HIGH-TEMPERATURE RHEOLOGICAL PROPERTIES OF LIGNIN MODIFIED ASPHALT BINDER

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ABSTRACT

This study aims to introduce lignin as a bio-additive to modify the base asphalt and investigate the high-temperature rheological properties of lignin modified asphalts and virgin asphalt. In this study, asphalt PG 58-28 was selected as the virgin asphalt, and four contents, 2%, 4%, 6% and 8%, of the total binder by weight of lignin were incorporated in the base binder. Rotational viscosity, dynamic shear rheometer, and multiple stress creep recovery tests were conducted to characterize the rheological performances of different types of asphalts. The results showed that the incorporation of lignin increased the viscosity of virgin asphalt at different rotational speeds. The activation energy showed an increasing trend as the lignin increased compared with the virgin asphalt. Meanwhile, the lignin incorporated into the asphalt binder increased the elastic components, and improved the resistance of asphalt binder to the permanent deformation regardless of the lignin contents. The addition of lignin in the asphalt binder could retard oxidation reactions that occurred in the asphalt during the rolling thin film oven aging. This study could provide a prospective foundation for the utilization of lignin extracted from waste biomass as an exceptional and renewable bio-additive in the field of asphalt pavement engineering.

Keywords: Lignin modified asphalt, rheological behavior, activation energy, master curve, multiple stress creep recovery.

1. INTRODUCTION

The construction, rehabilitation and maintenance of road pavement in the past few years has led to the massive consumption of asphalt binder. Meanwhile, the petroleum-based asphalt is dwindling because of the limitation of crude oil in the world (Su et al., 2018, Zhang et al., 2019). In addition, the conventional asphalt binder consumes lots of energy and emits a large number of greenhouse gases during the utilization (Xu et al., 2017, Ge et al., 2019). Thus, to seek the potential alternative for the petroleum-based asphalt or the effective additive to enhance the base asphalt binder has attracted more attention by the researchers in the field of road engineering (Gao et al., 2019).

Among the renewable energies, biomass energy has essential and great potential in the field of asphalt pavement (Yguatyara de Luna et al., 2019, Lv et al., 2018). Biomass such as wood saw dust, corn stalk, grass, and cereal straw is widely distributed in the world, and has low price and large yields. It can be transformed to gaseous, liquid, and solid fuel. Meanwhile, some researchers from road engineering also extracted bio-oil from the biomass through fast pyrolysis (Diebold, 2000), and studied the property of asphalt binder incorporating the bio-oil (Hosseinnezhad et al., 2019).

Lignin, a kind of byproduct from biomass, was shown to have the potential performance as an extender in asphalt (Sundstrom et al., 1983, Li et al., 2015). It constitutes about 20% of photosynthetic biomass and is an abundant renewable resource (Ben-Iwo et al., 2016). The cross-linking of three-dimensional hydrophobic and aromatic molecules of lignin makes it one of the most abundant organic polymers on the planet (Pan, 2012). Meanwhile, it has also been reported that lignin possesses the antioxidant, antifungal properties and antibiotic activity (Mai et al., 2000).

However, due to the heterogeneous nature of lignin, the chemical structure is complex, and the separation and extraction process is cumbersome. The condensation reaction is easy to occur, which seriously restricts the development and utilization of lignin. In the paper production process, millions of cellulose are separated annually from plant fiber, a large number of lignin by-products (about 50 million tons) are produced, it is directly discharged into natural water bodies in the form of pollutants “black liquor” (Li et al., 2015). Some of the products are concentrated and burned, and the lignin that can be effectively utilized is less than 20%. Among them, less lignin can be utilized for resource utilization, thus causing waste of organic resources (Chio et al., 2019).

