Journal of Renewable Materials
DOI:10.32604/jrm.2020.012054
Article

Tech Science Press

Analysis of the Mechanism and Effectiveness of Lignin in Improving the High-Temperature Thermal Stability of Asphalt

Cheng Cheng[1,2,*], Weiwei Sun[2], Bo Hu[3], Guixiang Tao[2], Chao Peng[2], Yanjuan Tian[4] and Shujuan Wu[4,5]

[1]Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products, Southwest Forestry University, Kunming, 650224, China
[2]School of Civil Engineering, Southwest Forestry University, Kunming, 650224, China
[3]Yunnan Tongqu Engineering Testing Co., Ltd., Kunming, 650500, China
[4]Key Laboratory for Special Area Highway Engineering of Ministry of Education, Chang'an University, Xi'an, 710064, China
[5]School of Civil Engineering, Lanzhou University of Technology, Lanzhou, 730050, China
[*]Corresponding Author: Cheng Cheng. Email: chengcheng_clx@swfu.edu.cn

Received: 12 June 2020; Accepted: 29 July 2020

Abstract: The use of lignin, which is a by-product of the pulp and paper industry, in the development of asphalt binders would contribute to waste reduction, providing environmental, economic, and social benefits. In this study, samples of lignin-modified asphalt binder samples with different content of lignin (3%, 6%, 9%, 12%, and 15%) and unmodified asphalt (control) were tested using Fourier transform infrared spectroscopy (FTIR), dynamic shear rheometer (DSR), and thermogravimetry. The mechanism and effectiveness of lignin in improving the thermal stability of asphalt at high temperatures were analyzed. The FTIR analysis shows that no new characteristic absorption peak is seen in the infrared spectral of the lignin-modified asphalt binder samples, and some bands characteristic of lignin-related peaks gradually increased with the increase of lignin content. This suggests that the modification of lignin-modified asphalt binder samples was due to physical blending rather than chemical modification. The increase of lignin content in the lignin-modified asphalt samples increases the complex shear modulus G* of the samples and decreases the phase angles of the samples. Similarly, the anti-rutting performance ($G^*/\sin\delta$)of the samples improves with the increase in lignin content, but this is not significant after any addition of lignin that exceeds 12% of asphalt mass. Thermal characterizations show that the thermal decomposition rate of lignin is lower, and its residual amount is higher compared to that of asphalt, which is a major reason for the improved stability of lignin-modified asphalt binders at high temperatures. The effect of lignin on the thermal stability of asphalt is dependent on both lignin content and temperature. It has a positive effect on the thermal stability of asphalt at high temperatures within the range of asphalt service temperature (25°C–200°C). Additionally, from the pyrolysis viewpoint, it was explained that excessive lignin addition is not beneficial to the thermal stability of asphalt at high temperatures, which is consistent with the DSR test result conducted high temperatures.

Keywords: Lignin modified asphalt; high-temperature stability; FTIR; TG

1 Introduction

Lignin is the second most abundant renewable polymer in nature. Its molecular chain contains several active reactive groups, such as phenolic hydroxyl group and aromatic group [1], and it can be used as a substitute for phenol and other petrochemical raw materials to prepare polymers such as phenolic resin [2–4], polyurethane resin [5–7], and epoxy resin [8–10]. It can also be used to modify polymers, enhancing their mechanical properties [11] and significantly improving their thermal stability [12], aging resistance [13], and flame retardancy [14].

The structure of lignin is similar to bitumen resin with large rings joined by alkyl chains [15–17]. Therefore, lignin can be used to improve the performance of asphalt. Lignins used for modifying asphalt include Kraft lignin [18–20], sulfonated lignin [21], Organosolv lignin, Klason lignin [19,22], and Enzymatic Hydrolysis lignin [23] and are mainly derived from pulp and paper mills and lignocellulosic biorefinery.

Test results of asphalt physical properties show that the addition of lignin reduces asphalt penetrability and increases its softening point. This means that the stability of asphalt is improved at high temperatures [18,23–25]. However, the addition of lignin will harden asphalt, decreasing its ductility, especially when the content of lignin added is higher than that of asphalt. Controlling the lignin content [25] or adding low dose styrene-butadiene-styrene [24] would prevent the above-mentioned issue. The rheological properties of asphalt binders directly affect the performance of asphalt pavements. When lignin is added to asphalt, the rheological properties of asphalt are changed. Lignin-modified asphalt binders have a greater viscosity than unmodified binders [18,26]. Rheological test results on Lignin-modified asphalt binders indicate that the addition of lignin can significantly increase the storage modulus (G') of asphalt binders, have little effect on the loss modulus (G") [27], and improve the rutting resistance of asphalt binders [25–29]. Meanwhile, lignin can improve thehigh-temperature performance grade of asphalt [25,30]. Harder lignin-modified asphalt may crack at low temperatures or degrade due to fatigue [31,32]. However, some researchers have reported that the addition of lignin does not significantly affect the susceptibility of asphalt to cracking at the low temperatures [20,21]. Chemically treated lignins could prevent the cracking of asphalt at low temperatures up to −24°C [30]. Pan [33] evaluated some asphalt samples and lignin samples using X-ray photoelectron spectrometry. Evaluation results indicated that lignin can be used as an antioxidant in bitumen on the condition that lignin is not oxidized. Compared to unmodified asphalt, the physical properties and rheological properties of lignin-modified asphalt are not significantly changed after aging [20,27], and its carbonyl index is reduced [32]. This is mainly due to the presence of phenolic hydroxyl groups in lignin that can effectively remove free radicals generated during asphalt aging [31]. Additionally, the stability of lignin-modified asphalt at high temperatures is one of the reasons for improving its oxidation resistance [34]. Generally, several related research studies have been done on the rheological properties and oxidation resistance of lignin-modified asphalt. The application of lignin to modify asphalt performance is widely recognized. However, there are few studies on the modification mechanism of lignin-modified asphalt and the effectiveness evaluation of asphalt thermal stability at high temperatures.

