospects in the energy industry and materials industry through chemical characterization tests such as ^{1}H NMR, GC–MS, and FTIR [24].

Bio-oil, as a sustainable and renewable green new energy source, is similar in chemical element composition and properties to petroleum asphalt, making it possible for bio-oil to be compatible with petroleum-based asphalt and improve asphalt performance. Chemical and microscopic methods revealed the oxidative polymerization reaction of bio-oil and petroleum asphalt, and the oxidative polymerization reaction could increase the consistency of the binder [26]. Fini tried to extract bio-oil from swine manure, corn stover, wood pellet, and miscanthus pellet to prepare bio-oil modified asphalt (BMA) to improve the low-temperature performance of asphaltFini et al. [27]. Wen used bio-asphalt as an alternative binder for petroleum-based asphalt, and the content of bio-oil was 0%, 10%, 30%, and 60%, respectively. It was shown that incorporating bio-oil improves the resistance to thermal cracking but reduces the permanent deformation resistance of the mixture at high temperatures [25]. Bio-oil can reduce the viscosity-temperature range of asphalt by 30 ~ 40 ℃ compared with virgin asphalt, which is beneficial to improve the workability of asphalt mixture and minimize energy consumption. However, the improvement in low-temperature performance is parallel with a decrease in high-temperature performance [28].

Researchers have tried composite modifications of bio-oil and other modifiers or additives to improve the negative impact of bio-oil on the high-temperature performance of the asphalt. Zhang enhanced the high-temperature performance by adding SBS to the BMA, adding 1 % SBS to the 5 %, 10 %, 15 %, and 20 % bio-oil-modified asphalt, respectively. It was shown that SBS could significantly improve the high-temperature viscosity and anti-rutting performance of composite modified asphalt and reduce the sensitivity of performance to temperature. However, the content of bio-oil has little effect on performance at high temperaturesZhang et al. [29,33]. Adding 10 % and 15 % rubber powder to the bio-asphalt, the results showed that the rubber powder and bio-asphalt have good compatibility, and the PG classification at high temperatures is improved [30]. Raouf modified oak-based bio-oil with 2 % and 4 % polyethylene, showed that the rheological properties of modified oak-based bio-oil were similar to asphalt, and verified its possibility as a renewable alternative to petroleum asphaltRaouf and Williams [31]. However, the research on OLMA is almost blank.

2. Objective

This study uses biomass, lignin, and bio-oil as substitutes or modifiers in asphalt to improve the various rheological and aging properties. Dynamic shear rheometer (DSR) methods were employed to evaluate the rheological performances of binders. The Frequency Sweep measured the viscoelastic behavior of the binders. Temperature Sweep and Multiple Stress Creep Recovery (MSCR) tests were performed to measure the high-temperature properties, including stability and resistance to rutting. The fatigue behavior was examined by Linear Amplitude Sweep (LAS) tests. The low-temperature properties, including the relaxation and thermal cracking resistance, were assessed by Relaxation

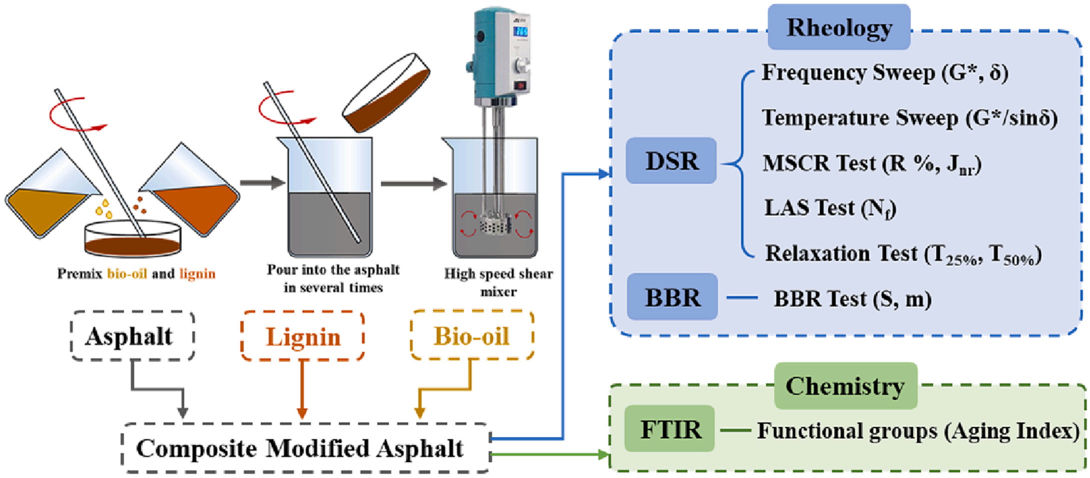
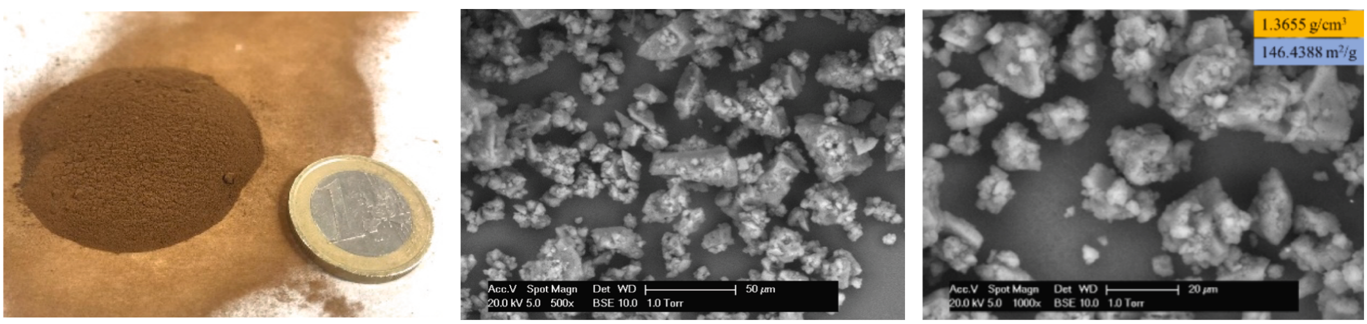


Fig. 2. The framework and research program.



(a) (b) (c)

Fig. 3. Images of lignin (a) Appearance; (b) ESEM image (×500); (c) ESEM image (×1000).

and Bending Beam Rheometer (BBR) tests. The Fourier transforms infrared spectroscopy (FTIR) tests were derived to characterize the aging states and anti-aging effects. Therefore, this study aims to (1) explore the various rheological properties and aging behaviors of the OLMA through rheological and chemical analysis; (2) verify whether the synergistic effect of lignin and bio-oil could improve the high-temperature performance of LMA and low-temperature performance of BMA; (3) reveal the anti-aging mechanism of OLMA; (4) determine the optimum dosage of composite modified asphalt based on the performance balance theory. The framework and research program of this study were showed in Fig. 2.

3. Materials and methodology

3.1. Materials

This study was implemented to solve the problem of environmental pollution and improve the efficient reuse of waste resources, lignin derived from the by-product "black liquor" of the paper and pulping industry. Organsolv lignin has the characteristics of low extraction conditions, no pollution from desulfurization, and high polymerization and purity. On the other hand, the modification and anti-oxidation effects of asphalt are more prominent.

The visual and Environmental scanning electron microscope (ESEM) images of lignin are shown in Fig. 3. Lignin was a nutbrown, fine, and homogeneous powder with a purity of over 90%. The microscopic surface was rough and porous, which could better bond with the asphalt to prevent segregation. The particle size differs from 20 to 100 μm, and some lignin particles have significant angularity.

The density and specific surface area of lignin were 1.3655 g/cm^3 and 146.4388 m^2/g measured by Helium Pycnometer and Dynamic Vapor Sorption (DVS), respectively. Other basic properties are listed in Table 1. Lignin is composed of 61.8 % carbon, 31.1 % oxygen, 5.4 % hydrogen, and 1.7 % other elements (Fig. 4).

The DTG (Derivative Thermal Gravity, DTG) curve of lignin was measured by Thermogravimetric Analysis (TGA), as illustrated in Fig. 4. Lignin suffers from a complex thermal decomposition process, which mainly contains three stages, and the peaks of mass loss rate occur at 111.098, 234.898, and 352.698 °C. When the temperature was 200 °C, the mass loss rate of lignin was only 5.086 %. Compared with asphalt, it had a lower thermal decomposition rate, higher quality preservation rate, and better thermal stability.

The plant-based pyrolysis bio-oil was employed in this study, mainly derived from waste crop straw. Bio-oil has fluidity at room temperature, and its appearance is a dark brown liquid, as shown in Fig. 5. Its basic properties, such as density, viscosity at room temperature, and PH, are shown in Table 1. The chemical element composition in the bio-oil was determined by an organic element analyzer (Elementar Vario EL cube). The results are illustrated in Fig. 5. The mass fractions of the main elements C, H, and O were 76.4 %, 11.9 %, and 11.4 %, and the elements N and S were less than 0.2 % and 0.1 %, respectively. The PG 64–22 virgin asphalt with a 71.4 penetration and a softening point of 47.5 °C was selected. The main performances are listed in Table 1.

3.2. Determination of modifier content and sample preparation

In order to study the effects of different contents of bio-oil and lignin on the rheological and anti-aging properties of asphalt, explore the

Table 1
The primary performance parameters of materials.

Materials	Properties	Unit	Value	Requirements
Organosolv Lignin	Purity	%	93.5	≥ 80
	Residual sugar	%	0.19	≤ 5
	Ash	%	1.6	≤ 5
	Density (Fresh)	g/cm^3	1.3774	–
	Specific surface area (Fresh)	m^2/g	147.0593	–
	Density (Aged)	g/cm^3	1.5029	–
	Specific surface area (Aged)	m^2/g	65.0475	–
Bio-oil	Density (25 °C)	g/cm^3	1.011	–
	Viscosity (25 °C)	Pa·s	0.25	–
	PH	–	3.2	–
	Flash Point	℃	7.2	–
	Moisture	%	265 ~ 305	–
Asphalt	Density (15 °C)	g/cm^3	1.021	–
	Penetration (25 °C)	0.1 mm	71.4	60 ~ 800
	Softening point	°C	46.5	≥ 43
	Ductility (5 cm/mm, 15 °C)	cm	> 100	> 100
	Flash Point	℃	312	≥ 260
	Wax Content	%	1.6	≤ 4.5
	TFOT Residue: Mass change	%	−0.22	−0.8 ~ +0.8
	TFOT Residue: Penetration ratio (25 °C)	%	68.2	≥ 61
	TFOT Residue: Ductility (10 °C)	cm	19.5	≥ 6

modification mechanism of the synergistic effect of bio-oil and lignin, and verify whether biomass could play a role in replacing petroleum-based asphalt. Based on large number of lignin modified asphalt (LMA) and bio-oil modified asphalt (BMA) research literature, the statistics of different content of lignin or bio-oil in the asphalt were shown in Fig. 6. The composite modified asphalt samples with various contents of lignin and bio-oil were designed, and the contents and labels of the composite modified asphalt samples were shown in Table 2.

