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Research Article

Study on Conventional and Rheological Properties of Corn Stalk Bioasphalt/PPA Composite Modified Asphalt

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As a new type of pavement material, bioasphalt has received more and more attention. However, the high-temperature behavior of bioasphalt is poor after blending with asphalt binder. In order to solve this problem and facilitate the waste utilization and resource conservation, the corn stalk bioasphalt/PPA composite modified asphalt was proposed. The conventional performance tests and rheological tests were conducted to evaluate high-temperature and low-temperature behavior. Fourier transform infrared reflection (FTIR) test was undertaken to analyze the mechanism of modified asphalt. The results indicated that blended asphalt penetration and ductility gradually decrease with the PPA content increasing. The softening point and viscosity of the modified asphalt increased, which led to an improvement of blended asphalt's rigidity. The PPA increased the rutting index of corn stalk bioasphalt/PPA composite modified asphalt. However, bioasphalt had a negative effect on its high-temperature performance. The corn stalk bioasphalt/PPA composite modified asphalt could meet the specification requirement at −18°C considering the creep rate and stiffness modulus, indicating it had outstanding crack resistance. When the PPA and bioasphalt respect to the weight of neat asphalt were 6%–8% and 10%–16%, respectively, the corn stalk bioasphalt/PPA composite modified asphalt performance was optimal. However, shear time and shear rate merely affected the proposed modified asphalt performance. The bioasphalt did not affect the chemical structure of asphalt. However, PPA generated new functional groups (P-O single bond, phosphate $(RO)_3P=O$, and P=O double bond) causing a chemical modification in the asphalt binder. This study can provide a basis for applying bioasphalt, making road engineering more economical and environmentally friendly.

1. Introduction

Since the start of the 21st century, the need for asphalt has sharply increased with the vigorous development of worldwide transportation construction. In the context of the global pandemic, the demand for crude oil has suddenly decreased, leading to increased pressure on the supply and demand of asphalt. Moreover, asphalt is a petroleum processing product, which means it is a nonrenewable resource [1]. Hence, finding an alternative to mitigate this problem has become a hotspot in current research works. Bioasphalt can be obtained from biomass materials through pyrolysis technology. It has attracted more attention from scholars because of its characteristics of being extremely cheap and environmentally friendly [2]. Assuming that bioasphalt can entirely or partially replace petroleum asphalt, the former material can reduce the dependence on the latter material, making road construction greener, environmentally friendly, and more economically viable.

The biomass resources are abundant in China. Bioasphalt is a by-product of the plant refining process. The bioasphalt performance is similar to that of petroleum asphalt. In this study, the waste product obtained during the refining process of corn stalks was selected as bioasphalt. Furthermore, bioasphalt reacts with polyurethane and rubber, but there are few studies on directly blending it with neat asphalt [3–6]. After the regeneration of aged asphalt with bioasphalt, the asphalt's stiffness modulus decreases, and the creep rate increases. Bioasphalt can positively affect the low-temperature behavior and fatigue performance of the recycled asphalt mixture.

However, it harms the high-temperature behavior [5, 7–9]. The creep rate of the rubber-modified asphalt has been increased by using bioasphalt. Bioasphalt improves and increases the low-temperature and rutting index of neat asphalt, respectively [6, 10]. Adding bioasphalt to the neat asphalt decreases its viscosity and high-temperature behavior. Besides, dynamic stability, splitting strength, and compressive resilience modulus of asphalt mixture will decrease, but the low-temperature behavior increases [11–13]. In summary, the application of corn stalks bioasphalt has not been efficiently studied yet. The low-temperature behavior of bioasphalt has been improved, but the high-temperature behavior needs to be further enhanced.

In order to expand the application of bioasphalt and enhance the high-temperature behavior of blended asphalt, the most effective method has been polymer modification, such as SBS or SBR [14]. SBS modified asphalt has been the most widely used because of its excellent performance, but its price is high [15]. Polyphosphoric acid (PPA) has been successfully applied because of its lower cost and superior compatibility with neat asphalt, and it shows a remarkable improvement in the high-temperature behavior of asphalt [16–18]. After using PPA modified asphalt, the colloidal structure and system change, the resin decreases, and the asphaltene content gradually rises [19]. It enhances the asphalt high-temperature behavior and improves storage stability [20]. After using PPA modified asphalt, the rutting index can be increased so that the pavement has positive resistance to permanent deformation [18, 21]. PPA can improve the cohesiveness, elasticity, and rutting resistance of SBR modified asphalt. SBR modified asphalt has higher toughness and recovery rate. The asphalt high-temperature behavior is prominent when the PPA content increases [17]. PPA can significantly enhance the creep recovery of rubber-modified asphalt. The temperature scanning test results have demonstrated that PPA can increase the rutting index of rubber asphalt [22, 23]. However, PPA harms the water stability of the bioasphalt mixture [24]. Many studies have manifested that PPA can significantly enhance the high-temperature behavior of different types of asphalt.

In summary, if the bioasphalt is blended with neat asphalt and then modified with PPA, on the one hand, bioasphalt may partially replace the content of petroleum asphalt, and, on the other hand, PPA will enhance the high-temperature behavior of the blended asphalt. The bioasphalt will produce economic benefits and make road engineering greener and environmentally friendly. This study will adopt an orthogonal test design. The bioasphalt contents will be set at 10%, 12%, 14%, or 16% and PPA contents will be 2%, 4%, 6%, or 8%. Furthermore, the shear time and shear rate will be considered for preparing corn stalk bioasphalt/PPA composite modified asphalt. In this study, the conventional performance and rheological tests to evaluate the modified asphalt behavior and determine its best preparation plan will be undertaken. Finally, FTIR test will be conducted to analyze the mechanism of modified asphalt. This research work provides a theoretical basis for promoting the practical application of corn stalk bioasphalt/PPA composite modified asphalt.

2. Raw Materials and Test Methods

2.1. Raw Materials. The neat asphalt from Chongqing Huiming Company was utilized in this study. Its technical indexes are shown in Table 1. Bioasphalt was the product of the corn stalks refining process, and it was a dark brown viscous liquid; its technical indicators are displayed in Table 2. Polyphosphoric acid (PPA) was obtained from Henan Hui-Fa Chemical Company. The technical indicators are shown in Table 3.

2.2. Preparation of Corn Stalk Bioasphalt/PPA Composite Modified Asphalt. The experimental scheme was determined by orthogonal design. The factors and levels are described in Table 4. Then, the corn stalk bioasphalt/PPA composite modified asphalt was prepared using the FM300 high-speed shear apparatus. First, the neat asphalt and bioasphalt were preheated in a bake-out furnace at 135°C for 2 hours. Second, the neat asphalt was blended with bioasphalt. The bioasphalt contents were 10%, 12%, 14%, and 16% of the neat asphalt mass, and the shear rate was 1500r/min for 20 minutes. Finally, corn stalk bioasphalt/PPA composite modified asphalt was prepared by adding a specific content of PPA according to Table 5. At the same time, different shear times and shear rates were utilized to prepare corn stalk bioasphalt/PPA composite modified asphalt.

