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Study on the Performance and Modification Mechanism of Polyphosphoric Acid (PPA)/Styrene–Butadiene–Styrene (SBS) Composite Modified Asphalt

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Abstract: In order to address the high preparation cost of styrene–butadiene–styrene block copolymer (SBS) modified asphalt, four kinds of polyphosphoric acid (PPA) content (0%, 0.5%, 0.75%, and 1% PPA by weight of the matrix asphalt) were selected to prepare composite modified asphalt with better high-temperature performance. The physical properties of composite modified asphalt were evaluated by conventional performance tests. The rheological properties of composite modified asphalt were evaluated by dynamic shear rheometer (DSR) test and bending beam rheometer (BBR) test. The synergistic modification mechanism of PPA and SBS was revealed by the Fourier transform infrared spectroscopy test. The results show that with the increase of PPA content, the penetration of PPA/SBS composite modified asphalt is reduced by 20.92%, 25.07% and 28.94%, respectively, compared with matrix asphalt, and the softening point is increased by 5.46%, 22.69% and 34.03%, respectively. In addition, PPA can improve the thermal oxidative aging resistance of asphalt. PPA can improve the shear resistance, high-temperature performance and temperature sensitivity of asphalt. At 82 °C, compared with SBS modified asphalt, the phase angle of PPA/SBS composite modified asphalt can be decreased by 8.63%, 13.23% and 19.24%, respectively, and $G^*/\sin\delta$ can be increased by 41.97%, 67.62% and 70.97%, respectively. SBS mainly exists in asphalt in the form of physical blending, and PPA has a new chemical reaction with asphalt, which increases the macromolecules and chain hydrocarbon components in asphalt, and the macroscopic performance is the improvement of high-temperature performance of asphalt. However, PPA has a negative effect on the low-temperature performance of the SBS modified asphalt.

Keywords: polyphosphoric acid; modified asphalt; rheological properties; zero shear viscosity; temperature sensitivity; microscopic mechanism

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1. Introduction

Asphalt pavement is widely used in road construction because of its comfortable driving performance and low noise. However, in the service process of asphalt pavement, it is susceptible to rutting, cracks and potholes due to the coupling of climatic change, load, light and other factors, which seriously affect the service life of asphalt pavement [1–3]. As a by-product of crude oil processing, the extensive use of asphalt will inevitably lead to frequent exploitation of crude oil, resulting in environmental pollution and energy shortage, which is contrary to current global green initiatives and concepts related to environmental protection and sustainable development [4–6].

Researchers usually use styrene–butadiene–styrene block copolymer (SBS), styrene butadiene rubber (SBR), polyethylene (PE) and other polymers to modify asphalt, which is a common method to solve the deterioration of pavement materials [7–10]. Among these modifiers, SBS modifier is widely used because it has the advantage of significantly improving the high- and low-temperature performance of matrix asphalt, but its compatibility with matrix asphalt is poor, and it is prone to segregation during transportation. In the actual use process, there are problems such as road performance degradation and weak anti-aging ability, which in turn lead to the reduction of pavement service life and the increase of life cycle construction cost [11–13]. Polyphosphoric acid (PPA) is an inorganic acid modifier formed by the polymerization of various phosphoric acids, but its acidity is less than that of sulfuric acid and nitric acid. It is a colorless, transparent and viscous liquid at room temperature, and the viscosity is positively correlated with the content of phosphoric acid (H_3PO_4). It plays a corresponding chemical role as a different functional admixture in organic synthesis [14]. PPA has the characteristics of easy access and low cost, so it has quickly attracted the attention of researchers. The physical properties, high-temperature properties and anti-aging properties of PPA modified matrix asphalt were studied [15–17]. For example, Ramayya et al. [18] found that PPA significantly increased the proportion of asphaltene to improve the high-temperature performance of asphalt by studying the rheological properties of PPA modified asphalt in the middle and high temperature range. Xiao F et al. [19] analyzed the rotational viscosity, anti-rutting factor, phase angle and failure temperature of polyphosphate modified asphalt and found that the rotational viscosity and anti-rutting factor of polyphosphate modified asphalt showed a gradually increasing trend with the increase of PPA content. Peng Liang et al. [20] found that polyphosphoric acid increased the viscosity and elasticity of modified asphalt at high-temperatures by gelation. Zhang et al. [21] used chemical composition analysis and atomic force microscopy to observe that the proportion and dispersion of asphaltenes are directly related to the content of PPA. With the continuous increase of its content, the proportion of asphaltenes increases and the dispersion is more uniform, so the physical properties and rheological properties of asphalt can be improved.

Although polyphosphoric acid can improve the high-temperature performance and aging resistance of asphalt, it will also weaken the low-temperature performance of asphalt to a certain extent [22,23]. For example, Jun Liu et al. [24] found that the low-temperature crack resistance of warm mix modified asphalt decreased after adding polyphosphoric acid by means of BBR test. Cui [25] studied the low-temperature performance of PPA modified asphalt and its mixture by low-temperature ductility, bending creep stiffness test and low-temperature bending test. It was found that the feasibility of improving the low-temperature crack resistance of asphalt and its mixture by PPA alone was low, and it needed to work together with other polymers or rubber modifiers. Therefore, in recent years, researchers have gradually turned to the study of multiphase composite modified asphalt [26–29]. For example, Yajin Han et al. [30] found that an appropriate amount of PPA can reduce the phase separation phenomenon of SBR modified asphalt, and its low-temperature performance degradation is not significant. Liu et al. [31] found that the incorporation of SBR modifier significantly made up for the deficiency of PPA modified asphalt in low-temperature performance through a semi-circular bending test.

Based on the analysis of the findings, the research object is mainly based on PPA single modified asphalt, and the research on PPA/polymer composite modified asphalt is insufficient. Therefore, PPA modifier was selected to partially replace the SBS modifier, and PPA/SBS composite modified asphalt was prepared by double doping of PPA and SBS. The road performance of composite modified asphalt was evaluated by conventional asphalt performance tests. The rheological properties of composite modified asphalt were evaluated by dynamic shear rheometer (DSR) test and bending beam rheometer (BBR) test. The synergistic modification mechanisms of PPA and SBS were revealed by Fourier transform infrared spectroscopy tests.

2. Raw Materials

2.1. Asphalt

The grade A 70# road petroleum asphalt provided by Zhengfa Municipal Construction Co., Ltd. in Zhengzhou City, Henan Province, China was used. The technical indicators are shown in Table 1, which meets the requirements of the specification.

Table 1. Technical properties of matrix asphalt.

Item		Unit	Result	Specification
Penetration (25 °C, 100 g, 5 s)		0.1 mm	69.8	60~80
5 °C ductility (5 cm/min)		cm	10.3	——
10 °C ductility (5 cm/min)		cm	51	≥20
15 °C ductility (5 cm/min)		cm	>150	≥100
Softening point		°C	47.6	≥46
Penetration index PI		——	−0.768	−1.5~1.0
Rolling thin-film oven test (RTFOT)	Mass variation	%	−0.264	−0.8~0.8
	Residual penetration ratio (25 °C)	%	62.6	≥61
	Residual ductility (10 °C)	cm	7.1	≥6

2.2. Polyphosphoris Acid (PPA)

The industrial-grade polyphosphoric acid 115% H_3PO_4 base provided by Anhui Longhua Chemical Co., Ltd. (Chizhou, China) was used. It is a transparent viscous liquid, and its specific technical indicators are shown in Table 2.

Table 2. Technical properties of polyphosphoric acid.

Item	Unit	Result
P_2O_5 Concentration	%	84.7
25 °C Vapor pressure	Pa	2.64×10^{-6}
Boiling point	°C	552
Chloride (Cl) content	%	0.0002
Iron (Fe) content	%	0.0013
Arsenic (As) content	%	0.0068
Heavy metal (Pb) content	%	0.0017

2.3. SBS Modifier

SBS1401E-modified material produced by Baling Petrochemical Branch of Sinopec Asset Management Co., Ltd. (Baling, China) was used. It is a white solid particle. Its basic technical indicators are shown in Table 3, which meet the requirements of the specification.

Table 3. Technical properties of the SBS modifier.