Based on the physical and chemical characteristics, the functions and situations of lignin, studies on the lignin combining with asphalt binder were conducted in recent years to modify petroleum-based asphalt in the field of road pavement. Batista et al. analyzed the physical and chemical performances of asphalts modified with lignin, and tested the high-temperature, low-temperature and weathering aging properties of the modified asphalts. The results illustrated that the asphalt binder with lignin had a lower carbonyl indicator, and exhibited higher resistance to the weathering aging, except for the modified asphalt binder with 4% content of lignin under the condition of 200 hours weathering aging (Batista et al., 2018). Arafat et al. investigated the influences of small portion of lignin on the aged and unaged asphalt binder and asphalt mixture. It found that the asphalt with lignin had a higher strain tolerance than the virgin asphalt binder during the strain sweep; asphalt with lignin from rice hulls and black liquor had longer aging indicator than that of the conventional asphalt (Arafat et al., 2019).

Overall, lignin has great potential to modify the properties of petroleum-based asphalt as a green and environmentally-friendly bio-additive. However, the performances, especially the high-temperature rheological property of asphalt modified by lignin are studied insufficiently because of the test methods and the lignin content in the previous research. Motivated by these, this study investigates the incorporation of four contents of lignin into virgin asphalt to determine its influence on the properties of lignin modified asphalt.

2. OBJECTIVE OF THE STUDY

This study aimed to investigate the high-temperature rheological property of lignin modified asphalt (LMA) binder. The LMA binder was prepared with virgin asphalt binder and four contents of lignin, which were 2%, 4%, 6% and 8%, respectively. Rotational viscosity (RV), dynamic shear rheometer (DSR), and multiple stress creep recovery (MSCR) tests were employed to investigate the high-temperature rheological properties of different kinds of lignin modified asphalts in the laboratory.

3. MATERIALS AND METHODS

3.1 Materials

The base asphalt binder used in this research was PG 58-28, which was generally used in the region of upper peninsula of Michigan and many areas of Midwest in the U.S.A. The performances of PG 58-28 could meet the requirement. The parameters, rotational viscosity, rutting factor, and fatigue factor, met the requirements of specification AASHTO M 320 for the PG 58-28. The lignin was used as a bio-additive in this study, and it was produced by Shanghai Jack Gump Industrial Co. Ltd. It was converted from the waste wood chips. The color of the powder was brown. The average molecular weight was about 10350, the water content was 3.55%, and the pH value was 7.5. The composition of this lignin was about 64.2% carbon, 5.8% hydrogen, 29.2% oxygen, and 0.8% ash.

3.2 Preparation of Lignin Modified Asphalt

The LMA binder was prepared by virgin asphalt binder and lignin. Firstly, the virgin asphalt in the container was heated to the flow stage at 160°C. Then the prepared lignin was added to the asphalt in quantities of 2%, 4%, 6% and 8% of the total binder by weight. The mixed mixture was sheared and further mixed by a shear mixer at the speed of 6000 rpm for 40 min (Xu et al., 2017, Batista et al., 2018). To simplify the name of the lignin modified asphalt, the asphalt with 2%, 4%, 6% and 8% of lignin were denoted as L02, L04, L06 and L08 in the following study and result analysis.

3.3. Test Methods

3.3.1 Viscosity

Different types of asphalt binder were tested using the Brookfield DV-III produced by AMETEK Brookfield. Spindle size 27 was employed in this study. Four different test temperatures, 110, 135, 150 and 165°C, three speeds, 10, 20 and 50 rpm, were set for the tests. For the FAE calculation, the rotational speed was 20 rpm.

3.3.2 Dynamic Shear Rheometer

The rheological behavior of different types of asphalt binder could be characterized by DSR through temperature sweep based on AASHTO M320. The rheometer used in this study was MCR 302 produced by Anton Paar. The asphalts tested were unaged and RTFO-aged binder. The test temperature range was 46°C-76°C in intervals 6°C. Complex modulus, phase angle, and rutting factor were obtained and calculated.

3.3.3 *Multiple Stress Creep and Recovery*

Asphalt used in MSCR test was firstly aged by RTFO. The test device was also MCR 302 produced by Anton Paar. The test temperatures were 58, 64, 70 and 76°C, respectively. The specific process of MSCR was based on the specification AASHTO T 350.