2.3. Test Method. According to the specification (JTG E20-2011), the penetration, ductility, softening point, and viscosity tests of 16 groups of corn stalk bioasphalt/PPA composite modified asphalt were implemented. The dynamic shear rheometer (DSR) test was used for temperature scanning. The temperature scanning range was 40°C–88°C. The low-temperature behavior of corn stalk bioasphalt/PPA composite modified asphalt was tested by using the bending beam rheometer (BBR) test. The rolling thin-film oven aging (RTFO-aging) test and pressurized aging vessel (PAV) test of asphalt were carried out before the BBR test. Finally, FTIR analyzed the functional groups of neat asphalt, bioasphalt, blended asphalt, PPA modified neat asphalt, and corn stalk bioasphalt/PPA composite modified asphalt. The preparation and test process are shown in Figure 1.

3. Analysis and Discussion of Test Results

3.1. Conventional Physical Properties. According to the specification (JTG E20-2011), the 16 groups of corn stalk bioasphalt/PPA composite modified asphalts were tested for conventional physical properties. The results are displayed in Table 6. Furthermore, the visual and variance analysis of conventional physical properties are shown in Tables 7 and 8.

3.1.1. Penetration. According to Table 7, the influence order of the factors on the penetration is as follows: PPA content > bioasphalt content > shear time > shear rate. As shown in Table 8, PPA content has a particularly significant effect on penetration. The bioasphalt content impact on

Table 1: Technical index of neat asphalt.

Index	Test results	Technical requirements
Penetration (25°C)/0.1 mm	62.3	60–80
Ductility (15°C), cm	147	≥100
Softening point, °C	46.8	≥46
Flash point, °C	316	≥260
Wax content, %	1.56	≤2.2

Table 2: Technical indicators of bioasphalt.

Index	Test results
PH	2.6
Density, g/cm^3	0.97
Trichloroethylene solubility, %	87.1

Table 3: Technical indicators of PPA.

Index	Test results
Content (P_2O_5), %	80.36
Density (25°C), g/cm^3	2.1
Boiling point, °C	532
Sulfide (Cl), %	<0.001

Table 4: Orthogonal test table of factor level.

Variables	Unit	Coded and actual factor			
PPA content	%	2	4	6	8
Bioasphalt content	%	10	12	14	16
Shear time	min	20	30	40	50
Shear rate	r/min	1000	2000	3000	4000

penetration is higher than those of the shear time and shear rate. Shear time and shear rate do not affect penetration. Figure 2 reveals that the penetration of corn stalk bioasphalt/PPA composite modified asphalt gradually decreases with the increase of PPA content from 2% to 6%. However, penetration does not significantly change when the PPA contents are 6% and 8%. When PPA content is 8%, the penetration is the smallest. The average penetration is 64.8 when the PPA content is 8%, and the decrease ratio is 4% compared with neat asphalt. Penetration gradually decreases with PPA content increasing. This fact shows that PPA has an evident hardening influence on the corn stalk bioasphalt/PPA composite modified asphalt. According to Figure 2, the penetration gradually increases with the bioasphalt content increasing. It indicates that the bioasphalt would have a specific softening effect. In particular, the penetration obviously increases with the increase of bioasphalt. Compared with the neat asphalt, when PPA content is 2% and bioasphalt contents are 10%, 12%, 14%, and 16%, the penetration increases by 102.6%, 118.5%, 140.1%, and 193.6%, respectively. Bio-oil is a kind of light material, and, during high-temperature preparation, the unstable light material volatilizes because of the aging phenomenon. However, the constant part is modified with the neat asphalt, which causes the asphalt to soften at ambient temperature and increase the penetration [25].

3.1.2. Softening Point. According to Table 7, the influence order of the factors on the softening point is as follows: PPA content > bioasphalt content > shear rate > shear time. As shown in Table 8, the PPA content had a particular effect on the softening point. Shear time and shear rate merely affect the softening point. Figure 3 shows that the softening point would increase with PPA content changing from 2% to 8%. It indicates that the PPA can enhance the high-temperature behavior and temperature sensitivity. When the PPA content is 2%, 4%, 6%, or 8%, the average softening point is 44.35°C, 59.9°C, 68.13°C, or 72.83°C, respectively, and the enhanced ratio compared with the neat asphalt is −5.24%, 27.99%, 45.57%, or 55.61%, respectively. The softening point gradually decreases with the bioasphalt content increasing, indicating that bioasphalt would harm the high-temperature behavior. When the PPA content is 8% and bioasphalt content is 10%, 12% 14%, or 16%, the softening point is 78.6°C, 75.2°C, 70.6°C, or 66.9°C, respectively, and, compared with the neat asphalt, the enhanced ratio is 67.95%, 60.68%, 50.85%, or 42.95%, respectively. The softening point is enhanced because PPA changes the asphalt components: the resin continues to decrease, and the asphaltene content gradually increases, which increases its stiffness and hardness [6, 26, 27]. Due to the reconstitution of colloidal structure in asphalt, the softening point of asphalt has been significantly improved.

3.1.3. Ductility. The ductility was tested at 5°C and the results are shown in Figure 4. The neat asphalt ductility is 168 mm at 5°C. According to Table 7, the influence order of the factors on the ductility is as follows: bioasphalt content > PPA content > shear time > shear rate. According to Table 8, the PPA and bioasphalt content effects on ductility are significant. However, the shear time and shear rate have no effect on it. It can be observed that the ductility is maximum when the PPA content is 2% and the bioasphalt content is 16%. Ductility does not significantly change when the PPA content is in the range of 6%–8%. When the PPA content is 6% and bioasphalt content is 10%, 12%, 14%, or 16%, the ductility is 287.2 mm, 346.2 mm, 374.7 mm, or 432.2 mm, respectively, and, compared with the neat asphalt, the enhanced ratio is 70.95%, 106.07%, 123.04%, or 157.26%, respectively. The ductility gradually increases with bioasphalt content increases. It reveals that plasticity increases. However, the ductility results show a descending trend with the rise of PPA content. It indicates that PPA decreases the plasticity of the asphalt binder. Compared with neat asphalt, the ductility of the modified asphalt dramatically rises. A previous research work has shown that bioasphalt increases the fracture energy of asphalt and significantly enhances ductility [28]. At the same time, the bio-oil made the asphalt have enough light components at high temperature and correspondingly increases the proportion of oil in the asphalt, so the ductility increases [25].

3.1.4. Viscosity. Asphalt with greater viscosity will produce less shear deformation under load. It has better elastic recovery performance and less residual permanent

Table 5: Orthogonal test table.