Item	Unit	Result	Specification
Molecular structure	——	line style	line style
Ash	%	0.09	≤0.20
300% Stress at definite elongation	MPa	4.1	≥3.5
Tensile strength	MPa	27.8	≥24.0
Tensile elongation	%	736	≥730
Volatile	%	0.57	≤0.70
S/B mass ratio	——	20/80	20/80

3. Test Method

3.1. Preparation of Composite Modified Asphalt

SBS modified asphalt and PPA/SBS composite modified asphalt were prepared by high-speed shear method. The preparation process is shown in Figure 1. The specific steps are as follows:

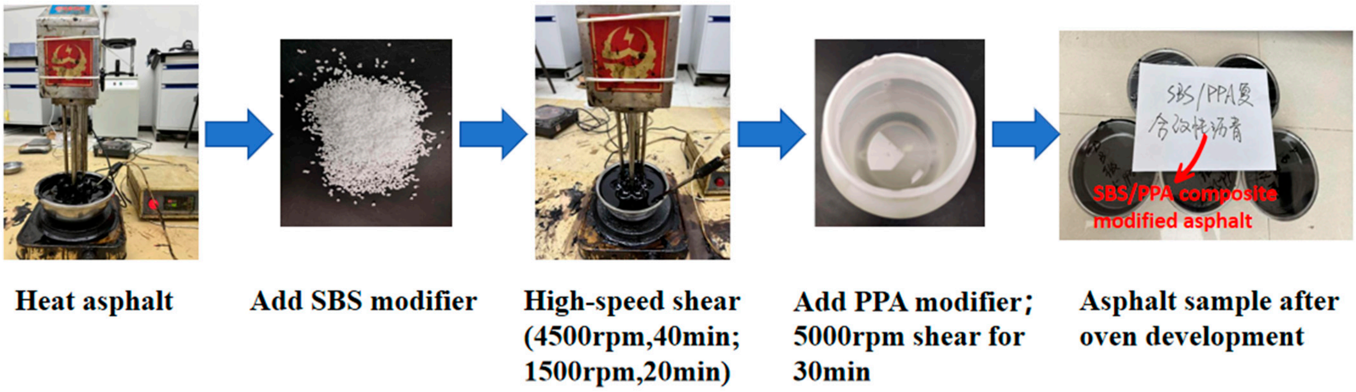


Figure 1. Preparation process of composite modified asphalt.

(1) The matrix asphalt was placed in an electric blast drying oven at 160 °C and heated to full melting and dehydration.

(2) The asphalt was taken out and placed on a constant temperature heating table for heat preservation. The SBS modifier was slowly and uniformly added at 3000 rpm, and sheared at a speed of 4500 rpm for 40 min. Finally, the constant temperature was maintained, and the SBS modified asphalt was fully swelled at a low speed for about 20 min.

(3) The temperature was raised to 170 °C, the speed was increased to 4500 rpm and certain amounts of PPA (0.5%, 0.75% and 1% PPA by weight of the matrix asphalt) were added at a constant speed. After complete addition, the shear was continued at 5000 rpm for 30 min.

(4) The sheared SBS modified asphalt and PPA/SBS composite modified asphalt were placed in an oven at 180 °C for 1 h to fully swell and develop.

3.2. Conventional Performance Test

Three index tests (penetration test, softening point test and ductility test) and Brinell rotational viscosity test were carried out to evaluate the physical properties of asphalt according to the test method of JTG E20-2011 (referred to as the Specification). The rolling thin-film oven test (RTFOT) was carried out on the asphalt according to the specification [32]. The quality, penetration and softening point of the aged asphalt were tested, and the quality change, residual penetration ratio and softening point increment of asphalt before and after aging were calculated to evaluate the anti-aging performance of asphalt.

3.3. DSR Test

The DSR test can better reflect the viscoelastic properties of asphalt materials. The principle is to apply sinusoidal strain to the sample. The sample generates corresponding stress with the strain. The applied sinusoidal strain and the sinusoidal stress generated by the sample will generate two amplitudes with a time difference. The complex modulus G^* can be obtained by amplitude, and the phase angle δ of the test sample can be obtained by calculating the time difference before and after the two signals. Through these two indexes, more evaluation indexes of rheological properties can be obtained to evaluate the high-temperature rheological properties of asphalt.

According to the test method of T 0628-2011 in the Specification [32], the sample size was 25 mm in diameter and 1 mm in thickness, and the DHR-1 dynamic shear rheometer was used, as shown in Figure 2. The frequency sweep test and temperature sweep test were carried out, respectively. Among them, the test temperature of the frequency sweep test was 40~88 °C, the test interval was 12 °C, the angular frequency changes from 0.1 rad/s to 100 rad/s, and the strain level was controlled to be 1% during the test. The temperature range of the temperature sweep test was 46~82 °C, the test interval was 6 °C, the angular frequency was adjusted to 10 rad/s, and the strain level was controlled to 10% during the test.

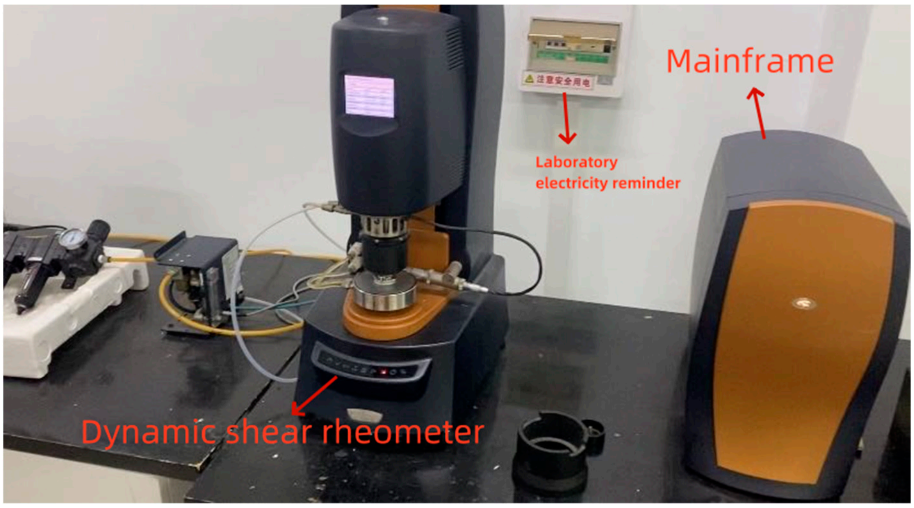


Figure 2. DHR-1 dynamic shear rheometer.

3.4. BBR Test

The low-temperature crack resistance of asphalt was studied with BBR test. The test applies the theory of a simply supported beam. The bending beam rheometer is used to apply creep load to the beam specimen to simulate the mechanical response of asphalt under the action of pavement temperature stress. The ATS low-temperature bending rheometer is shown in Figure 3. The 127 mm × 12.7 mm × 6.35 mm trabecular specimens were formed according to the test method of AASHTO T313 [33], and the test temperatures were −12 °C, −18 °C and −24 °C. The creep stiffness modulus (S) and creep rate (m) under different loading times can be obtained by experiment. According to the specification requirements of the American Highway Strategy Research Program (SHRP), $S \leq 300$ MPa, $m \geq 0.3$ at 60 s [34].

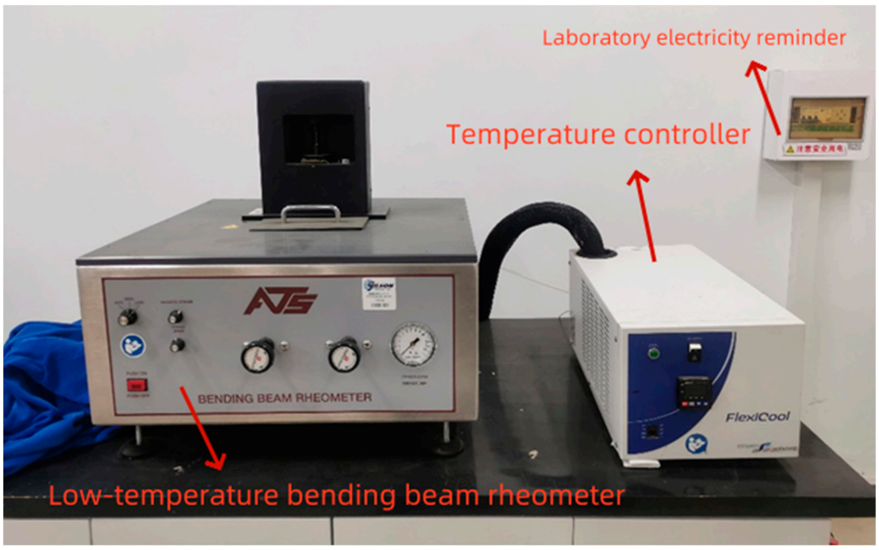


Figure 3. Low-temperature bending beam rheometer.