4. RESULTS AND DISCUSSION

4.1 Viscosity

The viscosity for virgin asphalt and lignin modified asphalt at different temperatures with a speed of 20 rpm are shown in Fig. 1. As displayed in Fig. 1, it was noteworthy that the rotational viscosity of virgin asphalt PG 58-28 and four kinds of lignin modified asphalt could meet the requirement of specification, which should be no more than 3000 mPa·s at the temperature of 135°C. This meant that the addition of lignin, even with the content up to 8%, was still sufficiently flowable for the workability and mixability during construction.

The rotational viscosity of different types of asphalt, virgin asphalt PG 58-28, LMA (i.e. L02, L04, L06, L08), decreased with the increase of temperature. However, when the temperature was higher, the variation in decrease was less. For instance, the viscosity of L02 was 1.616 Pa·s at 110°C, and it decreased about 74.94% at 135°C; while it decreased about 50.62% at 150°C compared with that at 135°C; and the decrease value was 37.50% at 165°C compared with that at 150°C. This was because the asphalt binder was a kind of viscoelastic material, which was affected by the temperature. The higher the temperature, the easier it flowed. Moreover, the addition of the lignin enhanced the viscosity of the asphalt. As the content of the lignin increased, the viscosity of LMA had an increasing trend, and the trend was reduced when the temperature was higher than 135°C. For example, at 110°C, the increases of viscosity of L02, L04, L06, L08 were 25.17%, 38.26%, 50.12%, 56.16% compared with PG 58-28, respectively; at 150°C, the increases were 14.29%, 35.71%, 40.00%, 45.71%, respectively. This could be explained by that the stiffening of asphalt increased with the addition of lignin, and the influence also became significant with the increasing concentration of the lignin.

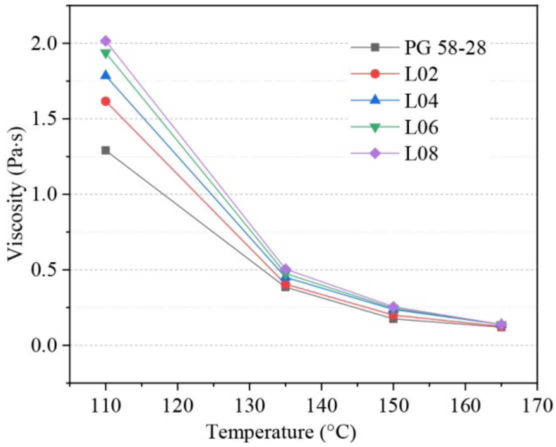


Figure 1: The relationship between viscosity of asphalt PG 58-28 and LMA and temperature

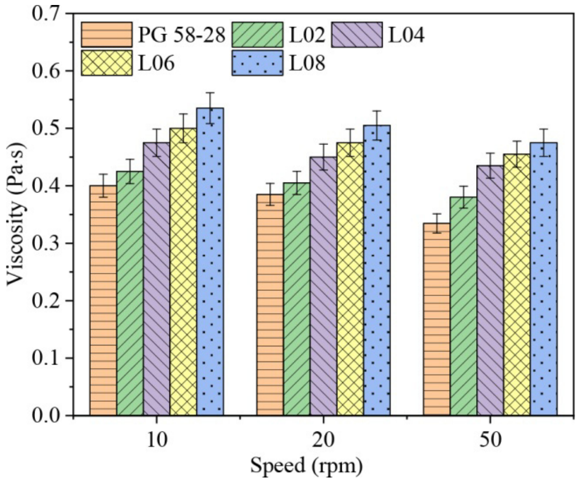
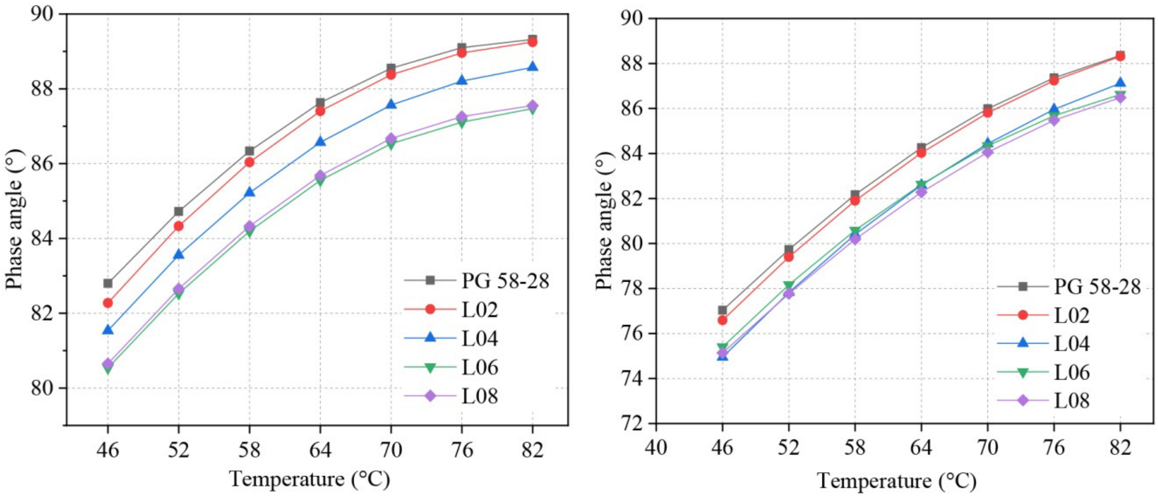