Number	PPA content/%	Bioasphalt content/%	Shear time/min	Shear rate/r/min
1	2	10	20	1000
2	2	12	30	2000
3	2	14	40	3000
4	2	16	50	4000
5	4	10	30	3000
6	4	12	20	4000
7	4	14	50	1000
8	4	16	40	2000
9	6	10	40	4000
10	6	12	50	3000
11	6	14	20	2000
12	6	16	30	1000
13	8	10	50	2000
14	8	12	40	1000
15	8	14	30	4000
16	8	16	20	3000

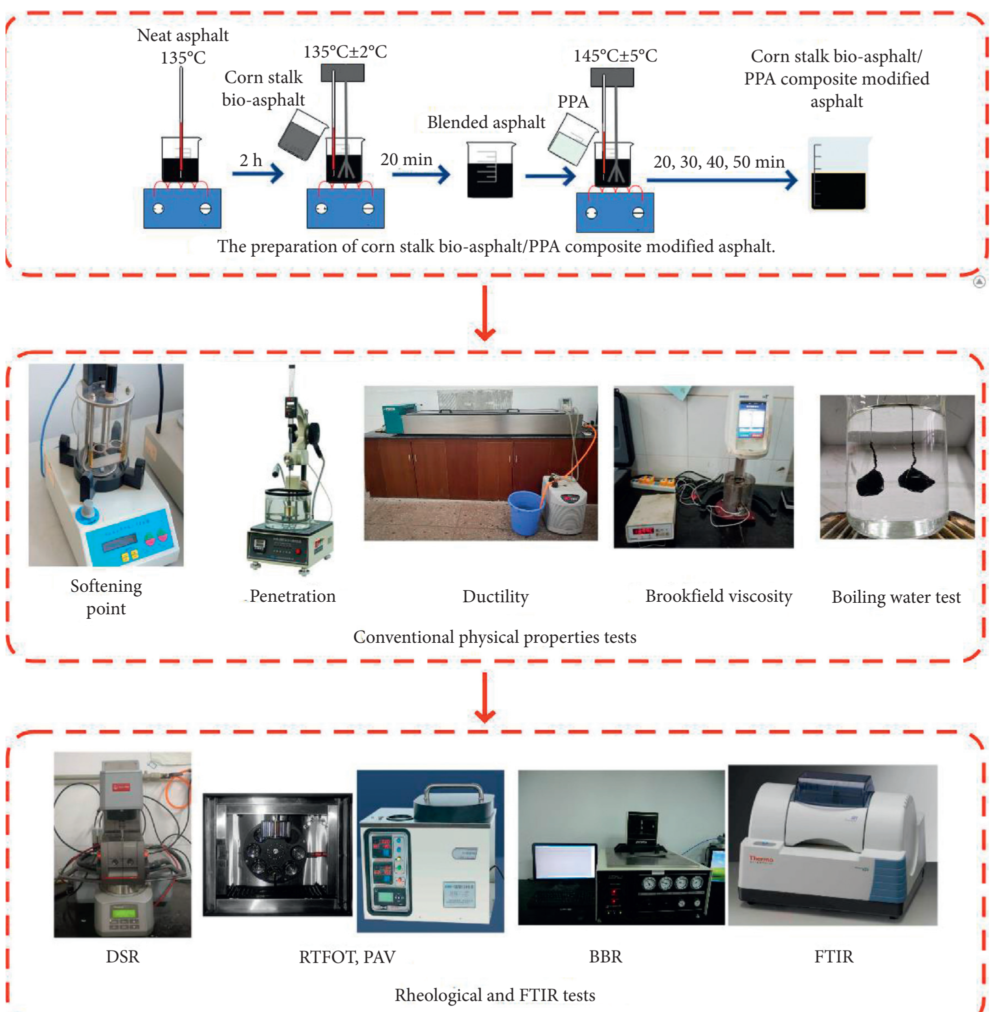


Figure 1: Preparation and test process of corn stalk bioasphalt/PPA composite modified asphalt.

deformation so that the asphalt mixture has a better high-temperature behavior. The viscosity test was performed at 135°C. The test results are depicted in Figure 5. The viscosity of neat asphalt is 476 MPa·S at 135°C. According to Table 7, the influence order of the factors on the viscosity is as follows: PPA content > bioasphalt content > shear

Table 6: Conventional physical properties.

No.	Penetration/0.1 mm	Softening point/°C	Ductility/mm	Viscosity(135°C)/MPa·S
1	126.2	52.2	396.2	375.5
2	136.1	46.1	430.8	316
3	149.6	42.3	541.7	279
4	182.9	36.8	590.8	226
5	70.3	65.4	326.3	589.7
6	80.6	60.5	352.7	423
7	95.6	60.1	403.3	402.7
8	116.8	53.6	468.6	359
9	61.3	73.2	287.2	801
10	63.8	68.6	346.2	716
11	65.2	66.1	374.7	698.7
12	74.2	64.6	432.2	584.3
13	59.3	78.6	279.4	1031
14	62.2	75.2	328.1	952
15	67.3	70.6	356.7	752.5
16	70.4	66.9	410.3	624

Table 7: Visual analysis of conventional physical properties.

Index	Factor	PPA	Bioasphalt	Shear time	Shear rate
Penetration	Average value 1	148.7	79.28	85.6	89.55
	Average value 2	90.83	85.68	86.98	94.35
	Average value 3	66.13	94.43	97.48	88.53
	Average value 4	64.8	111.08	100.4	98.03
	Range	83.9	31.8	14.8	9.5
Softening point	Average value 1	44.35	67.35	61.43	63.03
	Average value 2	59.9	62.6	61.68	61.1
	Average value 3	68.13	59.78	61.08	60.8
	Average value 4	72.83	55.48	61.03	60.28
	Range	28.48	11.88	0.65	2.75
Ductility	Average value 1	489.88	322.28	383.48	389.95
	Average value 2	387.73	364.45	386.5	388.38
	Average value 3	360.08	419.1	406.4	406.13
	Average value 4	343.63	475.48	404.93	396.85
	Range	146.25	153.2	22.93	17.75
Viscosity	Average value 1	299.13	699.3	530.3	578.63
	Average value 2	443.6	601.75	560.63	601.18
	Average value 3	700	533.23	597.75	552.18
	Average value 4	839.88	448.33	593.93	550.63
	Range	540.75	250.98	67.45	50.55

Table 8: Analysis of variance of conventional physical properties.

Index	Factor	Deviation sum of squares	Degrees of freedom	Mean-squared	*F*-value	*P* value	Significance
Penetration	PPA	18496.5	3	6165.5	22.92	0.001	***
	Bioasphalt	2280.67	3	760.22	0.47	0.71	
	Shear time	660.98	3	220.32	0.13	0.94	
	Shear rate	233.6	3	77.87	0.043	0.99	
Softening point	PPA	1874.68	3	624.89	23.6	0.001	***
	Bioasphalt	298.2	3	99.4	0.63	0.61	
	Shear time	1.13	3	0.38	0.002	1.0	
	Shear rate	17.27	3	5.76	0.032	0.99	
Ductility	PPA	51651.66	3	17217.22	3.64	0.045	**
	Bioasphalt	53115.37	3	17705.12	3.84	0.039	**
	Shear time	1732.48	3	577.49	0.065	0.98	
	Shear rate	784.64	3	261.55	0.029	0.99	
Viscosity	PPA	716324.21	3	238774.74	16.89	0.001	***
	Bioasphalt	135528.28	3	45176.09	0.72	0.56	
	Shear time	12019.04	3	4006.35	0.055	0.98	
	Shear rate	6950.81	3	2316.94	0.032	0.99	

*$P \leq 0.1$ is generally significant. **$P \leq 0.05$ is significant. ***$P \leq 0.001$ is particularly significant.