In this study, Fourier transform infrared spectroscopy (FTIR) will be used to test the functional groups of lignin and asphalt samples to explain the mechanism of lignin-modified asphalt, and the dynamic shear rheological (DSR) test will be used to evaluate the dynamic shear modulus (G*) and phase angle (δ) of asphalt samples with different lignin content and analyze the effect of lignin content on the rheological properties of asphalt at high temperatures. The pyrolysis test on lignin and asphalt samples is conducted using a thermogravimetric analyzer. Reasons for the improvement of the thermal stability of asphalt at high temperature are analyzed, and the effect of lignin on the thermal stability of asphalt at high temperatures is also discussed.

2 Materials and Methods

2.1 Preparation of Lignin-Modified Asphalt Binders

Asphalt used was $70^{\#}$ base asphalt produced by SK Group of Korea and was supplied by Yunnan Asphalt Oil Reserve and Guarantee Center in China. The technical properties of bitumen are shown in Tab. 1.

Table 1: Technical properties of 70# asphalt binder

Technical Indices	Result	Requirement	Unit
Penetration/(25°C, 5 s, 100 g)	65.4	60–80	0.1 mm
Softening point	46.6	>46	°C
Ductility/(15°C)	150	>100	cm
TFOT penetration ratio/(25°C)	76.9	>61%	%
Residual ductility/(15°C)	132.9	>100	cm

The commercial lignin used herein was produced by Jinan Yanghai Chemical Co., Ltd. (Shandong Province, China). Main indicators, including lignin content, ash content, sugar content, and pH are shown in Tab. 2.

The preparation process of lignin-modified asphalt samples was conducted following these three steps:

1. Matrix asphalt was heated to a liquid state in an oven at 120°C, then poured into an iron container with a certain quality and heated to 150°C in an oil bath pot.
2. Asphalt and lignin were first mixed at a shear rate of 500 rpm until the lignin was completely immersed in the asphalt, and then the shear rate was gradually increased and stirred at the shear rate of 5000 rpm for 1 h.
3. Finally, the mixture was put into an oven at 120°C for 1 h, and lignin-modified asphalt samples were prepared.

Table 2: Main indicators of lignin

Indicators	Result	Unit
Lignin content	85–90	%
Ash content	1	%
Sugar content	1–3	%
pH	7–8	–

The preparation process of lignin-modified asphalt is shown in Fig. 1.

In this study, different lignin-modified asphalt samples were prepared. The content of lignin in the samples accounted for 3%, 6%, 9%, 12%, and 15% of asphalt mass and termed SK-3, SK-6, SK-9, SK-12, and SK-15, respectively. To eliminate the effect of the preparation process on the test results, the matrix asphalt was used as a comparative sample after the preparation of the same sample and termed SK-0.

2.2 Fourier Transform Infrared Spectroscopy Test on Lignin and Asphalt Samples

The asphalt samples and lignin were sufficiently milled in an agate mortar with a KBr crystal (spectral purity) in a ratio of 1:100 (mass ratio) when fully dissolved in petroleum ether. Afterward, the solvent evaporates, and equal masses of the mixture were weighed and tableted, as shown in Fig. 2a. The

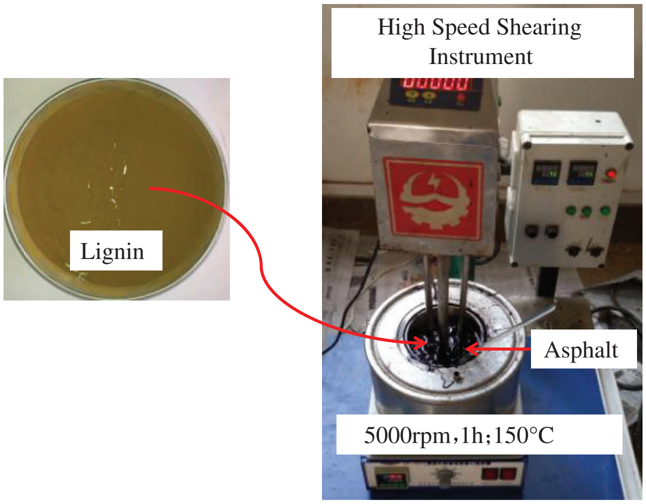
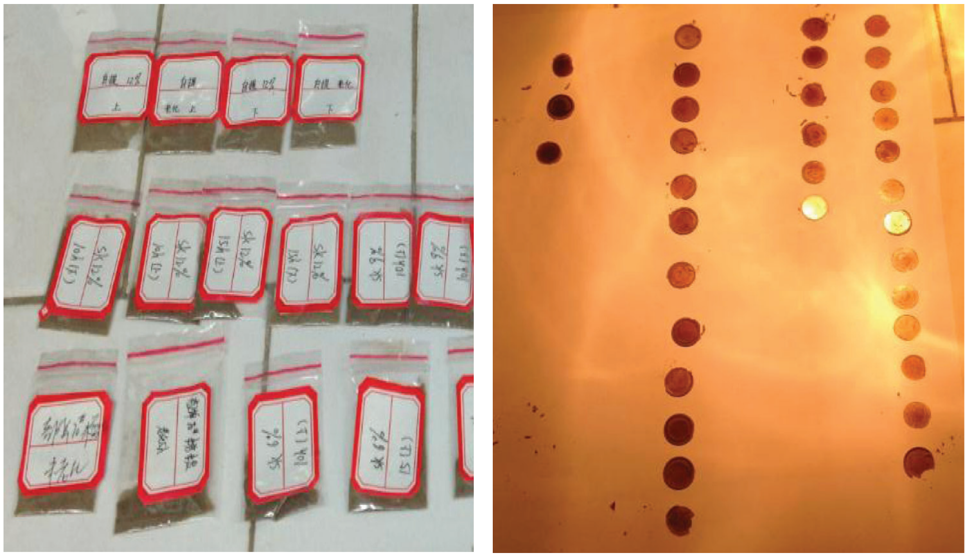


Figure 1: Preparation of lignin-modified asphalt



(a) (b)

Figure 2: Photographs of FTIR lignin-modified asphalt preparation. (a. Lignin or asphalt mixed with KBr powder. b. Samples (mixture) kept dried under an infrared spectral lamp)

tableted samples were kept dry under an infrared lamp, as shown in Fig. 2b, which prevents the samples from absorbing moisture in the air. The FTIR test was used to determine the functional groups present in the samples using a spectrophotometer (Bruker TENSOR27, Germany) with an infrared region median (4000–400 cm^{-1}), 32 scanning times, and a resolution of 4 cm^{-1}.

