Evaluation of high temperature rheological performance of Polyphosphoric acid-SBS and Polyphosphoric acid-crumb rubber modified asphalt

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Abstract

This study explores the effects of polyphosphoric acid (PPA) on the rheological performance of styrene butadiene styrene (SBS) and crumb rubber (CR) modified asphalt binders at high temperatures. Four PPA concentrations were selected: 0.4%, 0.8%, 1.2%, and 1.6% by weight of virgin asphalt, and one SBS modified binder with 5% SBS by weight was used as a reference binder. Laboratory tests were performed to simulate short-term and long-term aging. Temperature sweep, frequency sweep, multiple stress creep recovery (MSCR) and repeated creep recovery (RCR) tests were also conducted to investigate the rheological properties of asphalt binders (i.e., PPA-SBS, PPA-CR and SBS modified). Fourier transform infrared spectroscopy (FTIR) test was used to study the chemical reaction of modifiers in the asphalt. Results showed that PPA improved the asphalt's resistance to permanent deformation and enhanced their elastic recovery behavior. Moreover, results of the rutting factor ($G^*/\sin\delta$), complex modulus (G^*), zero shear viscosity (ZSV), recovery percentage (R), non-recoverable compliance (Jnr) and viscous stiffness modulus (Gv) suggested that PPA-SBS had the best modification effects, followed by PPA-CR. Besides, results of the viscosity-temperature susceptibility (VTS) indicated that the additives decreased the temperature susceptibility of composite modified asphalt binders. PPA modified asphalt binder had good anti-aging behavior when the PPA content was no less than 0.8% of the virgin asphalt. Additionally, CR-modified asphalt binder with PPA additives exhibited the most improved aging and loading resistance.

Key words: Polyphosphoric acid (PPA); Crumb rubber (CR); Composite modified binder; Rheological properties; Temperature susceptibility.

1. Introduction

Deformation of asphalt pavement at high temperatures has been a worldwide issue since the beginning of modern road construction, and bitumen behavior is proved influential in the rheological performance of asphalt mixtures [1]. Polymers have been widely used in recent years for modification, which can increase elasticity, and decrease temperature sensitivity, of the binders. The polymers used for this purpose include styrene-butadiene-styrene (SBS), natural rubber (NR), styrene-butadiene-rubber (SBR), polyethylene (PE) and polyvinyl chloride (PVC), etc. [2-4]. However, poor storage stability and degradation of these polymers have prompted an industry-wide search for novel bitumen modifiers [5]. Polyphosphoric acid (PPA) has attracted increasing attention for its advantages such as low cost, simple modification process and excellent storage stability [6]. What's more, laboratory research has recognized the effect of PPA on enhancing the rheological performance of asphalt at high temperatures [7, 8].

PPA-modified asphalt is considered the most promising among acid-modified asphalts [7]. PPA changes the chemical composition of asphalt binder, such as conversion of saturates into asphaltenes [9]. Meanwhile, this additive acts as an anti-condensing agent reacting with asphaltenes, which results in the dispersion of asphaltene [10]. Overall, the modulus of asphaltene is enhanced, and consequently the elastic performance of the binder improved [9, 11]. However, the effect on low-temperature (LT) performance is largely unknown except some researchers believed it is dependent on the virgin asphalt [12, 13]. Moreover, the modification by PPA is often applied in conjunction with another additive [8, 14, 15]. Considering the characteristics of PPA-modified asphalt binders, researchers have been looking for a more effective modification, such as in conjunction with SBS or crumb rubber (CR) [16-19]. Among the studied polymer modifiers, SBS block copolymers is widely recognized as the best modifier of asphalt for their physical performance and rheological characteristics. D’Angelo [20] revealed the modification mechanism of PPA-SBS asphalt binder using laboratory experiments. He indicated that PPA could interweave with the SBS particles to form a spatially interlocking structure. Furthermore, the esterification of PPA with sulfoxide groups in asphaltene colloid enhanced the cohesion of the SBS modifier in asphalt. Some studies [17, 21, 22] discovered that the addition of PPA improved high-temperature stability and anti-aging characteristics of SBS-modified asphalt binder and meanwhile, its low-temperature (LT) performance also met the requirements of the specification. However, its disadvantages are high cost, difficulty in preparation and poor storage stability [23-25]. Sarnowski et al. [26] modified virgin asphalt and SBS-modified asphalt with PPA, and the difference in LT performance between the two modified asphalts was insignificant. Aflaki et al. [27] concluded that the PPA had positive effects on binder’s LT performance.

In order to improve the crack resistance of asphalt binders at low temperatures, PPA-CR composite modified asphalt has been prepared and tested. Yadollahi G et al. [11] claimed that the modification reduced the risk of cracking at low temperatures and rutting at high temperatures, and the performance of modified asphalt was further enhanced when the CR content increased [28]. Domingos et al. [18] found that CR and PPA can effectively enhance stiffness and elasticity of the bitumen, and they were more effective when used in combination. Cao et al. [19] recommended the optimal ratio of PPA-CR composite modified asphalt based on variance analysis. The aforementioned studies all found that the modification by PPA-CR composite was promising, which improved thermal stability of the asphalt. However, the content of CR powder in those studies was no more than 15%, and there are no observations so far about the effect of PPA blended with high content (＞15%) of CR modifier on rheology and microstructure.

The application of PPA combined with SBS- and CR-modified asphalt is a new cost-effective way of binder modification. However, studies that involve a quantitative comparison with 5% SBS modified asphalt binder are few, which provided limited guidance for the application of PPA-SBS composite modified asphalts. Furthermore, no study is found on the effect of PPA in comparison with PPA-SBS and PPA-CR modified asphalt. Literature suggested that the rheological behavior is crucial for evaluating the effect of different modifiers on asphalt binders [2, 29]. In terms of PPA-CR modified asphalt, Zarei et al. [30] claimed that the stiffening effect of PPA did not contribute substantially to elastic responses at high temperatures. Although they expected that those results would be different with PPA-SBS modified asphalts, they did not test and compare the rheological performance of the two modified asphalts under the same conditions. To conclude, other researchers studied rheological behaviors of PPA-SBS and PPA-CR modified asphalts at high temperatures but the results did not agree, thereby a comparative analysis of the two PPA-added composite modified asphalts under the same conditions is imperative.

Objectives of this paper are to investigate the rheological performance of PPA (0.4%, 0.8%, 1.2% and 1.6% by weight) combined with SBS- and CR-modified asphalt, including the rheological performance at high temperatures, temperature sensitivity, resistance to aging and the chemical components. Meanwhile, the two asphalts (PPA-SBS and PPA-CR) were compared with 5% SBS modified asphalt binder. Furthermore, this paper presented in detail the rheological behavior of CR-modified asphalt with varying PPA contents, to test the feasibility of PPA-CR modified asphalt at high CR contents.

2. Materials and samples preparation

2.1 Materials

The physical properties of PPA are shown in Table 1. The two modifiers in use were SBS and desulfurized CR powder. The SBS was denoted as 2116-06 linear SBS polymers, physical properties are presented in Table 2. The CR was obtained from waste tires, using the method of ambient grinding and the particle size is 60-mesh (0.25mm). The physical properties of CR are reported in Table 3.

In this study, the virgin asphalt binder was SK90# (produced in Korea in compliance with the Chinese specification, JTG F40-2004 [31]). Table 4 summarizes the technical properties of the virgin asphalt binder.

Table 1
Basic physical properties of PPA modifier.

Test indicators	Values
P_2O_5 content (%)	115
Steam pressure @ 25°C (Pa)	2.61×10^{-6}
Surface tension (N/cm)	81×10^{-5}

Specific heat capacity (J/g)	2.054
Density @ 25 °C (g/cm^3)	1.433
Boiling point (°C)	558

Table 2

Basic physical properties of SBS modifier.

Test indicators	Values
Structure	Linear
Ash content (%)	0.02
Tensile strength (MPa)	28.4
300% Extended stress (MPa)	4.5
Elongation at break (%)	674
Shao's A hardness (Shore A)	92
Permanent set (%)	44

Table 3

Basic physical properties of CR modifier.

Test indicators	Values	Specification
Relative density (g/cm^3)	1.15	—
Moisture content (%)	0.4	<1.0
Metal content (%)	0.007	<0.01
Fiber content (%)	0.002	<1.0

Table 4

Properties of virgin asphalt binder.