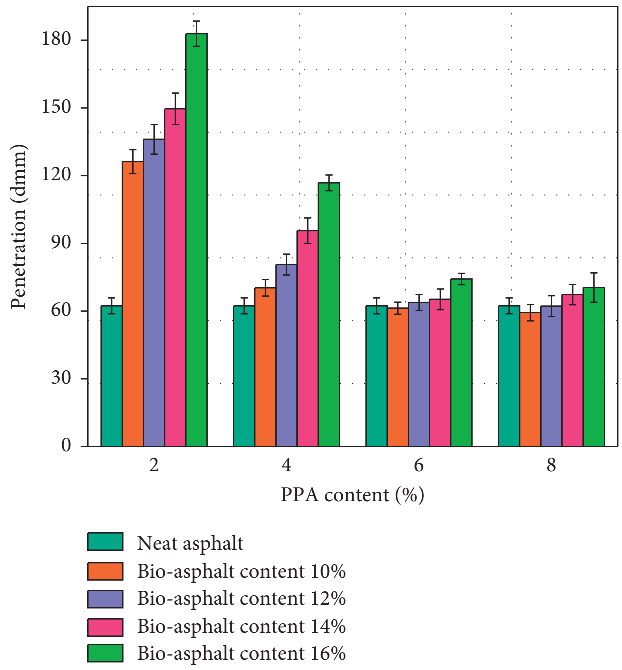


Figure 2: Penetration.

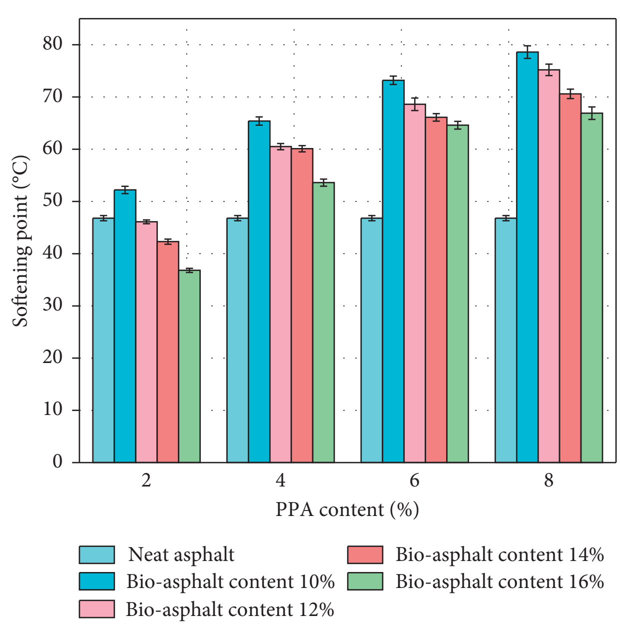


Figure 3: Softening point.

time > shear rate. From Table 8, it can be concluded that PPA content has a particularly significant effect on viscosity. As shown in Figure 5, the viscosity of the modified asphalt is better than that of the neat asphalt when PPA content is higher than 6%. Obviously, the viscosity gradually increases when the PPA content increases. When the PPA content is 8% and the bioasphalt content is 10%, 12%, 14%, or 16%, the viscosity is 1031 MPa·S, 952 MPa·S, 752.5 MPa·S, or 624 MPa·S, respectively, and the enhanced ratio is 116.6%, 100%, 58.09%, or 31.09%, respectively. The increase in the viscosity will improve the high-temperature behavior of the asphalt mixture [29].

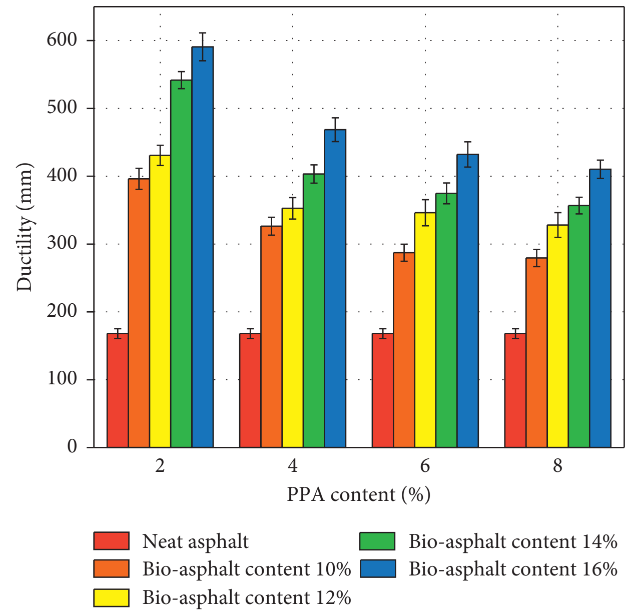


Figure 4: Ductility.

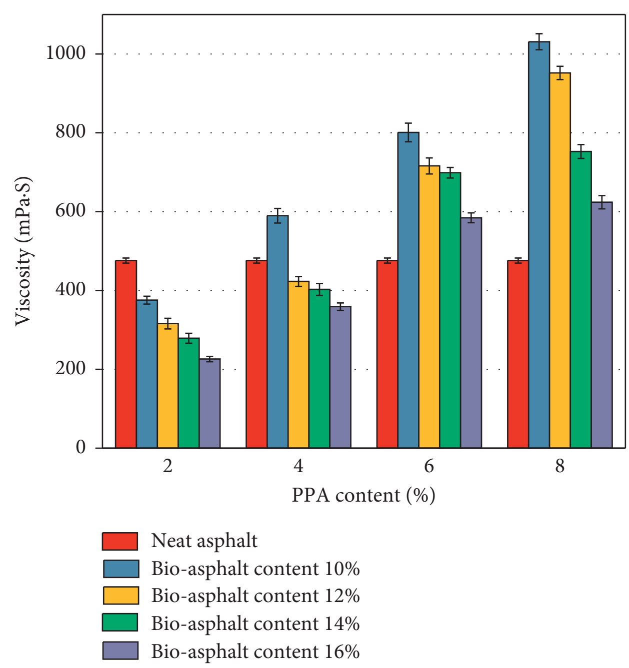


Figure 5: Viscosity.

3.2. Rheological Properties. This study carried out the DSR and BBR tests to evaluate the rheological behavior of the asphalt binder. In summer, the asphalt pavement is exposed to sunlight, which increases the upper layer's temperature. The actual temperature is about 60°C [30]. This study focuses on the rutting index at 60°C to evaluate high-temperature behavior. After RTFO-aging and PAV tests, the corn stalk bioasphalt/PPA composite modified asphalt was placed into asphalt trabeculae and subjected to BBR test at −18°C. Furthermore, the creep rate and stiffness modulus were used as low-temperature evaluation indicators. The results of the rheological properties are shown in Table 9.

Table 9: Rheological properties.