3.5. Fourier Transform Infrared Spectroscopy Test

With the help of the Nicolet iS10 Fourier transform infrared spectrometer produced by Thermo Fisher Scientific(Waltham, MA, USA), as shown in Figure 4, the evolution behavior of characteristic groups in the spectra after the addition of the modifier was analyzed. Firstly, the KBr wafer was prepared with the tabletting method, and the asphalt was evenly coated on it. Then, the absorption infrared spectra of each asphalt sample were collected by transmission light with a wavelength range of 500~4000 cm^{-1}, and the scanning times were 64 times.

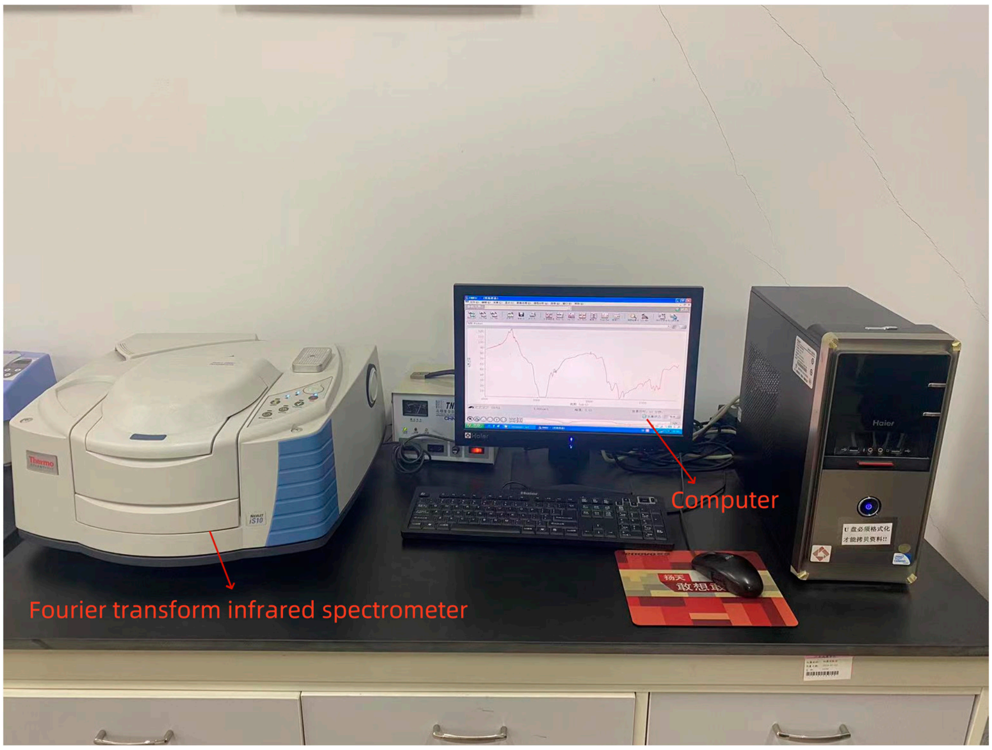


Figure 4. Nicolet iS10 Fourier transform infrared spectrometer.

4. Results and Analysis

4.1. Conventional Performance Test Analysis

The purpose of this section is to study the influence of the PPA modifier on the road performance of the SBS modified asphalt. According to the above test method, the conventional performance test of four kinds of asphalt was carried out. The test results are shown in Table 4.

Table 4. Conventional performance test results.

Item		Unit	Matrix Asphalt	5%SBS	0.5%PPA/3.5%SBS	0.75%PPA/3.5%SBS	1%PPA/3.5% SBS
Penetration (25 °C, 100 g, 5 s)		0.1 mm	69.8	52.4	55.2	52.3	49.6
Softening point		°C	47.6	67.0	50.2	58.4	63.8
Ductility (5 cm/min, 5 °C)		cm	10.3	30.1	26.9	20.5	17.0
Brookfield viscosity (135 °C)		Pa·s	0.47	1.16	1.56	2.02	2.72
RTFOT	Mass variation	%	0.264	0.220	0.206	0.194	0.169
	Residual penetration ratio	——	62.6	65.9	62.9	64.1	67.0
	Softening point increment	——	6.6	8.5	6.8	6.2	3.9

It can be seen from Table 4:

(1) Compared with the matrix asphalt, the penetration of the 5%SBS modified asphalt decreased by 24.9%, and the softening point increased by 40.8%. The 5 °C ductility of the 5%SBS modified asphalt is 2.9 times that of matrix asphalt, which further verifies the improvement effect of SBS on the high- and low temperature properties of asphalt. Compared with 5%SBS modified asphalt, the penetration of the 0.5%PPA/3.5%SBS composite modified asphalt increased by 5.3%, and the softening point decreased by 25.1%. This is mainly because the high-temperature performance of asphalt is weakened after reducing

the content of the SBS modifier, and the content of the 0.5%PPA modifier alone cannot make up for the deficiency of high-temperature performance. However, the high-temperature performance of the 0.5%PPA/3.5%SBS composite modified asphalt is still better than that of matrix asphalt.

The content of the PPA modifier changes from 0.5% to 1%, the penetration of PPA/SBS composite modified asphalt decreases from 55.2 to 49.6, while the softening point increases from 50.2 to 63.8. This may be because the PPA modifier increases the viscous component of the asphalt, thereby improving the high-temperature performance of the asphalt. The ductility index of asphalt decreases with the increase of the content of the PPA modifier. It can be found that although the content of the PPA modifier is very small, the ductility value shows a significant change, indicating that the SBS modified asphalt is gradually hardened due to the addition of PPA, and the low temperature ductility deformation ability of asphalt is weakened. The 135 °C Brookfield rotational viscosity of the SBS modified asphalt was 1.16 Pa·s. Compared with it, the 135 °C Brookfield rotational viscosity of the three groups of composite modified asphalt increased by 34.5%, 74.1% and 134.5%, respectively, and all of them met the requirements of no more than 3 Pa·s. This may be that polyphosphoric acid reacts with asphalt while changing the composition of asphalt, to improve the viscosity of asphalt.