Test indicators		Values	Specification	Test methods
Penetration (25°C, 5s, 100g, 0.1mm)		85	80-100	ASTM D5
Ductility (15°C,cm)		>150	≥100	ASTM D113
Softening point (°C)		45.6	≥45	ASTM D36
TFOT (163°C, 5h)	Residual penetration ratio(%)	65.6	≥57	ASTM D1754/ D5
	Ductility (10°C,cm)	9	≥8	ASTM D1754/D113
	Ductility (15°C,cm)	134	≥8	ASTM D1754/D113

2.2 Samples preparation

The dosage of CR, SBS, and PPA was determined making reference to previous studies [32-35], where 5% SBS modified asphalt was widely used. PPA-SBS composite asphalt is commonly modified with a ratio of 1.2%± 0.4% PPA and 3% SBS. Considering the high purity of PPA in this study, the commonly used 3% SBS content was reduced to 2.8%. The PPA-SBS modified asphalt binder was prepared as follows: (1) SBS was added to the SK 90# in a quantity of 2.8% by weight of the virgin asphalt binder. The mixture was stirred at 160°C for 2h, and then mixed further at 165-170°C by a high-speed shearing machine at a speed of 5000 rpm for 45 min. (2) PPA of 0.4%, 0.8%, 1.2% and 1.6% (by weight of the virgin asphalt binder) was added, using a high-speed shearing machine for 20 min. (3) Place the mixtures in the oven at 170°C for 60 min. The preparation of the PPA-CR modified asphalt binder followed the same steps (1) to (3), except that the modifier added in step (1) was CR (60-mesh) at 18% by weight of the virgin asphalt binder.

The reference sample (SBS modified asphalt) was also produced using a high-speed shear mixer. The preparation process was as follows: (1) 5% SBS polymer was blended with the virgin asphalt binder at 160°C, at a low speed of 600 rpm for 2h. (2) increase the shearing speed to 5000 rpm for 45 min. (3) Keep the mixture in the oven at 170°C for 60 min.

The softening point and penetration tests were carried out in accordance with ASTM-D5 and ASTM D36, respectively. Results are summarized in Table 5. It is observed that penetration of the modified binders decreased and the softening point increased, when the PPA dosage increased. This can be explained by a previous study which found that an interlock was formed in the asphalt binder during the blending process by polymer additives [36]. The same conclusions were made by Xiao [37], despite the rate of increase to PPA dosage was found different.

For simplicity, the PPA-SBS modified asphalt with 0.4%, 0.8%, 1.2% and 1.6% PPA content were denoted as PS04, PS08, PS12 and PS16; the PPA-CR modified asphalt with 0.4%, 0.8%, 1.2% and 1.6% CR content were denoted as PC04, PC08, PC12 and PC16 in this paper.

Fig.1 illustrates the main experimental designs and procedures.

Table 5

Penetration, softening point and PG grade of the modified binders.

Binders	Penetration (25°C,0.1mm)	Softening Point (°C)	High-temperature of PG(°C)	Binders	Penetration (25°C,0.1mm)	Softening Point (°C)	High-temperature of PG(°C)
SK 90#	85	45.6	PG64	5%SBS	54.7	76.5	PG70
PS04	57.8	55.8	PG70	PC04	70.4	56.6	PG70
PS08	54.3	69.3	PG76	PC08	65.0	57.8	PG70
PS12	52.1	71.6	PG76	PC12	62.3	58.7	PG70
PS16	50.6	73.6	PG76	PC16	61.4	60.1	PG76

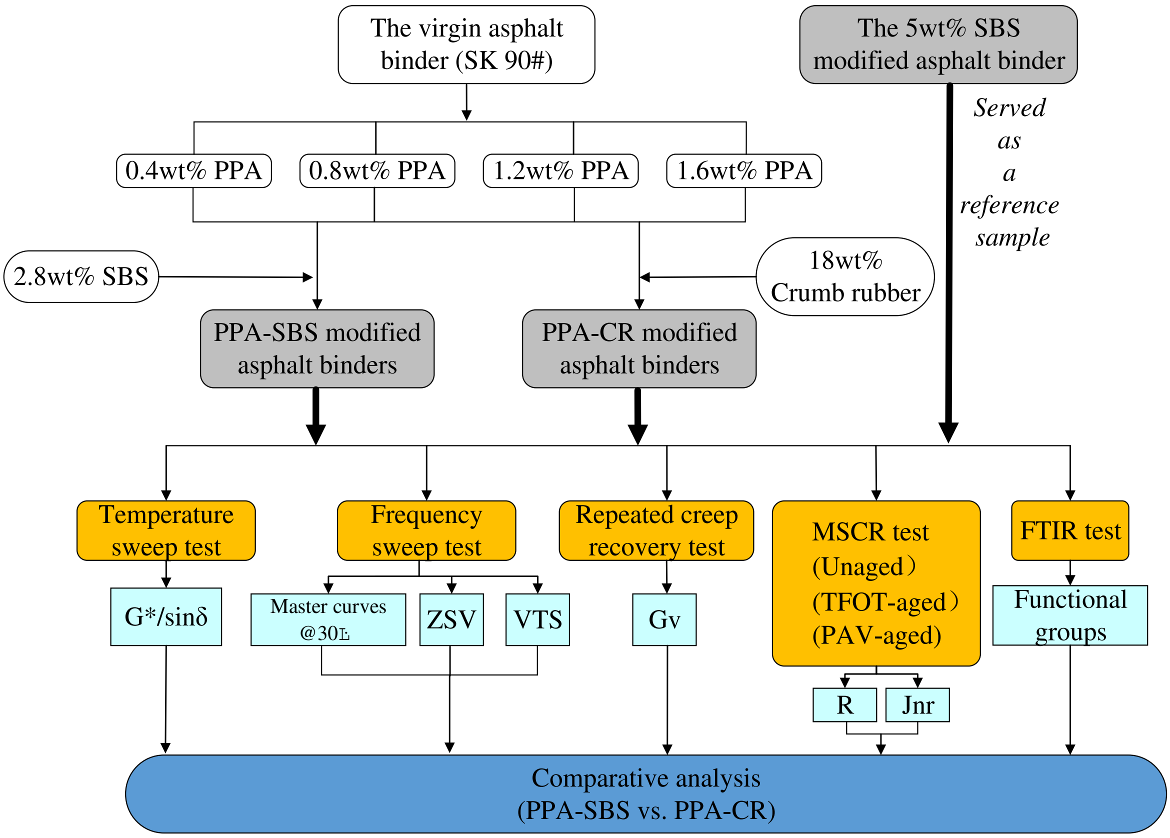


Fig.1. Flowchart of experiments in the study.

2.3 Test methods

2.3.1 Temperature sweep test

Temperature sweep tests were carried out using a dynamic shear rheometer (DSR) to characterize the viscoelastic behavior of asphalt binders. PG specifications for asphalt binders use a stiffness-based factor ($G^*/\sin\delta$) as the rutting factor at high temperatures. A stiffer binder provides more rutting resistance. This test was conducted on tablet specimens contained in a 25mm-diameter plate with a 1 mm gap at 10 rad/s shear rate, and the temperatures were maintained at 30°C, 40°C, 50°C, 60°C and 70°C. Then, the rutting factor ($G^*/\sin\delta$) was calculated in accordance with ASTM D7175.

2.3.2 Frequency sweep test

Frequency sweep test was conducted at loading frequencies from 0.01 to 100 rad/s and at temperatures of 30°C, 40°C, 50°C, 60°C and 70°C. The combination of temperatures and loading frequencies ensured sufficient representation of the material responses [38]. The William-Landel-Ferry (WLF) equation based on free volume theory was defined using substantial experimental data, which is shown in Eq.(1). The horizontal shift factors for all samples were calculated using the WLF functions and dynamic modulus master curves over a wide range of frequencies at a reference temperature of 30°C. In addition, the stress levels for frequency tests were chosen to be linear.

$$log\,\alpha_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \quad (1)$$

Where α_T = shift factor which ranges from 0.01 to 100 rad/s; T_1 = tested temperature; T_r = reference temperature (30°C); C_1, C_2 = constant which is obtained from the G* master curves, such that $C_1 \times C_2 \approx 900$.