Figure 2: The viscosity of asphalt PG 58-28 and LMA with different rotational speeds at 135°C

Fig. 2 illustrates the viscosity of asphalt PG 58-28 and LMA with different rotational speeds at 135°C. As displayed in Fig. 2, the influence of the rotational speed to the viscosity of different types of asphalt binder was similar. In addition, the viscosity of PG 58-28 and LMA decreased with the rotational speed. Taking asphalt binder L02 as an example, the viscosity was 0.425 Pa·s at the speed of 10 rpm while it was 0.405 Pa·s and 0.38 Pa·s at 20 rpm and 50 rpm, respectively. This was because the asphalt binder exhibited the characteristics of a non-Newtonian fluid at the test temperature and speeds (Gao et al., 2018b). The addition of lignin increased the viscosity of virgin asphalt at any given rotational speeds, but the viscosities still could meet the requirements of specification for the mixing and construction of asphalt binder, which is no more than 3.00 Pa·s at 135°C.

4.2 Temperature Sweep

4.2.1 Phase Angle vs. Temperature



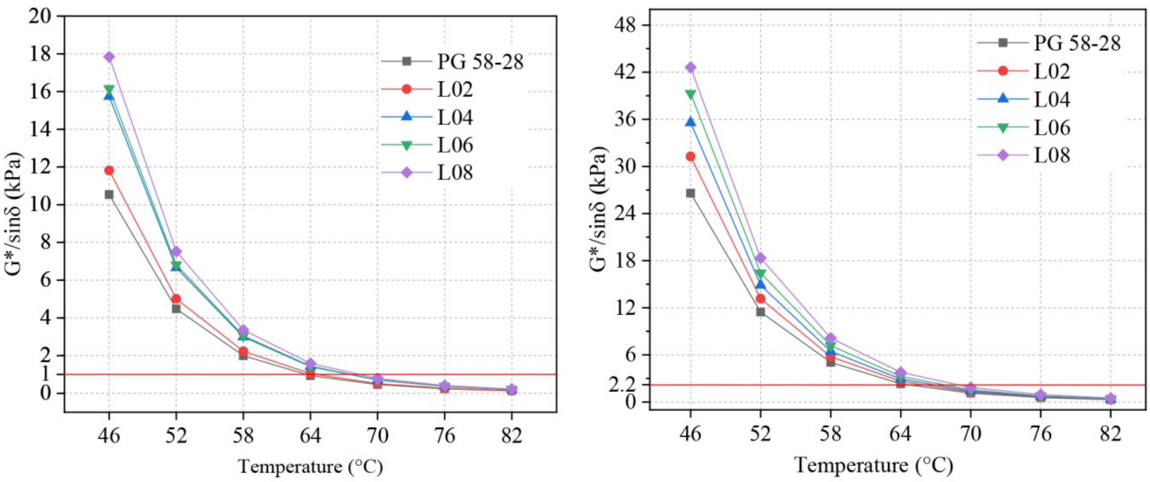
(a) Unaged (b) RTFO-aged

Figure 3: The phase angle of asphalt binder vs. temperature at 10 rad/s

In Fig. 3 (a), the δ of five types of asphalt binder increased as the temperature increased, which meant there were more viscous components when the temperature was high. However, the increasing rate of the phase angle became lower with the increasing of temperature. For example, the phase angle of L04 at 46°C was 82.28°, and it increased 6.23% at 64°C compared with that at 46°C; while it increased 2.11% from 64°C to 82°C, which had the same interval value. Meanwhile, the incorporation of lignin reduced the phase angle of virgin asphalt, which lowered the viscous components. It was also notable that when the concentration of lignin was more than 6%, the increasing trend was insignificant. It also could be found from Fig. 3 (b) that the change rule of phase angle for the RTFO-aged asphalt with the change of temperature was consistent with that of the unaged asphalt binder. In general, the RTFO-aged asphalt binder showed lower phase angle compared to the unaged. This was because the aging decreased the light component in the asphalt binder, such as aromatic compounds. Meanwhile, the lignin modified asphalt binder L04, L06, and L08 showed nearly the same change of phase angle with the change of temperature after RTFO-aging.

4.2.2 *Rutting Factor vs. Temperature*

Fig. 4 (a) and (b) show the rutting factor ($G^* / \sin\delta$) changes of different types of asphalt binders with the changes of test temperature, respectively. A higher rutting factor of asphalt binder indicated a better ability to resist deformation.



