



Article Study on the Performance of SBS/Polyphosphoric Acid **Composite Modified Asphalt**

Chaojie Li^{1,2,3}, Zhenxia Li^{3,4,5}, Tengteng Guo^{3,4,5}, Yuanzhao Chen^{3,4,5,*}, Qi Liu³, Jing Wang³ and Lihui Jin³

- Henan Transportation Research Institute Co., Ltd., Zhengzhou 450006, China; lcj13676936229@163.com 2
 - Xi'an Changda Highway Engineering Inspection Center Co., Ltd., Xi'an 710064, China
- 3 School of Civil Engineering and Communication, North China University of Water Resources and Electric Power, Zhengzhou 450045, China; zhenxiali2009@ncwu.edu.cn (Z.L.); guotth@ncwu.edu.cn (T.G.); lq_9898@163.com (Q.L.); wj@ncwu.edu.cn (J.W.); lihuijin2023@163.com (L.J.)
- 4 Technology Innovation Center of Henan Transport Industry of Utilization of Solid Waste Resources in Traffic Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045, China
- 5 Henan Province Engineering Technology Research Center of Environment Friendly and High-Performance Pavement Materials, Zhengzhou 450045, China
- Correspondence: cyz740513@ncwu.edu.cn

Abstract: To address the issue of bad compatibility between a single polymer modifier and asphalt and high preparation cost, the composite modified asphalt with polyphosphoric acid (PPA) and SBS as a modifier was prepared. Basic properties, viscosity characteristics, high-temperature and low-temperature rheological performance, and aging-resistant performance of SBS/PPA composite modified asphalt were comprehensively evaluated, and the best content of PPA was obtained through the experimental results below. By performing an infrared spectrum test and a scanning electron microscope test, structural changes and modifying mechanisms of composite modified asphalt were analyzed. The results indicate the optimal PPA content is 0.75%. After adding PPA, the penetration and ductility of composite modified asphalt were reduced, while the softening point increased. At 135 °C, the viscosity was 1.2 times that of SBS modified asphalt. The average weight loss ratio was 0.163%. When the content of PPA was 0.75% and 1%, the rutting factor increased significantly. Therefore, PPA can not only improve the thermal oxidation aging resistance of asphalt, it can also improve the shear resistance, high-temperature performance, and temperature sensitivity of asphalt. Between 1027 and 1150 $\rm cm^{-1}$, the composite modified asphalt forms a new absorption peak, and from 1610 cm^{-1} , the absorption peak presents an upward trend, suggesting that PPA reacts chemically with asphalt, produces the new substance, and also increases a large number of hydrocarbon components with chain structure. The surface appearance of the compound modified asphalt gradually presents a smooth wrinkle state due to the increase of PPA, so the issue of easy segregation of SBS in asphalt is improved.

Keywords: environmental protection material; composite modified asphalt; rheological properties; polyphosphoric acid; microscopic analysis

1. Introduction

Hole cracks, pit collapse, and other diseases occur in asphalt pavement all year round. In addition to construction reasons, pavement aging is also an important cause. The principal cause for pavement aging is the decrease of cohesion and even movement of aggregate and asphalt in asphalt mixture subjected to repeated heavy loads and high temperatures [1]. Conventional polymer modified asphalt has the problems of poor compatibility with asphalt and easy segregation during transportation, which ultimately results in a decrease in service life and a rise in the cost of building and maintaining [2]. Therefore, it is of great significance for practical road applications to combine modifiers with different modification



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mechanisms into base asphalt to achieve complementary advantages among modifiers to improve asphalt performance.

As the third generation of synthetic rubber, an SBS modifier is widely used because of its excellent thermal stability and high-temperature performance, but it still cannot avoid the problem of transportation segregation caused by poor blending compatibility, and the performance deterioration is also common [3–6]. Cortizo et al. [7] indicated that the penetration of SBS modified asphalt was reduced and the softening point was raised after RTFOT. The infrared spectrum showed that changes in performance were mainly due to changes in microstructure, as well as the molecular weight of SBS modified asphalt under thermal oxidative degradation. The modification of asphalt with a different modifying agent was investigated. It was found that although both SBS and rubber powder were physically modified, its performance was obviously superior to single mixing [8–12]. The physical index, storage stability, and aging resistance of SBS modified asphalt can be improved by applying surface-active nanomaterials to produce composite modified asphalt [13,14]. When the chemical modifier gradually entered the academic field of vision, the composite modified asphalt co-doped with the reactive modification agent based on polyurethane precursor (PRM) and SBS appeared, which increased the compatibility of the polymer modifier and asphalt by chemical crosslinking and formed a more stable network structure [15,16].