Viscosity relates to the high-temperature fluidity and workability of asphalt [29]. After DSR frequency sweep test, results were analyzed to derive a correlation between the viscosity and frequency, a simplified Carreau model was used to describe the data [39]. The formula for the model is presented in Eq.(2), and the viscosity η_0 at low frequency was obtained, named the zero shear viscosity (ZSV) of asphalt binders.

$$\eta = \eta_{\infty} - \frac{\eta_0 - \eta_{\infty}}{[1+(\lambda D)^2]^{\frac{1-c}{2}}} \tag{2}$$

Where λ = characteristic time of material; c = material constant; D = shear rate; η = viscosity; η_{∞} = viscosity at infinite shear rate

Since the complex shear modulus G* was measured by a frequency sweep test, Eq.(3) showed the complex viscosity η' obtained by using the complex shear modulus G* and frequency ω. Specially, the index of VTS (viscosity-temperature susceptibility) was used to evaluate the sensitivity to temperature [40, 41], as shown in Eq.(4).

$$\eta' = \frac{(\sin\delta)^{-4.8628}\left|G^*\right|}{\omega} \tag{3}$$

$$VTS = \frac{\lg(\lg\eta_{T_2} - \lg\eta_{T_1})}{\lg T_2 - \lg T_1} \tag{4}$$

Where G* = complex shear modulus; η' = complex viscosity of asphalt binders; η_{T1}、η_{T2} = dynamic viscosity values at T_1 and T_2 temperature, respectively.

2.3.3 Multiple stress creep recovery (MSCR) test

The rutting susceptibility of asphalt binders refers to its creep behavior [42]. Since the high-temperature performance of modified asphalts can't be evaluated effectively by the rutting factor (G*/sinδ) [43, 44], multiple stress creep recovery (MSCR) test was adopted in NCHRP 9-10 (National Cooperative Highway Research Program). This test evaluates the resistance of asphalts to permanent deformation, by determining the elastic response of asphalt binder under shear creep and recovery at two stress levels (0.1 kPa and 3.2 kPa). During the test, the binder is subject to 10 cycles of creep stress (1s-duration per cycle) and recovery (9s-duration per cycle). Then, two parameters (recovery rate R and non-recoverable creep J_{nr}) will be characterized. ASTM D7405 describes the testing process and sample preparation, and the evaluation was carried out at temperatures of 56 °C, 64 °C and 72 °C.

2.3.4 Repeated creep recovery test

The repeated creep recovery (RCR) test was adopted in NCHRP 9-10, which introduced the viscous stiffness modulus G_V based on repeated creep test using creep stiffness as the index of high-temperature performance [45]. The cycle of loading for 1s and unloading for 9s was repeated 100 times, and the median (50^{th} and 51^{st}) results were taken [46]. The creep compliance Jv of the tested asphalt binder was calculated in accordance with Eq.(5).

$$J(t) = J_0 + J_1[1 - exp(-\frac{t}{\eta_1 J_1})] + J_v \tag{5}$$

Where Jv = Creep compliance of asphalt binder; J_0 = Transient or glassy shear compliance; J_1 = Delay compliance; η_1= Viscosity of Burgers model (Pa.s)

The G_V =1/ J_V was calculated to quantitatively assess the influence of PPA on composite modified binders for high-temperature performance. The test temperatures were 56°C, 64°C and 72°C, at the stresses were 30Pa, 100Pa and 300Pa.

2.3.5 Short- and long-term aging test

In order to shorten the time spent on getting the materials aged for testing, the simulation (accelerated) aging test was adopted. The asphalt binder was subject to “short-term” aging in a thin film oven test (TFOT), which was specified in ASTM D1754. The binders were exposed to airflow and maintained at 163°C for 5h.

Pressure aging vessel (PAV) test protocols were provided in ASTM D6521. The samples were placed in a heated and pressurized vessel, in which the air was maintained at 100°C and

2.1MPa for 20h to stimulate the state of aging in roads for 5 to 10 years. Therefore, PAV was called a “long-term” aging test. In this study, the TFOT and PAV conditioned samples were collected for multiple stress creep recovery (MSCR) test.

2.3.6 FTIR test

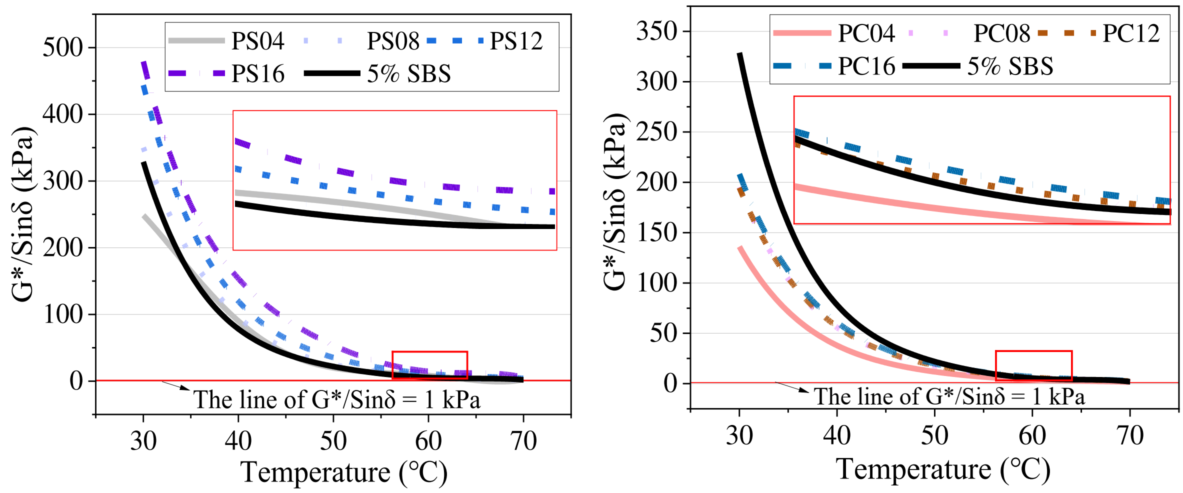
Fourier transform infrared spectroscopy (FTIR) test has been widely used to investigate the chemical composition of modified asphalt, as a simple analytical technique [42]. This study applied an FTIR spectrometer (Thermo Fisher Nicolet iS5) to observe the chemical composition of PPA-SBS and PPA-CR modified asphalt binders in the range of $4000cm^{-1}$-$400cm^{-1}$. Identification of functional groups is essential to find the difference between SBS- and CR-modified asphalt binders with added PPA modifier.

3. Results and discussion

3.1 Temperature sweep test results

Figs. 2 (a) and (b) show temperature sweep test results of rutting factor ($G^*/\sin\delta$, where G^* is the complex shear modulus). When the temperature increased, the rutting factor $G^*/\sin\delta$ continuously decreased for all asphalt binders. At the same PPA concentration, PPA-SBS had the highest $G^*/\sin\delta$ value, followed by 5% SBS, and PPA-CR binder had the lowest one. The reason could be that the plasticity of rubber increased after desulfurization, contributing to a decreased elastic recovery of the PPA-modified asphalt [47]. It was believed that PPA contributed to some sulfoxide groups, leading to more C=C stretches in the butadiene block. The PPA-SBS composite can, to some degree, promote the graft copolymerization reaction between SBS and asphalt binders. Fig.2 (b) indicated that the optimal content of PPA in CR asphalt binder was between 1.2% and 1.6%. At high temperatures (> 60℃), the $G^*/\sin\delta$ result between PPA-CR and 5% SBS was close, which indicated similar deformation resistance. As expected in Figs. 2 (a) and (b), after adding 1.2% PPA , both PPA-SBS and PPA-CR samples had enhanced anti-rutting performance, and the increase in $G^{*}/\sin\delta$ value of the former outpaced that of the later. This could be explained by that, a combined effect of the increased acid concentration and high CR content in the PPA-CR asphalt binder played a key role in modifying its rutting behavior. In other words, owing to depolymerization and devulcanization with added CRs, the transition from a sol to a gel structure was limited by the colloidal structure of PPA–CR-modified asphalt binder.

In comparison with PPA-CR asphalt at a same PPA concentration, PPA–SBS had better rutting resistance; thus verifying the desirable effect of PPA combined with SBS-modified asphalt. Herein, in terms of high-temperature performance, PPA had limited contribution to CR-modified asphalt binder.