2.3 Dynamic Shear Rheological Test Lignin-Modified Asphalt at High Temperatures

Rheological tests on asphalt samples were conducted using a rheometer (Malvern CVO100, UK) equipped with a parallel plate geometry (1 mm in gap, 25 mm in diameter) and a Peltier system (±0.1°C) for temperature control. Experiments were conducted at 58°C, 64°C, and 70°C; the shear frequency used was 10 rad/s, and the strain was controlled at 12%. Dynamic shear modulus G*, phase angle δ, and

$G^*/\sin\delta$ were calculated to evaluate the effect of lignin on the rheological properties of asphalt at high temperatures.

2.4 Thermogravimetry Test on Lignin and Asphalt Samples

Thermal analysis was performed using a synchronous thermogravimetric analysis instrument (METTLER TOLEDO TGA/SDTA851e, USA). The samples (3 mg–5 mg in mass) were heated in a standard aluminum oxide crucible. All experiments were conducted in a nitrogen atmosphere with a flow rate of 20 ML min^{-1} and a heating rate of 10°C min^{-1} from 25°C up to 700°C.

3 Experimental Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy Analysis

FTIR test results for the lignin and asphalt samples are shown in Fig. 3. The lignin sample has a broad and strong peak around 3400 cm^{-1}, which is a hydrogen bond stretching vibration peak in -OH. The comparative sample SK-0 due to high-speed shear processing completely volatilized the internal water. As a result, no obvious -OH stretching vibration absorption peak appears close to 3400 cm^{-1}. To better analyze the change of functional groups in asphalt after lignin addition, the infrared spectral of the lignin fingerprint region between 1800 and 800 cm^{-1} were selected for comparison.

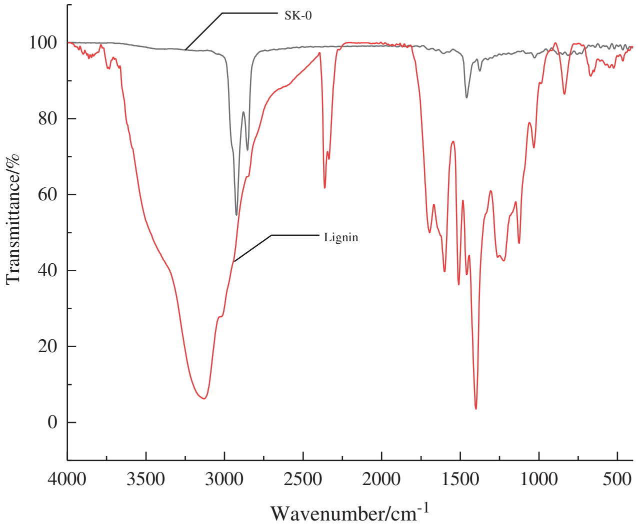


Figure 3: FTIR test results of lignin, asphalt sample (SK-0)

Fig. 4 shows a comparison of the six lignin-modified asphalt samples with different lignin content. Comparing the FTIR spectrum of each sample shows that the infrared spectrum base of each lignin-modified asphalt sample has only the characteristic peaks of lignin and asphalt. No new characteristic absorption peak is attributable to the chemical reactions of lignin and asphalt. The increase of lignin content from 3% to 15% of asphalt mass gradually increased the intensities of the 1512 cm^{-1} and 1265 cm^{-1} bands and other lignin-related peaks (1126 cm^{-1}, 1602 cm^{-1}, 1650 cm^{-1}, 1695 cm^{-1}). This shows that the asphalt binders were uniformly well-mixed [28]. It can be inferred that the modification of asphalt by lignin is merely physical blending.

3.2 High-Temperature Stability

Dynamic shear modulus (G*) is an index to evaluate the total deformation resistance of asphalt. The larger the G*, the stronger the deformation resistance of asphalt binders at high temperatures. The phase