The asphalt and lignin were preheated in a 165 ℃ oven and turned on a heating system of the high shear mixer. When the temperature reached 165 °C, the corresponding amount of lignin and bio-oil were poured into the stirring pan and pre-mixed with a stirring rod. Afterward, the preheated asphalt and lignin-bio-oil were transferred into the mixer pot, and a stirring rod was used for pre-mix. Finally, a high shear mixer was employed to mix the composite modified binders at 165 °C, 4000 rpm, and for 30 min.

The long-term aging of binders was performed with the Pressure Aging Vessel (PAV) device according to ASTM D6521. The PAV aging program was conducted after a Thin-film oven test (TFOT) at 163 °C and 5 h for short-term aging based on ASTM D1754. Then the samples were put in the PAV unit at 100 °C, 2.1 MPa for 20 h.

3.3. *Frequency sweep and temperature sweep*

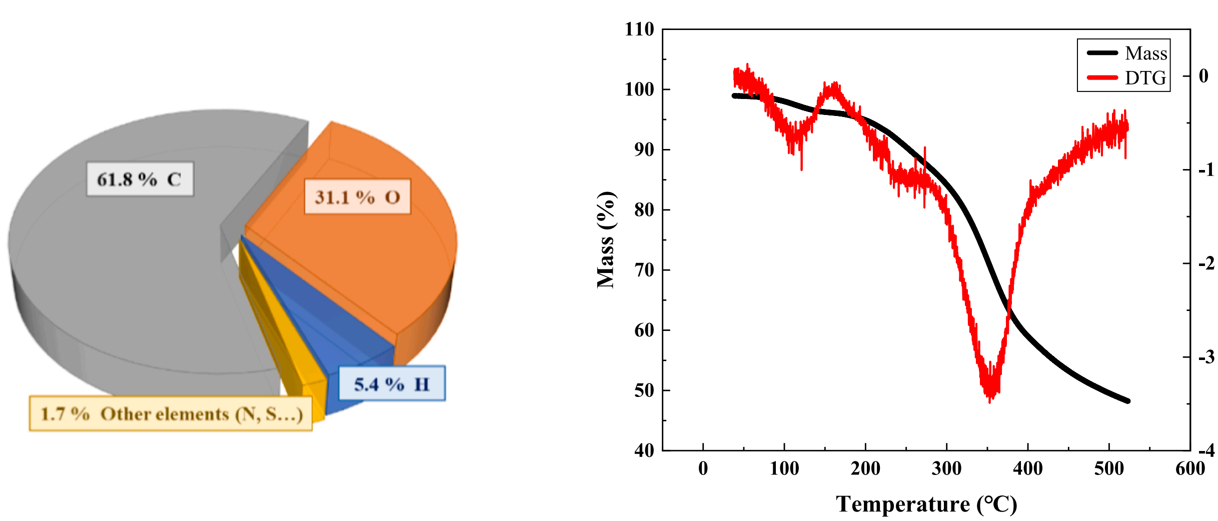
The complex shear modulus (G*) and phase angle (δ) of asphalt were tested by a DSR following AASHTO T 315–19. The configuration geometry of the testing parallel plate was a 2 mm gap and 8 mm in diameter, and the testing temperature range was 0 to 30 °C. The configuration of the 25 mm diameter and 1 mm gap was subjected to the elevated temperature, 30 to 60 °C. The frequency was performed from 100 to 0.1 rad/s. The 30 °C was the reference temperature, then the master curves of G* and δ were constructed by the sigmoidal model [32]. Three replications of each binder in fresh and PAV aged were tested. Moreover, the temperature sweep test was performed on the asphalt samples at 52, 58, 64, 70, and 76 °C with a constant sweep frequency of 10 rad/s, and the rutting factors (G*/sinδ) of binders in short-term aged were calculated to assess the properties and resistances.

3.4. *Multiple stress creep and recovery (MSCR)*

The MSCR tests measured the elastic response and stress dependence of asphalt binders under representative stress levels and temperatures

(a) (b)

Fig. 5. Image and elemental analysis of bio-oil (a) Appearance; (b) Elemental composition.



(a) (b)

Fig. 4. Elemental analysis and TGA of lignin (a) Elemental composition; (b) DTG Curves.

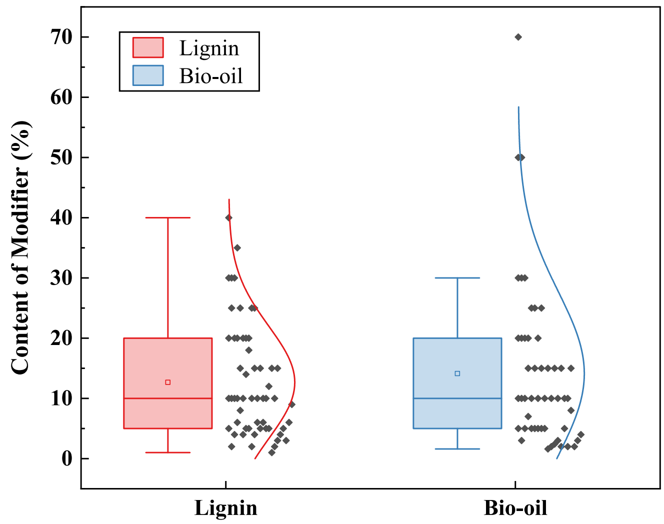


Fig. 6. Content statistics of bio-oil and lignin.

Table 2
Sample content and label of OLMA.

Label		Lignin dosage (wt%)			
		0	10	20	30
Bio-oil dosage (wt%)	0	Bref	BL10	BL20	BL30
	5	BO5	BO5L10	BO5L20	BO5L30
	10	BO10	BO10L10	BO10L20	BO10L20
	15	BO15	BO15L10	BO15L20	BO15L20

(ASTM D 7405–15). The binders were tested by a load for 1 s and recovered for 9 s in every cycle. Twenty cycles were applied first at 0.1 kPa and then ten cycles under the 3.2 kPa stress level. The first 10 cycles under 100 Pa were performed for the preconditioning of binders. The testing temperature was 52, 58, 64, and 70 °C. The recoverability to the initial mechanical condition is characterized by the R%, while the J_{nr} implies the residual strain after the cycle.

3.5. Linear amplitude sweep (LAS)

The cyclic load with strain amplitudes increases linearly to evaluate the fatigue performance of binders. The testing plates with a 2 mm gap and 8 mm diameter were used in LAS tests according to AASHTO TP 101–14. The LAS test was programmed as follows: the first step was the frequency sweep to evaluate the rheological properties of asphalt. The test applied an oscillatory shear load of 0.1% strain at 12 typical frequencies from 0.2 to 30 Hz. The studied samples were performed on the strain sweep at 10 Hz in the second step. At the temperature of 20 °C, continuous oscillatory cycles with strain increasing from 0% to 30% were employed to accelerate the fatigue damage. The fatigue life of asphalt binders is significantly affected by the aging process. Fresh and long-term aged samples were measured by the LAS test.

3.6. Relaxation test

The ability of binders to release stress after the stress relaxation tests determined an invariable strain. The configuration geometry of the testing parallel plate was 2 mm in the gap and 8 mm in diameter was performed in DSR. The test was under strain-controlled mode, the temperature was 0 °C, and the aging condition was fresh and PAV aged. The experiment was designed in two parts, the first part was the strain rose from 0 to 1 % in 0.1 s, and the second part was to keep the constant 1% shear strain in a relaxation time of 100 s.

3.7. Bending Beam Rheometer (BBR) test

To better evaluate the low-temperature properties, thermal cracking, and relaxation of asphalt, the stiffness modulus (s) and creep rate (m) were measured by the Bending Beam Rheometer (BBR). The Pressure Aging Vessel (PAV) aged asphalt was poured into the standard aluminum mold, the configuration geometry of the demolded beam was 6.35 mm thick by 12.7 mm wide by 127 mm long, and then was conducted at −6, −12, and −18 °C under seating load 980 ± 50 mN. The data acquisition system of the rheometer automatically recorded the load and displacement at the loading time of 0, 0.5, 8, 15, 30, 60, 120, and 240 s.

3.8. Fourier transforms infrared spectroscopy (FTIR) test

The Fourier transform infrared spectrometer with attenuated total reflectance (ATR) was employed in this research to measure the spectra of samples. The different absorption spectra were directly related to the chemical functional groups contained in the material. The wavenumber ranged from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Nine replications for each sample were analyzed. Changes in functional group

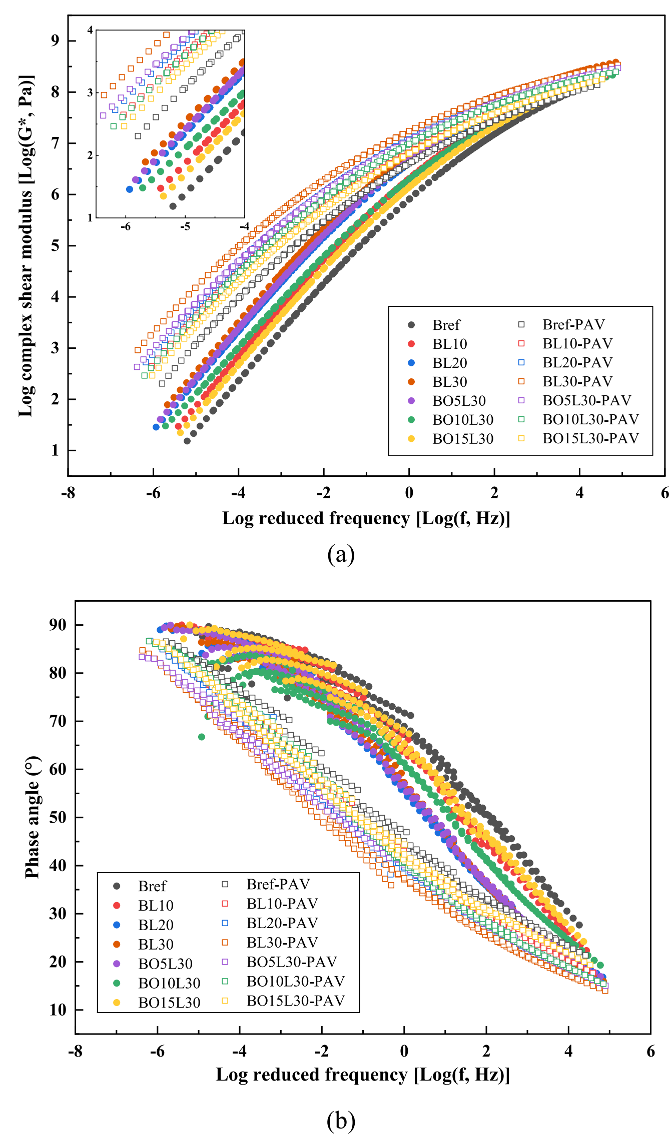


Fig. 7. (a) The complex shear modulus G* and (b) the phase angle δ master curves.