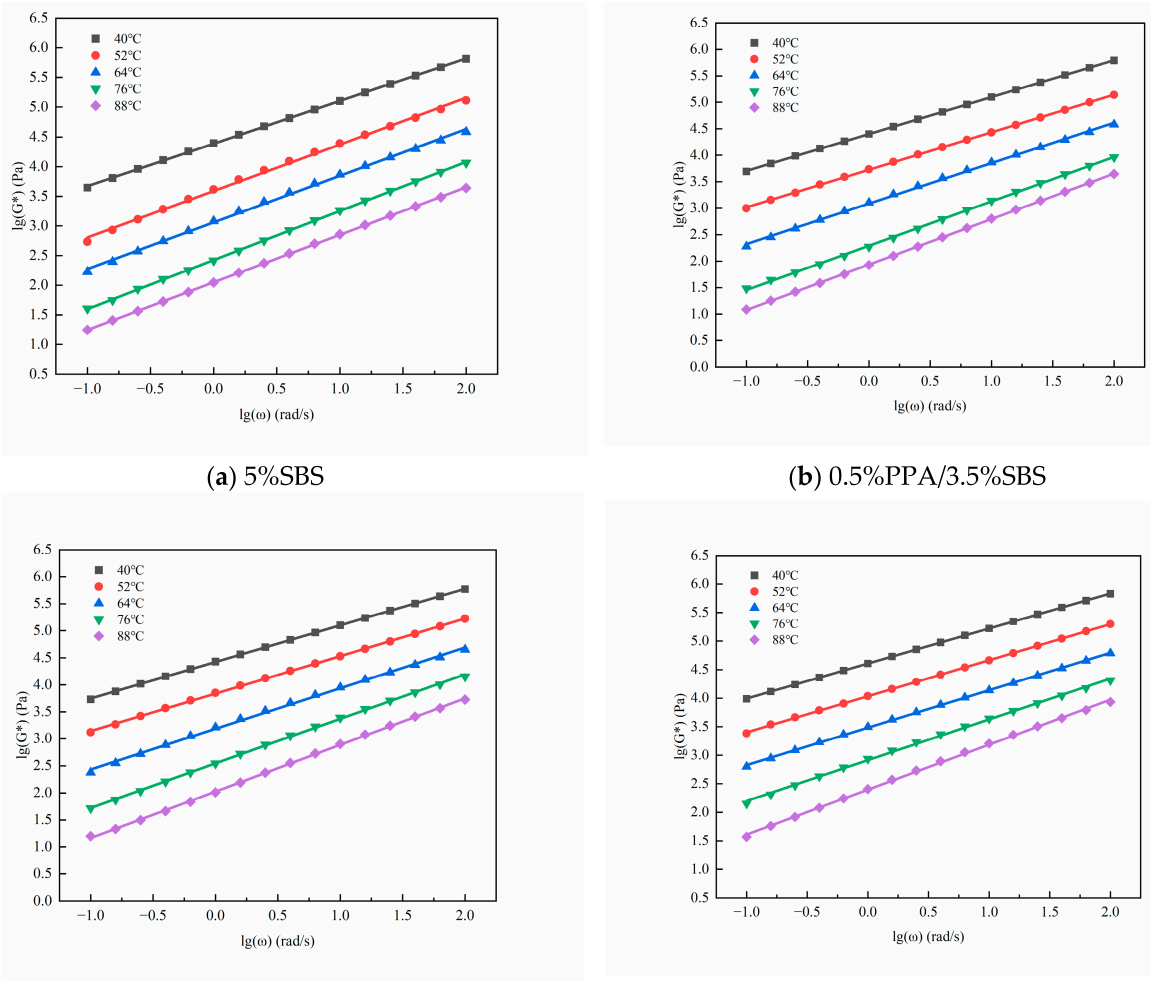
(2) The five groups of asphalt after RTFOT all suffered mass loss, which was caused by the loss of light components in the asphalt during heating and aging. However, PPA reduced the mass change of asphalt, indicating that PPA played a positive role in anti-aging performance. Aged asphalt generally shows increased consistency and hardness, which will reduce its penetration and increase its softening point. With the increase of PPA content, the residual penetration ratio gradually increases, and the softening point increment gradually decreases, which also shows that PPA can play a beneficial role in the anti-aging performance of the SBS modified asphalt, so that it can meet the performance requirements during production mixing and construction.

4.2. Frequency Sweep Test Analysis

4.2.1. High-Temperature Rheological Properties Analysis

Due to the complex chemical composition of asphalt, conventional performance tests cannot fully characterize the performance of asphalt. Therefore, in this section, the frequency sweep test of asphalt was carried out to obtain the complex shear modulus of asphalt in the temperature range of 40~88 °C (interval 12 °C) and frequency change (0.1~100 rad/s) to analyze the variation of complex shear modulus of four modified asphalts with angular frequency under different temperature conditions. The test results are shown in Figure 5.

By observing the complex modulus change curves of four kinds of asphalt in Figure 5, it can be concluded that at any experimental temperature, the complex modulus of the four modified asphalt shows an increasing trend with increasing angular frequency. The increase in angular frequency in the experiment can be used to characterize the increase in road load frequency in practical applications. Therefore, the more vibration generated by the road surface per unit time, the increase in vibration leads to a decrease in strain generated by asphalt, and thus the complex modulus shows an increasing trend. It can also be understood that when the vehicle load is constant, when the speed of the road vehicle is accelerated, the impact on the road surface is instantaneous, the deformation is small, the stiffness is large, and the complex modulus shows an increasing trend. Especially under high-frequency and low-temperature conditions, the complex modulus is the largest and has little effect on the pavement. Under high-temperature conditions, when the vehicle runs slowly, brakes sharply or stops, the load frequency is small, resulting in a low complex modulus, and the road surface is prone to permanent deformation.



(**a**) 5%SBS (**b**) 0.5%PPA/3.5%SBS

(**c**) 0.75%PPA/3.5%SBS (**d**) 1%PPA/3.5%SBS

Figure 5. The variation trend of complex shear modulus of asphalt with frequency.

In the test temperature range of 40~88 °C, there is almost no difference in the change trend of G* of the same kind of asphalt under five temperature conditions, and the curves are generally parallel. The G* values of the four kinds of asphalt reduce with the rise in temperature, which indicates that the rise in temperature leads to the softening of asphalt, and the asphalt gradually turns from elastomer to viscoelastic body, its G* value degrades gradually.

4.2.2. Viscoelastic Characteristic Analysis of Principal Curve

The frequency sweep test is to study the viscoelastic properties of asphalt binder at different loading frequencies under the proposed temperature state. When quantitatively measuring the mechanical properties of asphalt, the test frequency cannot be infinitely expanded based on the test. Therefore, the mechanical response data in a wider frequency range can be obtained by using the time-temperature equivalence principle (TTSP) to observe the change of material properties in a wider frequency or temperature range.

(1) Determination of displacement factor

Through the displacement factor, the complex modulus curves at different temperatures are translated to obtain the complex modulus master curve [35,36]. Taking 5%SBS modified asphalt as an example, the complex modulus change curves at 40~88 °C in Figure 5a were linearly fitted one by one to obtain the double logarithmic fitting equations at different temperatures. The relationship between lgG* and lgω was clarified by the fitting equation. The fitting results are shown in Table 5.

Table 5. SBS modified asphalt double logarithmic fitting curve equation table.

Temperature/°C	Curve-Fitting Equation	R^2
40	y = 4.3875 + 0.71555x	0.99982
52	y = 3.58965 + 0.78339x	0.99798
64	y = 3.05983 + 0.78662x	0.99849
76	y = 2.42496 + 0.82765x	0.99985
88	y = 2.04866 + 0.80207x	0.99993

The angular frequency logarithm lgω (G* = 1 kP, rad/s) was obtained by bringing G* = 1 kPa into the fitting equation at each temperature in Table 5, and the displacement factor was obtained by taking 40 °C as the reference temperature. The results are shown in Table 6.

Table 6. Displacement factor of the 5%SBS modified asphalt.

Temperature/°C	lgω(G* = 1 kP, rad/s)	Displacement Factor
40	−1.9391	0
52	−0.7527	1.1864
64	−0.0761	1.8630
76	0.6948	2.6339
88	1.1861	3.1252

Through this idea and method, the linear fitting equations and displacement factors of the other three modified asphalts were obtained, respectively. The results are shown in Tables 7 and 8.

According to the calculated results in Tables 5–8, the complex modulus of four kinds of asphalt at different temperatures was translated, and the complex modulus master curve at 40 °C was obtained, as shown in Figure 6.

Table 7. PPA/SBS composite modified asphalt double logarithmic fitting curve equation summary table.

Scheme	Temperature/°C	Curve-Fitting Equation	R^2
0.5%PPA/3.5%SBS	40	y = 4.401 + 0.69712x	0.99997
	52	y = 3.72489 + 0.70901x	0.99989
	64	y = 3.08663 + 0.76396x	0.99898
	76	y = 2.29102 + 0.83766x	0.99957
	88	y = 1.93556 + 0.85827x	0.99993
0.75%PPA/3.5%SBS	40	y = 4.42343 + 0.67596x	0.99992
	52	y = 3.83727 + 0.69351x	0.9997
	64	y = 3.18477 + 0.75266x	0.99835
	76	y = 2.5458 + 0.82381x	0.99951
	88	y = 2.02573 + 0.86171x	0.9996
1%PPA/3.5%SBS	40	y = 4.60696 + 0.61414x	0.99998
	52	y = 4.03362 + 0.63192x	0.99986
	64	y = 3.48315 + 0.65615x	0.99972
	76	y = 2.91344 + 0.71499x	0.99875
	88	y = 2.3976 + 0.78802x	0.99915

Table 8. Summary of displacement factors of PPA/SBS composite modified asphalt.