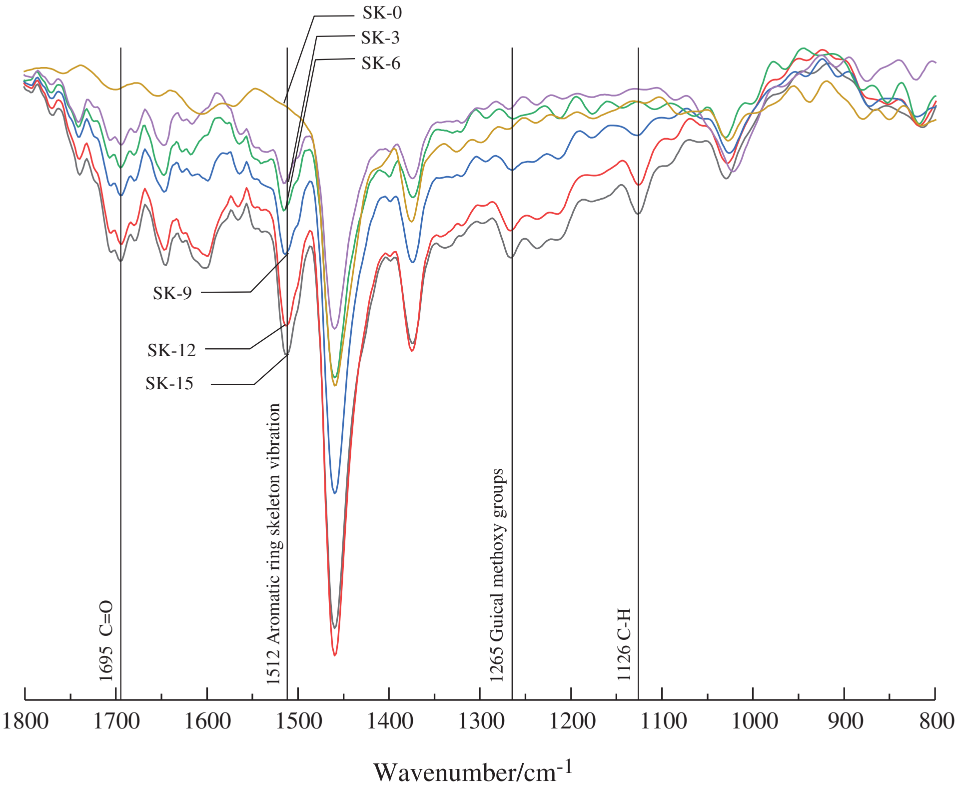


Figure 4: Comparison of FTIR spectra of lignin modified asphalt samples

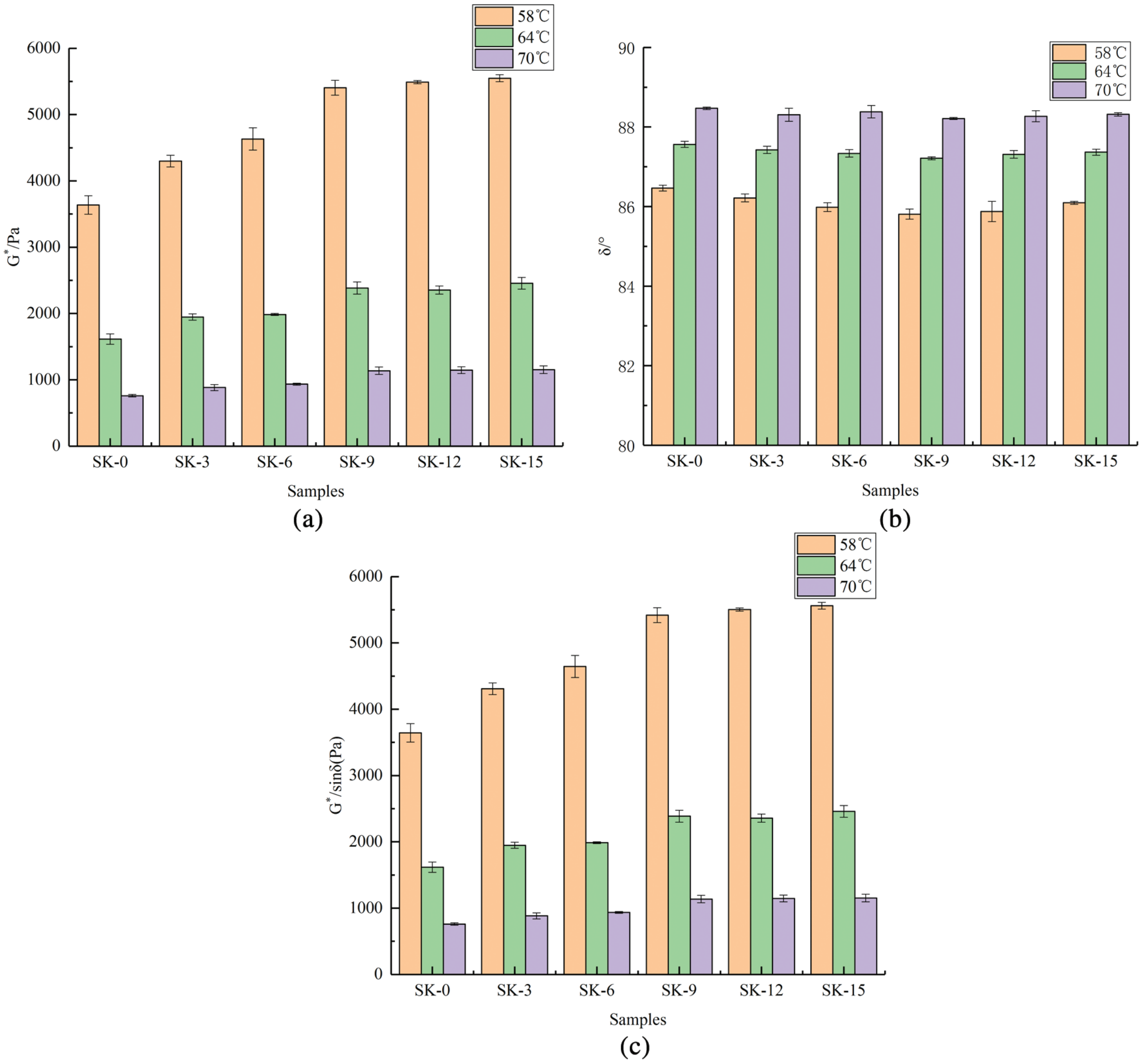
angle (δ) is the proportion index to evaluate the components of asphalt viscosity (non-recoverable part) and elasticity (recoverable part). The smaller the phase angle of the asphalt, the higher its elasticity and the better its stability at high temperatures [35,36]. According to the test method described in 2.3, the test results of asphalt samples at 58°C, 64°C, and 70°C are shown in Fig. 5.

As shown in Fig. 5, compared to the matrix asphalt, the complex shear moduli G^* of the modified asphalt samples are increased and the phase angles are reduced. This indicates that the addition of lignin increased the elasticity of asphalt and is beneficial to the improvement of the matrix asphalt stability at high temperatures.