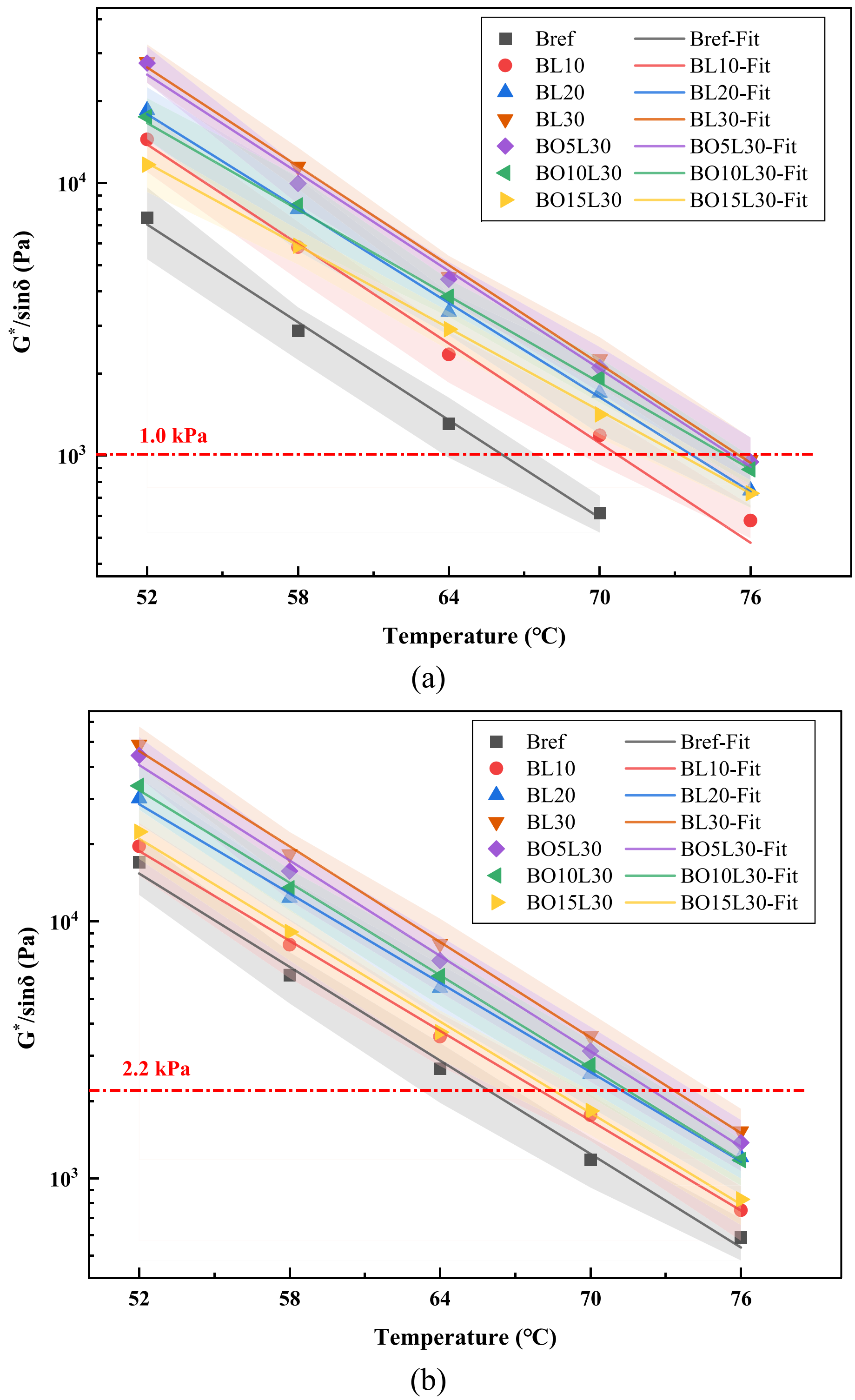


Fig. 8. Rutting factor and fitted curves of fresh (a) and short-term aged asphalt (b).

concentration were assessed by the absorption index (AI), which was determined as

$$AI = \frac{A_{ab}}{\sum A} \quad (1)$$

where A_{ab} is the integral area of absorption band ab, $\sum A$ is the sum of the integral areas of several characteristic functional group peaks. The wavenumbers of typical bands of chemical functional groups of different materials were summarized in previous studies [1,22].

The carbonyl and sulfoxide were analyzed as conventional aging indices for lignin-bio-oil-asphalt systems. Lignin and bio-oil, as biomass, also had carbonyl and sulfoxide, which would influence the analysis of the anti-aging effect of binders. The carbonyl and sulfoxide aging indexes were added to obtain the Combined Aging Index (CAI) for further analysis, which was calculated as shown follows

$$CAI = AI_{c=o} + AI_{s=o} = \frac{A_{c=o}}{\sum A} + \frac{A_{s=o}}{\sum A} \quad (2)$$

$$\Delta CAI = \Delta AI_{c=o} + \Delta AI_{s=o} = \frac{A_{c=o,Aged} - A_{c=o,Fresh}}{\sum A} + \frac{A_{s=o,Aged} - A_{s=o,Fresh}}{\sum A} \quad (3)$$

4. Results and discussion

4.1. Frequency sweep and temperature sweep

During the frequency sweep tests, the complex shear modulus (G*) and phase angle (δ) of each sample in the temperature range of 0 to 60 °C were measured. The complex shear modulus-frequency curve and the phase angle-frequency curve were obtained by fitting the data at different temperatures through the sigmoidal function model. The frequency range was wide, and the overall curve was smooth. To more accurately estimate the influence of lignin and bio-oil on the master curve, the G* and δ master curves of asphalt samples were selected and analyzed, as shown in Fig. 7.

The X-axis coordinate was the frequency, and the Y-axis coordinate was the G* and δ. Generally, asphalt with a higher G* shows greater resistance to deformation, while the larger the δ, the more viscous the asphalt is. The smaller the δ, the shorter the response delay between stress and strain, and the stronger the elasticity of asphalt. The G* increased with increasing frequency, and conversely, the δ decreased. The G* of all samples was relatively close in the high-frequency region (low temperature), while the difference was larger in the low-frequency range (high temperature).

As the aging progressed, the G* of the PAV aged binders rose, and the δ declined. It was attributed to the conversion of light components with smaller molecular weights into heavy components with larger molecular weights in the asphalt by thermal oxygen reaction; At the same time, there were also physical changes in the volatilization of lightweight components and the aggregation of heavy components, which will lead to the hardening effect of asphalt. Harder asphalt exhibited more elasticity and greater resistance to deformation.

As the lignin content in asphalt increased from 0 % to 30 % (for example, Bref, BL10, BL20, and BL30), the G* increased and the δ decreased, and the curves of modulus had an upward trend with the increase of lignin content, and the δ curves had a downward trend. Lignin enhanced the molecular polarity and intermolecular forces in the modified asphalt binder.

With the increase of bio-oil content in the composite modified asphalt (BL30, BO5L30, BO10L30, and BO15L30 as examples), the G* master curve showed a gradually decreasing trend, while the δ curve showed an increasing trend. The higher the content of bio-oil, the more obvious the changing trend. It was indicated that bio-oil reduced the binder hardness and recoverable ability, making the asphalt softer and more prone to plastic deformation.

The rutting factor (G*/sinδ) is the main index to characterize the high-temperature performance of the binder, and it is also an important basis for the performance grading of asphalt. To explore the effects of lignin and bio-oil on the rutting factor of asphalt at different temperatures, the rutting factors of some samples were selected and plotted in Fig. 8, where the light-colored filled area represented the error bar.

It can be seen that there is a significant relationship between the rutting factor and the test temperature in the logarithmic coordinate system. Importantly, the rutting factor decreased with the increase in temperature, indicating that the higher the temperature, the worse the rutting resistance. As the temperature rises, the asphalt changes from viscoelastic to viscous, the G* decreases, the strain response and stress delay time increase, so the G*/sinδ decrease. As the aging progressed, the rutting factor at the same temperature increased significantly, and the correlation curves of the rutting factor shifted upwards accordingly. It was corroborated that the permanent deformation resistance and high-temperature stability of asphalt after aging were improved, strongly related to the hardening effect in the aging process. Therefore, the critical conditions for PG classification under different aging states differ significantly. The G*/sinδ should not be less than 1.0 kPa for fresh specimens and should not be less than 2.2 kPa for short-term aged samples.

Table 3
Rutting factor fitting function and critical temperature.

Label	Fresh G*/sinδ fitting curve	T_c	Short-term aged G*/sinδ fitting curve	T_c	PG Temp
Bref	$y = 9.123 \times 10^6 e^{-0.1378x}$	66.17	$y = 2.197 \times 10^7 e^{-0.1397x}$	65.92	64
BL10	$y = 2.045 \times 10^7 e^{-0.1403x}$	70.75	$y = 2.029 \times 10^7 e^{-0.1343x}$	67.98	64
BL20	$y = 1.807 \times 10^7 e^{-0.1330x}$	73.70	$y = 2.963 \times 10^7 e^{-0.1335x}$	71.22	70
BL30	$y = 3.723 \times 10^7 e^{-0.1393x}$	75.56	$y = 7.744 \times 10^7 e^{-0.1428x}$	73.31	70
BO5	$y = 7.937 \times 10^6 e^{-0.1361x}$	65.98	$y = 1.452 \times 10^7 e^{-0.1345x}$	65.39	64
BO5L10	$y = 1.485 \times 10^7 e^{-0.1382x}$	69.50	$y = 1.677 \times 10^7 e^{-0.1327x}$	67.36	64
BO5L20	$y = 1.522 \times 10^7 e^{-0.1324x}$	72.73	$y = 2.747 \times 10^7 e^{-0.1332x}$	70.81	70
BO5L30	$y = 3.326 \times 10^7 e^{-0.1383x}$	75.29	$y = 6.751 \times 10^7 e^{-0.1426x}$	72.45	70
BO10	$y = 3.367 \times 10^6 e^{-0.1240x}$	65.50	$y = 6.396 \times 10^6 e^{-0.1275x}$	62.55	58
BO10L10	$y = 5.592 \times 10^6 e^{-0.1264x}$	68.27	$y = 9.983 \times 10^6 e^{-0.1293x}$	65.12	64
BO10L20	$y = 7.074 \times 10^6 e^{-0.1233x}$	71.89	$y = 1.758 \times 10^7 e^{-0.1281x}$	70.15	70
BO10L30	$y = 9.410 \times 10^6 e^{-0.1219x}$	75.06	$y = 4.310 \times 10^7 e^{-0.1383x}$	71.46	70
BO15	$y = 1.963 \times 10^6 e^{-0.1184x}$	64.04	$y = 4.871 \times 10^6 e^{-0.1224x}$	62.93	58
BO15L10	$y = 2.457 \times 10^6 e^{-0.1207x}$	64.68	$y = 6.884 \times 10^6 e^{-0.1257x}$	64.03	64
BO15L20	$y = 3.649 \times 10^6 e^{-0.1197x}$	68.52	$y = 1.042 \times 10^7 e^{-0.1272x}$	66.53	64
BO15L30	$y = 5.046 \times 10^6 e^{-0.1164x}$	73.25	$y = 2.553 \times 10^7 e^{-0.1366x}$	68.51	64

The rutting factor under different aging conditions enlarged with lignin content increased from 0 % to 30 %. Meanwhile, the G*/sinδ at 64 ℃ increased from 1306 Pa to 2351, 3365, and 4527 Pa, which were raised by 1.80, 2.58, and 3.47 times, respectively; While increased from 616 Pa to 1185, 1698, and 2257 Pa, correspondingly increased by 1.92, 2.768 and 3.66 times at 70 ℃; After short-term aging, the G*/sinδ at 64 °C increased from 2667 Pa to 3565, 5504, and 8191 Pa, which were increased by 33.67 %, 106.37 %, and 207.12 %, respectively; While increased from 1180 Pa to 1760, 2552, and 3580 Pa, with an increase of 49.15 %, 116.27 %, and 203.39 % at 70 ℃. It was demonstrated that lignin could enhance the rutting factor and significantly improve the high-temperature rutting resistance of asphalt.