As an acidic modifier, polyphosphoric acid was first popularized abroad, accounting for more than 16% of the modified asphalt market in the United States [17]. This is enough to show that polyphosphoric acid can play an active role in modified asphalt, and its cost is only half or even lower than that of polymer. Therefore, for large-volume asphalt pavement construction projects, the use of polyphosphoric acid is a choice to save economic costs and has economic benefits for practical road applications. Jafari et al. [18,19] found that adding PPA could improve the properties of high-temperature and aging resistance through various rheological tests. Amirkhanian et al. [20,21] found that the addition of phosphorus-containing acidic modifiers represented by PPA could facilitate the conversion of asphalt colloids to asphaltenes, so that asphalt can be transformed into a solution-gel type asphalt colloid structure; the effect of improving the high-temperature property of asphalt is realized by a stable homogeneous system. Cao et al. [22] used a standard penetration test (SD) method and a semi-circular bending (SCB) test, pointed out that PPA can change the asphalt structure and that the high-temperature stabilization is enhanced, and revealed that the reason for the increase of asphalt brittleness is that PPA increases the viscosity. Adding PPA into asphalt mixture makes low-temperature crack resistance worse, and the negative impact is greater. Wang [23] put forward that the phosphorylation reaction caused the macromolecular long-chain hydrocarbon components to appear in the asphalt, so the asphalt became hard and the penetration decreased. Hou [24], through multiple stress creep recovery (MSCR) tests, found that when the content of PPA was 1~1.25%, high-temperature stability can be enhanced regardless of whether the polymer is added into asphalt through the MSCR test.

Nowadays, there are some problems in combining SBS with base asphalt, such as unstable compatibility, easy segregation, and insufficient anti-aging performance, which will have a non-negligible impact on the asphalt structure. The content of PPA as a modifier in composite modified asphalt still needs to be carefully studied. It is generally believed that the content of PPA in 0.5~2% is more appropriate. In addition, the modification mechanism of PPA is still controversial, so it is important to systematically study its modification mechanism from the micro level. For this reason, SBS/PPA compound modified asphalt was prepared, and its properties and modifying mechanism were compared and explored. The changes in conventional properties and rheological properties of SBS modified asphalt with different PPA contents were revealed; then, further analysis about microstructure changes in modified asphalt was carried out.

2. Raw Materials

2.1. Asphalt

A-grade 70# road petroleum asphalt, produced by Zhengzhou Municipal Engineering Corporation, was adopted in this study. Basic properties of base asphalt were tested in accordance with the test program [25], and its technical indicators were assessed against the technical specifications [26]. The experimental results are shown in Table 1, which suggests the asphalt specification is up to standard.

Table 1. Technical indicators of 70# base asphalt.

Test Items		Unit	Test Results	Technical Requirements	Test Method
Penetration $(100 \text{ g}, 5 \text{ s})$		0.1 mm	67.6	60~80	T0604
Ductility (5 cm/min, 10 °C)		cm	48	≥ 20	T0605
Softening point		°C	46.5	≥ 46	T0606
Penetration index PI		_	-0.768	$-1.5 \sim +1.0$	T0604
	Quality change	%	-0.272	$-0.8 \sim +0.8$	T0610
After RTFOT	Penetration ratio (25 °C)	%	62.4	≥ 61	T0604
	Ductility (5 cm/min, 10 °C)	cm	6.8	≥ 6	T0605

2.2. Polyphosphoric Acid

The polyphosphoric acid (PPA) with a purity of 117% (H3PO4 content), provided by Lanjue Chemical Co., Ltd. (Zhongshan, China), is used in this study. It is a transparent viscous liquid. The results presented in Table 2 show that the polyphosphate modifier meets the specification.

Table 2. Technical indicators of polyphosphoric acid.

Test Items	Unit	Test Results	
P_2O_5 concentration	%	82.6	
25 °C vapor pressure	Pa	$2.61 imes 10^{-6}$	
Boiling point	°C	558	
Chloride (Cl) content	%	0.0002	
Iron (Fe) content	%	0.0010	
Arsenic (As) content	%	0.0066	
Heavy metal (Pb) content	%	0.0014	

2.3. Styrene-Butadiene-Styrene Block Copolymer

In this study, SBS-YH791 SBS1301 modified material, produced in Yueyang, Baling Petrochemical (Yueyang, China), was used, and its state is white solid particles. It can be concluded from the test results presented in Table 3 that the SBS modifier satisfies the specification.

Table 3. Technical indicators of SBS.