(a) Unaged (b) RTFO-aged

Figure 4: The rutting factor of asphalt binder vs. temperature at 10 rad/s

In Fig. 4 (a), the rutting factor of different types of asphalt decreased significantly as the temperature increased. This was because the higher temperature made the asphalt binder softer, and the viscous portion increased. Thus, it decreased the resistance to the deformation. However, the decrease rate became lower when the temperature was more than 64°C. Moreover, the addition of lignin increased the rutting factor, and the more lignin content, the higher the rutting factor. This law illustrated that the incorporation of lignin to the asphalt has the potential to enhance the resistance to deformation during the high-temperature condition. For example, when the temperature was 52°C, compared with PG 58-28, the rutting factor of LMA binder, L02, L04, L06, L08, increased 11.90%, 24.70%, 48.80%, 67.90%, respectively.

RTFO aging was a kind of process that the oxidation reactions occur in the asphalt. After the asphalt binder was RTFO-aged, as displayed in Fig. 4 (b), the rutting factor of all kinds of asphalt dramatically increased at the same temperature. For instance, when the temperature was 52°C, compared with the unaged asphalt, the $G^* / \sin\delta$ of RTFO-aged asphalt PG 58-28, L02, L04, L06, L08 increased by 155.74%, 152.48%, 146.33%, 146.45%, 143.86%, respectively. The reason was that the RTFO-aging decreased the light components in the asphalt, and made the asphalt stiffer. It was also interesting to observe that the increasing portion of rutting factor for the aged compared to the unaged asphalt binder varies differently. For the LMA binder, i.e., L02, L04, L06, L08, the increasing percentages were lower than PG 58-28. This may be affected by the content of lignin; higher content of lignin may lead to the higher modulus of lignin modified asphalt binder in original state, and the rutting factor of lignin modified asphalt with higher lignin may exhibit more stable during aging. This could also mean that the incorporation of lignin in the asphalt could retard the oxidation reactions that occurred in the asphalt during the RTFO aging and would make the aged asphalt less rigid. The reason was that lignin possessed hydroxyl and methoxy functional groups, and may neutralize the free radicals, which were formed during the oxidation reaction in the asphalt (Batista et al., 2018, Azadfar et al., 2015, Dizhbite et al., 2004, Boeriu et al., 2004). The finding was also certified by Xu (Xu et al., 2017) through the calculated amount of carbonyl structure (C=O) detected by Fourier-transform infrared spectroscopy (FTIR) for the unaged and aged asphalt.