No.	G^*(60°C) KPa	δ(60°C)	$G^*/\sin\delta$/KPa (60°C)	Creep rate (−18°C)	Stiffness modulus/MPa (−18°C)
1	1.72	79.4	1.75	0.48	40.3
2	1.33	81.36	1.35	0.47	32.4
3	1.13	82.7	1.14	0.48	31.9
4	0.84	85.46	0.84	0.49	31.5
5	4.75	68.23	5.11	0.33	44.6
6	3.15	68.63	3.38	0.41	41.3
7	3.07	71.96	3.23	0.44	32.9
8	2.07	66.75	2.25	0.43	32.8
9	7.06	60.88	8.08	0.35	62.5
10	4.94	62.78	5.55	0.35	51.7
11	3.80	65.57	4.17	0.34	42.5
12	3.36	66.09	3.67	0.35	38.2
13	9.16	57.82	10.82	0.34	86
14	6.46	60.8	7.4	0.31	58.9
15	5.72	65.32	6.3	0.32	49.7
16	4.55	62.81	5.11	0.38	43.6

3.2.1. Temperature Scanning. Asphalt resistance to shear deformation could be reflected by the complex shear modulus [31, 32]. The complex shear modulus (60°C) of the neat asphalt was 2.82 KPa. As shown in Figure 6, when PPA content is 8% and the content of bioasphalt is 10%, 12%, 14%, or 16%, the complex shear modulus is 9.16 KPa, 6.46 KPa, 5.72 KPa, or 4.55 KPa, respectively. The increase ratio was 224.75%, 129.06%, 103%, or 61.18%, respectively. Besides, the complex shear modulus gradually decreases with the bio-oil content increasing. However, the complex shear modulus gradually increases with PPA content increasing. When bioasphalt content is 10% and the content of PPA is 2%, 4%, 6%, or 8%, the complex shear modulus is 1.72 KPa, 4.75 KPa, 7.06 KPa, or 9.16 KPa, respectively. The increase ratio is −39%, 68.28%, 150.31%, or 224.75%, respectively. It indicates that PPA can significantly enhance the high-temperature behavior of asphalt.

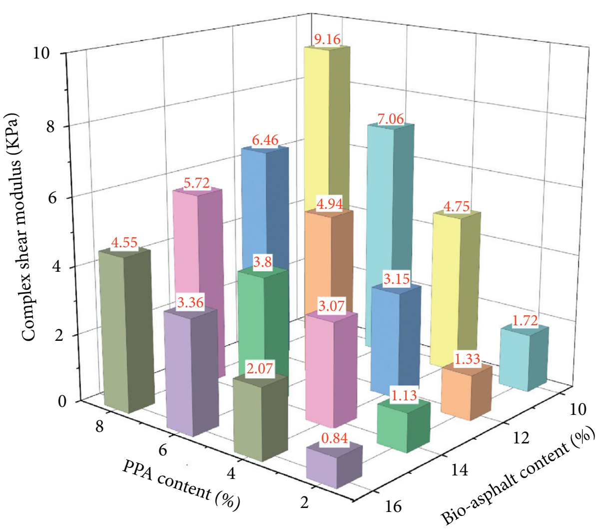


Figure 6: Complex shear modulus (60°C).

The phase angle reflects the asphalt's elasticity (recoverable part) to viscosity (unrecoverable part). It indicates that the asphalt is transformed from elastic to viscous. When the phase angle decreases, the modulus's less dense component is under load in the high-temperature state. The asphalt has excellent deformation resistance when the unrecoverable part was smaller. The phase angle of neat asphalt is 86.86°. Figure 7 shows that the phase angle is significantly lower than that of neat asphalt. When PPA content is 8% and the content of bioasphalt is 10%, 12%, 14%, or 16%, the phase angles were 57.82°, 60.8°, 65.32°, or 62.81°, respectively. The reduction ratio is 33.43%, 30%, 24.8%, or 27.69%, respectively. The phase angle decrease is due to the fact that PPA made the corn stalk bioasphalt/PPA composite modified asphalt more elastic. The phase angle decrease shows that it increases the asphalt's rebound rate under load, thereby improving the asphalt's high-temperature stability [33, 34].

Table 10 and Table 11 illustrate the visual and variance analysis of the rutting index ($G^*/\sin\delta$) at 60°C. According to Table 10, the influence order of the factors on the rutting index (60°C) is as follows: PPA content > bioasphalt content > shear time > shear rate. As shown in Table 11, the impact of PPA content on this parameter is significant. The implication of bioasphalt content on the rutting index is significantly higher than that of the other two factors.

As shown in Figure 8, the rutting index (60°C) gradually increases with the PPA content increasing. The rutting index has a significant increase when PPA content is higher than 6%. When the PPA content is 6% and the content of bioasphalt is 10%, 12%, 14%, or 16%, the rutting index (60°C) is 8.08 KPa, 5.55 KPa, 4.17 KPa, or 3.67 KPa, respectively. The increase ratio is 186.52%, 96.81%, 47.84%, or 30.14%, respectively. When bioasphalt content is 10% and the PPA content is 2%, 4%, 6%, or 8%, the rutting index (60°C) is 1.75 KPa, 5.11 KPa, 8.08 KPa, or 10.82 KPa, respectively. The increase ratio is −37.94%, 81.21%, 186.52%, or 283.69%, respectively. It indicates that PPA can enhance the high-temperature behavior of the modified asphalt. It happens because of the asphalt composition changes: the asphaltene increases, and the colloid decreases. The new colloidal structure made the high-temperature behavior significantly improved [16, 22, 35].

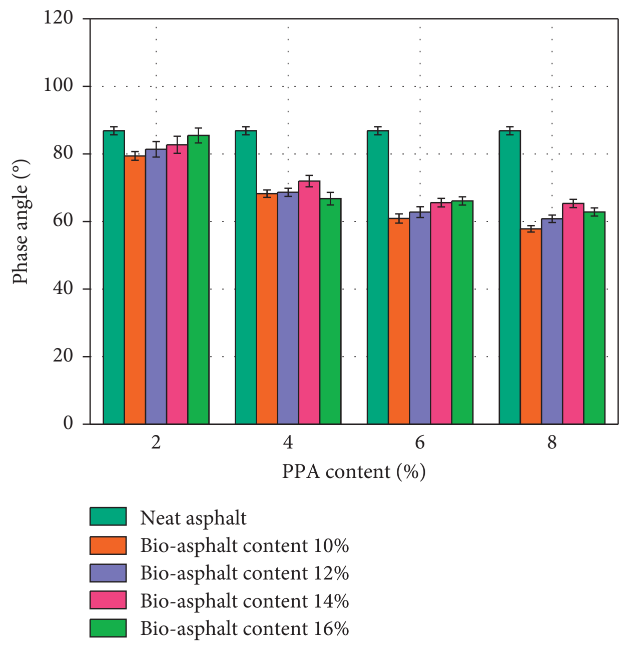


Figure 7: Phase angle (60°C).

Table 10: Visual analysis of rutting index (60°C).

Factor	PPA	Bioasphalt	Shear time	Shear rate
Average value 1	1.27	6.44	3.60	4.01
Average value 2	3.49	4.42	4.11	4.65
Average value 3	5.37	3.71	4.72	4.23
Average value 4	7.41	2.97	5.11	4.65
Range	6.14	3.47	1.51	0.64

Table 11: Analysis of variance of rutting index (60°C).

Factor	Deviation sum of squares	Degrees of freedom	Mean-squared	*F*-value	*P* value	Significance
PPA	82.40	3	27.47	9.54	0.002	**
Bioasphalt	26.76	3	8.92	1.19	0.356	
Shear time	5.3	3	1.77	0.19	0.90	
Shear rate	1.21	3	0.40	0.042	0.99	

* $P \leq 0.1$ is generally significant. ** $P \leq 0.05$ is significant. *** $P \leq 0.001$ is particularly significant.