The rutting factor decreased slightly with the increase of bio-oil content in the composite modified asphalt (BL30, BO5L30, BO10L30, and BO15L30). The G*/sinδ at 64 ℃ decreased from 4527 Pa to 4438, 3229, and 3108 Pa, which reduced by 1.97%, 28.67%, and 31.35%, respectively; While decreased from 2257 Pa to 2105, 1924, and 1413 Pa at 70 ℃, correspondingly decreased by 6.73 %, 14.75 %, and 37.39 %. It indicated that bio-oil would slightly reduce the rutting factor of the composite modified asphalt, thereby affecting the high-temperature stability. The rutting factors were fitted to obtain function curves. Taking G*/sinδ = 1.0 kPa and 2.2 kPa as the critical conditions, the temperature sensitivity of the rutting resistance and critical temperature (T_c) of the composite modified asphalt were calculated and analyzed, as shown in Table 3.

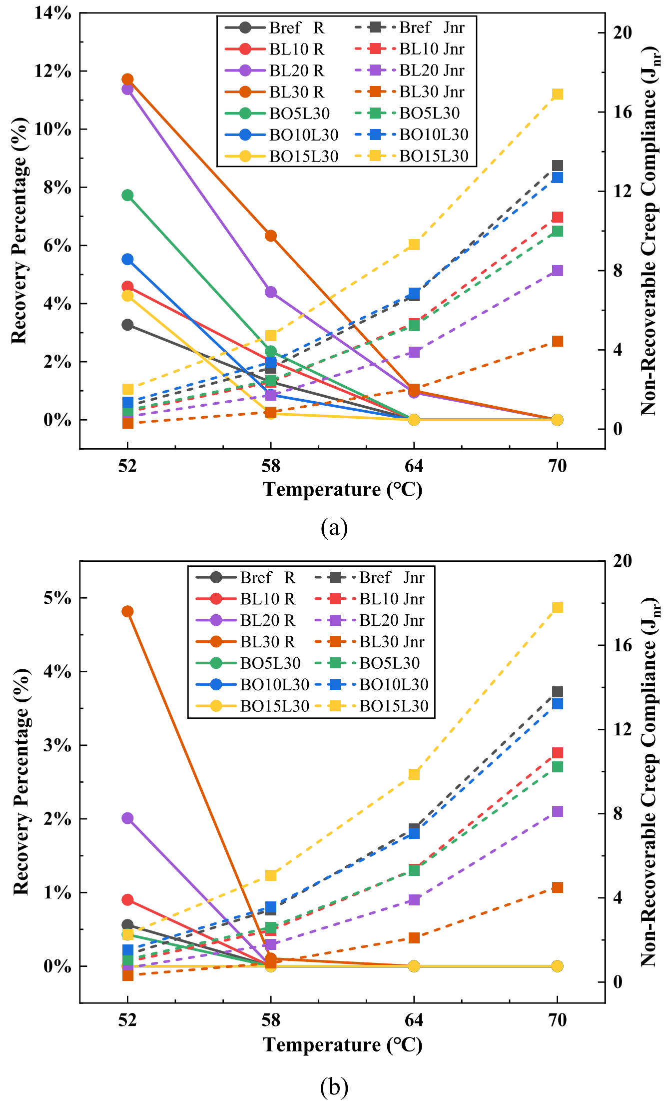


Fig. 9. R and J_{nr} of modified asphalt (a) 0.1 kPa and (b) 3.2 kPa.

The slope parameters of the correlation functions in the logarithmic coordinate system represent the temperature sensitivity. The larger the slope value, the more sensitive the material is to temperature, and the faster the rutting factor decreases with temperature increase. Table 3 displays that the slope of the function of the samples in both aged and unaged became flat with the increment in bio-oil content. It implied that bio-oil could reduce the temperature sensitivity of composite modified asphalt high-temperature performance, while lignin has no significant effect on the temperature sensitivity. The slope of the function tends to become steeper with the increase of lignin content.

Lignin significantly improved the performance grading of asphalt. With the increase of lignin content in asphalt (from 0 % to 30 %), the critical temperature of modified asphalt increases from 66.17 ℃ to 70.75, 73.70, and 75.56 ℃, from PG 64 to PG 70, especially BL30 was very close to PG 76. The improvement effect after aging was also obvious, increasing from 65.92 ℃ to 67.98, 71.22, and 73.31 ℃. Although bio-oil will slightly reduce the critical temperature, an appropriate dosage of lignin and bio-oil could still improve T_c of the high-temperature performance of composite modified asphalt.

4.2. MSCR test

MSCR tests were conducted at a low-stress level of 0.1 kPa and a high-stress level of 3.2 kPa with test temperatures of 52, 58, 64 and 70 °C respectively. To quantify the effect of lignin and bio-oil on high-temperature performance. The MSCR test load curves were processed and the Recovery Percentage (R %) and Non-Recoverable Creep Compliance (J_{nr}) of the samples were calculated according to the specification ASTM D7405-15. Generally a higher R % indicates a more elastic material while a lower J_{nr} indicates a stiffer and more rigid material. R % and J_{nr} were plotted for different doses of modified asphalt at different stress levels (0.1 and 3.2 kPa) respectively as shown in Fig. 9.

It can be seen that the stress level and temperature conditions have significant effects on the R and Jnr of the samples from Fig. 9. As the stress level rises from 0.1 kPa to 3.2 kPa, R decreases while Jnr slightly increases. As the temperature gradually increased from 52 °C to 70 °C, R decreased and Jnr increased remarkably, and the change trends were consistent for all samples. The R of Bref decreased from 3.27 % to 0 %, and Jnr increased from 1.17 to 13.3 when the temperature rose from 52 °C to 70 °C. It results from the asphalt being more fluid, less viscous and stiff, worse elastic resilience at high temperatures, so it is more prone to deformation at high temperatures.

Lignin had a distinct effect on the R % and J_{nr}, R significantly increasing and Jnr significantly decreasing with increasing lignin incorporation. For example, the R at 52 °C was 4.58 %, 11.38 %, and 11.71 % for asphalt with 10 %, 20 %, and 30 % lignin, respectively, 1.40, 3.48, and 3.58 times that of the virgin asphalt, while the J_{nr} at 70 °C was 10.7, 8.0 and 4.43 respectively, a reduction of 19.5 %, 39.8 %, and 66.7 % compared to the neat asphalt.

The following effects of lignin are mainly caused: (1) lignin as a granular modifier, with a porous, rough surface and large specific surface area, etc., will adsorb some of the lighter components when mixed into asphalt; (2) lignin contains a large number of molecules with molar masses in the range of 600 ~ 1000 g/mol and aromatic compounds, the benzene ring structure is the most important rigid group that will cause an increase in asphalt hardness. And there is π-π stacking interaction (face-to-face and edge-to-face interaction) between aromatic molecules, which is a covalent bonding interaction as important as hydrogen bonding and a special spatial arrangement between aromatic molecules; (3) lignin also contains a large number of polar functional groups such as carboxylic acid groups (–COOH), phenolic hydroxyl groups (Ar-OH), hydroxyl groups (–OH), and amino groups (–NH2). On the other hand, the incorporation of lignin into asphalt increases the molecular polarity of the system and enhances dipole–dipole interactions. In summary, the addition of lignin makes the asphalt harder, on the one hand, increases the molecular polarity and intermolecular forces in the system and improves the adhesion properties of the asphalt, thus improving the resistance to deformation and rutting, and high-temperature stability of the asphalt.

As the bio-oil content of the composite modified asphalt increased, R decreased while J_{nr} increased. The R at 52 °C were 7.73, 5.52, and 4.27 % for the 30 % lignin blending with 5 %, 10 %, and 15 % bio-oil, which were 33.99 %, 52.86 %, and 63.54 % lower than BL30, but all higher than the neat asphalt; While The R at 58 °C were 2.36, 0.86, and 0.21 %, which were 62.72, 86.41, and 96.68 % lower than BL30, and the BO10L30 and BO15L30 were lower than that of Bref; The J_{nr} at 70 °C was 10.1, 12.7, and 16.9, was 2.28, 2.87, and 3.81 times that of BL30 respectively. The properties of the BO10L30 were similar to those of the Bref, and the hardness of BO15L30 was less than that of the Bref. Bio-oil reduced the hardness and recoverability, making the binder softer and more susceptible to plastic deformation, and therefore bio-oil had a negative impact on high-temperature performance. It is mainly explained that bio-oil contains molecules with molar masses in the range of 100 ~ 200 g/mol, which is close to the molecular weight and properties of the lighter components of asphalt. The involvement of bio-oil supplements the lighter components of the system. It has a similar effect to that of rejuvenators and regenerators, reducing the hardness and stiffness of the system and increasing its fluidity.

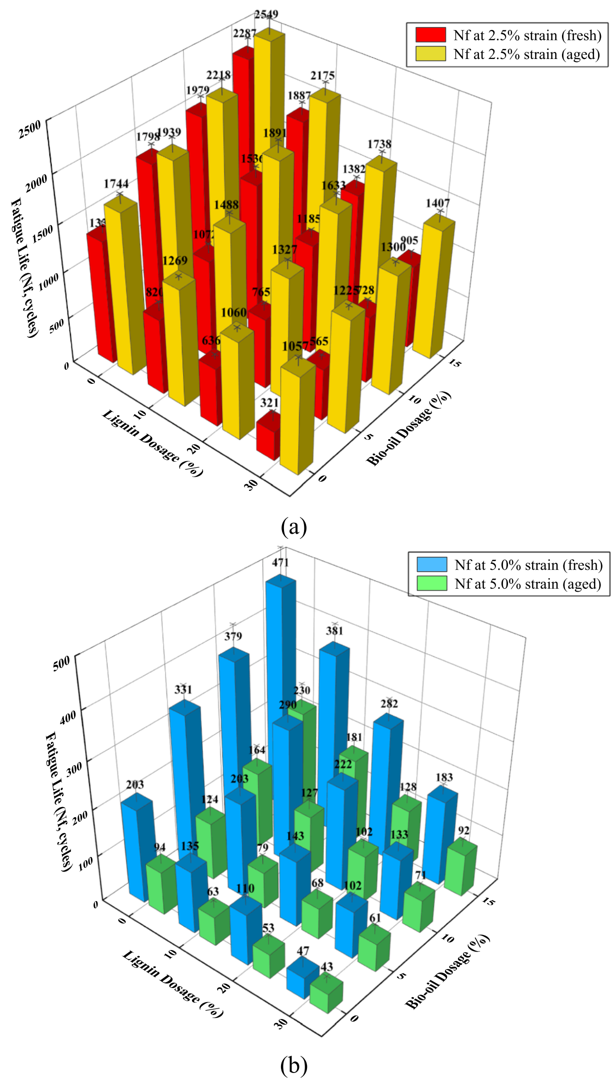


Fig. 10. Fatigue life at different strain levels (a) 2.5 % and (b) 5.0 %.