Test Items	Unit	Test Results	Technical Requirements
Molecular structure	_	Linear	Linear
Ash	%	0.07	≤ 0.20
300% tensile stress	MPa	4.8	\geq 3.5
Tensile strength	MPa	28.4	$\geq \! 24.0$
Elongation at break	%	742	\geq 730
Volatile matter	%	0.54	≤ 0.70
Styrene/Butadiene mass ratio	—	20/80	20/80

3. Experimental

3.1. Formulate Sample Content and Modified Asphalt Preparation Method 3.1.1. Preliminary Formulation of Sample Content

According to the actual construction situation of the current pavement and the comprehensive analysis of fuzzy mathematics, it was finally determined that the comprehensive evaluation of various physical properties is the best when the SBS content is 5% [27]. As a result, SBS content in SBS modified asphalt was 5% [28–30]. Considering the advantages of PPA in high-temperature performance and its negative influence on low-temperature performance [31], a large number of studies [32,33] believe that the content of PPA should not be higher than 1%. Because a small amount of PPA can achieve a high amount of polymer modification effect, it is appropriate to reduce the amount of SBS when preparing composite modified asphalt. In this study, the SBS content was selected to be 3.5% of the asphalt quality, and the contents of PPA were 0.5%, 0.75%, 1.0%, 1.25%, and 1.5% of asphalt quality, respectively.

3.1.2. Preparation of SBS Modified Asphalt

First, the asphalt was heated to its melting flow in an electrothermal blast drying oven at 160 °C, then taken out and placed on a constant temperature heating table. The weighed 5% SBS was slowly and uniformly added at 3000 r/min. After that, shear 45~50 min at 4500 r/min. During the shearing period, glass rods were continuously stirred to prevent uneven shearing. After the stirring was completed, the rotational speed was set to 1500 r/min for 30 min, so that SBS was further dissolved in asphalt in a finer state. Finally, the sheared sample was put into an electrothermal blast drying oven at 180 °C to swell and develop for 1 h to achieve the purpose of full compatibility between the modifier and the asphalt.

3.1.3. Preparation of SBS/PPA Composite Modified Asphalt

First, the asphalt was put into the electric hot blast drying box, and the asphalt was heated to melt and dehydrate. It continued to heat to 165 °C, then was taken out and placed on a constant temperature heating table. A total of 3.5% SBS was added at a slow and uniform speed of 3000 r/min; then, the asphalt was sheared at a speed of 4500 r/min for $35\sim40$ min and finally maintained a constant temperature. It was mixed at a low speed for about 25 min to fully swell SBS modified asphalt. After the sample was fully prepared and swelled, the constant temperature heating platform was heated to 170 °C, and the speed was increased to 4500 r/min. A different dosage of PPA modifiers, which were weighed by the electronic balance, were added at a constant speed, and the speed was set to 5000 r/min for 30 min after complete addition. Lastly, the sheared sample was put into an electrothermal blast drying oven at 180 °C to swell and develop for 1 h.

3.2. Basic Performance Test

According to the specification [25], the short-term aging of asphalt and the above prepared samples were carried out by an SYD-3061 rotating film oven. A total of 14 groups of samples prepared above were tested for three major indicators, and the basic property changes of samples with or without aging were compared.

3.3. Brookfield Viscosity Test

In accordance with the T 0625-2011 test method in the specification [25], the NDJ series Brookfield viscometer of Changji Geological Instrument Co., Ltd. in Shanghai, China was used to carry out 135 °C and 175 °C rotational viscosity tests on above prepared samples. The effect of the modifier on viscosity-temperature characteristics was studied.

3.4. DSR

In accordance with the T 0628-2011 test method in specification [25], the temperature scanning experiments were conducted on the prepared samples in the original sample group and the aging group by using the instrument. A large sample with a diameter of

25 mm and a thickness of 1 mm was used. The angular frequency was adjusted to 10 rad/s, the experiment temperature was set to start from 46 °C, and the interval was 6 °C until 82 °C. The phase angle δ and rutting factor G*/sin δ of all samples were compared. In addition, frequency scanning tests were performed on 6 groups of modified asphalt in the original and aging groups. The experiment temperature was set to start from 40 °C, and the interval was 12 °C until 88 °C. The frequency was set from 0.1 to 100 rad/s and the strain level was 1%. The change trend of logG*/sin δ , with frequency at 52 °C and 76 °C, was analyzed to study the high-temperature property and aging resistance of composite modified asphalt.

3.5. BBR

According to the T 0627-2011 in the specification [25], the trabecular bending specimens of all samples were prepared, as shown in Figure 1. The specimen size is $127 \times 12.7 \times 6.35$ mm. Experiment temperature was set at -12 °C, -18 °C, and -24 °C, and all specimens were loaded, unloaded, and dead loaded. The stiffness modulus and creep curve slope of each asphalt group before and after aging were compared to study its low-temperature crack resistance.