Asphalt anti-rutting performance is improved as the content of lignin is increased, but further addition of lignin content that exceeds 12% of asphalt mass has an insignificant effect on asphalt anti-rutting performance. This is mainly because the modification mechanism of lignin-modified asphalt is primarily physical blending, and lignin mainly increases the viscosity of asphalt. Therefore, with the increase of lignin content, the viscosity of the lignin-modified asphalt samples was increased and the high-temperature stability of the samples was also improved. However, if excess lignin was added to the asphalt binder, it would saturate the asphalt binder and not significantly improve the properties of the asphalt binder and could worsen the properties of the asphalt binder due to a change in the phase state of the asphalt binder.

3.3 Thermogravimetry Analysis

The thermogravimetric test results of the lignin and asphalt samples are shown in Figs. 6 and 7, respectively. Fig. 6 shows that the derivative thermogravimetric (DTG) curve of SK-0 has only a single peak at 455°C, indicating that there is only one pyrolysis stage, which is slightly different from what is



(a) (b) (c)

Figure 5: Experimental results of lignin-modified asphalt DSR

described in the literature [37]. This is mainly caused by the volatilization of some light components in the preparation of SK-0 or by the conversion of some light components into heavy components due to aging. The TG curve of SK-0 shows no thermal decomposition at temperatures below 200°C. Taking a weight loss temperature of 5% as the initial pyrolysis temperature, the initial temperature of unmodified asphalt was 360°C, and the thermogravimetric loss rate was $0.6\%\cdot°C^{-1}$. The mass loss rate increased rapidly with the increase in temperature and reached a maximum of $4.5\%\cdot°C^{-1}$ close to 455°C. This indicates that the main components of asphalt are pyrolysis. Then, the mass loss rate decreased gradually and remained weakly changed above 500°C. At the same time, the asphalt sample had been carbonized and the quality retention rate of the sample was 15.9%.

As can be seen from Fig. 7, the first mass loss peak of the lignin sample appeared in the range of 50°C–60°C, which is mainly caused by the loss of free water in the lignin sample. In the temperature range of 200°C–300°C, there are several small mass loss peaks due to the loss of water in the lignin sample and the production of methane, ethane, carbon dioxide, and so on [38,39]. The maximum mass loss rate of the lignin sample is seen at 345°C, and its mass retention percentage was approximately 68%. The lignin

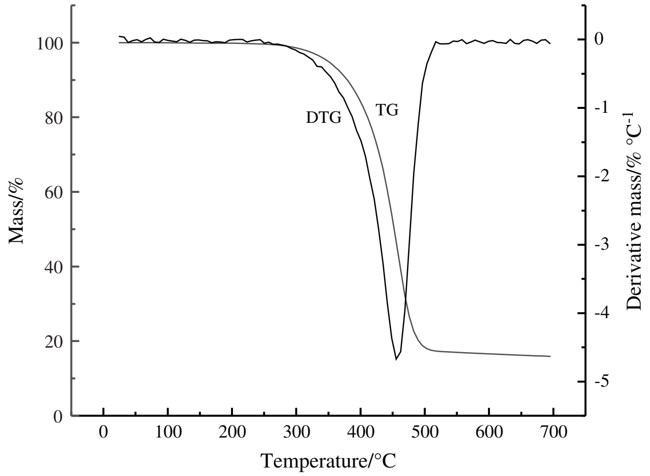


Figure 6: TG/DTG curves for asphalt sample (SK-0)

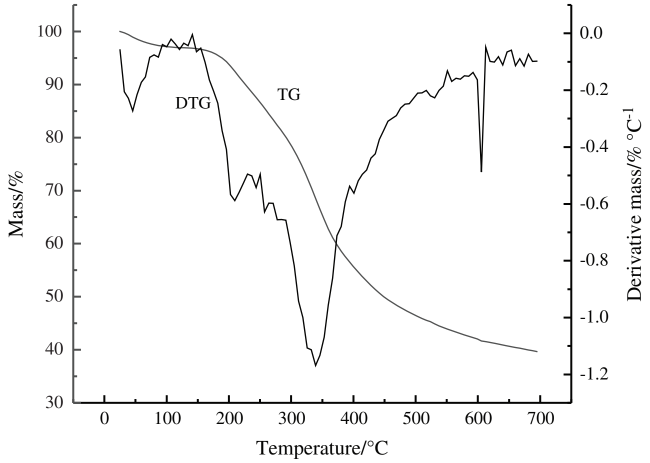


Figure 7: TG/DTG curves for lignin

sample could be used to modify the asphalt samples because at 190°C the retention percentage of the sample was above 95%. It was worth noting that the maximum mass loss and mass retention rates of the lignin sample were 25% and 2.5 times higher than those of the unmodified asphalt SK-0, respectively. Compared to the asphalt sample, the thermal decomposition rate of the lignin sample was lower and the mass retention rate was higher, which was an essential reason for the improved thermal stability of lignin-modified asphalt at high temperatures.