The results of rutting index are shown in Figure 9. It can be noticed from this figure that the rutting index gradually decreases with the temperature increasing. The rutting index increases with the PPA content increasing. It is observable that PPA can enhance the high-temperature behavior. Its rutting index decreases with bioasphalt content increasing.

When the PPA content is 2%, the rutting index of the modified asphalt is much lower than that of the neat asphalt, as can be seen in Figure 9(a). As demonstrated in Figure 9(b), when PPA content is 4% and the bioasphalt contents are 10% and 12%, the rutting indexes are the same as those of neat asphalt at 47.18°C and 55.57°C. It can be seen in Figure 9(c) that the rutting index exceeds that of neat asphalt when the PPA content is 6%, and the bioasphalt contents are 10% and 12%. When the bioasphalt contents are 12%, 14%, and 16%, the rutting index is consistent with the neat asphalt when the temperatures are 47.07°C, 50.69°C, and 53.29°C, respectively. Figure 9(d) illustrates that when PPA content is 8% and the bioasphalt content is 10%, 12%, or 14%, the rutting index exceeds that of neat asphalt. In summary, the rutting index increases with the PPA content increasing compared with neat asphalt.

When the content of PPA is 8% and the bioasphalt content is 10%, the rutting index is 33.11 KPa, 19.83 KPa, 12.34 KPa, 7.79 KPa, or 4.9 KPa, respectively, at 46°C, 52°C, 58°C, 64°C, or 70°C, respectively. The rutting index increases by 62.62%, 130.05%, 253.58%, 422.82%, or 528.21%, respectively. When PPA content is 8% and the content of bioasphalt is 14%, the rutting index is 20.29 KPa, 12.68 KPa, 7.34 KPa, 4.21 KPa, or 2.65 KPa at 46°C, 52°C, 58°C, 64°C, or 70°C, respectively. The rutting index increases by –0.34%, 47.1%, 110.32%, 182.55%, or 239.74%, respectively. This fact

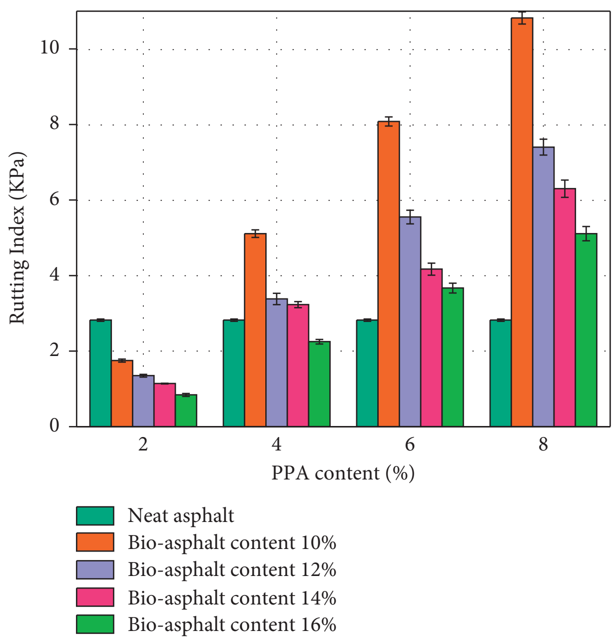


Figure 8: Rutting index (60°C).

shows that the rutting index decreases with bioasphalt content increasing. The PPA improves the high-temperature properties of the corn stalk bioasphalt/PPA composite modified asphalt with the temperature rise.

3.2.2. BBR Test. Before the BBR test, the neat asphalt and corn stalk bioasphalt/PPA composite modified asphalt were subjected to RTFO-aging and PAV tests. The low-temperature behavior indexes of these asphalt samples were stiffness modulus and creep rate. They reflected the asphalt's temperature stress and relaxation ability. Generally, the smaller stiffness modulus and the higher creep rate can reflect outstanding crack resistance asphalt. The test results must meet the following requirements: the stiffness modulus should be less than 300 MPa, and the creep rate must be higher than 0.3.

The BBR test was conducted on neat asphalt and the results are shown in Table 12. In this table, it can be analyzed that the creep rate of neat asphalt gradually decreases, and the stiffness modulus gradually increases as the temperature decreases. The neat asphalt creep rate is 0.29 at −12°C, which does not meet the specification requirements.

According to Table 13, the influence order of the factors on the creep rate (−18°C) and stiffness modulus (−18°C) is as follows: PPA content > bioasphalt content > shear time > shear rate. As shown in Table 14, the PPA content shows a particularly significant impact on the creep rate of corn stalk bioasphalt/PPA composite modified asphalt. However, the PPA content has a significant impact on the stiffness modulus. The PPA influence on low-temperature behavior is significant.

Figure 10 shows that the creep rate is higher than 0.3 at −18°C. When the PPA content is 4%, the creep rate has its maximum values. Figure 11 shows that the stiffness modulus values are all less than 300 MPa. It can be seen from Figures 10 and11 that the low-temperature rheological properties gradually decrease with the PPA content increasing. In summary, the creep rate and stiffness modulus meet the requirements, indicating that the corn stalk bioasphalt/PPA composite modified asphalt has excellent low-temperature behavior.

3.3. Fourier Transform Infrared Reflection (FTIR). To reveal the modification mechanism and functional group information, the neat asphalt, PPA modified neat asphalt, bioasphalt, blended asphalt, and corn stalk bioasphalt/PPA composite modified asphalt were subjected to FTIR test. The FTIR results are shown in Figures 12(a) and 12(b).

As presented in Figure 12(a), the absorption peaks at 2921 cm^{-1} and 2852 cm^{-1} increase by methylene -CH2 stretching vibration and alkane C-H stretching vibration [36, 37]. The peak at 1458 cm^{-1} represents methyl-assisted C-H bending vibration [38]. The wavelength at 1374 cm^{-1} is caused by -CH2 [14]. The wavelengths at 811 cm^{-1} and 724 cm^{-1} are caused by C-H bending vibration and C-O-S symmetrical stretching on the benzene ring [39, 40].

As shown in Figure 12(a), the corn stalk bioasphalt/PPA composite modified asphalt has peaks of 1709 cm^{-1}, 1150 cm^{-1}, and 1002 cm^{-1}, which are not present in the neat asphalt. The peaks at 1150 cm^{-1} and 1002 cm^{-1} appeared in PPA modified neat asphalt and corn stalk bioasphalt/PPA composite modified asphalt. However, these two peaks are not present in the blended asphalt, indicating that PPA causes the two of them. The absorption peak at 1150 cm^{-1} is produced by the P-O single bond and P=O double bond [41, 42]. The newly generated mixed absorption peak at 1002 cm^{-1}, which is wide and large, is mainly caused by the antisymmetrical expansion and contraction of P-O-C in the phosphate $(RO)_3P=O$ formed after the reaction of PPA and asphalt [43]. Figure 12(b) shows that bioasphalt, blended asphalt, and corn stalk bioasphalt/PPA composite modified asphalt all have prominent peaks at 1709 cm^{-1} because of the fatty acid of C=O stretching vibration in bioasphalt [6]. It indicated that the bioasphalt and the neat asphalt were physically blended.