Figure 1. Low-temperature bending beam specimens.

3.6. FTIR

With the help of the Nicolet iS10 FTIR spectrometer produced by Thermo Fisher Scientific (Waltham, MA, USA), as shown in Figure 2, the infrared spectrum test of 7 kinds of asphalt in the original sample group was carried out, the change rule of absorbance in the spectrum after the addition of a modifier was analyzed, and the reaction type between modifier and asphalt was judged. The test parameters mainly include a scanning range of 500 cm^{-1} ~4000 cm⁻¹, scanning time of 64 times, and a minimum resolution of 0.019 cm⁻¹.



Figure 2. Infrared spectrometer.

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3.7. SEM

The test of SEM was carried out by SU8010 field-emission scanning electron microscope produced by HITACHI in Tokyo, Japan, the combination of the modifier and asphalt was observed, and its microstructure change was analyzed. The preparation process for the specimens was as follows: first, the prepared sample was put into the oven and heated to melt. Then, the sample was dipped quickly with a glass rod, and the sample with a volume of 10 mm \times 10 mm \times 1 mm (or 2 mm) was formed on the clean glass slide. After cooling, the specimens were sprayed with gold and then the experiments were conducted. The test specimens are illustrated in Figure 3.



Figure 3. SEM test specimens.

4. Test Results and Analysis

4.1. Analysis of Basic Performance Results

4.1.1. Analysis of Performance Results of Original Group Modified Asphalt

The tests of penetration, softening point, and ductility performance were conducted on asphalt and six groups of modified asphalt in the original group. The test results are presented in Table 4.

Table 4. Three index results of composite modified asphalt.

Test N	umber and Schemes	Penetration (25 $^{\circ}$ C, 0.1 mm)	Softening Point (K)	Ductility (5 $^\circ$ C, cm)
1	70# Base asphalt	67.6	319.7	10.3
2	5% SBS	51.9	339.5	29.7
3	0.5% PPA + 3.5% SBS	54.7	322.9	26.6
4	0.75% PPA + 3.5% SBS	51.8	331.0	20.3
5	1.0% PPA + 3.5% SBS	49.1	336.4	16.8
6	1.25% PPA + 3.5% SBS	44.7	342.6	14.4
7	1.5% PPA + $3.5%$ SBS	42.4	73.2	12.9

After adding SBS, the penetration is reduced by 23.2%, the softening point increased from 319.7 K to 339.5 K—an increase of 6.2%—and the ductility is 2.9 times that of asphalt, suggesting that SBS can remarkably improve the high- and low-temperature properties of asphalt. The penetration of each modified group is smaller than that of asphalt, and it will be reduced gradually as the dosage is increased. The ductility of each modified group exceeds that of asphalt, but when the content exceeds a certain limit, the ductility will show a downward trend. When PPA content is 1.5%, it tends to be closer to basic asphalt. The softening point of each modified group exceeds that of the asphalt, and when PPA content is 1.5, it is 1.5 times that of the asphalt, indicating that even a little amount of PPA can increase the viscosity of asphalt, which makes a positive function on the property of asphalt at both high and low temperatures.

The penetration of each composite modified asphalt group decreases as the increment of the dosage. When PPA dosage is 0.75%, the penetration is similar to that of SBS modified asphalt. When PPA dosage is less than 1%, although the softening point is smaller than that of SBS modified asphalt, the softening point is increased as the dosage is increased, indicating that adding PPA will increase the viscosity of SBS modified asphalt and enhance its high-temperature performance [34]. The 5 °C ductility of each composite modified asphalt group reduces as the increment of the dosage; even if PPA dosage is 0.5%, it is not as good as 5% SBS modified asphalt, illustrating that adding PPA makes it gradually harden so that its ability to extend and deform at a low temperature decreases. Therefore, adding PPA is not conducive to the low-temperature property of SBS modified asphalt.

4.1.2. Analysis of Performance Results of Aging Group Modified Asphalt

Experimentation results of the mass change, 25 °C penetration, 5 °C ductility, and softening point of seven groups of asphalt after aging are presented in Table 5.

Test Number and Schemes		Mass Change (%)	Penetration (25 $^{\circ}$ C, 0.1 mm)	Softening Point (°C)	Ductility (5 °C, cm)
1	70# Base asphalt	0.272	42.2	54.2	7.8
2	5% SB\$	0.218	34.2	74.7	21.4
3	0.5% PPA + 3.5% SBS	0.204	34.4	56.4	20.7
4	0.75% PPA + 3.5% SBS	0.192	33.2	63.9	14.9
5	1.0% PPA + 3.5% SBS	0.167	32.9	67.1	12.6
6	1.25% PPA + 3.5% SBS	0.133	32.1	72.7	11.2
 7	1.5% PPA + 3.5% SBS	0.119	31.3	75.1	10.3

Table 5. Aging test results of composite modified asphalt.