The DTG curves of the lignin modified asphalt samples are the same as that of the unmodified asphalt sample, and there are no multiple heat loss peaks, as seen in the lignin DTG curve (in Fig. 8). This was mainly due to the relatively less content of lignin in the modified asphalt samples and the free water contained in the lignin sample or because its low-temperature pyrolysis products had been volatile and dispersed in processing. The addition of lignin resulted in a slight decrease in temperature during the initial pyrolysis of the modified asphalt samples and at the maximum mass loss, which could be ignored for the unmodified asphalt sample. Fig. 9 shows a graph of the variation of mass retention rate and maximum pyrolysis rate to lignin content. As the lignin content increase, the residual carbon ratio of the asphalt

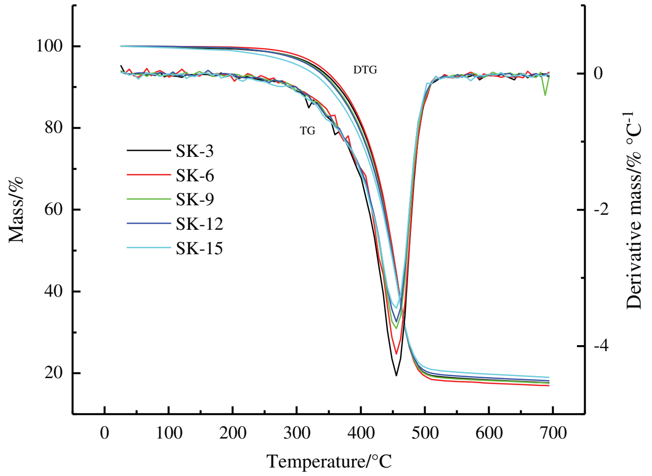


Figure 8: TG/DTG curves for lignin-modified asphalt samples

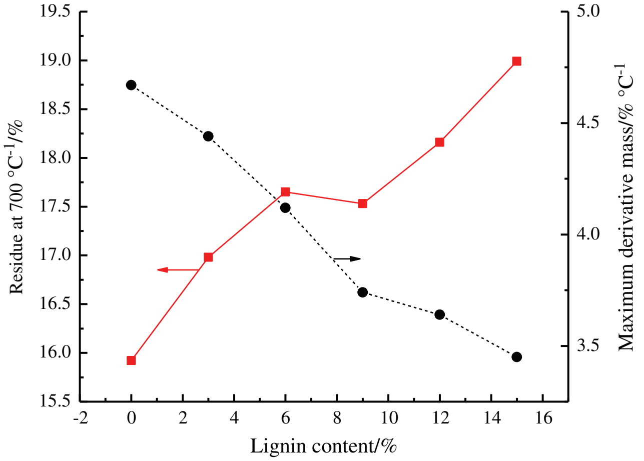


Figure 9: Effect of lignin content on residue and maximum derivative mass

sample increases, while the maximum pyrolysis rate decreases. This further proves that lignin can significantly improve the thermal stability of asphalt.

3.4 Effectiveness Analysis

The properties of lignin-modified asphalt can be considered the superposition of lignin and asphalt because there is no chemical reaction (only physical modification) when lignin is added to asphalt. Therefore, this study defines a variable $W_{T,\ A+L}$ to represent the mass loss rate of asphalt and lignin when the temperature is T and adds them according to their proportion in the mixture, as shown in Eq. (1).

$$WT, A + L = WT, A \times 100/(100 + C_L) + W_{T,L} \times C_L/(100 + C_L) \tag{1}$$

Mass loss rates of asphalt and lignin at temperature T were represented by $W_{T,\ A}$, and $W_{T,\ L}$, respectively, C_L is the lignin content (0, 3, 6, 9). W_T is the mass loss rate of lignin-modified asphalt at temperature T, and the difference between $W_{T,\ A\ +\ L}$ and W_T at temperature T is used to analyze the effect of lignin on the thermal stability of asphalt.

When the difference between $W_{T,\ A\ +\ L}$ and W_T is greater than 0, the thermal stability of the modified asphalt is improved by the addition of lignin; otherwise, the addition of lignin will have a negative effect on the modified asphalt. The effect of lignin on the thermal stability of asphalt is depended on both lignin content and temperature, as shown in Fig. 10.

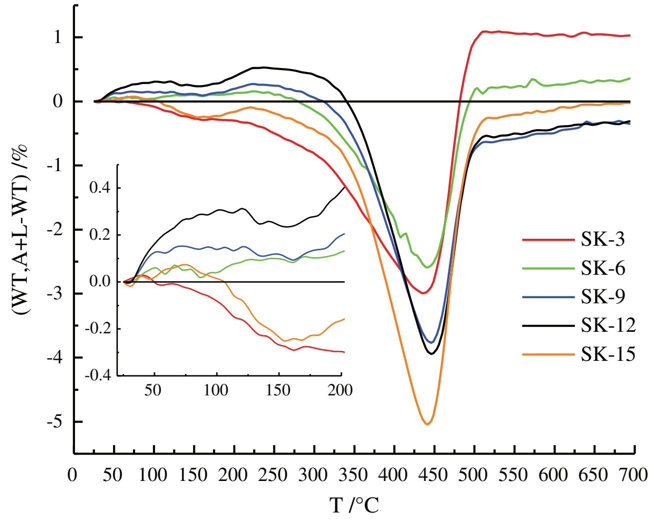


Figure 10: Relationship between $W_{T,\ A\ +\ L}$ - W_T of modified asphalt samples and temperature

Fig. 10 shows thatin the range of 25°C–350°C (3%) has no significant effect on improving the thermal stability of asphalt, especially in the road asphalt use and processing temperature range (<200°C). The quantity of lignin content added has a gradual positive effect on the thermal stability of asphalt, but the thermal stability of the asphalt sample was negatively impacted by the addition of lignin content of 15% of asphalt mass, especially at higher temperatures. This is mainly due to a large amount of thermal decomposition of lignin in lignin-modified asphalt, which means that the lignin content must be controlled.

4 Conclusions

In this paper, the rheological properties of lignin-modified asphalt binders at high temperatures with different lignin content were tested using DSR. The mechanism and effectiveness of lignin in improving the thermal stability of asphalt at high temperatures were analyzed by FTIR and TG. The main conclusions are as follows:

1. According to the FTIR analysis, only the characteristic peaks of both the lignin and the asphalt samples were present in the infrared spectral of the lignin-modified asphalt samples, and no new characteristic absorption peak was observed. Therefore, the modification mechanism of the lignin-modified asphalt samples was physical blending rather than chemical modification.
2. The rheological test results showed that the addition of lignin to asphalts can effectively improve the stability of asphalt at high temperatures, but the content of lignin added should be controlled, and the recommended optimum lignin content was 12% asphalt mass.
3. Compared to the pyrolysis process of lignin and asphalt, it was found that the thermal decomposition rate of lignin was lower and the residual carbon rate of lignin was higher than that of asphalt, respectively. An increase of lignin content decreased the pyrolysis rate and increased residual carbon rate of lignin-modified asphalt. This explained that lignin could improve the stability of asphalt at high temperatures.