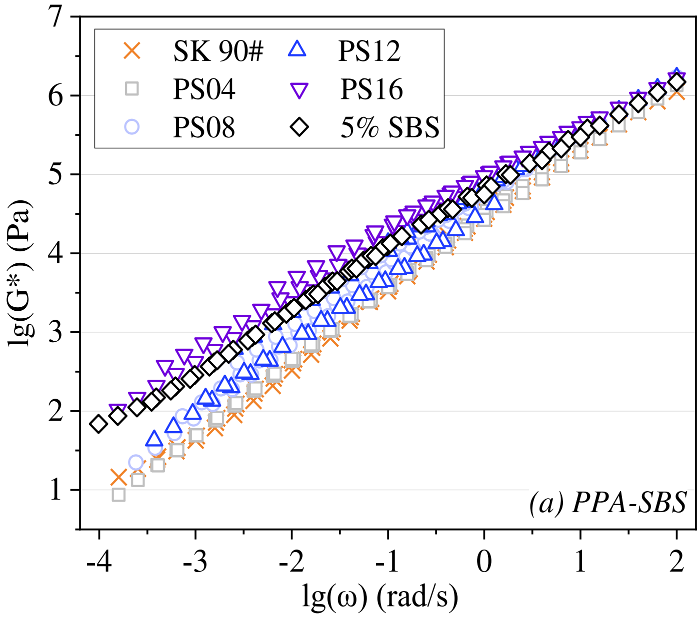
(a) **(b)**

Fig.2. Rutting factor $G^{*}/\sin\delta$ for binders at various temperatures: (a) PPA-SBS; (b) PPA-CR.

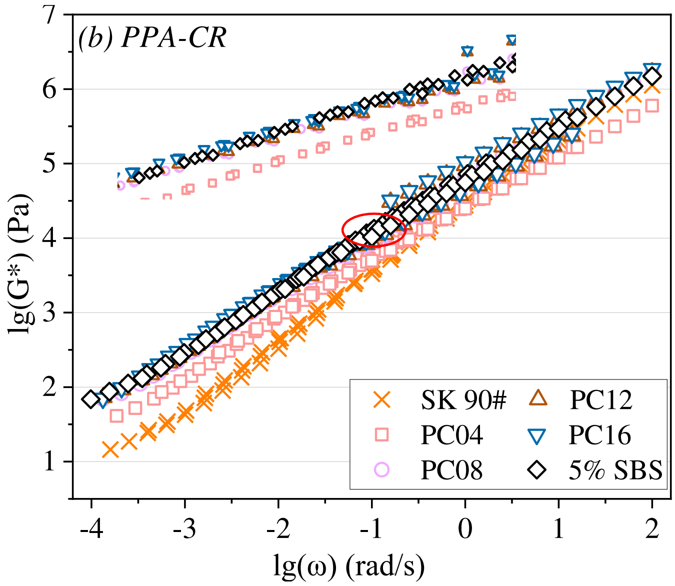
3.2 Frequency sweep test results

3.2.1 Master curves of complex modulus

Frequency sweep test was conducted at different frequencies to the bitumen samples. It can be seen from Fig. 3 that, with increased PPA, the improvement on G* of the two PPA-modified asphalts was clearly visible, proving that PPA made a major contribution to the growth of G*. Additionally, G* values of all binders increased across the frequency ranges, among which SK 90# had the greatest increase, verifying that PPA satisfactorily decreased the temperature susceptibility of modified binders. In Fig. 3(b), there was a distinct gap in performance in the low-frequency region between PC04 and the other PPA-CR asphalts. It showed that the stiffening effect of the PPA-CR asphalt containing 0.4% PPA was obviously lower in comparison with those containing 0.8%, 1.2% and 1.6% PPA. As depicted in Figs. 3 (a) and (b), by comparing the G* values of PPA-SBS and PPA-CR binders (in high-frequency region), the former exhibited a higher G* than the latter. That is, PPA–CR asphalt binders exhibited a weaker loading susceptibility. Herein, the high-frequency region corresponded to a shorter loading time where binders exhibited more elastic responses. With the above results, it was difficult to distinguish the difference in performance among PPA-SBS binders, while PPA-CR binders exhibited distinct rheological behavior. In this case, the later exhibited a superior viscoelastic response irrespective of the loading time.



(a)



(b)

Fig.3. G* master curves at 30°C for binders: (a) PPA-SBS; (b) PPA-CR.

3.2.2 Zero shear viscosity

The zero shear viscosity (ZSV) is defined as the maximum viscosity when the asphalt material is in the first Newtonian region, assuming the shear rate is at the minimum. The value of ZSV is highly correlated with the high-temperature performance of the asphalt [48]. Results of the frequency sweep test of PPA-SBS, PPA-CR, and 5% SBS modified asphalt binders are analyzed using the Carreau model (Eq.2), and shown in Table 6.

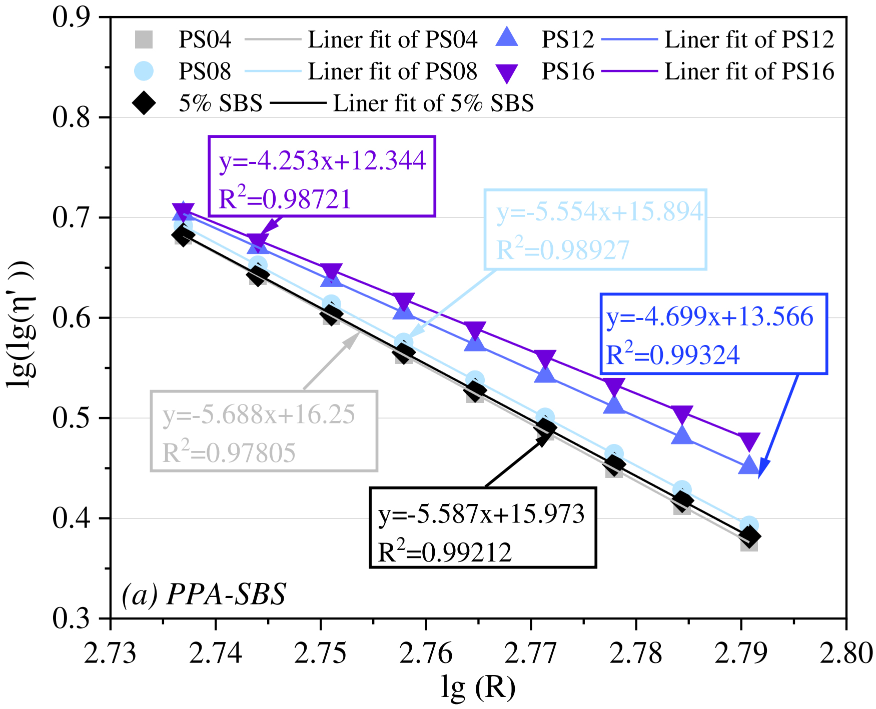
Table 6
ZSV parameters of PPA-SBS、PPA-CR and 5% SBS modified asphalt binders.

Binders	Temperature (°C)	η_0 (Pa·s)	λ	c	R^2
PS04	60	777.37	0.015	0.42	0.99933
PS08	60	1801.65	0.158	0.61	0.99904
PS12	60	4166.72	3.80	0.63	0.99987
PS16	60	6059.48	1.75	0.59	0.99997
PC04	60	2218.31	1.34	0.65	0.99184
PC08	60	2407.89	0.55	0.58	0.99521
PC12	60	2505.50	0.65	0.57	0.9978
PC16	60	2722.78	0.61	0.55	0.99981
5%SBS	60	4059.75	28.19	0.53	0.99176

A satisfactory correlation (R^2>0.99) can be found for all asphalt binders, indicating that the Carreau model fits well with the ZSV results of PPA-SBS, PPA-CR, and 5%SBS modified asphalts, which is similar with the findings by Abdullah [49]. Specially, the ZSV values of PPA-SBS at low PPA contents (i.e. 0.4% and 0.8%) were lower than those of PPA-CR asphalt. The ZSV values in both types of modified asphalts grow with an increase in PPA content, but the growth rate of ZSV in PPA-SBS was higher. This can be explained that, PPA alters the solvation of asphaltenes and increases the solid fraction in asphalt binder, strengthening the anti-flow ability of CR-modified asphalt. However, the viscous flow of PPA-CR was still remarkably higher than 5% SBS and PPA-SBS samples. It relates to the fact that degraded rubber particles undergo a devulcanization and depolymerization during the curing, retarding the formation of interlock structure within the CR-modified asphalt.