As shown in Table 5, as the increment of PPA dosage increases from 0.5% to 1.5%, the average mass loss rate of composite modified asphalt is 0.163%, which is less than 0.264% of base asphalt and 0.218% of 5% SBS modified asphalt. The results suggest that adding PPA could enhance the thermal oxidation resistance of asphalt, and the more the content, the less the weight loss. The penetration of seven groups of aged asphalt decreases after aging, and the higher the PPA dosage, the smaller the penetration, and the base asphalt decreases the most. When the PPA content increases from 0.5% to 1.5%, the residual penetration ratio increases from 62.9% to 73.8%, and the change range is more than 10%. The residual penetration ratio of SBS modified asphalt is between the composite modified asphalt group with PPA content of 0.75~1.0%, indicating that adding PPA could decrease the thermal oxidation of SBS/PPA compound modified asphalt and improve its aging resistance. After aging, the softening point of seven groups of asphalt increases, and the increment of PPA content causes the increment of the softening point of each compound modified asphalt to reduce, indicating that adding PPA is beneficial to greatly improving the aging resistance of SBS modified asphalt. After aging, the ductility of the seven groups of asphalt decreases, and the greater the PPA content, the lower the difference in ductility pre- and post-aging, and the residual ductility ratio increases from 70% to nearly 80%. The ductility of composite modified asphalt and its ductility difference is less than 5% SBS modified asphalt, but still better than matrix asphalt, indicating that thermal oxygen aging will weaken the ductility and low-temperature property of compound modified asphalt.

4.2. Analysis of Viscosity-Temperature Characteristics Results

The viscosity experiment results of seven groups of samples at 135 °C and 175 °C are summarized in Figure 4. Through analysis, adding SBS to the base asphalt at 135 °C can increase the viscosity by 1.4 times, and the viscosity is increased by 3.8 times at 175 °C. At 135 °C, the viscosity of each compound modified asphalt group increased by 34%, 73.7%, 134.2%, 166.7%, and 179.8%, respectively, compared with SBS modified asphalt. However, when PPA dosage exceeds 1% to 1.25%, the viscosity exceeds 3 Pa·s, which does not meet

the construction requirements. At 175 °C, the viscosity of the seven groups of asphalt has decreased by no less than 50%, but the viscosity after adding PPA is always greater than that without PPA. This is because the viscosity is mainly determined by the asphaltene content; adding PPA will increase the asphaltene content—which is mainly converted from the resin—and further enhance the high-temperature property of asphalt. It proves that adding PPA can increase the shear deformation resistance of asphalt mixture.



Figure 4. Brookfield viscosity test results.

4.3. Analysis of DSR Test Results

4.3.1. Analysis of Temperature Sweep

Figure 5 illustrates the change curves of $G^*/\sin\delta$ and δ concerning temperature in the original group, and Figure 6 presents the change curves of $G^*/\sin\delta$ and δ concerning temperature in the aging group. The analysis shows that:

- (1) As the experimental temperature gets higher and higher, the experimental results of all samples in the original group and the aging group are generally that $G^*/\sin\delta$ decreases and δ increases. The main cause of this phenomenon is that the higher the temperature is, the weaker the close force between asphalt molecules is. The asphalt binder presents a viscous fluid at high temperature, which leads to a decrease in its recovery deformation ability and a poor anti-deformation ability.
- (2) Regardless of aging or not, the G*/sinδ of each composite modified asphalt group increases with increasing PPA content, suggesting the viscosity is further strengthened by adding PPA. At the same test conditions, when the content of PPA is 0.75% and 1%, the G*/sinδ value increases significantly, and the absolute value of slope reaches more than 0.5, indicating that the best dosage range of PPA in composite modified asphalt is 0.75~1%.
- (3) Regardless of aging or not, the δ of each group has a significant downward trend with increasing PPA dosage. When the PPA dosage is 0.75%, the phase angle is significantly smaller than that of others, suggesting that under high temperature load, when the PPA dosage is 0.75%, the improvement degree of elastic element in the composite modified asphalt is the largest, closest to the elastomer, and is easier to recover after load deformation.



Figure 5. Rutting factor and phase angle-temperature change curve of the original group.



Figure 6. Rutting factor and phase angle-temperature change curve of the aging group.

