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# Laboratory Evaluation of the Effects of Long-Term Aging on High-Content Polymer-Modified Asphalt Binder

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Haopeng Wang<sup>5</sup>; and Chuanqi Yan<sup>6</sup>

**Abstract:** One of the most widely used polymer-based modifiers in asphalt binders is styrene–butadiene–styrene (SBS), which results in binders of increased modulus, strength, toughness, and resistance to permanent deformation. These properties are further improved with the increase of SBS polymer content in asphalt binders, producing binders such as high-content polymer-modified asphalt (HCPMA). Although the HCPMA binders commonly are used in porous asphalt pavements, limited research has been conducted on their aging performance. This paper used gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, and the dynamic shear rheometer (DSR) to explore the evolution of chemical and rheological properties of aging HCPMA binders. The study found that the aging of HCPMA is a combination of oxidation of the base asphalt binder and degradation of the SBS polymer, leading to modulus increase and phase angle decrease. The degradation of SBS happened mostly at the beginning and slowed after pressure-aging vessel (PAV) conditioning for 20 h, which resulted in the lowest rutting resistance of HCPMA binders. When SBS content was higher than 7.5%, more than half the SBS polymer remained after 80 h of PAV conditioning. Although the molecular weight of SBS decreased from 230,000 to 70,000 due to degradation, its modification effect was still significant. Moreover, high modification of SBS can retard the oxidation and hardening of base asphalt binder, especially after PAV conditioning for 20 h. Principal component analysis showed that 10 parameters used in this study could be explained by SBS content and asphalt binder aging extent. Based on PCA results, the complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) of HCPMA binders can be well fitted by the exponential function of SBS content and aging index. DOI: [10.1061/\(ASCE\)MT.1943-5533.0003208](https://doi.org/10.1061/(ASCE)MT.1943-5533.0003208). © 2020 American Society of Civil Engineers.

**Author keywords:** High-content polymer-modified asphalt; Asphalt binder; Long-term aging; Rheology; Chemistry.

## Introduction

Oxidative aging of asphalt binders is one of the main defects that cause embrittlement of asphalt and subsequently contribute to the total in-service deterioration of asphalt pavements (Apostolidis et al. 2017). From the chemical point of view, through the aging process of asphalt binders, oxygen reacts with certain molecules leading to the formation of polar functional groups called carbonyl and sulfoxide compounds (Petersen 2009). From the mechanistic point of view, this chemical process influences the flexibility and

the stiffness of materials (i.e., a decrease of phase angle and increase of complex modulus), and has a negative effect on the adhesion characteristics of asphalt binders.

Due to the acceleration of the total deterioration of asphalt pavement structures by continuously increasing traffic loading and volume, the incorporation of polymer modifiers in asphalt binders is becoming very critical. Additionally, because the infrastructure of road networks in developed countries such as the Netherlands and China demands long-lasting pavements with high permeability, skid resistance, and sound absorption, open-graded (porous) asphalt pavements have attracted increasing attention (Jia et al. 2017; Van Rooijen et al. 2005). The internal structure of open-graded pavements has high air-void content, and for this reason they are more vulnerable to environmental effects, making the option of polymer modifiers of high importance. Polymers such as styrene–butadiene–styrene block copolymers (SBS) are widely used as modifiers, producing ordinary SBS-modified asphalt binder (<5%) (SBSMA) which is able to improve the ultimate performance of asphalt pavements (Polacco et al. 2015; Zhu et al. 2014).

In addition to SBSMA, high-content polymer-modified asphalts (HCPMA) are prepared by the addition of high SBS content (>6%), and have improved toughness and thus increased resistance against raveling in porous asphalt pavements (i.e., loss of aggregates from the surface of pavements) (Alvarez et al. 2011; Geng et al. 2016; Griebel et al. 2016; Habbouche et al. 2018; Liang et al. 2017; Xu et al. 2016; Zhang and Hu 2017). Nevertheless, the primary challenge faced by many researchers in applying HCPMA in porous asphalt pavements is aging. Because of the open gradation of porous pavement, plenty of oxygen is introduced, which results in severe aging. Due to the high viscosities of HCPMA, they usually have higher mixing (180°C–190°C) and paving (170°C–180°C)