3.2.3 Viscosity-temperature susceptibility

To study the temperature sensitivity of asphalt, the VTS (viscosity-temperature susceptibility) was calculated using Eqs.(3) and (4). The relationship between lg(R) and lg(lg(η')) is presented in Figs.4 (a) and (b), in which the value of VTS was the gradient of the regression curve. The relationship between VTS and PPA content of modified asphalt binders is shown in Fig. 4(c), which indicates the changes in viscosity of modified asphalt in relation to the type and rate of modifier. As seen from Fig. 4(c), increasing PPA content led to a decrease of the VTS for both PPA-SBS and PPA-CR samples. The smaller the value of VTS, the less the viscosity changed with temperature [40, 50], which implied that the addition of PPA caused a decrease in temperature sensitivity of those two asphalts. When the content of PPA exceeded 0.8%, the VTS values were in the order of (at the same PPA concentration): 5% SBS > PPA-CR asphalt > PPA-SBS asphalt, showing that SBS asphalt modified with PPA was the least susceptible to temperature change. This can be attributed to the theory that CR particles, dispersed in the binder, tend to be oriented at elevated temperatures. Interestingly, both PPA-SBS and PPA-CR asphalt binders behaved better than 5% SBS regarding temperature sensitivity [28].



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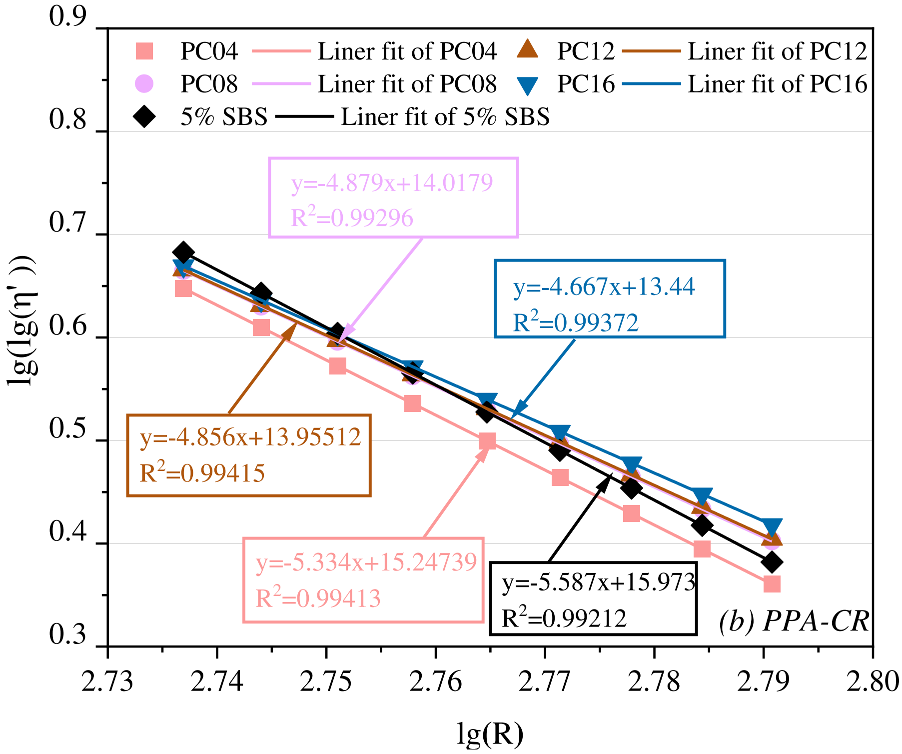

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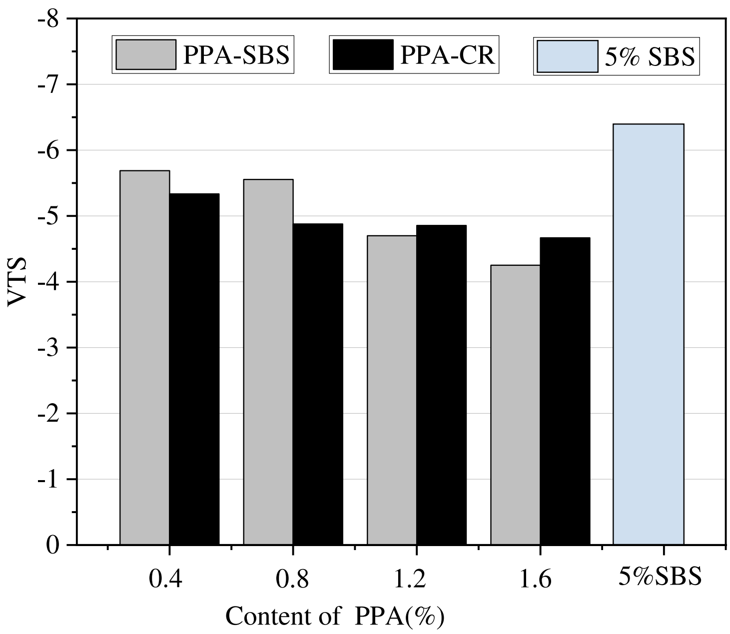


（c）

Fig.4. Viscosity-temperature susceptibility for binders:

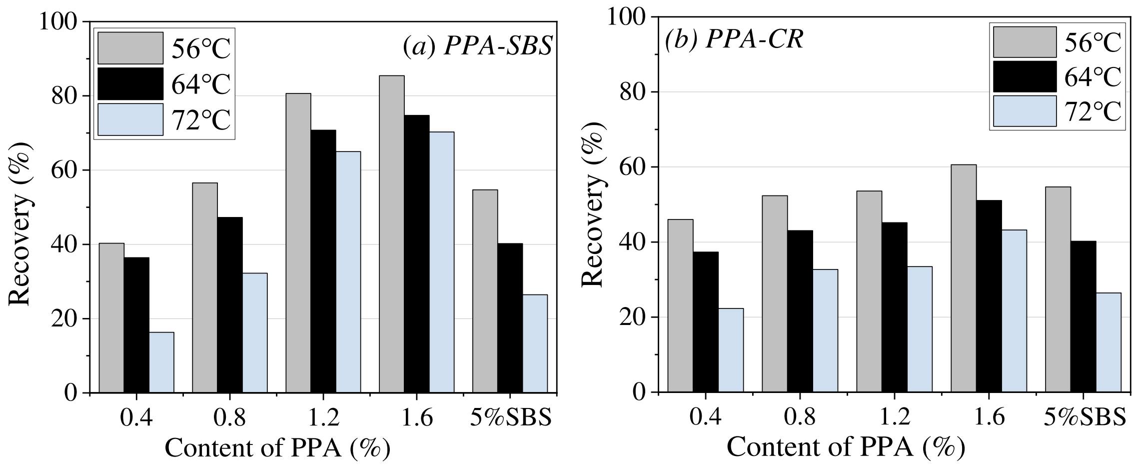
(a) Linear fitting results of PPA-SBS; (b) Linear fitting results of PPA-CR; (c) VTS

value for binders.

3.3 MSCR test results

3.3.1 Percent recovery

To evaluate the rheological behaviors of PPA-modified asphalts, two rheological parameters were selected, namely the percent recovery R and non-recoverable creep compliance Jnr. Binders with a higher value of R and a lower value of Jnr are expected to have better rutting resistance [51]. The percent recovery rates R of 5% SBS- and PPA-modified asphalt binders under 0.1 kPa and at various temperatures are illustrated in Figs. 5(a) and (b).



(a) **(b)**

Fig.5. Percent recovery: (a) PPA-SBS; (b) PPA-CR.

In Fig. 5(a), R value of PPA-SBS asphalt binder gradually increased with an increase in PPA content. Meanwhile, at all three temperatures, R value of 5% SBS was between PS04 and PS08. More importantly, when PPA content increased from 0.8% to 1.2%, the elevation of R value was the greatest. The improvement was about 14% (PS08 to PS12), three times more than the elevation from PS12 to PS16. To conclude, for sake of the percent recovery improvement on PPA-SBS, 1.2% PPA was the recommended choice.