3.4. Moisture Susceptibility Analysis. Some studies have shown that the bioasphalt moisture sensitivity is poor, and also this material affects the adhesion between aggregate and asphalt [14]. Asphalt spalled off from aggregate surface will affect the road durability. The moisture sensitivity of aggregate asphalt was evaluated by boiling water test. The aggregate in the boiling test was limestone. In order to evaluate the adhesion between asphalt and aggregate more accurately, this research work used Image-Pro software to measure the asphalt falling off from the aggregate surface after the boiling test and then the spalling rate was calculated, as shown in Figure 13. Taking the corn stalk bioasphalt/PPA composite modified asphalt (bioasphalt content of 10% and PPA content of 8%) as an example, the moisture sensitivity comparison with neat asphalt is shown in Table 15.

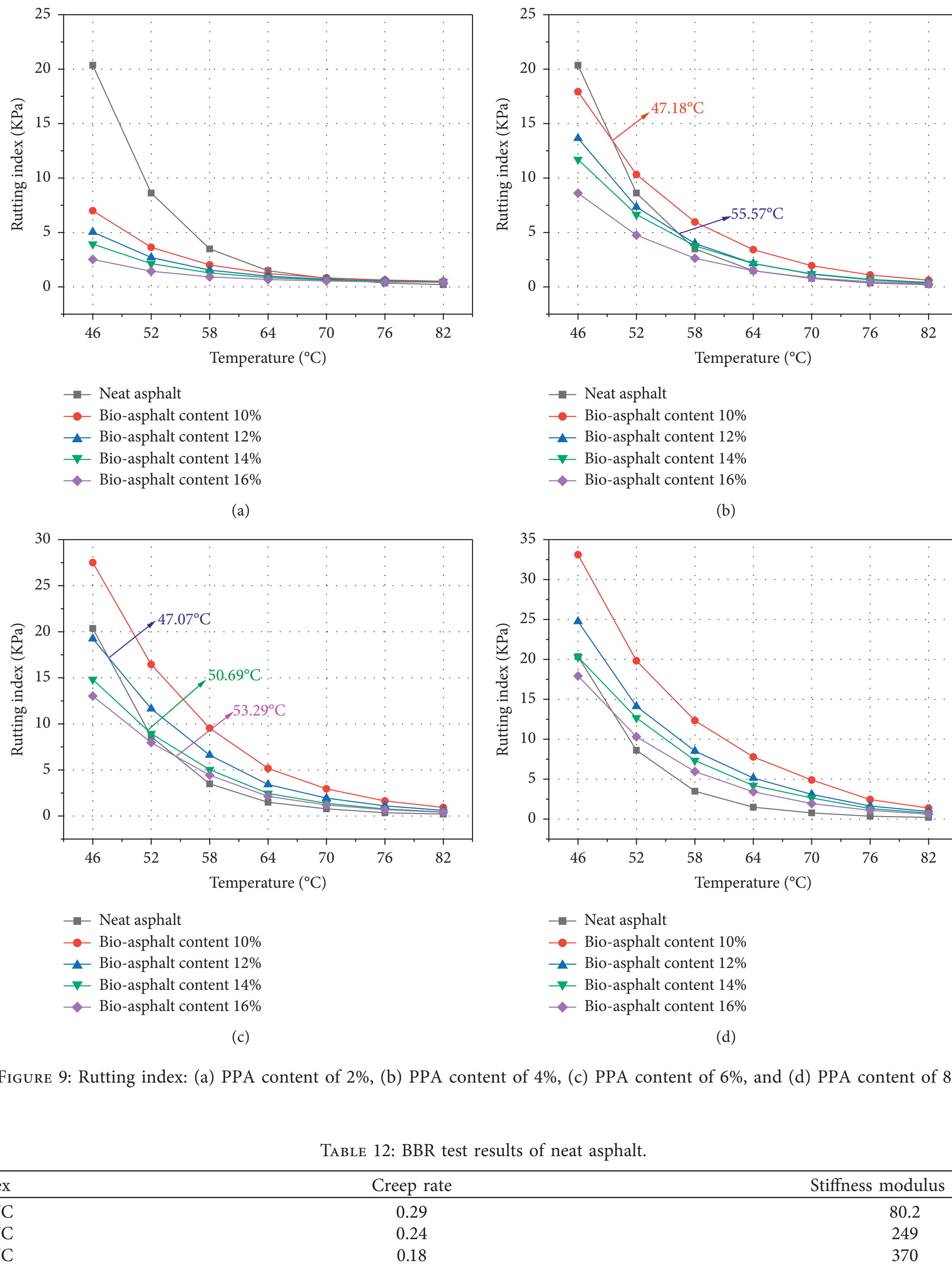


FIGURE 9: Rutting index: (a) PPA content of 2%, (b) PPA content of 4%, (c) PPA content of 6%, and (d) PPA content of 8%.

TABLE 12: BBR test results of neat asphalt.

Index	Creep rate	Stiffness modulus (MPa)
−12°C	0.29	80.2
−18°C	0.24	249
−24°C	0.18	370

The results show that the neat asphalt's spalling rate is 20.3%. However, the corn stalk bioasphalt/PPA composite modified asphalt's spalling rate is 23.6%. The corn stalk bioasphalt/PPA composite modified asphalt's moisture sensitivity is slightly higher than that of neat asphalt. Some studies have shown that the antistripping agent does not

Table 13: Visual analysis of BBR results.

Index	Factor	PPA	Bioasphalt	Shear time	Shear rate
Creep rate	Average value 1	0.48	0.375	0.402	0.395
	Average value 2	0.402	0.385	0.367	0.395
	Average value 3	0.348	0.395	0.392	0.385
	Average value 4	0.338	0.412	0.405	0.393
	Range	0.142	0.038	0.037	0.01
Stiffness modulus	Average value 1	34.025	58.35	41.925	42.575
	Average value 2	37.9	46.075	41.225	48.425
	Average value 3	48.725	39.25	46.525	42.95
	Average value 4	59.55	36.525	50.525	46.25
	Range	25.525	21.825	9.3	5.85

Table 14: Analysis of variance of BBR.

Index	Factor	Deviation sum of squares	Degrees of freedom	Mean-squared	*F*-value	*P* value	Significance
Creep rate	PPA	0.051	3	0.017	19.28	0.001	***
	Bioasphalt	0.003	3	0.001	0.21	0.89	
	Shear time	0.004	3	0.001	0.24	0.87	
	Shear rate	0.000	3	0.001	0.02	0.99	
Stiffness modulus	PPA	1585.72	3	528.57	4.07	0.03	**
	Bioasphalt	1137.03	3	379.01	2.26	0.13	
	Shear time	226.19	3	75.4	0.310	0.82	
	Shear rate	93.47	3	31.16	0.122	0.95	

* $P \leq 0.1$ is generally significant. ** $P \leq 0.05$ is significant. *** $P \leq 0.001$ is particularly significant.