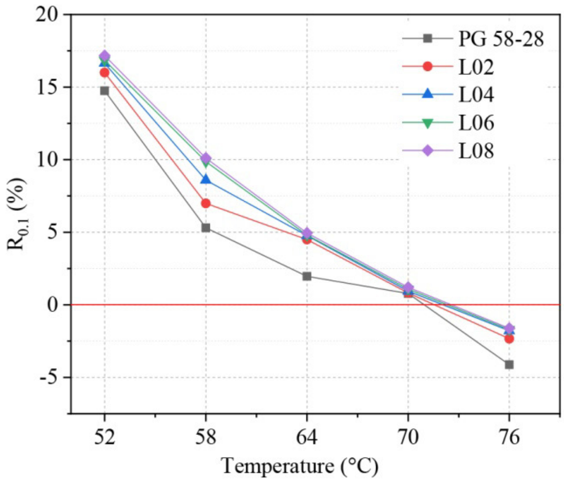
The antioxidant activity of lignin added to the asphalt binder showed a great potential application combining with bio-asphalt. The bio-asphalt made of bio-oil and petroleum asphalt exhibits high aging degree after RTFO-aging (Lei et al., 2018, Gao et al., 2018b).

Additionally, it was actually an environmentally friendly and renewable pavement material, which utilized waste wood chips or crops as a resource for bio-oil (Gao et al., 2018a).

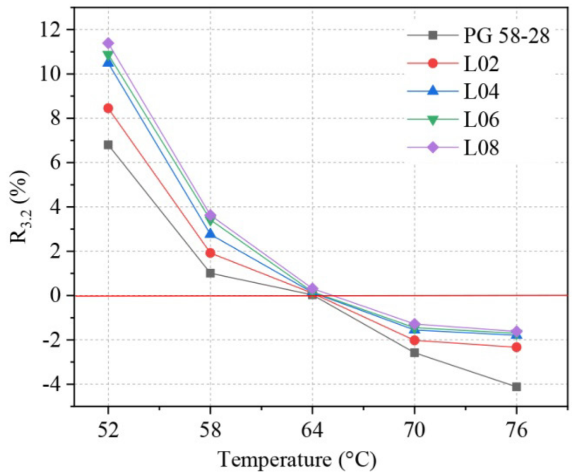
4.3 MSCR Test

4.3.1 Average Percent Recovery and Non-Recoverable Creep Compliance

The average percent recovery of different types of asphalt binder at the 0.100 kPa stress level and 3.200 kPa stress level are presented in Fig. 5 (a) and (b).