PPA also enhanced the percent recovery of PPA-CR asphalt binder. It can be seen in Fig.5 (b) that the most dramatic improvement was about 7% (PC12 to PC16), six times that of change from 0.8% to 1.2% added PPA (PC08 to PC12). This meant that PC16 had greater elastic recovery compared to other PPA-CR binders. To sum up, the good elasticity of SBS and its bonding effect provided PPA-SBS modified asphalt with a better recovering ability, outperforming PPA-CR. Besides, the enhancement of recovering ability was subtle for PPA-CR samples with the addition of PPA. It could be deduced that, the improvement of recovery performance was mainly influenced by the increase in acid concentration, and a high content of rubber powder did not have a significant effect.

3.3.2 Non-recoverable creep compliance

Figs. 6 (a) and (b) illustrate the non-recoverable creep compliance Jnr values of 5% SBS and two types (PPA-SBS and PPA-CR) of modified asphalt binders with PPA contents of 0.4%, 0.8%, 1.2% and 1.6% under three temperatures and at a pressure of 0.1kPa.

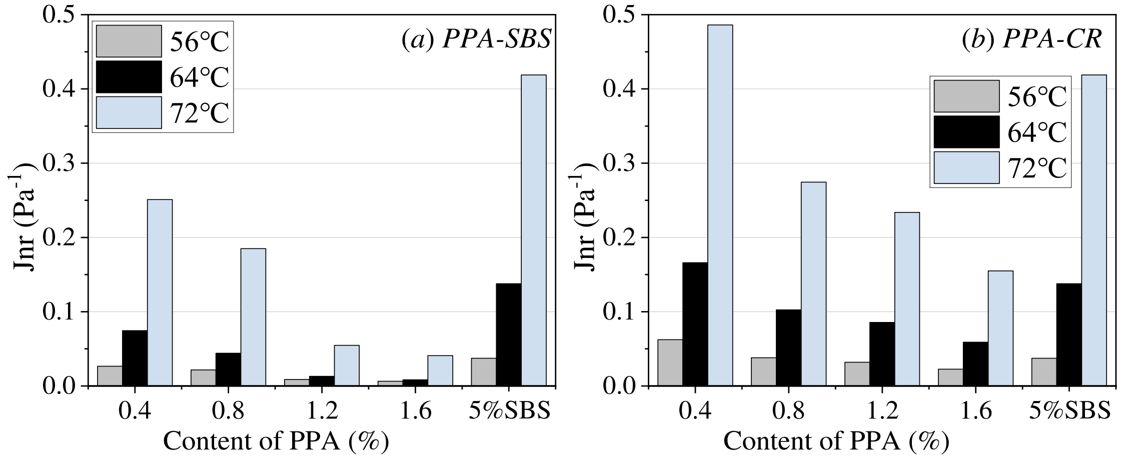


Fig.6. Non-recoverable creep compliance value: (a) PPA-SBS; (b) PPA-CR.

Binder's suitability was evaluated based on a Jnr value at 0.1kPa. According to Figs. 6 (a) and (b), with an increasing amount of PPA, non-recoverable compliance Jnr of PPA-SBS gradually decreased for all three temperatures, confirming the effect of PPA on improving binder's recovery from elastic deformation. The deformation resistance of PPA-SBS was enhanced most significantly when the content of PPA increased from 0.8% to 1.2%. Meanwhile, the sample was more sensitive to temperature in the range of 64°C to 72°C. In terms of PPA-CR modified asphalt, the Jnr value decreased rapidly at the whole temperature ranges. The deformation resistance of PPA–CR asphalt was the highest (relates to lowest Jnr) when the PPA content was 1.6% (PC16). In comparison, the Jnr value of 5% SBS–asphalt binder was between that of PC04 and PC08. In other words, PC08, PC12 and PC16 all had better deformation resistance compared to the 5% SBS modified asphalt.

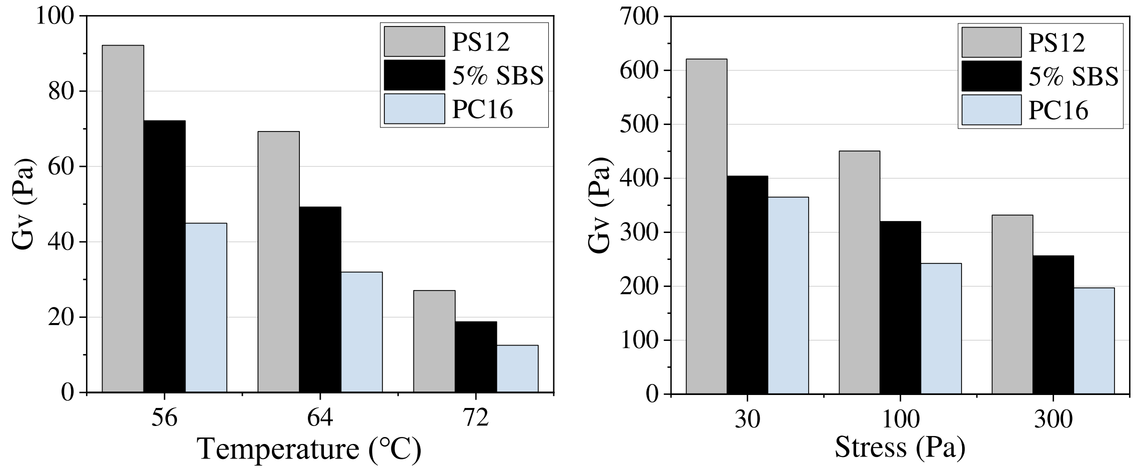
3.4 Repeated creep recovery (RCR) test results

According to the MSCR test, when the content of PPA stays at 1.2% and 1.6%, respectively, the increase in recovery of elastic deformation is the highest for PPA-SBS and PPA-CR modified asphalts. Based on the 50th and 51st percentile G_V creep stiffness obtained from repeated creep recovery tests (RCR) for PPA-SBS, PPA-CR and SBS modified asphalt, three samples were considered to have optimal blending and subsequently tested: PS12, PC16 and 5% SBS. Table 7 shows the G_V test results of these modified asphalts under three temperatures and at three stresses. Results are illustrated in Figs.7 (a) and (b).

Table 7
G_V test results of modified asphalts under optimal blending.

Stress	T	PS12			PC16			5%SBS		
(Pa)	(°C)	$G_V(50)$	$G_V(51)$	G_V	$G_V(50)$	$G_V(51)$	G_V	$G_V(50)$	$G_V(51)$	G_V
30	56	625.0	617.3	621.2	367.6	362.3	365.0	406.5	401.6	404.1
	64	452.5	448.4	450.5	243.9	241.0	242.5	321.5	318.5	320.0
	72	333.3	330.0	331.7	198.0	195.7	196.9	257.7	255.1	256.4
100	56	92.6	91.7	92.2	45.1	44.7	44.9	72.5	71.8	72.2
	64	69.4	69.2	69.3	32.0	31.9	32.0	49.3	49.2	49.3
	72	27.1	27.1	27.1	12.5	12.5	12.5	18.8	18.8	18.8

	56	28.3	28.2	28.2	12.7	12.5	12.6	24.4	24.2	24.3
300	64	19.1	19.1	19.1	8.2	8.2	8.2	14.7	14.7	14.7
	72	6.9	6.9	6.9	3.0	3.0	3.0	5.1	5.1	5.1