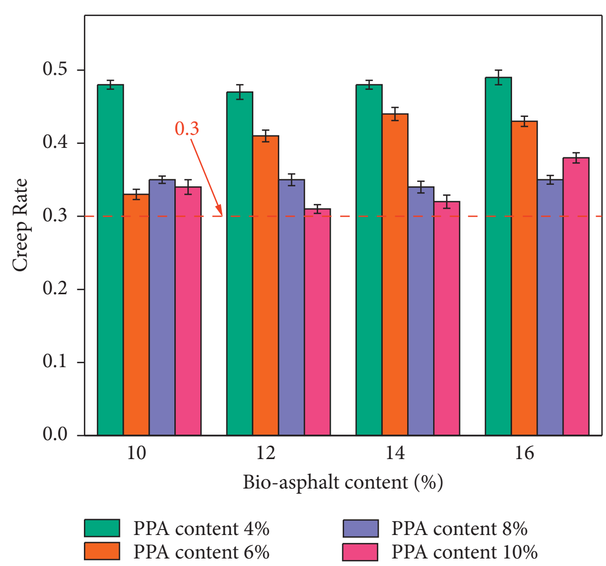


Figure 10: Creep rate (−18°C).

affect the performance of asphalt [44, 45]. A 0.3% BHW511 antistripping agent was added to corn stalk bioasphalt/PPA composite modified asphalt to improve its adhesion. The result of the boiling water test is shown in Table 15. After adding BHW511, the corn stalk bioasphalt/PPA composite modified asphalt's spalling rate is 8.4%, and the adhesion of asphalt is enhanced by 64.4%. The BHW511 reacts with the hydroxyl groups in the asphalt to generate hydrogen bonds and covalent bonds, which results in the asphalt and the aggregate being tightly packed together [46].

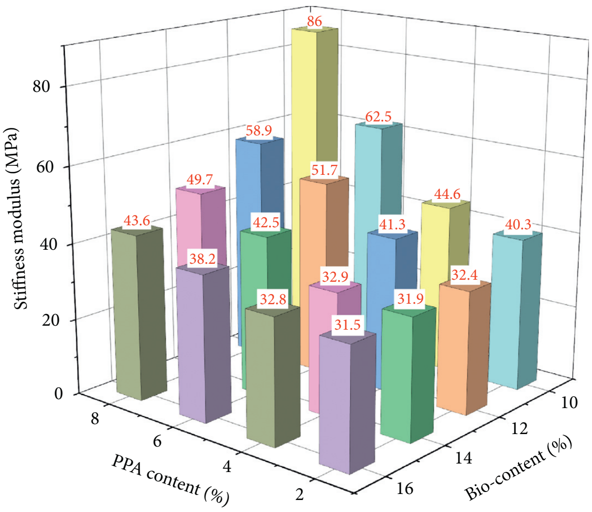
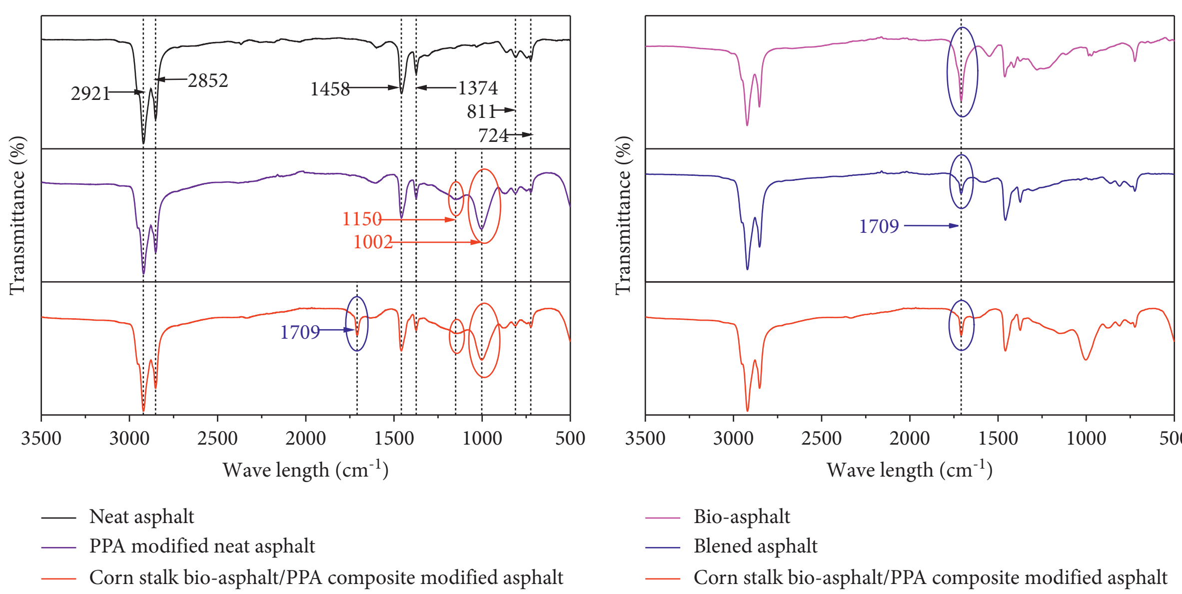


FIGURE 11: Stiffness modulus (−18°C).



(a) (b)

FIGURE 12: FTIR: (a) FTIR of neat asphalt, PPA modified neat asphalt, and corn stalk bioasphalt/PPA composite modified asphalt; (b) FTIR of bioasphalt, blended asphalt, and corn stalk bioasphalt/PPA composite modified asphalt.

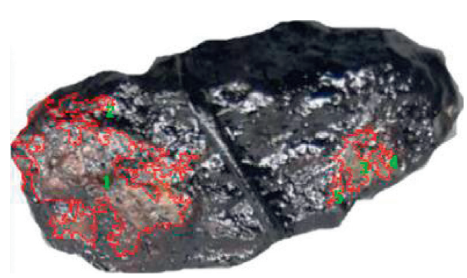


FIGURE 13: Asphalt spalling area.

Table 15: Boiling water test results.

Types of asphalt	Aggregate surface area	Asphalt spalling area	Spalling rate (%)
Neat asphalt	695842	196066	20.3
Corn stalk bioasphalt/PPA composite modified asphalt	836874	197502	23.6
Corn stalk bioasphalt/PPA composite modified asphalt with BHW511	978566	82120	8.4

4. Conclusions

This study evaluated corn stalk bioasphalt/PPA composite modified asphalt's performance on penetration, softening point, ductility, DSR test, and BBR test. FTIR test was undertaken to analyze the mechanism of modified asphalt. According to the test results, the following conclusions can be drawn:

(1) PPA content has the most remarkable impact on corn stalk bioasphalt/PPA composite modified asphalt performance. Penetration and ductility gradually decrease with PPA content increasing. However, the softening point and viscosity remarkably increased with PPA content increasing. Besides, the rutting index gradually increases when PPA content rises. The corn stalk bioasphalt/PPA composite modified asphalt can meet the requirements at −18°C. The corn stalk bioasphalt/PPA composite modified asphalt's moisture sensitivity is slightly higher than that of neat asphalt.

(2) Considering the low-temperature and high-temperature behavior, the optimal PPA content range is 6%–8%, and the optimal bioasphalt content range is 10%–16%. However, shear time and shear rate merely affect the performance of corn stalk bioasphalt/PPA composite modified asphalt.

(3) The bioasphalt added to the neat asphalt does not affect its chemical structure. It only causes physical modification. Nevertheless, PPA will produce new functional groups P-O single bond, phosphate $(RO)_3P=O$, and P=O double bond with asphalt, which results in the chemically blended binder.

(4) This work mainly studied the high-temperature and low-temperature behavior and did not conduct storage stability and aging tests. Future research works will focus on the aging behavior of bioasphalt and the mixture's fatigue characteristics.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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