Scheme	Temperature/°C	lgω(G* = 1 kP, rad/s)	Displacement Factor
0.5%PPA/3.5%SBS	40	−2.0097	0
	52	−1.0224	0.9873
	64	−0.1134	1.8963
	76	0.8464	2.8561
	88	1.2402	3.2499
0.75%PPA/3.5%SBS	40	−2.1058	0
	52	−1.2073	0.8985
	64	−0.2455	1.8603
	76	0.5513	2.6571
	88	1.1306	3.2364
1%PPA/3.5%SBS	40	−2.6166	0
	52	−1.6357	0.9809
	64	−0.7363	1.8803
	76	0.1211	2.7377
	88	0.7644	3.3810

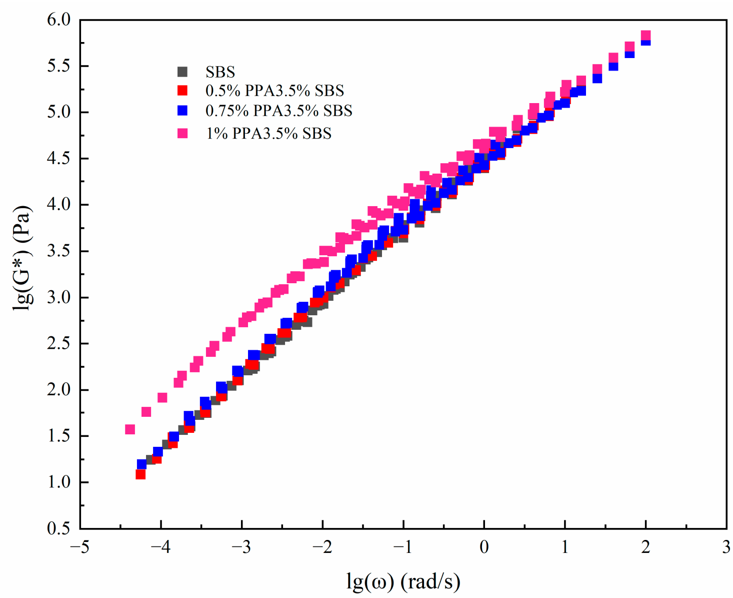


Figure 6. Principal curves of complex shear modulus of four asphalts.

It can be observed from Figure 6 that at the same frequency, due to the addition of the PPA modifier, the master curve of asphalt complex modulus shows an obvious change trend, and the more the content, the more obvious the change trend. When the PPA content increases from 0.75% to 1%, the modulus of PPA/SBS asphalt increases the most, indicating that the addition of PPA is the main factor for the modulus growth of PPA/SBS asphalt. In the low-frequency region, when the PPA content increases from 0.75% to 1%, the complex modulus difference of the composite modified asphalt is the most obvious, indicating that the addition of the PPA modifier under low-frequency and high-temperature conditions makes the asphalt have better high-temperature deformation resistance. It is assumed that the addition of PPA makes the asphalt sticky, so as to improve the high-temperature deformation resistance of the asphalt. In addition, the 0.5%PPA/3.5%SBS composite modified asphalt and the 5%SBS modified asphalt are at the same level. In the high-frequency region, the main curves of the complex shear modulus of the four kinds of asphalt tend to be concentrated, and the PPA/SBS composite modified asphalt is at the same level as the 5%SBS. This shows that the G* of PPA/SBS composite modified asphalt performs better at a lower driving speed. At a faster driving speed, the G* discrimination of PPA/SBS modified asphalt is not large.

4.3. Zero Shear Viscosity Analysis

The viscosity of asphalt material will gradually decrease with the increase of load shear rate in practical pavement application. The related research of DSR test using the limit shear rate level also shows that the viscosity of asphalt material tends to be stable under the condition of too high or too low shear rate [37]. At this time, the increase or decrease of shear rate has no obvious effect on the viscosity of asphalt material. When the shear rate is extremely low, the stable viscosity value is the zero shear viscosity (ZSV) of the asphalt material. The viscosity value at an extremely high shear rate usually means that the asphalt material is in the second Newtonian fluid state, and the asphalt material is already in the shear thinning state [38].

Under the action of an external load, the matrix asphalt is mainly flow deformation, and its deformation increases linearly with the load. However, due to its nonlinear viscoelasticity and delayed elasticity, the modified asphalt contains delayed elastic deformation in addition to flow deformation, so it is more accurate to characterize the high-temperature viscosity of modified asphalt by zero shear viscosity (ZSV) [39,40].

The frequency sweep of each group of asphalt samples was carried out at 64 °C, and the four-parameter Cross model and Carreau model were used to fit the complex modulus shear rate non-curve. The Cross and Carreau models are shown in Equations (1) and (2).

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (k\omega)^m} \tag{1}$$

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{\left(1 + (k\omega)^2\right)^{m/2}} \tag{2}$$

where η is the complex viscosity, Pa·s, ω is the angular frequency, rad/s, k and m are the characteristic constants of the material, η_0 is First Newtonian viscosity, i.e., ZSV, Pa·s, η_∞ is viscosity of the Second Newtonian region of the flow curve, Pa·s.

In the frequency sweep test, the set shear frequency is generally 0.1~100 rad/s; in this range, $\eta_0 \geq \eta \geq \eta_\infty$ can be considered. In the actual fitting process, when the test shear frequency is large enough, the asphalt is completely elastic, and the viscosity is basically zero; that is, η_∞ = 0, so the equation can be simplified as a parameter expression, as shown in Equations (3) and (4).

$$\frac{\eta}{\eta_0} = \frac{1}{1 + (k\omega)^m} \tag{3}$$

$$\frac{\eta}{\eta_0} = \frac{1}{\left(1 + (k\omega)^2\right)^{m/2}} \tag{4}$$

where η is the complex viscosity, Pa·s, ω is the angular frequency, rad/s, k and m are the characteristic constants of the material, η_0 is First Newtonian viscosity, i.e., ZSV, Pa·s.

The complex shear viscosity values of four kinds of asphalt with the change of angular frequency are shown in Figure 7. The fitting results of the Cross model and Carreau model of different asphalts are shown in Table 9.

Table 9. Cross model and Carreau model fitting results.

Scheme	ZSV		R^2	
	Cross Model	Carreau Model	Cross Model	Carreau Model
5%SBS	2347.69435	1662.84815	0.99959	0.99316
0.5%PPA/3.5%SBS	3145.37399	1937.65434	0.99996	0.99699
0.75%PPA/3.5%SBS	3516.56269	2385.98834	0.9999	0.99657
1%PPA/3.5%SBS	20,935.59206	7371.37261	0.99989	0.99982

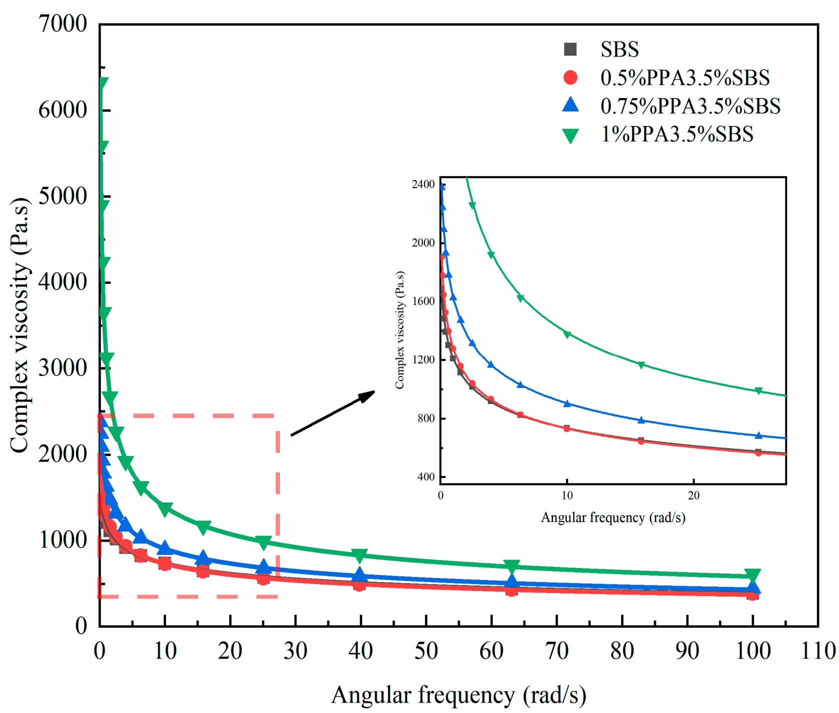


Figure 7. Curve of complex shear viscosity changing with angular frequency.