(a) At 0.100 kPa

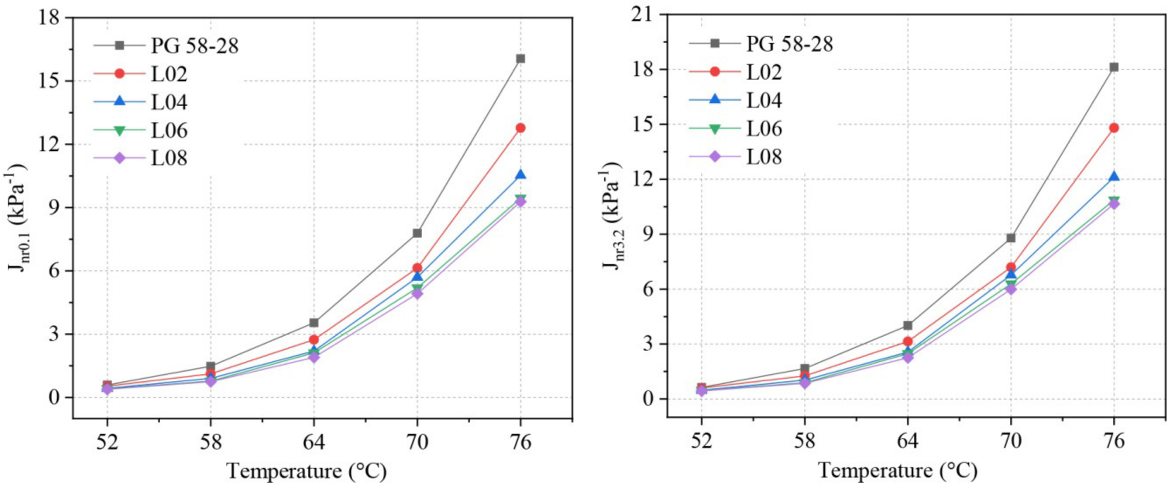


(b) At 3.200 kPa

Figure 5: Average percent recovery of different types of asphalt binder

It could be found from Fig. 5 (a) and (b) that the average percent recovery of all kinds of asphalt binders at 0.100 kPa and 3.200 kPa descended as the test temperature increased. This meant that the increased temperature changed the component portions in asphalt binder: the viscous component increased while the elastic component decreased. As a result, the resistance to deformation and the recoverability of asphalt binder was reduced. The change was more pronounced with a higher stress level. In addition, the recovery of LMA binder was higher than that of base asphalt, and the trend increased with the concentration of lignin. For example, L08 had higher percent recovery than PG 58-28, L02, L04 and L06. This illustrated that the incorporation of lignin ascended the ability to resist the permanent deformation of asphalt binder. Moreover, when the temperature was higher than 70°C, the average percent recovery at 0.100 kPa was negative; and when the temperature was higher than 64°C, the recovery at 3.200 kPa was also negative. This was because the viscous characteristic of asphalt binder at these temperatures was more significant and the elastic characteristic had nearly disappeared. Thus, it was difficult for the asphalt binder after loading to recover to its original deformation, and the resistance to deformation had also nearly disappeared. From Fig. 5 (a) and (b), it also could be found that for the same asphalt, when the stress level increased from 0.100 to 3.200 kPa, the average percent recovery decreased. This was in accordance with the fact that the heavy vehicle load would lead to deeper deformation on the road.

The non-recoverable creep compliance (J_{nr}) of different kinds of asphalt at the 0.100 and 3.200 kPa stress levels are compared in Fig. 6 (a) and (b).



(a) At 0.100 kPa (b) At 3.200 kPa

Figure 6: Non-recoverable creep compliance of different types of asphalt binder

As seen in Fig. 6 (a) and (b), the J_{nr} of different types of asphalt binder was amplified with test temperature, and the increment between the lignin modified asphalt and virgin asphalt also increased. This illustrated that the temperature had a vital influence on J_{nr}.

Furthermore, the addition of lignin reduced the J_{nr}, which meant the LMA binder was expected to have a higher resistance to deformation. However, when the content of lignin increased from 6% to 8%, the decrement of non-recoverable compliance of asphalt binder was not obvious.

5. CONCLUSIONS

In this study, lignin was introduced as a bio-additive in concentrations of 2%, 4%, 6% and 8% to modify the virgin asphalt. RV, DSR, and MSCR tests were utilized to investigate the high-temperature rheological performances of LMA binders and virgin asphalt binder.
The following conclusions can be obtained:

- The addition of lignin increased the viscosity of virgin asphalt at different rotational speeds. Meanwhile, the viscosity of modified asphalt can still meet the requirement for mixing and construction of asphalt binder in the specification. The activation energy showed an increasing trend with the increase of lignin compared with the virgin asphalt.
- The lignin incorporated to the asphalt increased the elastic components, made the base asphalt binder stiffer, and improved the resistance of the asphalt to the deformation during the high-temperature condition.
- The incorporation of lignin in the asphalt could retard the oxidation reactions that occurred in the asphalt during the RTFO aging.
- The LMA binder had high percent recovery compared with the virgin asphalt. The addition of lignin reduced the stress sensitivity of percent difference in recovery, while improving the non-recoverable creep compliance at different temperatures.

6. ACKNOWLEDGMENT

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