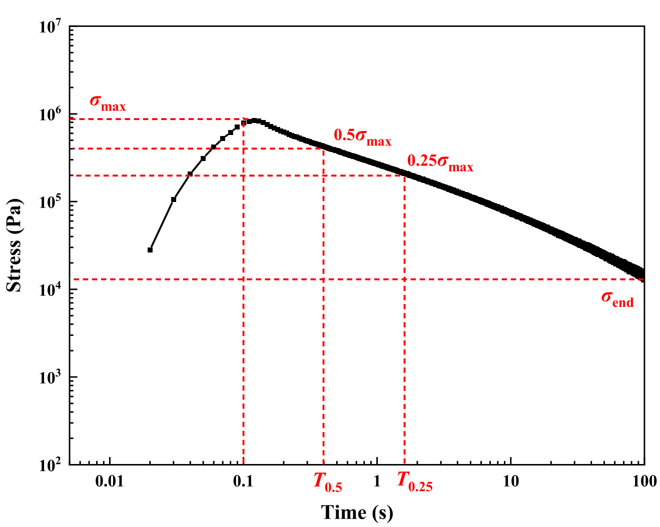


Fig. 11. Schematic diagram of the relaxation test load.

4.3. LAS test

The LAS test assesses the fatigue behavior of different asphalt binders utilizing cyclic loading with linearly increasing strain amplitude. The fatigue damage parameters were calculated according to AASHTO TP 101–14. The fatigue performance parameter N_f (fatigue life) was specifically analyzed for two typical strain levels ($\gamma = 2.5$ % and $\gamma = 5.0$ %). N_f also represented the number of load cycles at failure. The N_f of the sample before and after aging is shown in Fig. 10 and Fig. 11.

The X-axis is the lignin dosage, the Y-axis is the bio-oil dosage, and the Z-axis is the fatigue life. The N_f of Bref was 1335 at 2.5 % strain level and 203 at 5.0 % strain level. It was clear that the N_f decreased significantly with increasing strain levels, suggesting that the binder was more susceptible to damage failure at higher strain levels. After the aging process, the N_f increased at low strain levels, from 1335 to 1744, and decreased at high strain levels, from 203 to 94, indicating that the hardening effect of aging caused the binder to be more susceptible to damage at high strain levels while had a slight strengthening effect on low strain levels.

When the lignin content in asphalt was increased from 0 % to 30 %, the N_f at 2.5 % decreased from 1335 to 820, 636, and 321 with a decrease of 38.58 %, 52.36 %, and 75.96 %, respectively, while the N_f at 5.0 % decreased from 203 to 135, 110 and 47 with a decrease of 33.50 %, 45.81 %, and 76.85 % respectively. It revealed that the higher the lignin dosage, the greater the decrease in fatigue life and the worse the fatigue performance of the asphalt. A major reason for this was that lignin increased the cross-linkage and hardness of the asphalt. Stiffer asphalt binders, although more resistant to deformation at high temperatures, were more susceptible to damage under repeated loads with linearly increasing strains.

Bio-oil considerably increased the fatigue performance of asphalt. With a gradual increase in bio-oil content, the N_f increased from 1335 to 1798, 1979 and 2287 at 2.5 %, corresponding to 34.68 %, 48.24 % and 71.31 %, respectively, and from 203 to 331, 379 and 471 at 5.0 %, corresponding to 63.05 %, 86.70 % and 132.02 %. In addition, the composite modification improved and resolved the effect of lignin on fatigue performance. Take the BL30, BO5L30, BO10L30, and BO15L30 as examples, when the bio-oil content was 5 %, 10 %, and 15 %, the N_f at 2.5 % increased from 321 to 565, 728, and 905, an increase of 1.76, 2.27 and 2.82 times; while the N_f at 5.0 % increased from 47 to 102, 133 and 183, an increase of 2.17, 2.83 and 3.89 times. This was attributed to the incorporation of bio-oil, changing the component distribution of the OLMA system, supplementing the lighter components of the asphalt, and softening the binder while increasing the fatigue life and reducing fatigue damage sensitivity.

4.4. Relaxation test

The Relaxation Test is designed to characterize the relaxation behavior and assess the relaxation performance of asphalt. The shear strain increases to 1 % in 0.1 s. The stress reaches maximum value σ_{max} in a very short time after 0.1 s (0.01 ~ 0.02 s delay), the strain remains 1 % for 100 s, and σ_{end} is the stress at the end of the relaxation time (100 s). The $\sigma_{end}/\sigma_{max}$ is defined as the residual stress ratio (R_s) to characterize the ability to release the stress. Calculate and analyze the relaxation times ($T_{0.5}$ and $T_{0.25}$) for the reduction of stress from the maximum value σ_{max} to 50 % and 25 % to evaluate the relaxation rate of asphalt. Generally, longer relaxation times mean that it takes longer to release stored stresses at the end of one load and is more vulnerable to residual stresses.

The vehicle traffic loads are continuous, and if the stresses from the previous vehicle load are not recovered and released within a short period, the next vehicle load will work on the pavement again, thus causing an accumulation of residual stresses. Therefore, the relaxation time should be as short as possible to prevent damage to the pavement caused by accumulated stresses.

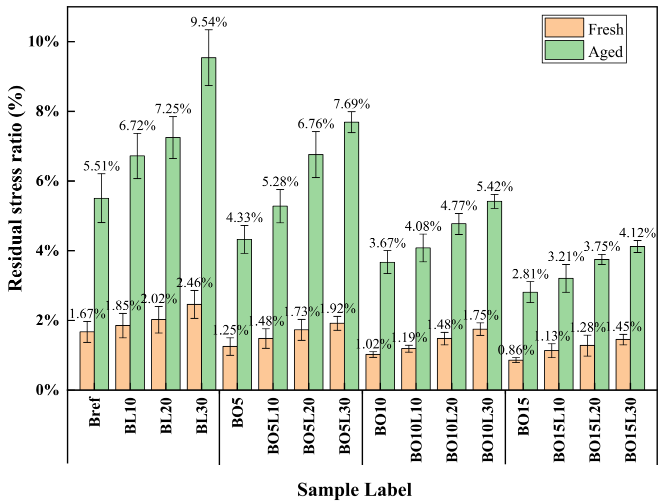


Fig. 12. Residual stress ratio (R_s).

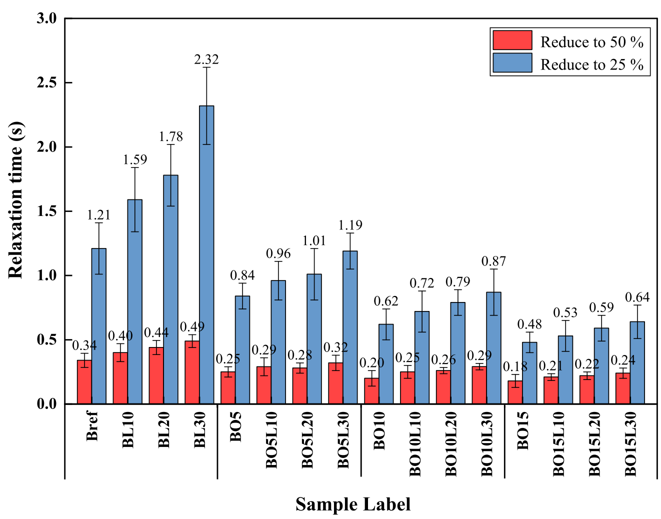


Fig. 13. Relaxation time ($T_{0.25}$ and $T_{0.5}$).

The residual stress ratio (R_s) was calculated to quantify the relaxation performance and represents the ratio of stress accumulation to release at the end of the relaxation test. The larger the R_s, the more residual stress at the end and the worse the recovery ability. Conversely, the smaller the R_s, the more pressure was released in the same relaxation time, and the better the relaxation performance. Compared to the aged sample, the fresh one had lower R_s and better elasticity and recoverability. It also showed that the relaxation properties decrease with aging. The R_s values are demonstrated in Fig. 12.

The R_s of the asphalt decreased noticeably with the incorporation of bio-oil. When the amount of bio-oil in the asphalt was increased from 0 % to 15 %, the R_s was reduced from 1.67 % to 1.25 %, 1.02 %, and 0.86 %, while from 5.51 % to 4.33 %, 3.67 % and 2.81 % in the aged condition. It suggested that bio-oil reduced residual stresses in the asphalt after loading and improved the relaxation properties. Lignin had the opposite effect on relaxation properties, when lignin dosage in asphalt was increased from 0 % to 30 %, the R_s increased from 1.67 % to 1.85 %, 2.02 %, and 2.46 %, from 5.51 % to 6.72 %, 7.25 %, and 9.54 % in the aged condition. The composite modification was able to solve and improve this problem. Only BO5L20 and BO5L30 had higher R_s than Bref. The relaxation properties of the other combinations of the composite-modified asphalt were improved.