（a）　　　　　　　　（b）

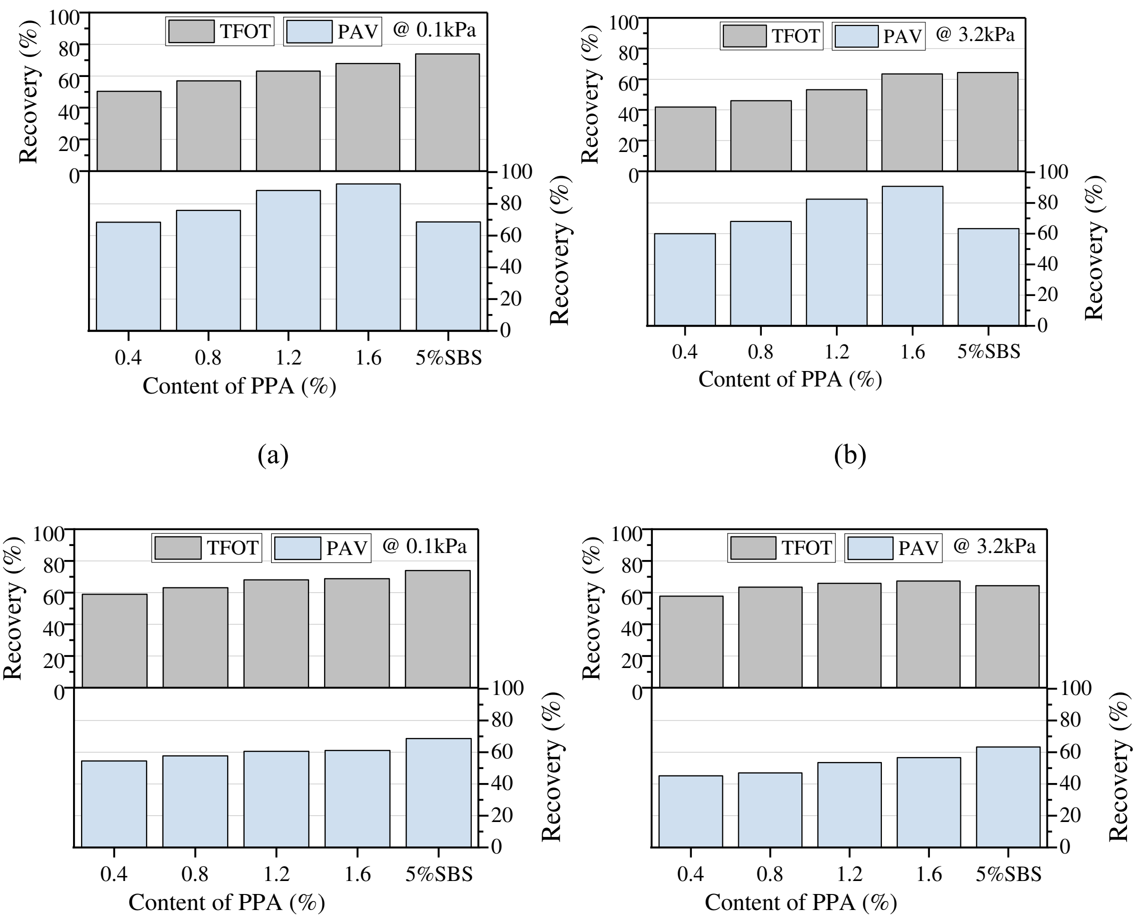
Fig. 7. G_V test results for binders under optimal blending: (a) G_V values at various temperatures (at 100Pa); (b) G_V values at various stresses (at 56°C).

Fig.7 (a) shows that with the increase of temperature, G_V of PS12, PC16 and 5% SBS modified asphalt all decreased significantly. This could be explained by the decreased creep properties of PPA-modified samples. At the same temperature, G_V values of samples were in the descending order of: PS12 > 5% SBS > PC16. For instance, at 56℃, PS12 had the largest G_V value, which was 1.3 times and 3.4 times that of 5% SBS and PC16, respectively. The temperature sensitivity of the three types of modified asphalt was similar.

Fig. 7 (b) illustrates the test results at a temperature of 56°C and varied loading stresses of 30 Pa、100 Pa, and 300 Pa. PS12 had the largest G_V value at all three loading stresses, while PC16 had the smallest one. When the stress increased from 30 Pa to 100 Pa and 300 Pa, the G_V value of PS12 decreased by 27% and 46%, the G_V of PC16 decreased by 33% and 46%, the G_V of 5% SBS decreased by 18% and 36%, concluding that the sensitivity of 5% SBS modified asphalt to stress was lower than the other two.

3.5 Aging behavior

Comparative analysis of aging behavior between PPA-SBS and PPA-CR asphalt was conducted via MSCR test. At 0.1kPa and 3.2kPa loading stress, the percent recovery R for the asphalts was compared using the TFOT-aged and PAV-aged samples, which is shown in Fig. 8.



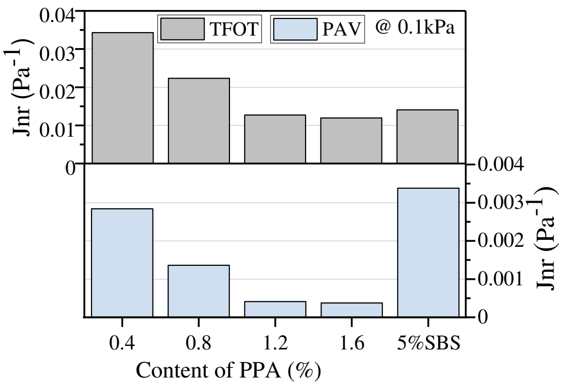
(a) (b)

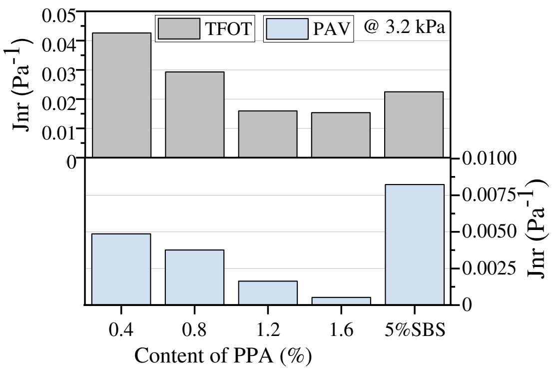
(c) (d)

Fig.8. Percent recovery after aging: (a) PPA-SBS at 0.1kPa; (b) PPA-SBS at 3.2kPa; (c) PPA-CR at 0.1kPa; (d) PPA-CR at 3.2kPa.

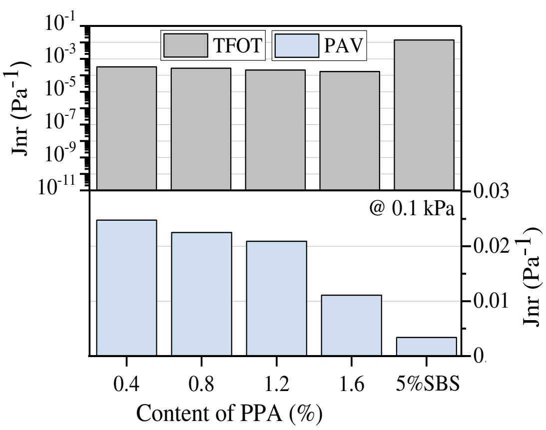
It can be seen from Figs.8 (a) and (b) that the recovery for PPA-SBS showed an upward trend with an increasing PPA content, indicating that the proportion of recoverable deformation increased. For example, at a low stress level (0.1kPa), R-value of PPA-SBS in PAV-aged samples increased, compared with TFOT-aged samples, by approximately 18.1%, 18.8%, 25.4%

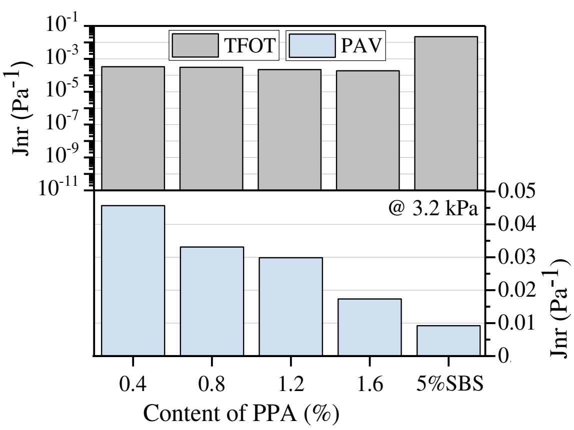
and 24.8%, respectively, for PPA contents of 0.4%, 0.8%, 1.2% and 1.6%. Conversely, a declined recovery was found for PAV-aged PPA-CR specimens, shown in Fig.8 (c) and (d). As for 5% SBS, the high-temperature creep properties of the samples were also weakened after PAV aging at both stress levels, being opposite to the trend of PPA-SBS but superior to the PPA-CR. For example, for PC04, PC08, PC12, PC16 and 5% SBS modified asphalt, the decline of percent recovery in PAV-aged samples was 4.5%, 5.4%, 2.5%, 7.7% and 5.2%, compared to TFOT-aged samples. The main reason is that as the temperature increases, wax in the CR-based asphalt transforms into a fluid state, which compensates for the reduced light components of PPA-CR modified asphalt obtained from the aging process, thereby alleviating the aging impact. Conversely, the damaged interlocking structure of SBS modifier exacerbates the negative impact of aging on PPA-SBS samples at high temperatures. Hence, PPA-SBS was more susceptible to long-term aging than PPA-CR.