4.3.2. Analysis of Frequency Scanning

Figure 7 illustrates the logarithmic curve of the change about $G^*/\sin\delta$ in the six groups of modified asphalt in the original group and the aging group at 52 °C and 76 °C. The analysis shows that:

- (1) The G*/sin δ values in the original sample group and the aging group generally increase in parallel with the change curve of frequency, and the logarithm of the rutting factor has a good linear correlation with the logarithm of frequency, illustrating that the influence of each modified asphalt group on frequency is basically the same. The increase of G*/sin δ value in the aging group is larger than that in the original group, and the logarithmic value of G*/sin δ in each group gradually approaches with increasing frequency, suggesting the high-temperature performance has changed significantly as a result of aging. The reason why G*/sin δ in the aging group is higher than that in the original sample group is that under the action of aging, asphalt lightweight component volatilizes, asphaltene increases, elasticity of the asphalt gets stronger, and the load resistance and deformation resistance are strengthened.
- (2) With regard to the G*/sinδ value, the composite modified asphalt of the original group and the aging group is always greater than the SBS modified asphalt in all

frequency ranges. Especially for 0.75% SBS/PPA composite modified asphalt, no matter how much the temperature is, the $G^*/\sin\delta$ value corresponding to this dosage is the highest. This is mainly because adding PPA can accelerate the change of asphalt structure to gel type more quickly, and the elastic behavior is more obvious when the aging effect is applied to the same degree.

(3) At 76 °C, the G*/sinδ value of the compound modified asphalt with 0.75% content increases by 40.4% after aging, while the measured G*/sinδ values of the SBS modified asphalt original group and the aging group are relatively low, and the G*/sinδ value increases by 27.7% after aging. The effect of aging reduces the volatilization of the light components, which results in a lower viscosity and a hardening of the asphalt binder. However, aging will also destroy the original stable spatial structure that was initially formed by SBS decomposition, so its high-temperature rutting resistance is worse than that of composite modified asphalt.



Figure 7. Logarithmic curves of the rutting factor and frequency of modified asphalt.

4.4. Analysis of BBR Test Results

Figures 8 and 9 show the variation curves of stiffness modulus S and creep rate m with respect to temperature in the original group and the aging group, respectively. The analysis shows that:

(1) Before aging, the lower the temperature of the original sample group is, the larger the S is, and the smaller the m is. Comparing the S value and m value at the same temperature, the base asphalt has the highest S value and the minimum m value. The S value and m value of each composite modified asphalt group are all below the SBS modified asphalt, indicating that after adding PPA, its deformation resistance and stress relaxation property have different degrees of decline, but compared with the matrix asphalt, the low-temperature creep ability of the modified group is still better. By comparing the different PPA content of compound modified asphalt, the S value is increased and the m value is reduced as the PPA content is increased, indicating that PPA will weaken the low temperature creep property of SBS modified asphalt, and that the degree of low temperature variation is positively correlated with PPA content. Therefore, the low-temperature property of SBS modified asphalt in the original sample group is the best.

(2) After aging, the variation tendency in asphalt with temperature is consistent with that in the original group. The S value of the compound modified asphalt in the interval of -18~-24 °C is the same as that in the original sample group. The slope is significantly larger, and the S value of all asphalts in this temperature range increases the fastest, indicating that adding PPA will reduce its low-temperature performance regardless

of aging or not. The aging group asphalt is still hard in this temperature range, and the load acting on it makes it more easily damaged by load deformation. The increment of S value becomes smaller after aging, indicating that adding PPA could weaken the aging effect and further improve the aging resistance, but it will have a reverse effect on the low-temperature creep property.



Figure 8. Stiffness modulus and creep rate of the original group.



Figure 9. Stiffness modulus and creep rate of aging asphalt.

4.5. Determination of Optimum Dosage Combination

Based on the basic property test, it is found that adding PPA can decrease the penetration and ductility of SBS modified asphalt, increase the softening point, and reduce mass loss after aging. It shows that the more PPA content there is, the more obvious the improvement effect on high-temperature properties, thermal oxidation resistance, and aging resistance of SBS modified asphalt, while it is negatively correlated with the lowtemperature anti-cracking performance. The Brookfield viscosity test indicates that the more PPA content there is, the higher the viscosity increases, but it should not exceed 1%. The high-temperature rheological test shows that the improvement effect is the best when 0.75% PPA is added. The low-temperature creep test shows that the higher the PPA content is, the more unfavorable the low-temperature ductility is. Therefore, taking into account the properties of the high and low temperature, viscosity temperature characteristics as well as aging resistance of composite modified asphalt, the optimum amount of PPA is recommended to be 0.75%.