After analyzing the residual stresses, the time for the shear stress to

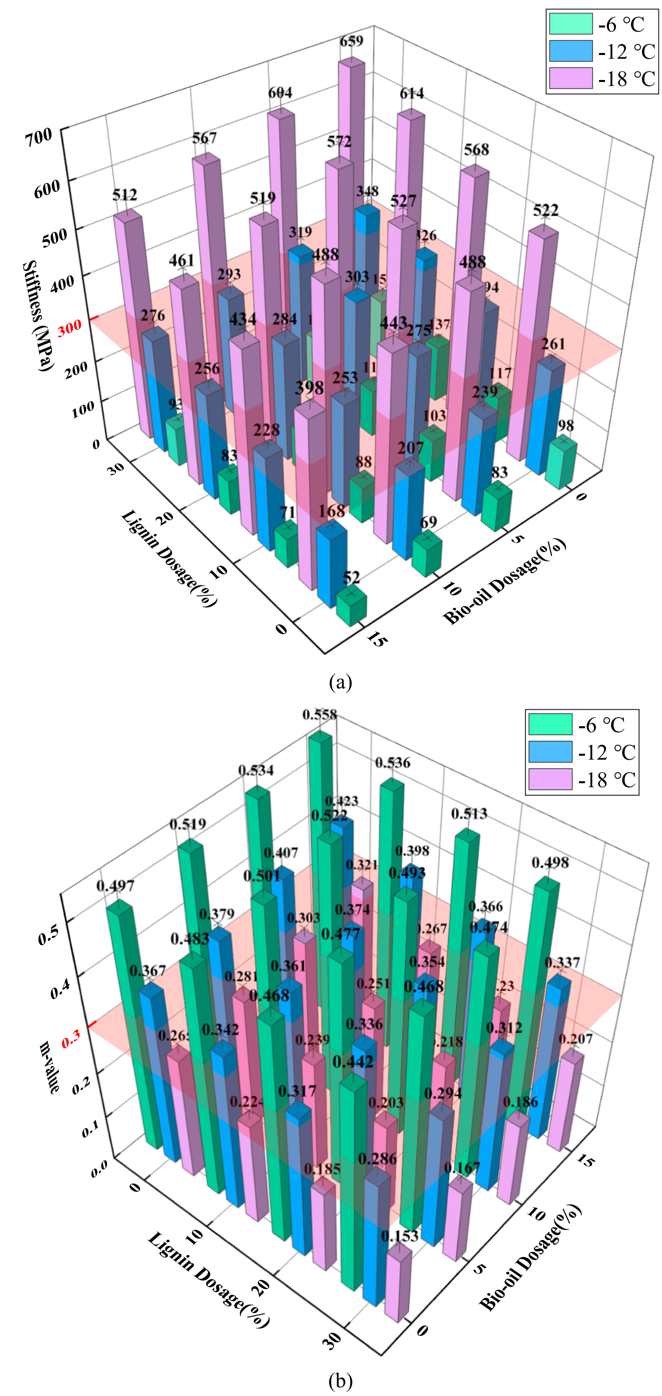


Fig. 14. BBR test results at different temperatures (a) creep stiffness and (b) m-value.

reduce to 50 % and 25 % of the initial (i.e., the relaxation rate) could also be used to assess the relaxation properties. The $T_{0.5}$ and $T_{0.25}$ of each sample were shown in Fig. 13. The bio-oil dramatically reduced the relaxation time. As the amount of bio-oil incorporated in asphalt increased from 0 % to 15 %, the $T_{0.5}$ reduced from 0.34 to 0.25, 0.20, and 0.18 s; $T_{0.25}$ decreased from 1.21 to 0.84, 0.62, and 0.48 s, a reduction of 30.58 %, 48.76 %, and 60.33 % respectively. However, lignin increased relaxation time when lignin dosing was increased from 0 % to 30 %, with $T_{0.5}$ increasing from 0.34 to 0.40, 0.44, and 0.49 s; and $T_{0.25}$ increasing from 1.21 to 1.59, 1.78, and 2.32 s, an increase of 31.40 %, 47.11 %, and 91.74 % respectively. The analysis results were consistent with the load curve and residual stress ratio. The bio-oil

Table 4
Sample low-temperature Tc (℃).

Label	Tc-s	Tc-m	Label	Tc-s	Tc-m	Label	Tc-s	Tc-m	Label	Tc-s	Tc-m
Bref	−12.9	−15.9	BL10	−12.1	−14.1	BL20	−11.2	−13.0	BL30	−10.5	−11.5
BO5	−13.5	−16.8	BO5L10	−12.6	−15.1	BO5L20	−11.9	−13.7	BO5L30	−11.4	−11.8
BO10	−14.4	−18.0	BO10L10	−13.2	−15.6	BO10L20	−12.4	−14.4	BO10L30	−12.2	−12.6
BO15	−15.4	−18.8	BO15L10	−14.1	−16.5	BO15L20	−13.3	−14.9	BO15L30	−12.6	−13.7

incorporated substantially lower relaxation times for the composite modified asphalt, even lower than neat asphalt.

4.5. BBR test

Based on ASTM D6648-16, BBR is used to assess the low-temperature performance and classification of the binder. The test measured flexural creep stiffness (S) and m-value at −6, −12, and −18 ℃ (Fig. 14). The creep stiffness represented the ability to resist creep deformation at low temperatures. In contrast, the m-value reflected the rate of change of the stiffness modulus with creep time. The specification (ASTM D6373) requires PAV aged asphalt binders to have a creep stiffness of less than 300 MPa and an m-value greater than 0.3 after aging. Generally, the larger the S and the smaller the m-value, the more elastic and the less viscous the asphalt, and the less flexibility and ductility at low temperatures.

It can be seen from Fig. 14 that as the temperature descended, the creep stiffness gradually increased while the m-value decreased. It revealed that the resistance to low-temperature cracking and relaxation properties weakened with the fall in temperature. It was because the stiffness and brittleness of asphalt increased visibly at low temperatures. As a result, the ability of the binder to resist deformation and release residual stress is weakened, and brittle failure is more likely to occur.

The creep stiffness decreased while the m-value increased with bio-oil incorporation in asphalt. When the bio-oil dosage was increased from 0 % to 15 %, the creep stiffness at −6 °C decreased from 98 MPa to 83, 69 and 52 MPa, a decrease of 15.3 %, 29.6 % and 46.9 %, respectively, and the m-value increased from 0.497 to 0.519, 0.534 and 0.558, an increase of 4.4 %, 7.4 % and 12.3 %, respectively. The test results showed consistent trends at −12 °C and −18 °C.

In addition, the low-temperature PG classification of the virgin asphalt (Bref) was –22, with a creep stiffness of 398 MPa and an m-value of 0.259 at −18 °C. When the bio-oil exceeded 10 %, it improved the low-temperature PG classification of the asphalt to −28. The creep stiffness of BO10 and BO15 in −18 ℃ was 0.303 and 0.321, respectively. It indicated that the bio-oil significantly improved the low-temperature performance of the asphalt. According to S = 300 MPa and m = 0.3, the low-temperature T_c of samples was calculated in Table 4.

The incorporation of lignin increased the creep stiffness and reduced the m-value. When the dose was increased from 0 % to 30 %, the creep stiffness at −6 °C increased from 98 MPa to 117, 137, and 157 MPa, an increase of 19.4 %, 39.8 %, and 60.2 %, respectively, and the m-value decreased from 0.497 to 0.483, 0.468, and 0.442, a decrease of 2.8 %, 5.8 %, and 11.1 %, respectively. The m-value of BL30 at −12 °C even was 0.286. It was mainly due to the strong adsorption of lignin, which ultimately led to an elevated amount of structural asphalt in the system, manifesting in reduced fluidity and increased modulus, making the binder more susceptible to low-temperature cracking. However, the composite modified asphalt with bio-oil and lignin improved this negative effect and increased the Tc of composite modified asphalt. It showed that the bio-oil could eliminate the hardening effect of lignin on the asphalt and supplement the lighter components of the system, thus increasing and improving the resistance to low-temperature cracking and relaxation.

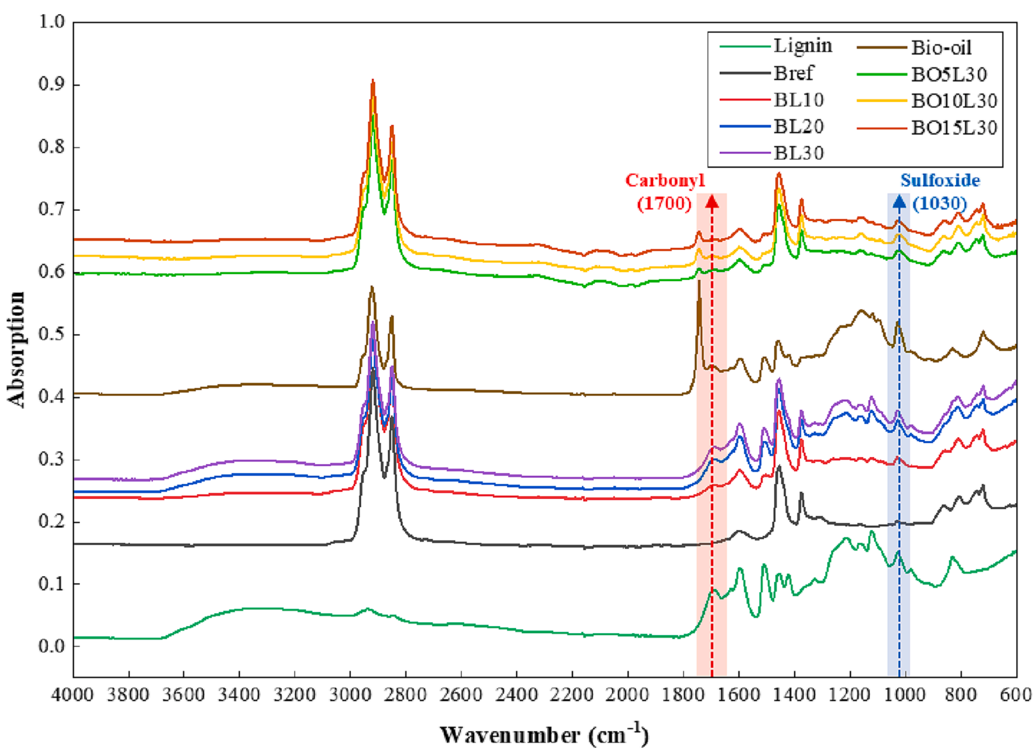
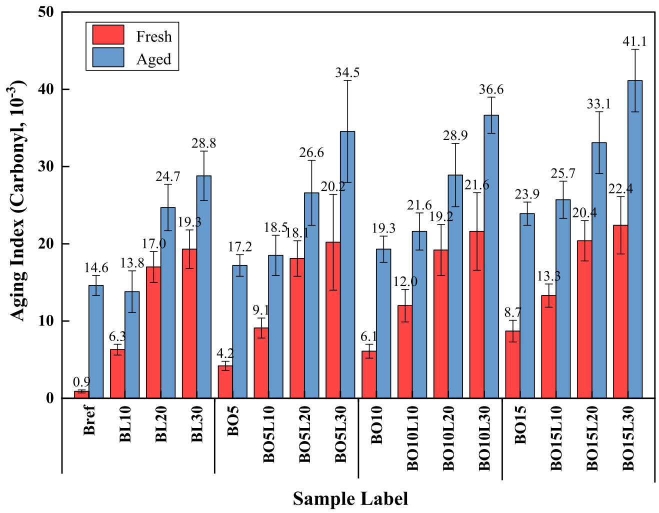
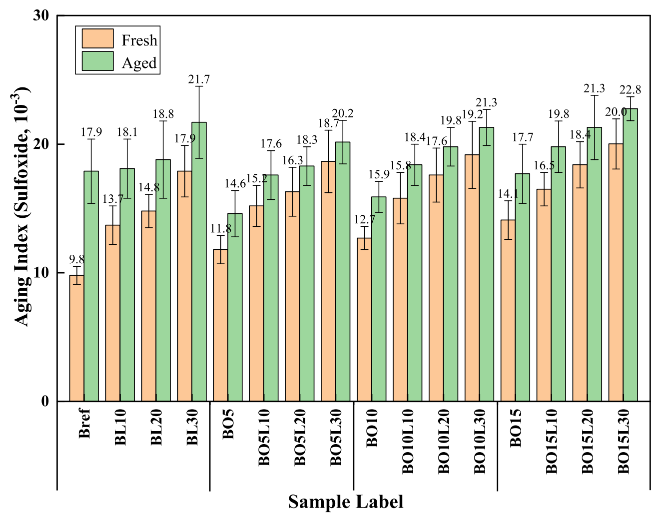


Fig. 15. FTIR spectra of lignin, bio-oil, and modified bitumen with various components.