From Figure 7 and Table 9, it can be concluded that the complex viscosity of PPA/SBS composite modified asphalt gradually reduces with increasing frequency at different dosages. The complex viscosity curve of the 0.5%PPA/3.5%SBS composite modified asphalt almost coincides with the complex viscosity curve of the 5%SBS modified asphalt, and with the continuous increase of PPA content, the complex viscosity curve of PPA/SBS composite modified asphalt is obviously superior to that of the 5%SBS modified asphalt, indicating that the shear performance of PPA/SBS composite modified asphalt is superior to that of the SBS modified asphalt.

The fitting correlation between three types of PPA/SBS composite modified asphalt and 5%SBS modified asphalt is good, with R^2 above 0.99. The fitting effect of the Cross model is better than that of the Carreau model, but the ZSV result obtained after the Cross model fitting is significantly higher than that of the Carreau model fitting. The results of accelerated loading tests in the United States showed that the ZSV value obtained by the Carreau model was better than the ZSV result fitted by the Cross model. In addition, the study of Wu et al. [41] also found that the ZSV value obtained by the Cross model has the characteristics of a virtual high. However, both the Cross model fitting results and the Carreau model fitting results show that the zero shear viscosity (ZSV) of asphalt shows a significant growth trend with the increase of PPA content. In the Carreau model fitting results, the PPA content changed from 0.5% to 1%, and the ZSV value of the asphalt increased by 16.53%, 23.14% and 208.94%, indicating that the PPA modifier has a remarkable improvement effect on the high-temperature shear resistance of the asphalt, and the more the content, the more obvious the improvement effect.

4.4. Temperature Sweep Test Analysis

4.4.1. Complex Modulus and Phase Angle Analysis

The complex modulus and phase angle of four kinds of modified asphalt at 46~82 °C were obtained by temperature sweep test, and the dependence of complex modulus and phase angle of four kinds of modified asphalt on temperature was analyzed. The test results are shown in Figure 8.

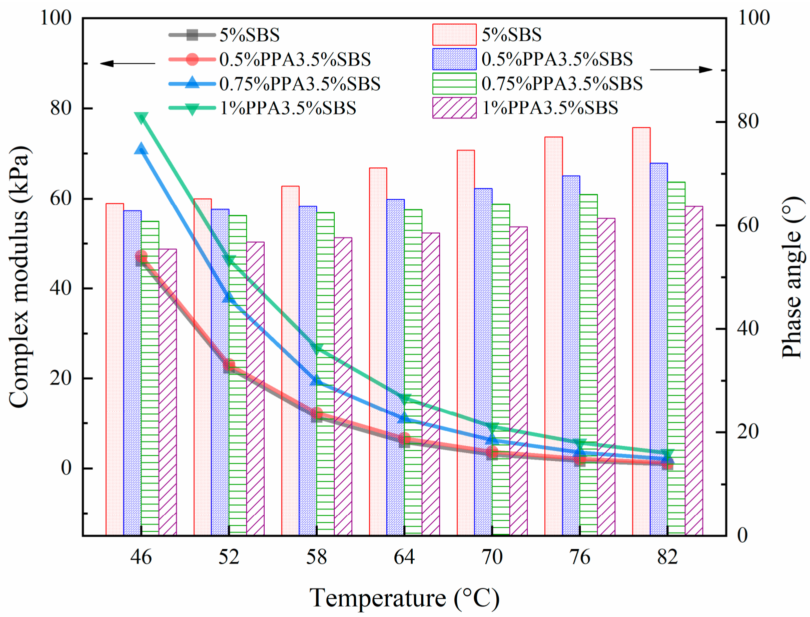


Figure 8. The curves of complex shear modulus and phase angle of asphalt with temperature change.

It can be obviously seen from Figure 8 that the complex shear modulus G* values of the four kinds of asphalt show a decreasing trend with the increase in temperature. Therefore, whether it is SBS modified asphalt or PPA/SBS composite modified asphalt, its high-temperature deformation resistance is weakening. Among them, in the temperature range of 52~64 °C, the decrease rate of complex shear modulus of asphalt is faster, while in the temperature range of 70~82 °C, the decrease rate is slower. This shows that the asphalt is greatly affected at the initial stage of temperature rise, and the degree of influence gradually decreases with the accumulation of temperature. The reason is that in the process of temperature rise, the molecular chain movement inside the asphalt becomes active, and the correlation between molecules decreases.

When the temperature changes from 46 °C to 82 °C, the phase angle δ of the four kinds of asphalt gradually increases, and the phase angle of the SBS modified asphalt is the largest. Due to the fact that the phase angle represents the ratio of elasticity to viscosity performance of asphalt, the larger phase angle means a larger proportion of viscosity, and it also means that asphalt begins to change from elasticity to viscosity, making it harder to recover its deformation after being loaded. Overall, the change in asphalt phase angle is SBS modified asphalt > 0.5PPA/SBS > 0.75PPA/SBS > 1PPA/SBS composite modified asphalt, indicating that the addition of PPA is beneficial for improving the ability of asphalt to resist deformation at high temperatures.

4.4.2. Anti-Rutting Factor Analysis

The anti-rutting factor of asphalt under the condition of 46~82 °C (interval 6 °C) was obtained by temperature sweep test, as shown in Figure 9. And its variation with temperature was studied. The effect of the PPA modifier on the anti-rutting performance of the SBS modified asphalt was analyzed.

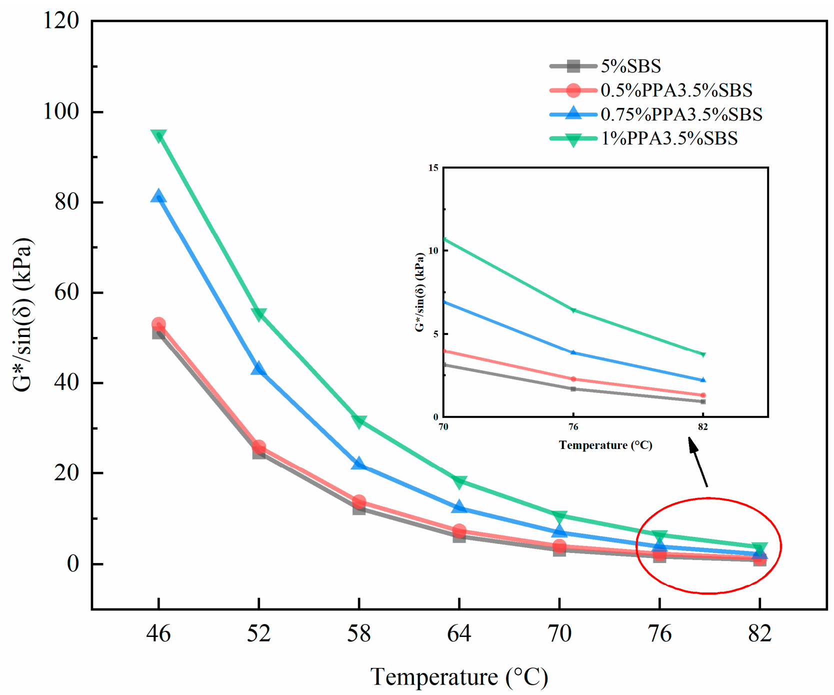


Figure 9. Rutting factor curve of asphalt.

It can be seen from Figure 9 that the rutting factors of the four kinds of asphalt show an evolution law that gradually decreases with increasing temperature, indicating that at a high temperature, the ability of asphalt to resist plastic deformation is weak, and it cannot better resist the driving load and increase the rutting deformation. However, in the high-temperature region, with the increase of PPA content, the G*/sinδ of asphalt increases. The G*/sinδ of asphalt with 0.5%PPA content is almost at the same level as that of the SBS modified asphalt, and the G*/sinδ of asphalt with 1%PPA content is the highest. Under the condition of 82 °C, the G*/sinδ increased by 41.97%, 67.62% and 70.97% when the content of PPA changed from 0.5% to 1%. This shows that the addition of the PPA modifier can improve the ability of asphalt to resist plastic deformation and improve the high temperature performance of asphalt.