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temperatures. Furthermore, due to the unsaturated double carbon bond (C=C) of SBS, this polymer is sensitive to oxygen and thus to oxidative aging damage (Lee et al. 2011; Wang et al. 2015; Zhang et al. 2017). Although the aging mechanism of SBS modified bitumen is quite complex, including the oxidation of base asphalt binder, chain scission of polybutadiene segments in SBS polymer, crosslinking or branching reactions between polymers, and grafting reactions between SBS polymer and asphalt binder components, the chain scission reaction at polybutadiene segments plays a primary role, which leads to a significant decrease of molecular weight of the SBS polymer and a dramatic decrease of the modification effect (Cortizo et al. 2004; Ouyang et al. 2006; Pospíšil et al. 1999; Wang et al. 2015). Because of the high content of SBS used in HCPMA, the degradation of SBS polymer will cause severe performance deterioration in asphalt pavements.

Based on the current literature, most research has focused on the impact of the aging of ordinary SBS-modified asphalts on their chemistry, physical, and rheological properties, using gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, and dynamic shear rheology testing methods (Tang et al. 2016; Wang et al. 2014; Yu et al. 2018). Atomic force microscopy (AFM), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) also are powerful test methods for aging investigation (Mikhailenko and Baaj 2019; Soenen et al. 2014; Yu et al. 2018). However, there is a significant difference between HCPMA and ordinary SBSMA binders, and there is limited available data about the properties of HCPMAs. Therefore, this paper explored the chemical and rheological changes of HCPMA during the aging process. Two types of base asphalt (i.e., Esso, Irving, Texas and SK asphalt binders, Gangnam-gu, Korea) and various SBS dosages from 4.5% to 15% were used. Rolling thin-film oven (RTFOT) and pressure-aging vessel (PAV) aging for different periods were applied to simulate different aging levels in the laboratory. Long-term aging was simulated with 20 h of PAV aging. However, the aging extent of HCPMA used in porous asphalt pavements is much more severe. The relationship between the rheological and chemical changes during aging were tracked with GPC, FTIR spectroscopy, and dynamic shear rheology. To further determine the relationship between performance- and component-related parameters, principal component analysis (PCA) and regression analysis were employed.

## Materials and Methods

### Materials

As mentioned previously, two types of base asphalt were used to prepare the HCPMA. These two type of base asphalt are characterized according to ASTM specifications [ASTM D36 (ASTM 2006), ASTM D113 (ASTM 2017), ASTM D5 (ASTM 2019), and ASTM D4124 (ASTM 2018)] and the results are illustrated in Table 1. The literature indicates that the constitution of the base asphalt binder has a significant influence on polymer–asphalt miscibility (Zhu et al. 2014; Habbouche et al. 2018). Esso asphalt binder had a relatively higher content of aromatic and asphaltene fractions compared with SK binder (Table 1). However, the saturate and resin fractions of Esso asphalt binder were relatively less.

Radial SBS with 230,000 g/mol average molecular weight (Mw) was chosen as the modifier (30% by weight of styrene). For the preparation of HCPMA, the added content of SBS modifier was from 4.5% to 15% by weight of base asphalt binder. In China, 4.5% and 7.5% by weight SBS are typical dosages for dense and porous asphalt pavements, respectively. Table 2 describes the samples. To

**Table 1.** Chemical composition and physical properties of base asphalt binders

Parameter	Esso asphalt	SK asphalt	Test specification
Saturates (%)	7.8	13.2	—
Aromatic (%)	54.6	45.7	—
Resin (%)	18.5	24.6	—
Asphaltene (%)	19.1	16.5	—
Softening (°C)	50.9	46.6	ASTM D36
Penetration (25°C 0.1 mm)	64	71	ASTM D113
Viscosity(135°C, Pa · s)	0.428	0.472	ASTM D5
Ductility(15°C, 0.1 cm)	>150	>150	ASTM D4124

**Table 2.** Description of studied asphalt binders

Asphalt category	Base asphalt	Radial SBS (%)	Resin (%)	Sulfur (%)	PG grade
E70	Esso 70	0	2	0.15	64-22
SK70	SK 70	0	2	0.15	64-22
E4.5S	Esso 70	4.5	2	0.15	76-28
E6S	Esso 70	6	2	0.15	76-28
E7S	Esso 70	7	2	0.15	76-28
E8S	Esso 70	8	2	0.15	76-28
E9S	Esso 70	9	2	0.15	82-28
E11S	Esso 70	11	2	0.15	82-28
E15S	Esso 70	15	2	0.15	88-28
S7S	SK 70	7	2	0.15	76-28
S9S	SK 70	9	2	0.15	82-28
S11S	SK 70	11	2	0.15	82-28

enhance the miscibility of asphalt and SBS polymer, a particular type of resin and 0.15% by weight sulfur as an agent to form crosslinks between polymers were added, which enhanced the storage stability to the HCPMA. All samples passed the segregation test [ASTM D5976 (ASTM 2000)] to ensure the uniformity of studied binders.