(a) (b)





(c) (d)

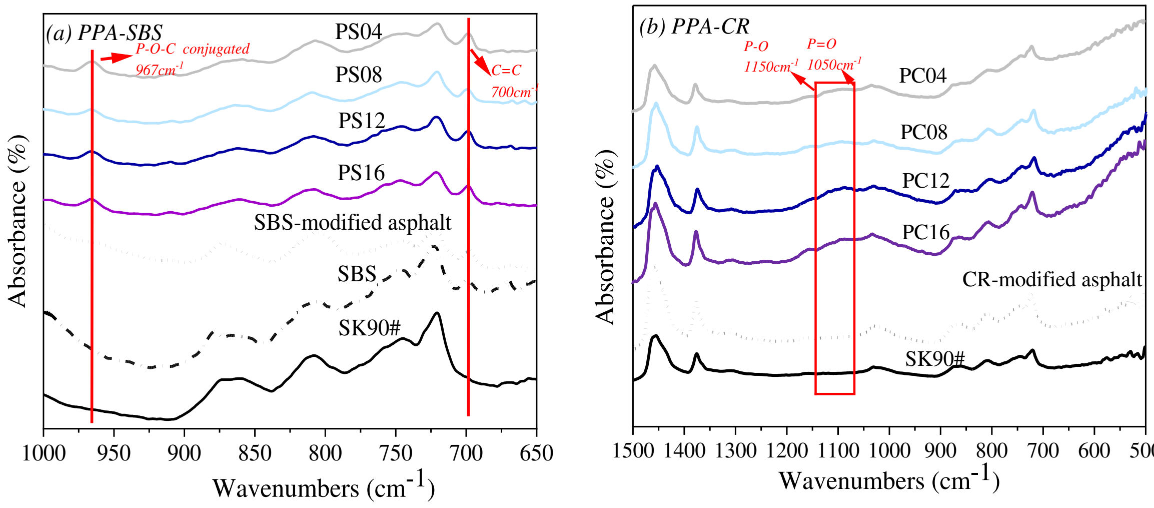
Fig.9. Non-recoverable creep compliance after aging: (a) PPA-SBS at 0.1kPa; (b) PPA-SBS at 3.2kPa; (c) PPA-CR at 0.1kPa; (d) PPA-CR at 3.2kPa.

As in shown in Figs. 9 (a) and (b), the Jnr value of PAV-aged PPA–SBS asphalt gradually decreased, where a higher PPA content is associated with higher deformation resistance. The Jnr value of 5% SBS modified asphalt was between PS08 and PS12, and after PAV aging, it was the highest. For PPA-SBS, chemical reactions occurred inside the composites after adding PPA, which reduced the condensation and degradation of SBS modifier thus increasing the aging resistance at high-temperatures, the same was found by Alam [21]. With regard to PPA-CR, Figs. 9 (c) and (d) showed the enhanced resistance to permanent deformation of PPA-CR compared with 5% SBS after TFOT aging, however it was reversed after PAV aging. That is, the introduction of PPA to CR-modified asphalt reduced the hardening effect from thermal oxygen aging. This is because PPA is not a polymer; and therefore, the stiffening effect of PPA–CR does not affect substantially elastic responses at high temperatures, whereas PPA–SBS samples maintain a steady recoverable property. Thus, we deduce that the aged-rubber modifier acts as a dominant factor in the PAV-aging process.

Overall, in view of the R and Jnr values, it can be concluded that the creep recovery performance of PPA-CR samples was weaker than PPA-SBS. The performance of 5% SBS is between these two composite modified binders. However, in terms of resistance to long-term aging (PAV), PPA-CR composite modified asphalt was superior to PPA-SBS. This provides interesting further work for researchers—more experimental work should be conducted to investigate the aging-resistance of PPA-CR modified asphalts produced with various types and contents of rubbers, in order to find the optimal design for PPA-CR composite modification.

3.6 FTIR test results

Figs. 10 (a) and (b) show the results of FTIR test on the PPA-SBS and PPA-CR modified asphalt binder.



(a) **(b)**

Fig.10. Infrared spectrum of PPA composite modified asphalt: (a) PPA-SBS binders at various PPA contents; (b) PPA-CR binders at various PPA contents.

Compared with virgin asphalt, the infrared spectrum of PPA-SBS composite modified asphalt had two distinct absorption peaks, which were located at 700 cm^{-1} (corresponding to the styrene block of SBS) and 967 cm^{-1}. In Fig. 10 (a), the peak at 967 cm^{-1} corresponded to the P-O-C symmetric stretching, generated by phosphorylation of functional groups in the SBS-modified asphalt with the added PPA [32]. The long-chain molecules in PPA-SBS modified asphalts were produced from the reaction between PPA and the -OH groups. These findings confirmed that chemical reaction occurred in the PPA modification process.

Fig. 10 (b) showed that only marginal differences were found between SK90# and CR-modified asphalt, confirming only physical interactions with the added CR particles. This result agreed well with a previous study [52]. It can be seen from Fig. 10 (b) that compared with CR-modified asphalt, the infrared spectrum of PPA-CR composite modified asphalt had a new absorption peak formed at 1050 cm^{-1} to 1150 cm^{-1}. It was mainly due to the vibration of P-O and P=O [53], and intensity of the peak was low due to the low PPA content. Intensities of those new peaks were enhanced with an increase in PPA, which agreed with the findings by Qian et al. [52] that PPA could chemically modify the virgin asphalt. However, there was no additional peak observed in the infrared spectra of PPA-CR modified asphalt binder, reinforcing the theory that there is only physical interaction between CR and PPA during blending.

Due to the complexity of chemical structure, in-depth investigation of the modification mechanism of PPA-SBS and PPA-CR composite modified asphalt is worth future research, in order to understand the material behavior and find the optimal modifier content.

4. Conclusions and Recommendations

This study evaluated the effects of PPA (polyphosphoric acid) on high-temperature performance, temperature susceptibility, and anti-aging performance of two modified asphalt, namely SBS- (styrene butadiene styrene) and CR- (crumb rubber) modified asphalt binders. It focused on the effect of PPA-CR composite modified asphalt at a high CR content, which is not found in literature. The main findings and conclusions are presented below.

(1) The addition of PPA enhanced the asphalt's resistance to temperature susceptibility. What's more, PPA played a significant role in improving asphalt performance at high temperatures. It indicated that the substitution of SBS polymers with PPA could enhance the

binder's resistance to permanent deformation and temperature sensitivity, with a PPA content between 0.4% and 1.6%. The effect on temperature sensitivity was more significant to PPA-SBS than to PPA-CR. However, in terms of aging resistance, PPA-CR composite modified asphalt was superior to PPA-SBS. The FTIR (Fourier Transform Infrared Spectroscopy) test helped to reveal the physical/chemical interactions that occurred during the production of PPA-SBS and PPA-CR.

(2) The PPA-CR asphalt binder had a superior viscoelastic response than PPA-SBS and 5% SBS modified asphalt binder. Also, the increased G*, failure temperature and R, and the decreased VTS and Jnr all indicated that a substitution of 5% SBS with 1.6% PPA-SBS was feasible. Moreover, PPA-CR modified asphalt with a high CR content has desirable rheology in its resistance to long-term aging.

(3) Due to the degradation of SBS polymer in the aging process, the PPA-SBS composite modified asphalt performed better after aging when the dosage of PPA increased, leading to the question of what is the optimal PPA content in real life considering both the cost and performance. After evaluating comprehensively the high-temperature performance, thermal-sensitivity and elastic recovery, the optimal content of PPA in PPA-SBS composite modified asphalt was considered between 0.8% and 1.2%, while in PPA-CR composite modified asphalt, the optimal PPA content was considered between 1.2% and 1.6%.

This study compared the PPA-SBS and PPA-CR modified asphalt under the same temperature and aging conditions. A quantitative chemical analysis of functional components of the modifiers is recommended, to explain the modification mechanism. Moreover, experiment on other binder properties such as low temperature performance, and cost-benefit analysis ideally using a lifecycle approach, will help to find the optimal PPA content for practical use.

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