4.6. Analysis of FTIR Test

Figure 10 is the infrared spectrum of 70# base asphalt. The small functional group absorption peak within 1000 cm⁻¹ is due to the presence of aromatics in the asphalt, and the bending vibration of the benzene ring C-H bond is generated. At 1028 cm⁻¹, the energy fluctuation is because of the extensional vibration of the sulfoxide group S=O in the asphalt molecule. At 1375 cm⁻¹, it is owing to the symmetric extensional vibration of the C-H bond in methyl -CH3-, and at 1457 cm⁻¹, it is for the sake of the antisymmetric extensional vibration, in which the antisymmetric stretching vibration is stronger. The absorption peak transmittance at 1616 cm⁻¹ is because the vibration of the toluene C=C double bond skeleton is low. Two absorption peaks with strong transmittance are generated at 2917 cm⁻¹ and 2847 cm⁻¹. The reason is that the methylene group has antisymmetric and symmetric stretching vibrations, and the vibration amplitude generated by antisymmetric is larger than the symmetry. In summary, the constituent of asphalt is complicated and is a hydrocarbon containing a variety of hydrocarbons.



Figure 10. Infrared spectrogram of base asphalt.

By analyzing the infrared spectra of each group of modified asphalt shown in Figure 11, it can be seen that:

- (1) After the addition of SBS, the vibration of the C-H bond in the benzene ring of the polystyrene block in SBS causes an absorption peak at 697 cm⁻¹, and the -C=C- double bond bending vibration of the butadiene block causes an absorption peak at 964 cm⁻¹. In the region of 1000~2000 cm⁻¹, the absorption peaks at 1027 cm⁻¹, 1457 cm⁻¹, and 1610 cm⁻¹ are simply superimposed compared with the base asphalt, so SBS and base asphalt only produce physical changes.
- (2) Compared with modified asphalt under different PPA dosages, the absorption peaks of SBS modified asphalt after adding PPA are mainly concentrated in the above five listed: 697 cm⁻¹, 964 cm⁻¹, 1027 cm⁻¹, 1457 cm⁻¹, and 1610 cm⁻¹. Among them, the absorption peak intensity at 964 cm⁻¹ is weakened because the addition of PPA will undergo a reduction reaction to open the -C=C- double bond of SBS, further promoting the copolymerization reaction between asphalt and SBS. The greater the content, the better the compatibility, and the stronger the high-temperature stability.
- (3) 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 964 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 697 cm⁻¹.



Figure 11. Infrared spectrogram of composite modified asphalt.

4.7. Analysis of SEM Test

4.7.1. Microstructure of Asphalt

The base asphalt is magnified 500 times to obtain Figure 12. It can be seen that there are some textures on the surface of the base asphalt, but no other substances or particles appear, indicating that the clean base asphalt is selected in this study.



Figure 12. Base asphalt scanning electron micrograph.

4.7.2. Microstructure of SBS Modified Asphalt

As shown in Figure 13, the microstructure of SBS modified asphalt has changed greatly after being enlarged by 2000 times. The SBS modifier is basically dissolved in asphalt due to shear action, forming a more uniform distribution of wavy mesh space structure. When

the magnification is 5000 times, it is observed that there are still stacked SBS particles in the lower right corner area and the particle size is different, indicating that there is an issue of poor compatibility between SBS and asphalt. The SBS modifier is crosslinked with asphalt in the state of elastic particles, so the surface is uneven [35].



Figure 13. SBS modified asphalt scanning electron micrographs. (**a**) Amplified 2000 times; (**b**) Amplified 5000 times.

4.7.3. Microstructure of SBS/PPA Composite Modified Asphalt

Figure 14a-j are the SEM images of compound modified asphalt amplified by 5000 times and 10,000 times under different dosages. Figure 14a,b show the compound modified asphalt with 0.5% PPA. It can be seen that the number of elastic particle protrusions formed by the SBS modifier is significantly reduced, forming uneven surface morphology. After 10,000 times magnification, it can still be seen that there are dispersed SBS particles on the surface of compound modified asphalt. Figure 14c,d are composite modified asphalt with 0.75% PPA content. When the magnification is 5000 times, there are still some SBS particles in the upper left corner of the picture. When the region is further enlarged, a smooth plane can be seen in the region, indicating that the increase of PPA dosage makes SBS particles more compatible with asphalt. The PPA content in Figure $14e_{f}$ is 1%. The graininess in the figure is obviously weakened, and the distribution is more scattered. After 10,000 times magnification, the smooth area increases significantly, and occasionally SBS particles exist. The PPA content in Figure 14g, h is 1.25%. The microstructure of composite modified asphalt with this content basically shows a slight wrinkle mechanism. The compatibility between SBS particles and asphalt is good, and there is almost no obvious particle bulge. The PPA content in Figure 14i, j is 1.5%. At this time, the microscopic image is smoother, there are many clear folds, and the SBS particles in the composite modified asphalt have completely disappeared.