To simulate the short- and long-term aging, all HCPMA samples were aged in a RTFOT at 163°C [AASHTO T240 (AASHTO 2013)] and in a PAV at 100°C [AASHTO R28 (AASHTO 2012b)], respectively. PAV aging of different durations (20, 40, and 80 h, denoted 1-PAV, 2-PAV and 4-PAV, respectively) was conducted after RTFOT aging to evaluate the chemomechanical changes of HCPMA.

## Experimental Methods

### Dynamic Shear Rheometer

**Frequency Sweep Test.** The dynamic oscillatory test was performed on a TA AR1500ex (TA Instruments, New Castle, Delaware) dynamic shear rheometer (DSR) to obtain the complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) of HCPMA binders. Because the high-temperature performance grade (PG) of HCPMA is from 82°C to 88°C, the dynamic oscillatory test was employed at 82°C. The test was conducted at 10 rad/s using a 25-mm plate with a 1-mm gap [AASHTO T315 (AASHTO 2012a)]. Two replicates were performed for each sample, and the average values were recorded.

**Multiple Stress Creep and Recovery Test.** The multiple stress creep recovery MSCR test is used to evaluate the viscoelastic properties of polymer-modified asphalt (PMA) binders (D'Angelo 2009; D'Angelo and Dongré 2009; Huang and Tang 2015). In this paper, the MSCR test was performed in the DSR to obtain nonrecoverable creep compliance ( $J_{nr}$ ) and percentage recovery ( $R$ ) at 0.1 and 3.2 kPa [AASHTO T350 (AASHTO 2014)]. Two replicates were performed for each asphalt sample, and the average values were recorded.

## Fourier Transform Infrared Spectroscopy

The infrared spectra values were collected using a Bruker (Billerica, Massachusetts) TENSOR FT-IR spectrometer equipped with a reflection diamond attenuated total reflectance (ATR) accessory. To quantify the oxidation-related change in IR absorption, band areas rather than peak absorbance values were used, and the functional groups of interest were identified. Three replicates of each sample were conducted, and their average values were recorded. The  $AR_{\bar{\nu}}$  values were normalized to the total sum of all band areas ( $\sum AR_{\bar{\nu}}$ ), and the indexes calculated as follows:

$$\text{Carbonyl index: } I_{CO} = AR_{1700} / \sum AR_{\bar{\nu}} \quad (1)$$

$$\text{Sulfoxide index: } I_{SO} = AR_{1030} / \sum AR_{\bar{\nu}} \quad (2)$$

$$\text{Polymer damage index: } I_{B/S} = AR_{965} / AR_{699} \quad (3)$$

where

$$\begin{aligned} \sum AR_{\bar{\nu}} = & AR_{1700} + AR_{1600} + AR_{1460} + AR_{1310} + AR_{1030} \\ & + AR_{965} + AR_{864} + AR_{814} + AR_{743} + AR_{725} + AR_{700} \end{aligned} \quad (4)$$

Carbonyl and sulfoxide compounds are the most commonly used indicators to measure the oxidation extent of asphalt binders, and the absorbance values of polybutadiene and polystyrene generally are considered to reflect the degradation of mechanical properties of the polymers. Therefore, in this study, the carbonyl index ( $I_{CO}$ ) and sulfoxide index ( $I_{SO}$ ) were employed to evaluate the oxidation extent of base asphalt binder and a polymer damage index ( $I_{B/S}$ ) was used to determine the degradation of SBS polymer. SBS consists of polybutadiene (PB) and polystyrene (PS), in which the PS segment possesses a corresponding peak at  $699 \text{ cm}^{-1}$  and the PB segment possesses a peak at  $965 \text{ cm}^{-1}$  (Lamontagne et al. 2001; Lin et al. 2017, 2018; Yut and Zofka 2011). Because the unsaturated C=C bond of the PB segment is an easy target for oxygen, it can be aged and subsequently degraded. PS is relatively stable, and exhibited a much smaller change after aging. Thus, the newly proposed  $I_{B/S}$  was employed to evaluate the damage level of SBS in PMA, which is not influenced by the SBS concentration and the scanning depth (Yan et al. 2017, 2018).