4. The proposed effectiveness evaluation index of high-temperature stability further proved that the addition of lignin has a positive effect on the improvement of the thermal stability of asphalt at high temperatures in the range of asphalt service temperature (25–200°C). Specifically, from the pyrolysis viewpoint, it was explained that excessive lignin addition was not beneficial to the thermal stability of asphalt at high temperatures. Additionally, this was consistent with the shear rheological test results conducted at high temperatures.

Acknowledgement: The authors are grateful to Professor Huijuan Li of the School of Chemical Engineering of Southwest Forestry University for the assistance.

Funding Statement: This research was funded by the Scientific Research Fund of Yunnan Provincial Department of Education (Grant No. 2020J0420) and Open Fund based on Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products (Grant No. 2015004). In addition, the authors would like to thank the reviewers of this paper for their ever-present support and valuable advice.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

References

1. Wen, J. L., Chen, T. Y., Sun, R. C. (2017). Research progress on separation and structural analysis of lignin in lignocellulosic biomass. *Journal Forestry Engineering, 2(5),* 76–84. DOI 10.13360/j.issn.2096-1359.2017.05.014.
2. Ren, L. F., He, Q. Q., Qing, T. T., Wang, X. C. (2016). Activation of enzymatic hydrolysis lignin and used for preparation of phenol-formaldehyde Resin. *New Chemical Materials, (9),* 47–49.
3. Ma, Z. M., Li, S. J., Yang, D. M. (2017). Activation of enzymatic hydrolysis lignin and used for preparation of phenol-formaldehyde resin. *Forest Engineering, 33(2),* 64–67.
4. Pinheiro, F. G. C., Soares, A. K. L., Santaella, S. T., Silva, L. M. A., Canuto, K. M. et al. (2017). Optimization of the acetosolv extraction of lignin from sugarcane bagasse for phenolic resin production. *Industrial Crops and Products, 96,* 80–90. DOI 10.1016/j.indcrop.2016.11.029.
5. Feng, P., Chen, F. G. (2010). Application progress of lignin in epoxy resin synthesis. *Journal of Materials Science & Technology, 2,* 54–60. DOI 10.3969/j.issn.1004-8405.2010.02.010.
6. Ferdosian, F., Yuan, Z., Anderson, M., Xu, C. (2016). Synthesis and characterization of hydrolysis lignin-based epoxy resins. *Industrial Crops and Products, 91,* 295–301. DOI 10.1016/j.indcrop.2016.07.020.
7. Zhao, Z., Chen, M. Q., Wang, Y. S., Ding, S. S., Yang, J. (2017). Synthesis and property of epoxy resin based on degrading lignin. *Journal of Materials Science & Technology, 3,* 46–52. DOI 10.16561/j.cnki.xws.2017.03.04.
8. Li, Y., Han, Y. M., Qin, T. F., Chu, F. X. (2011). Research progress of lignin is synthesis of polyurethane materials. *Chemical Industry & Engineering Progress, 30(9),* 1990–1997.
9. Arshanitsa, A., Krumina, L., Telysheva, G., Dizhbite, T. (2016). Exploring the application potential of incompletely soluble organosolv lignin as a macromonomer for polyurethane synthesis. *Industrial Crops and Products, 92,* 1–12. DOI 10.1016/j.indcrop.2016.07.050.
10. Kumari, S., Chauhan, G. S., Monga, S., Kaushik, A., Ahn, J. H. (2016). New lignin-based polyurethane foam for wastewater treatment. *RSC Advances, 6(81),* 77768–77776. DOI 10.1039/C6RA13308H.
11. Li, J. H., Liu, C. Z., Li, Q. L. (2017). Study on properties of lignin-filled polysulfide sealant. *Adhesion, (10),* 39–42. DOI 10.3969/j.issn.1001-5922.2017.10.005.
12. Natividade, L. F., Reinoldo, S. F., Elaine, W., Oliveira, B. R. L. D., Edna, P. et al. (2018). Thermal evaluation by DSC and tensile strength of extrudated blends from polyethylene terephthalate and kraft lignin. *Waste and Biomass Valorization, 6(15),* 367–373. DOI 10.1007/s12649-018-0367-x.
13. García, A., Alriols, M. G., Spigno, G., Labidi, J. (2012). Lignin as natural radical scavenger. Effect of the obtaining and purification processes on the antioxidant behaviour of lignin. *Biochemical Engineering Journal, 67,* 173–185. DOI 10.1016/j.bej.2012.06.013.