4.5. Temperature Sensitivity Analysis

During the service process of asphalt pavement, due to the change in temperature, the asphalt material will change accordingly. If the penetration index in the conventional physical test is adopted, it has certain disadvantages and great differences. VTS involves a wide temperature range, and the characterization of the temperature sensitivity of asphalt is more accurate [42].

This index was used to evaluate the temperature sensitivity of four kinds of asphalt. The complex shear modulus G^* and angular frequency ω of asphalt can be obtained by temperature sweep. The test temperature range was 46~82 °C (interval is 6 °C), the angular frequency was 10 rad/s, and the strain level was controlled to be 10% during the test.

Furthermore, the complex viscosity η^* can be obtained by complex shear modulus G^* and angular frequency ω, as shown in Equation (5). Because asphalt is a non-Newtonian fluid, in order to accurately calculate the equivalent viscosity η' of various types of temperature-regulated asphalt, the equivalent viscosity η' is calculated by the conversion method proposed by Cox–Merz, as shown in Equation (6). The research results of many scholars show that it is more accurate to calculate the *VTS* of modified asphalt by Kelvin temperature [43,44]. After calculating the equivalent viscosity η' of all kinds of asphalt, the viscosity temperature index VTS of all kinds of asphalt can be calculated by Equation (7). The calculation results of four kinds of asphalt are shown in Tables 10–13.

$$\eta^* = \frac{G^*}{\omega} \tag{5}$$

where G^* is the complex shear modulus and Pa, ω is the angular frequency, rad/s.

$$\eta\prime = \frac{(\sin\delta)^{-4.8628}|G^*|}{\omega} \tag{6}$$

where δ is the phase angle, G^* is the complex shear modulus and ω is the angular frequency.

$$VTS = \frac{\lg(\lg\eta_1 - \lg\eta_2)}{\lg_{T_{K,1}} - \lg_{T_{K,2}}} \tag{7}$$

where η is viscosity, ω is the angular frequency, η_1 and η_2 are the viscosity corresponding to the adjacent temperature and T_K is the Kelvin temperature.

Table 10. SBS modified asphalt equivalent viscosity.

Temperature/°C	Kelvin Temperature/K	G*/Pa	sinδ	η′/Pa·s	lg(lg(η′))
46	318.92	46,115.5	0.9011	7652.8754	0.5893
52	325.10	22,352.8	0.9079	3576.1537	0.5506
58	331.11	11,348.9	0.9247	1661.0299	0.5079
64	337.12	5797.77	0.9463	758.1339	0.4594
70	343.10	3024.18	0.9639	361.6789	0.4080
76	349.12	1643.94	0.9747	186.1669	0.3560
82	355.10	908.523	0.9812	99.6240	0.3007

Table 11. Equivalent viscosity of the 0.5% PPA3.5% SBS composite modified asphalt.

Temperature/°C	Kelvin Temperature/K	G*/Pa	sinδ	η′/Pa·s	lg(lg(η′))
46	318.92	47,193.5	0.8897	8331.7158	0.5934
52	325.10	23,119.1	0.8921	4027.5924	0.5569
58	331.11	12,314.7	0.8965	2094.8806	0.5213
64	337.12	6645.97	0.9069	1068.9688	0.4813
70	343.10	3667.66	0.9217	545.1113	0.4372
76	349.12	2138.89	0.9373	293.0784	0.3922
82	355.10	1250.69	0.9514	159.3204	0.3429

Table 12. Equivalent viscosity of the 0.75% PPA3.5% SBS composite modified asphalt.

Temperature/°C	Kelvin Temperature/K	G*/Pa	sinδ	η′/Pa·s	lg(lg(η′))
46	318.92	70,805.5	0.8727	13,729.9659	0.6168
52	325.10	37,805.3	0.8823	6949.2353	0.5846
58	331.11	19,368.2	0.8868	3473.2014	0.5491
64	337.12	10,950.1	0.8916	1913.1437	0.5161
70	343.10	6248.01	0.9001	1042.2974	0.4797
76	349.12	3530.76	0.9139	547.0778	0.4374
82	355.10	2049.36	0.9301	291.5504	0.3918

Table 13. Equivalent viscosity of 1% PPA 3.5% SBS composite modified asphalt.

Temperature/°C	Kelvin Temperature/K	G*/Pa	sinδ	η′/Pa·s	lg(lg(η′))
46	318.92	78,196.9	0.8231	20,153.8209	0.6339
52	325.10	46,442.8	0.8366	11,058.2239	0.6068
58	331.11	26,802.3	0.8443	6102.9137	0.5781
64	337.12	15,639	0.8532	3385.2959	0.5477
70	343.10	9250.52	0.8637	1886.0519	0.5153
76	349.12	5656.84	0.8775	1067.7738	0.4812
82	355.10	3377.48	0.8965	574.4235	0.4408

The above calculation results were linearly fitted, and the fitting results are shown in Figure 10.

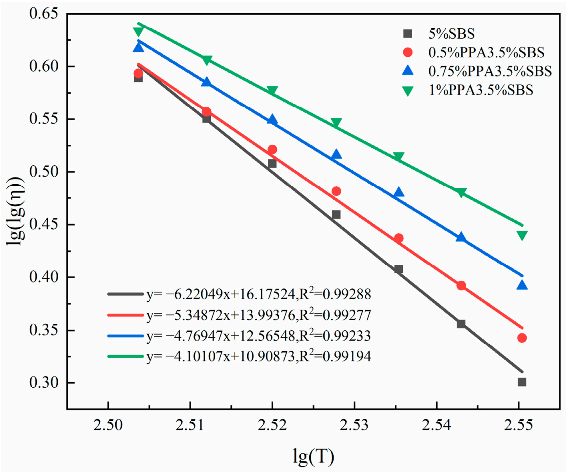


Figure 10. Linear fitting of equivalent viscosity of four kinds of asphalt.

It can be seen from Figure 10 that there is a great linear relationship between the double logarithm of the four asphalt viscosities and the logarithm of the absolute temperature T. The absolute values of VTS of the 5%SBS modified asphalt, 0.5%PPA/3.5% SBS composite modified asphalt, 0.75%PPA/3.5%SBS composite modified asphalt and 1%PPA/3.5%SBS composite modified asphalt are 6.22049, 5.34872, 4.76947 and 4.10107, respectively. In addition, with the incorporation of the PPA modifier, it showed a significant reduction in the absolute value of VTS. The smaller the absolute value of VTS of asphalt, the lower the temperature sensitivity. Therefore, PPA modifier can reduce the sensitivity of asphalt to ambient temperature, and with the increase of PPA content, the improvement of temperature sensitivity is more obvious.

4.6. BBR Test Analysis

The stiffness modulus S and creep rate m of four kinds of modified asphalt at −12 °C, −18 °C and −24 °C were obtained by BBR test. According to the requirements of American Highway Strategy Research Program (SHRP) specification, the stiffness modulus S and creep rate m at 60 s were selected to evaluate the low-temperature crack resistance of asphalt. The test results are shown in Figures 11 and 12.

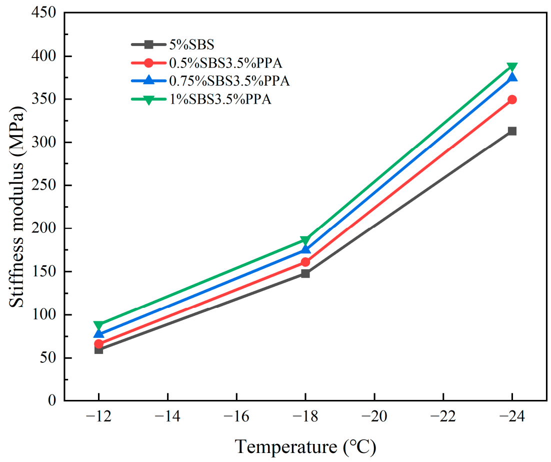


Figure 11. Variation of stiffness modulus with temperature.