## Gel Permeation Chromatography

In this study, a GPC device was used to characterize the molecular weight distribution of HCPMA binders for different aging periods after PAV conditioning. Before the GPC tests, a 20-mg modified asphalt binder sample was dissolved with tetrahydrofuran (THF) in a 10 mL volumetric flask for 24 h. The solution was filtered through a  $0.45\text{-}\mu\text{m}$  PTFE filter and collected in a 0.5-mL centrifugal tube for the GPC test. A Waters (Milford, Massachusetts) 1515 high-pressure liquid chromatography (HPLC) pump and Waters 2414 refractive index (RI) detector were used to conduct the GPC tests. The calibration curve was built with Shodex (Showa Denko America, New York) polystyrene standards to convert the retention time to molecular weight. Two replicates were performed for each sample, and their average values were recorded.

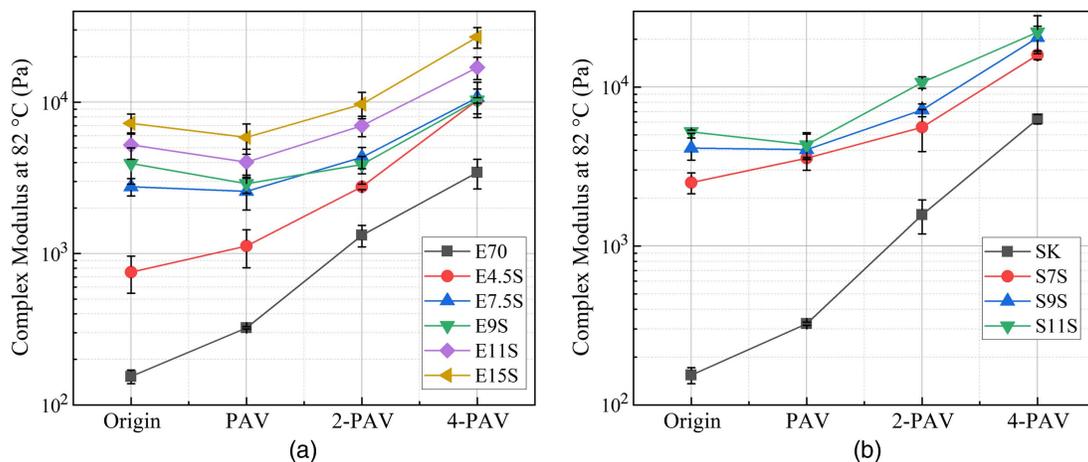
## Result and Discussion

### Rheological Characteristics

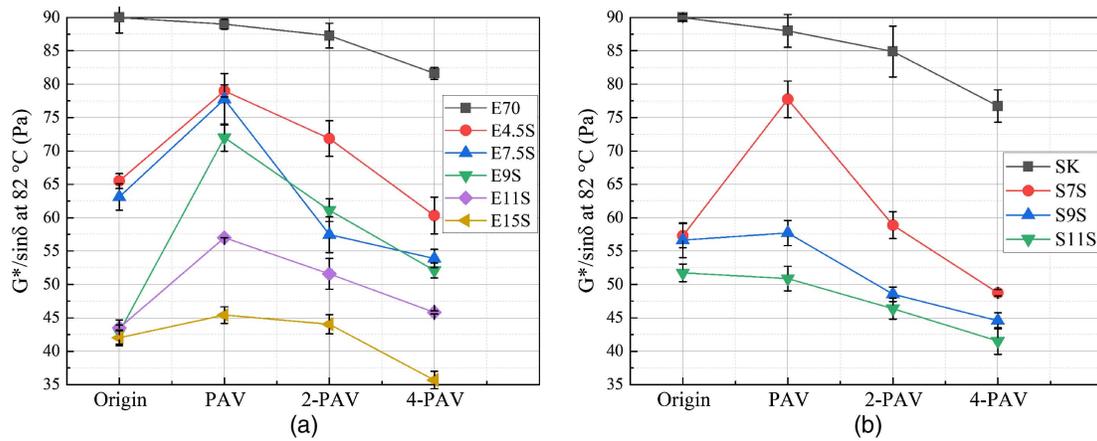
#### Complex Modulus

The high-temperature PG of the HCPMA ranged from  $76^\circ\text{C}$  to  $88^\circ\text{C}$  (Table 2);  $82^\circ\text{C}$  was chosen as the test temperature for the DSR test to fully distinguish the high-temperature properties of HCPMA. The evolution of the modulus of the base asphalt (Esso and SK) increased significantly during aging (Fig. 1). For E4.5S, the modulus increased, although the rate of increase was lower than that of Esso asphalt. When the SBS dosage reached 15%, the modulus decreased after PAV aging, due to the fact that the aging of HCPMA consisted of two parts. On the one hand, the oxidation of the base asphalt led to an increase of modulus. On the other hand, the severe degradation of SBS polymer had a softening effect on HCPMA, which caused modulus decrease. When SBS dosage was less than 7.5%, the aging of base asphalt played the dominant role and the modulus increased, whereas when the SBS dosage was more than 7.5%, the degradation of SBS played a more significant role, which led to a modulus decrease before 20 h of PAV aging. From this perspective, the increase of SBS content not only had a modification effect but also retarded the oxidation of the base bitumen, especially when the SBS content was more than 7.5%.

As aging proceeded, the modulus of the HCPMA samples increased from 1-PAV to 4-PAV. This indicates that the degradation rate of SBS polymer slowed through this process. For the HCPMA based on SK asphalt, the modulus evolution was similar to that of