14. Thankur, V. K., Thakur, M. K. (2015). Recent advances in green hydrogels from lignin: a review. *International Journal of Biological Macromolecules, 72,* 834–847. DOI 10.1016/j.ijbiomac.2014.09.044.
15. Brauns, F. E. (1952). *The chemistry of lignin*. New York: Academia Press Inc. Publishers.
16. Watkins, D., Nuruddin, M., Hosur, M., Tcherbi-Nateh, A., Jeelani, S. (2015). Extraction and characterization of lignin from different biomass resources. *Journal of Materials Research and Technology, 4(1),* 26–32. DOI 10.1016/j.jmrt.2014.10.009.
17. Mainka, H., Täger, O., Köner, E., Hilfert, L., Busse, S. (2015). Lignin–and alternative precursor for sustainable cost-effective automotive carbon fiber. *Journal of Materials Research and Technology, 4(3),* 283–296. DOI 10.1016/j.jmrt.2015.03.004.
18. Terrel, R. L., Rimsritong, S. (1979). Wood lignins used as extenders for asphalt in bituminous pavements. *Association of Asphalt Paving Technologists, 48,* 111–134.
19. Van Vliet, D., Slaghek, T., Giezen, C., Haaksman, I. (2016). Lignin as a green alternative for bitumen. In: EAPA and Eurobitumen, organizer. *Proceedings of the 6th Euroasphalt & Eurobitume Congress,* Prague, Czech Republic.
20. Slaghek, T. M., van Vliet, D., Giezen, C., Haaksman, I. K. (2017). U.S. Patent Application No. 15/125, 268.
21. Gao, J., Wang, H., Liu, C., Ge, D., You, Z. et al. (2020). High-temperature rheological behavior and fatigue performance of lignin modified asphalt binder. *Construction and Building Materials, 230,* 117063. DOI 10.1016/j.conbuildmat.2019.117063.
22. Asukar, S. D., Behl, A., Gundaliya, P. J. (2016). Utilization of lignin as an antioxidant in asphalt binder. *International Journal of Innovative Research in Technology, 2,* 198–207.
23. Liao, Y., Zhang, B., Li, M., Lin, L. (2014). Preparation and property of EHL modified asphalt. *New Chemical Materials, 42(7),* 99–101.
24. Zhao, Z. D., Xie, Y., Cheng, X. S., Jin, Y. Q., Xu, M. Y. (2011). Research on enzymatic hydrolysis lignin modified petroleum asphalt. *Advanced Materials Research, 306–307,* 1080–1083. DOI 10.4028/www.scientific.net/amr.306.
25. Cheng, C., Tao, G. X., Wang, Q., Han, X. Z. (2019). Experimental study on high temperature performance of lignin modified Asphalt. *Journal of Forestry Engineering, 4(1),* 148–154. DOI 10.13360/j.issn.2096-1359.2019.01.021.
26. Sundstrom, D. W., Klel, H. E., Daubenspeck, T. H. (1983). Use of byproduct lignins as extenders in asphalt. *Industrial & Engineering Chemistry Product Research and Development, 22(3),* 496–500. DOI 10.1021/i300011a022.
27. Cheng, C., Peng, C., Tao, G. X., Zhu, D. B. (2019). Study on effect of short-term aging on rheological rhroperties of lignin modified asphalt. *New Chemical Materials, 47(1),* 249–252+257.
28. Arafata, S., Kumarb, N., Wasiuddina, N. M., Owheb, E. O., Lynam, J. G. (2019). Sustainable lignin to enhance asphalt binder oxidative aging properties and mix properties. *Journal of Cleaner Production, 217,* 456–468. DOI 10.1016/j.jclepro.2019.01.238.
29. Pérez, I. P., Pasandín, A. M. R., Pais, J. C., Pereira, P. A. A. (2019). Use of lignin biopolymer from industrial waste as bitumen extender for asphalt mixtures. *Journal of Cleaner Production, 220,* 87–98. DOI 10.1016/j.jclepro.2019.02.082.
30. Xie, S., Li, Q., Karki, P., Zhou, F., Yuan, J. S. (2017). Lignin as renewable and superior asphalt binder modifier. *ACS Sustainable Chemistry & Engineering, 5(4),* 2817–2823. DOI 10.1021/acssuschemeng.6b03064.
31. Xu, G., Wang, H., Zhu, H. (2017). Rheological properties and anti-aging performance of asphalt binder modified with wood lignin. *Construction and Building Materials, 151,* 801–808. DOI 10.1016/j.conbuildmat.2017.06.151.
32. Batista, K. B., Padilha, R. P. L., Castro, T. O., Silva, C. F. S. C., Araújo, M. F. A. S. (2018). High-temperature, low-temperature and weathering aging performance of lignin modified asphalt binders. *Industrial Crops and Products, (111),* 107–116. DOI 10.1016/j.indcrop.2017.10.010.
33. Pan, T. Y. (2013). RETRACTED: coniferyl-alcohol lignin as a bio-antioxidant for petroleum asphalt: a quantum chemistry based atomistic study. *Fuel, 113(2),* 454–466. DOI 10.1016/j.fuel.2013.06.003.
34. Cheng, C., Peng, C., Hu, B., Sun, W. W. (2019). Study on short-term aging properties of lignin modified asphalt. *Journal Southwest Forestry University (Natural Science Edition), 39(3),* 149–154. DOI 10.11929/j.swfu.201811057.

35. Al-Khateeb, G. G., Al-Akhras, N. M. (2011). Properties of Portland cement-modified asphalt binder using Superpave tests. *Construction and Building Materials, 25(2),* 926–932. DOI 10.1016/j.conbuildmat.2010.06.091.
36. Rodríguez-Alloza, A. M., Gallego, J., Giuliani, F. (2017). Complex shear modulus and phase angle of crumb rubber modified binders containing organic warm mix asphalt additives. *Materials and Structures, 50(1),* 1–9. DOI 10.1617/s11527-016-0950-1.
37. Ma, F., Fu, Z., Sha, A. M. (2014). Aging mechanism of asphalt based on thermal property and mass spectrum analysis. *Journal Chang'an University (Natural Science Edition), 34(6),* 7–12.
38. Banu, D., El-Aghoury, A., Feldman, D. (2006). Contributions to characterization of poly(vinyl chloride)–lignin blends. *Journal of Applied Polymer Science, 101(5),* 2732–2748. DOI 10.1002/app.23026.
39. Liu, Q., Wang, S., Zheng, Y., Luo, Z., Cen, K. (2008). Mechanism study of wood lignin pyrolysis by using TG–FTIR analysis. *Journal of Analytical and Applied Pyrolysis, 82(1),* 170–177. DOI 10.1016/j.jaap.2008.03.007.