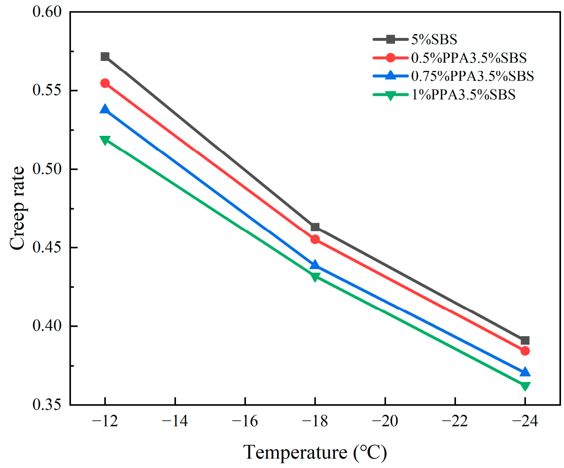


Figure 12. Creep rate changing with temperature.

From Figures 11 and 12, it can be seen that the slope of the stiffness modulus S value of the four kinds of asphalt in the range of −18~−24 °C becomes significantly larger, and the value increases the fastest, indicating that as the temperature continues to decrease, the low-temperature flexibility of the asphalt is worse, and the low-temperature anti-deformation ability is weakened. From the change rule of creep rate m value, the creep rate of the four kinds of asphalt decreases with the decrease in temperature from −12 °C to −24 °C, which indicates that the decrease in temperature leads to the decrease of stress relaxation performance of asphalt, which makes it more prone to brittle fracture. The stiffness modulus of the three groups of PPA/SBS composite modified asphalt is higher than that of the SBS modified asphalt, and the creep rate is lower than that of the SBS modified asphalt. At −12 °C, compared with SBS modified asphalt, its stiffness modulus increased by 11.17%, 29.78% and 48.86%, respectively, and the creep rate decreased by 3.00%, 5.93% and 9.18%, respectively. It shows that after PPA modifier partially replaces SBS modifier, its low-temperature deformation resistance and stress relaxation ability have different degrees of weakening effect.

4.7. Fourier Transform Infrared Spectroscopy Test Analysis

The infrared spectra of matrix asphalt, 5%SBS modified asphalt and 1%PPA/3.5%SBS composite modified asphalt were obtained by the Fourier transform infrared spectroscopy test. The results are shown in Figure 13, and then the synergistic modification mechanism of PPA and SBS was analyzed.

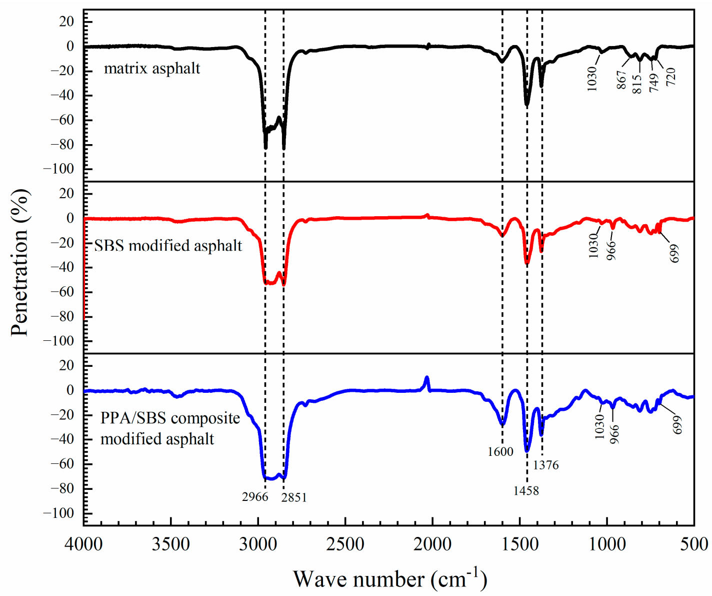


Figure 13. Infrared spectra of three kinds of asphalt.

From Figure 13, it can be observed that in the matrix asphalt map, the absorption peak near 3500 cm^{-1} is the stretching vibration of -OH, and there is an obvious absorption peak at 2800–3000 cm^{-1}, which is mainly due to the formation of-CH_2-stretching vibration. The vibration of the C=C double bond skeleton of toluene results in an absorption peak at 1600 cm^{-1}. The 1376 cm^{-1} is due to the symmetric stretching vibration of C-H bond in methyl-CH_3-, and the 1458 cm^{-1} is due to the characteristic peak caused by the anti-symmetric stretching vibration, in which the antisymmetric stretching vibration amplitude is stronger. The stretching vibration of sulfoxide group S=O in asphalt causes energy fluctuation, which is reflected at 1030 cm^{-1}. A small functional group absorption peak within 1000 cm^{-1} is due to the presence of aromatics in the asphalt, and the benzene ring in the aromatics has massive C-H bonds, so the absorption peak here is generated by the bending vibration of the C-H bond. It can be seen that the composition of matrix asphalt is complex, and it is a hydrocarbon containing a variety of hydrocarbons.

Because SBS is an immiscible system, the infrared spectrum of the SBS is only a simple superposition of the infrared spectrum of polystyrene and polybutadiene. The position and intensity of the absorption peak are basically unchanged, and no new absorption peak appears. The C=C double bond bending vibration of the butadiene block in the SBS modifier causes an absorption peak at 966 cm^{-1}, and the C-H bond out-of-plane bending vibration in the benzene ring of the polystyrene block in the SBS modifier causes an absorption peak at 699 cm^{-1}.

After adding PPA, the asphalt formed a new mixed absorption peak in the 800–1300 cm^{-1} band, indicating that PPA had a chemical reaction with asphalt and changed the chemical structure unit of the original SBS modified asphalt molecule. It is a chemical modifier. The strong absorption peak at 2800–3000cm^{-1} is mainly due to the formation of-CH_2-stretching vibration. In addition, a convex peak appeared in the PPA/SBS composite modified asphalt map near 2030 cm^{-1}, indicating that PPA as a chemical modifier, its addition and asphalt formed a new compound. It is assumed that PPA reacts with alcohols in asphalt, and -OH in alcohols is neutralized by phosphoric acid to form phosphate ester. The increase of esterification degree is manifested by the increase of macromolecules and chain hydrocarbon components in asphalt, which leads to its thickening, and the macroscopic performance is the reinforcement of the high-temperature performance of asphalt.

5. Conclusions

(1) Compared with matrix asphalt, when the content of the PPA modifier is increased from 0.5% to 1%, the penetration of PPA/SBS composite modified asphalt can be decreased by 20.92%, 25.07% and 28.94% respectively, and the softening point can be increased by 5.46%, 22.69% and 34.03%, respectively. However, even a low content of PPA will reduce the ductility of asphalt at 5 °C. In addition, PPA has the ability to inhibit the thermal oxidative aging of asphalt, and the more the content, the more obvious the effect.

(2) With the increase of PPA modifier content, the complex modulus of PPA/SBS composite modified asphalt in low-frequency and high-frequency regions is significantly improved. Compared with SBS modified asphalt, the ZSV (Carreau model fitting results) of PPA/SBS composite modified asphalt can be increased by 16.53%, 23.14% and 208.94%, which significantly improves the shear resistance of asphalt. At the same time, the temperature sweep results show that at 82 °C, the phase angle of PPA/SBS composite modified asphalt can be decreased by 8.63%, 13.23% and 19.24%, and the anti-rutting factor can be increased by 41.97%, 67.62% and 70.97%, indicating that PPA could improve the ability of asphalt to resist plastic deformation. The high-temperature performance of asphalt is greatly improved, and the absolute value of VTS of PPA/SBS composite modified asphalt is reduced by 14.01%, 23.33% and 34.07%, respectively.

(3) At −12 °C, compared with SBS modified asphalt, the stiffness modulus of PPA/SBS composite modified asphalt increased by 11.17%, 29.78% and 48.86%, respectively, and the creep rate decreased by 3.00%, 5.93% and 9.18%, respectively, indicating that after PPA modifier partially replaces SBS modifier, its low-temperature deformation resistance and stress relaxation ability have different degrees of a weakening effect. This is consistent with the conclusion that PPA has a negative impact on the low-temperature performance of asphalt in the survey results.

(4) After SBS modification, the molecular chemical structure and properties of asphalt remain unchanged. The modification process is mainly physical blending, while PPA and SBS modified asphalt undergo a new chemical reaction, manifested by the increase of macromolecules and chain hydrocarbon components in the asphalt, leading to the thickening of the asphalt, and the macroscopic manifestation is the improvement of the high-temperature performance of the asphalt.

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