**Fig. 1.** Complex modulus of HCPMA at different PAV aging periods: (a) HCPMA based on Esso asphalt; and (b) HCPMA based on SK asphalt.



**Fig. 2.** Phase angle of HCPMA at different PAV aging periods: (a) HCPMA based on Esso asphalt; and (b) HCPMA based on SK asphalt.

HCPMA based on Esso asphalt, and rendering base asphalt binder had little influence on modulus.

### Phase Angle

The phase angle of Esso asphalt binder decreased about  $10^\circ$  after RTFOT and 4-PAV conditioning [Fig. 2(a)]. For SK asphalt [Fig. 2(b)], the phase angle decreased about  $14^\circ$  after aging. The oxidation of the base asphalt binder during aging can result in a decrease of the phase angle.

For HCPMA, with the increase of SBS dosage, the phase angle in the original state decreased significantly from  $90^\circ$  to about  $42^\circ$  (E15S). The reason the phase angle decreased was that the addition of SBS polymer modifier enhanced the elasticity of HCPMA binders. The phase angle of HCPMA first increased and reached the peak at 1-PAV aging state, and then decreased significantly from 1-PAV to 4-PAV conditioning. This suggests that the SBS polymer degraded severely during the RTFOT and 1-PAV conditioning, and the polymer degradation reduced the effect of the modification. After 1-PAV, the asphalt oxidation played the primary role, which led to a decrease of the phase angle. However, when SBS dosage was more than 11%, the polymer network remained and had a considerable modification effect. Thus, the phase angle of HCPMA binder with 11% or 15% SBS content barely increased from the original state to 1-PAV.

### Rutting Factor

The evolution of rutting factor of HCPMA was very similar to that of modulus (Fig. 3). This was because the modulus changed more significantly than phase angle, and thus the rutting factor was

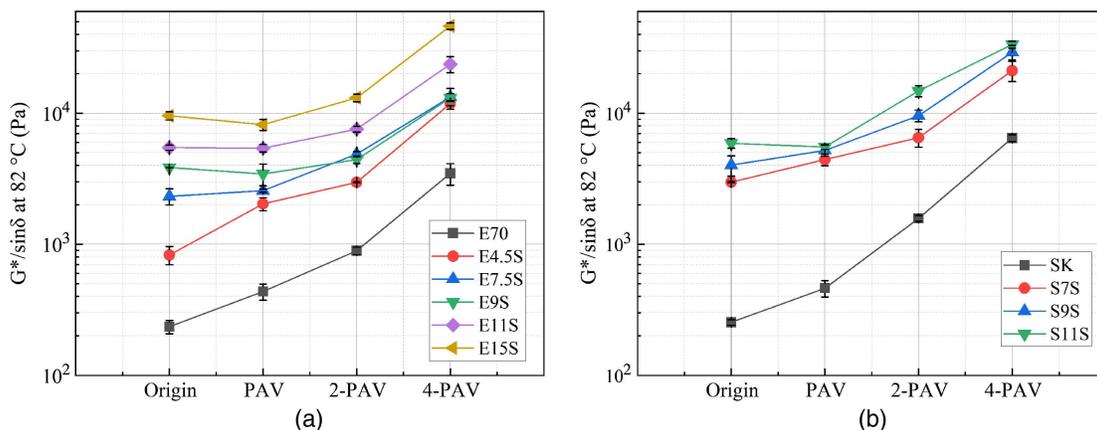
determined mainly by the modulus. Due to the point-to-point contact mode between aggregates in porous asphalt pavements, the high-temperature performance requirement of asphalt binders is stricter. When SBS content was higher, the rutting factor reached its lowest point at 1-PAV. Thus, to ensure the improved high-temperature performance of HCPMA binders, the rutting factor in the aging state needs to be considered.