(a)



(b)

Fig. 16. Composite modified asphalt aging functional group index (a) carbonyl and (b) sulfoxide.

4.6. FTIR test

Some of the composite modified asphalt samples were selected to analyze the changes in the FTIR spectra of asphalt blended with bio-oil and lignin (Fig. 15), with each sample spectrum obtained from nine parallel trials. The relationship between absorbance and wavenumber can be seen in the graph, with very significant differences in spectral absorption trends for virgin asphalt, lignin, bio-oil, and composite modified asphalt.

With the gradual increase of bio-oil and lignin blending in the modified asphalt, no new significant chemical functional group peaks were generated in the FTIR spectra of the composite modified asphalt. Instead, all chemical functional group peaks could be traced in the neat asphalt, bio-oil, and lignin spectra. Still, there were large changes in each chemical functional group's peak value and integrated area. This suggested that mixing bitumen with bio-oil and lignin did not result in significant chemical reactions and many new chemical products but did change the proportion of the original chemical composition of the asphalt.

Carbonyl ($C=O$) and sulfoxide ($S=O$) are the most important aging indices in asphalt. Although lignin contains carbonyl and sulphoxide groups, lignin hardly ages and does not influence the aging index of modified asphalt during the aging process. Therefore, the carbonyl and sulfoxide functional group indicators were calculated for each sample before and after the aging to characterize the antioxidant effect of the modifier (Fig. 16).

The virgin asphalt had only traces of carbonyl and a small amount of sulphoxide. The addition of lignin increased both aging indexes, with the amount of lignin increasing from 10 % to 30 %, the $AI_{C=O}$ increased from 0.9 to 6.3, 17.0, 19.3, and the $AI_{S=O}$ increased from 9.8 to 13.7, 14.8, 17.9. The integrated area of the carbonyl in the spectrum of lignin was much larger than that of the sulfoxide. With the increase of bio-oil from 5 % to 15 %, the $AI_{C=O}$ increased from 19.3 to 20.2, 21.6, and 22.4, an increase of 4.7 %, 11.9 %, and 16.1 % compared to BL30; the $AI_{S=O}$ increased from 17.9 to 18.7, 19.2, and 20.0, an increase of 4.4 %, 7.3 % and 11.7 % respectively. The $AI_{C=O}$ increased more significantly than the $AI_{S=O}$.

All samples showed an increase in both $AI_{C=O}$ and $AI_{S=O}$ after aging. The asphalt underwent an oxidation reaction to produce more carbonyl and sulfoxide, but the growth of the aging index of the different composite modified bitumen varied greatly. The $AI_{C=O}$ and $AI_{S=O}$ of the Bref increased from 0.9 and 9.8 to 14.6 and 17.9, an increase of 13.7 and 8.1, respectively; the $AI_{C=O}$ and $AI_{S=O}$ of the BL10 increased from 6.3 and 13.7 to 13.8 and 18.1, an increase of 7.5 and 4.4, respectively, a decrease of 42.3 % and 45.7 % over the increment of the Bref; the $AI_{C=O}$ and $AI_{S=O}$ of BL20 increased by 7.7 and 4.0 respectively, a decrease of 43.8 % and 50.6 % compared to Bref; while the $AI_{C=O}$ and $AI_{S=O}$ of BL30 increased by 9.5 and 3.8 respectively, a decrease of 30.7 % and 53.1 % compared to Bref. Lignin significantly reduced the increase of $AI_{C=O}$ and $AI_{S=O}$ during aging. Similar results were seen in previous studies [1,32].

The carbonyl and sulfoxide were formed by a chain reaction during aging (Fig. 17), where R can be a hydrogen atom, an alkyl, or a hydrocarbon group. Oxidation (2) occurred when molecules in asphalt lost their H atoms (1). C containing a peroxide bridge (-O-O-) was generated. Peroxides are unstable and very susceptible to decomposition to produce reactive radicals, which can lead to new free radical chain reactions. The peroxide C underwent a decomposition reaction (3) to produce ketones and alkoxides. Peroxide C reacted (4) with compounds containing thioether bonds (-S-) to form compounds containing sulphinyl groups (>S = O). The reaction (5) of the peroxide C with the H atom lost by the asphalt molecule produced the hydroperoxide H (R-OOH). Hydroperoxides H was also unstable and reacted (6) with compounds containing thioether bonds to form sulfoxide. A hydroperoxide rearrangement reaction (7) also occurred, where the peroxy bond (-O-O-) was broken, and the hydrocarbon group underwent nucleophilic rearrangement and formed ketones and alcohols. Oxidative aging of asphalt followed the free radical chain autocatalytic oxidation reaction mechanism. The process generated free radicals, including peroxy (ROO-), alkoxy (RO-), phenoxy (ArO-), etc.

Due to its unique chemical structure, lignin can act as a free radical inhibiting terminator, with three monomeric lignin (hydroxy-phenyl, syringyl, and guaiacyl lignin), all of which are phenol structures containing substituents. The antioxidant mechanism of lignin is to react with the free radicals formed during the aging process and generate stable structures, thus inhibiting the chain reaction and greatly reducing the generation of oxidation products, delaying the aging of asphalt. The free radical scavenging activity of lignin is shown below.

$$ArOH + ROO\cdot \rightarrow ArO\cdot + ROOH \tag{4}$$

$$ArOH + R\cdot \rightarrow ArO\cdot + RH \tag{5}$$

$$ArO\cdot + R\cdot \rightarrow ArOR \tag{6}$$

where Ar represents a structure containing an aromatic ring.

Reactions (7) and (8) were carried out by providing reactive hydrogen atoms which reacted with the free radicals generated during

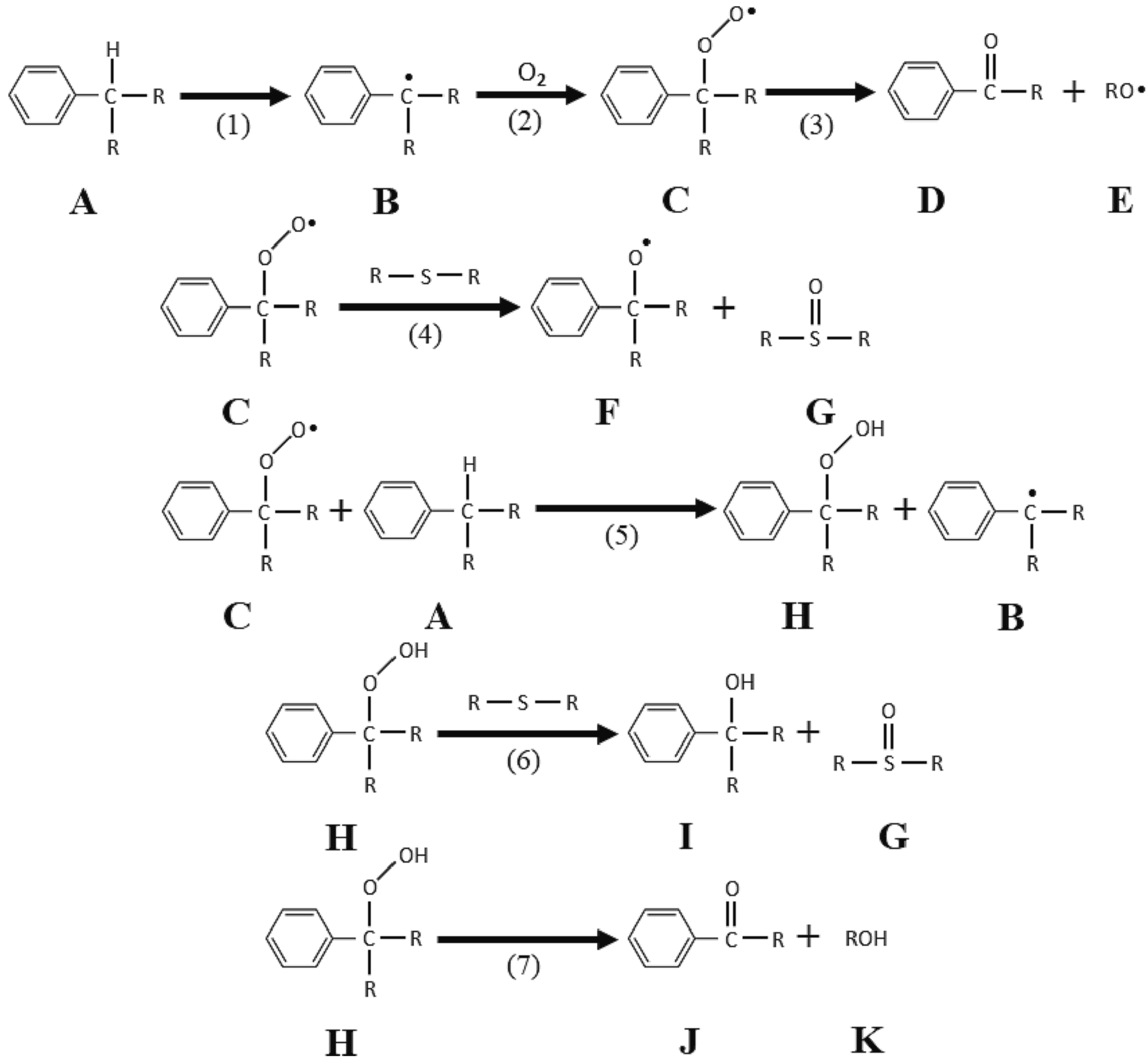


Fig. 17. The formation of carbonyl and sulfoxide during aging.

the aging and produced stable chemical substances. It converts free radicals to those that cannot participate in asphalt aging chain reactions or cause chain reactions. This mechanism is of the hydrogen atom-giving type. The oxygen atom of the phenolic hydroxyl group (Ar-OH) in the lignin molecular structure was able to undergo a p-π conjugation effect with the benzene ring. The oxygen atom exhibited electronegativity. When substituents were present at the ortho-, meta-, and *para*-positions of the phenolic hydroxyl group, the electron inductive effect weakened the polarity of the O-H bond in Ar-OH, making it easier for the O-H bond to break and release the active hydrogen atom.

Reaction (9) was of the radical trapping type, where the inhibitor could generate radicals in the process and react with the active radicals. After releasing hydrogen atoms, the phenol structure in lignin reacted with the reactive radicals to form aryl oxygen radicals, which can continue to react with the reactive radicals, thus terminating the chain reaction. Therefore, when lignin was incorporated into bitumen, it not only provided active hydrogen atoms but also reacted with the active radicals, thus enhancing and improving the antioxidant properties of bitumen. Due to the different reduction effects on carbonyl and sulfoxide, the CAI was proposed for analysis (Fig. 18).