Figure 14. Cont.



Figure 14. SBS/PPA composite modified asphalt scanning electron micrographs. (**a**) 0.5% PPA magnified 5000 times; (**b**) 0.5% PPA magnified 10,000 times; (**c**) 0.75% PPA magnified 5000 times; (**d**) 0.75% PPA magnified 10,000 times; (**e**) 1% PPA magnified 5000 times; (**f**) 1% PPA magnified 10,000 times; (**g**) 1.25% PPA magnified 5000 times; (**h**) 1.25% PPA magnified 10,000 times; (**i**) 1.5% PPA magnified 5000 times; (**j**) 1.5% PPA magnified 10,000 times.

As the increment of PPA dosage increases from 0.5% to 1.5%, the microstructure is basically smooth from the initial uniform bulge to the final smooth state, and the SBS particles are completely dissolved in the matrix asphalt. From the microscopic mechanism analysis, the surface of the cementing material is smooth because adding PPA will reduce the size and number of SBS particles. Therefore, the uniformity distribution of asphalt is improved, and a more stable phase structure is formed. The swelling adsorption between the light component (mainly oil) and SBS is enhanced by the rise of the dosage. Meanwhile, the addition of PPA has a chemical reaction, and the asphaltenes are increased; therefore, when the content is 1.25% and 1.5%, a large number of uniform folds will be distributed in the image, which is also the reason why adding PPA in SBS modified asphalt further improves the high-temperature stability.

5. Conclusions

(1) The softening point and viscosity of SBS/PPA composite modified asphalt increase with the increase of content, and the penetration decreases. The change range of resid-

ual penetration ratio, mass change rate, and softening point increment of aged composite modified asphalt are smaller than that of SBS modified asphalt, indicating that the addition of PPA can improve the thermal oxidation resistance, high-temperature performance, and anti-aging performance of SBS modified asphalt. After adding PPA, the ductility of composite modified asphalt decreases, and the residual ductility ratio increases after aging, indicating that PPA will weaken the low-temperature crack resistance. At 135 °C, the average viscosity of composite modified asphalt after PPA addition is 2.2 times that of SBS modified asphalt, indicating that PPA can improve the viscosity-temperature characteristics, but once the PPA content exceeds 1%, it will not meet the construction requirements due to high viscosity.

- (2) Under the same test temperature, when the PPA dosage is between 0.75% and 1%, the anti-rutting factor increases significantly, indicating the composite modified asphalt in this range is less sensitive to temperature, resulting in better plastic deformation resistance than other test groups. When the PPA content is 0.75%, the phase angle is the lowest. In summary, adding PPA will increase the elastic element in SBS modified asphalt and exert better high-temperature rheological properties. The S value is increased while the m value is reduced as the PPA content is increased. At -12 °C, as PPA dosage increases, the S value of aged composite modified asphalt is reduced from 40.2% to 5.3% compared with that before aging, and the creep rate m is reduced from 8.5% to 5.1%, suggesting that the aging resistance of the composite modified asphalt is improved, but adding PPA will make the low-temperature creep worse. Therefore, considering the above indexes of composite modified asphalt, the optimal PPA dosage in composite modified asphalt is 0.75%.
- The physical effect of SBS is mainly manifested in the bending vibration of the C-H (3) bond of the benzene ring and the bending vibration of the butadiene block C=C, resulting in new absorption peaks at 697 cm^{-1} and 964 cm^{-1} , while the remaining positions are simply superimposed with asphalt. The incorporation of PPA has undergone chemical modification. The reduction reaction weakens the absorption peak intensity at 964 cm⁻¹, new absorption peaks are produced from 1027 to 1150 cm⁻¹, and the absorption peak after 1610 cm^{-1} continues to rise. The microstructure of SBS modified asphalt shows a more uniform distribution of wavy mesh space structure, and there are still stacked SBS particles with different particle sizes, indicating that the combination of SBS and asphalt is difficult. The microstructure of composite modified asphalt gradually forms a smooth wrinkle state with an increasing PPA dosage, and SBS particles basically disappear in composite modified asphalt. PPA could improve the segregation state of SBS in asphalt, and the composite modified asphalt is existed in a more stable phase structure. The results indicate that adding PPA into low-content SBS modified asphalt could shape a more stable network structure, and the macro properties are the high-temperature properties, the viscosity-temperature characteristics, and the aging resistance of the compound modified asphalt.

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