The blue part showed the CAI before aging, the red part represented the increase in the combined functional groups during aging, and the sum of the blue and red parts was the CAI after aging. The CAI of Bref was 10.7, and the ΔCAI was 21.8. When the lignin dose was 10, 20, and 30 %, the ΔCAI was 11.9, 11.7, and 13.3, respectively, 45.4 %, 46.3 %, and 39.0 % lower than that of the virgin bitumen. This significantly slowed the generation rate of aging functional groups, again demonstrating a significant anti-aging effect on bitumen. The bio-oil also reduced the ΔCAI. When the bitumen with bio-oil was at 5 %, 10 %, and 15 %, the ΔCAI was 15.8, 16.4, and 18.8, respectively, 27.5 %, 24.8 %, and 13.8 % lower than the Bref. Bio-oil had a slightly lower inhibitory effect compared to lignin. Except for BO15L30, the ΔCAI of the composite modified asphalt samples was significantly lower than that of the matrix asphalt.

5. Determine optimal dosage of OLMA

In this study, the different properties of OLMA were investigated using tests such as DSR, BBR, and FTIR. DSR and BBR were used to analyze the rheological properties from low to high temperatures. The resistance to permanent deformation, fatigue, cracking, and Relaxation was assessed by MSCR, LAS, and relaxation tests. FTIR tests were applied to analyze the chemical functional groups and the anti-aging property. The rutting factor, creep stiffness, and m-value were determined for the

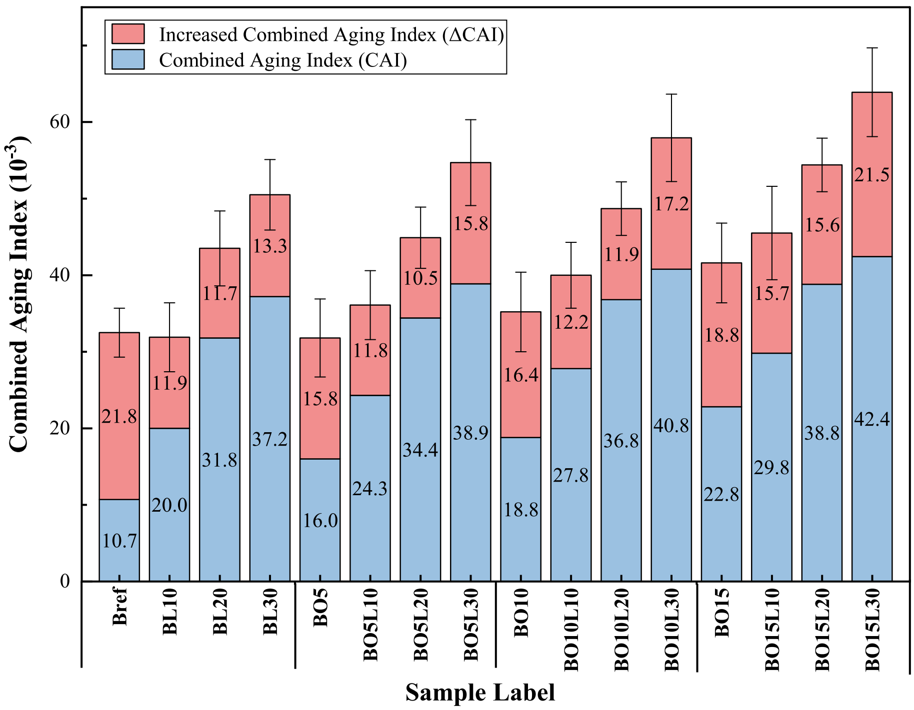


Fig. 18. Combined Aging Index of composite modified asphalt.

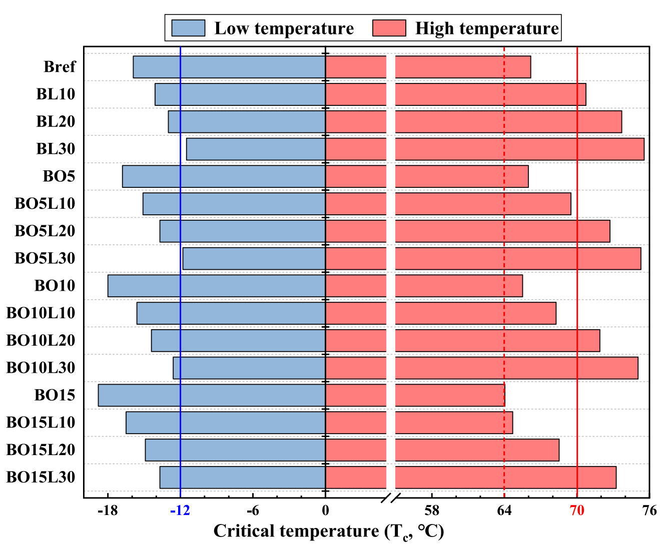


Fig. 19. High and low-temperature critical temperatures.

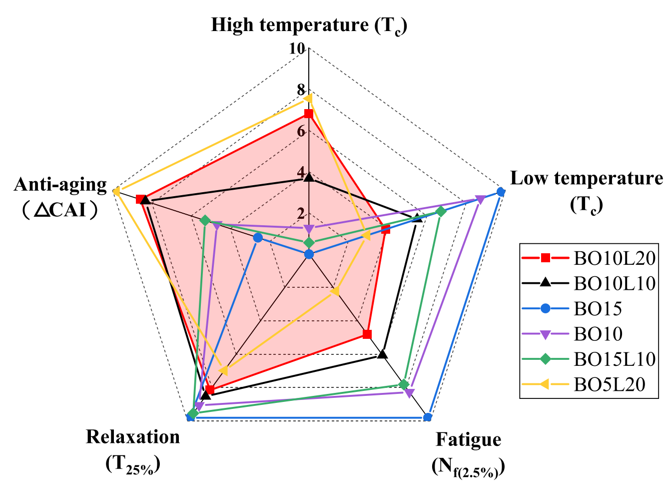


Fig. 20. Performance radar graph.

T_c of asphalt.

Fig. 19 showed that lignin significantly increased the high-temperature T_c, while bio-oil improved the low-temperature T_c. The virgin asphalt was PG 64–22. The high-temperature T_c of samples BL10, BL20, and BL30 had exceeded 70 °C, and even BL30 had a critical temperature close to 76 °C. On the other hand, samples BO10 and BO15 had a low-temperature T_c close to or above −18 °C. However, the single-modified asphalt can only increase a T_c at either low or high temperatures. Therefore, it is impossible to determine the optimum dosage for OLMA from the high and low-temperature properties. Thus, the different tests' results must be considered and quantified to determine the optimal proportion of OLMA.

The T_c can be a reference indicator for high-and-low temperature performance. In addition to this, the fatigue life cycle (N_f) at a 2.5 % strain level can be used as an indicator of fatigue performance, and the relaxation time ($T_{25\%}$) when the stress was reduced to 25 % of the initial stress after loading can be used as an indicator of relaxation performance, and ΔCAI after aging as an indicator of anti-aging performance. However, the units and physical meanings of the different indicators varied considerably. The test results needed to be dimensionless and normalized to compare and analyze the various performance indicators better. The Mapminmax function in Matlab was used to process the results.

To obtain the optimal proportion of OLMA with the best overall performance, the different property scores were summarized to get the overall score. BO10L20, BO10L10, BO15, BO10, BO15L10, and BO5L20 ranked 1st to 6th with 32.766, 32.660, 32.655, 32.623, 30.497, and 29.935, respectively. To compare the performance of these six samples more visually, they were plotted in the performance radar graph as shown in Fig. 20. BO15, BO10, and BO15L10 significantly improved relaxation, fatigue, and fatigue low-temperature performances. Nevertheless, they do not have a noticeable effect on aging property and even negatively impact high-temperature performance. Although BO5L20 can greatly improve the anti-aging, high temperature, and relaxation performances, the low temperature, and fatigue performance enhancement effect was not remarkable. The overall performance of BO10L20 and BO10L10 was superior.

The ΔCAI of BO10L20 is 11.9, slightly lower than the 12.2 of BO10L10, and BO10L20 exhibits better aging resistance. The residual stress ratio and relaxation time ($T_{50\%}$ and $T_{25\%}$) of BO10L10 were 1.19 %, 0.25 s, and 0.72 s, while those of BO10L20 were 1.48 %, 0.26 s, and 0.79 s, respectively. $N_{f(2.5\%)}$ and $N_{f(5.0\%)}$ of 1536 and 290 for BO10L10 and 1185 and 222 for BO10L20, respectively, giving BO10L10 a marginally better fatigue performance. BO10L20 does not improve the low-temperature performance as much as BO10L10, but there is no difference in the PG low-temperature classification of −12 for both. BO10L20 has a more dramatic improvement in high-temperature performance, with a critical temperature of over 70 °C, while BO10L10 does not exceed 70 °C. In addition, BO10L20 had the highest overall score and the largest area enclosed in the performance radar graph and was the best choice for both the principle of reducing the amount of petroleum-based bitumen and increasing the biomass content. Therefore, 10 % bio-oil and 20 % lignin were identified as the optimum dosage for the OLMA.

6. Conclusions and recommendations

In this paper, OLMA with different proportions were prepared, and the high-temperature stability, fatigue, anti-cracking, low-temperature, and anti-aging performance were investigated systematically by DSR, BBR, and FTIR. The effects of bio-oil and lignin on the properties were evaluated, and the mechanism was explained. The optimum dosage of bio-oil and lignin in the composite modified asphalt was determined based on the balance of performance theory. The main conclusions are as follows:

1. The frequency-temperature sweep and MSCR tests evaluated the effect laws of bio-oil and lignin on the viscoelastic properties and high-temperature performance of the asphalt. The composite modified bitumen increased the high-temperature classification and critical temperature and improved the resistance to rutting and stability.
2. The OLMA increased fatigue life, reduced the risk of cracking, improved low temperature and relaxation properties, and eliminated the effect of lignin on fatigue and low-temperature performance.
3. The ΔCAI were proposed to quantify the aging of OLMA. The OLMA can reduce the production of oxidation functional groups during aging. Furthermore, it revealed the mechanism of the anti-aging effect of scavenging reactive free radicals.
4. The high temperature, low temperature, fatigue, Relaxation, and aging properties of the OLMA were analyzed, quantified, and compared based on the balanced properties theory. The optimum dosage of 10 % bio-oil and 20 % lignin was determined.

This paper focused on the effects of different proportions of bio-oil and lignin on the rheological properties and the functional groups of asphalt. It ultimately concluded on the optimum dosage of OLMA. The microstructure, morphology, and other physical and chemical properties will be further investigated, such as molecular weight, sol–gel state, fractionation, and molecular thermal motion of OLMA.

CRediT authorship contribution statement

Yi Zhang: Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Chundi Si:** Supervision, Writing – review & editing. **Taotao Fan:** Data curation, Writing – review & editing. **Yuefeng Zhu:** Data curation, Writing – review & editing. **Song Li:** Resources, Writing – review & editing. **Shisong Ren:** Data curation, Writing – original draft, Writing – review & editing. **Peng Lin:** Methodology, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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