### Nonrecoverable Creep Compliance

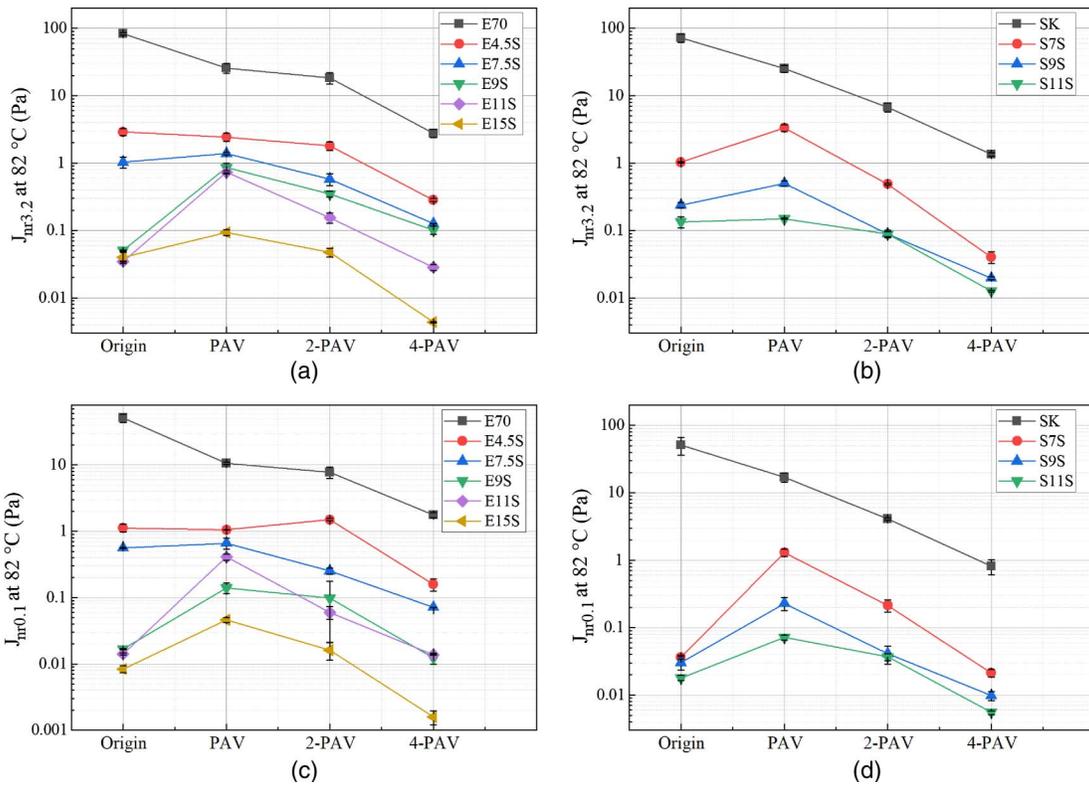
To fully distinguish the high-temperature properties of HCPMA binders with different base binders and SBS contents, the MSCR tests also were conducted at  $82^\circ\text{C}$ . The HCPMA binders had highest  $J_{nr}$  values (at 3.2 and 0.1 kPa) at 1-PAV, which coincided with the evolution of the phase angle (Fig. 4). As mentioned previously, the aging of HCPMA binders consists of oxidation of the base binder and degradation of the SBS polymer. From the original state to 1-PAV, the degradation of the SBS polymer played the primary role, which led to an increase of  $J_{nr}$ . As the aging process continued, the degradation of the SBS slowed, and the oxidation of base binder played the dominant role. For the HCPMA with high SBS content ( $>9\%$ ), the increase of  $J_{nr}$  was not as dramatic. This was because the undegraded SBS polymer still had a considerable modification effect.

### Percentage Recovery ( $R_{3,2}$ )

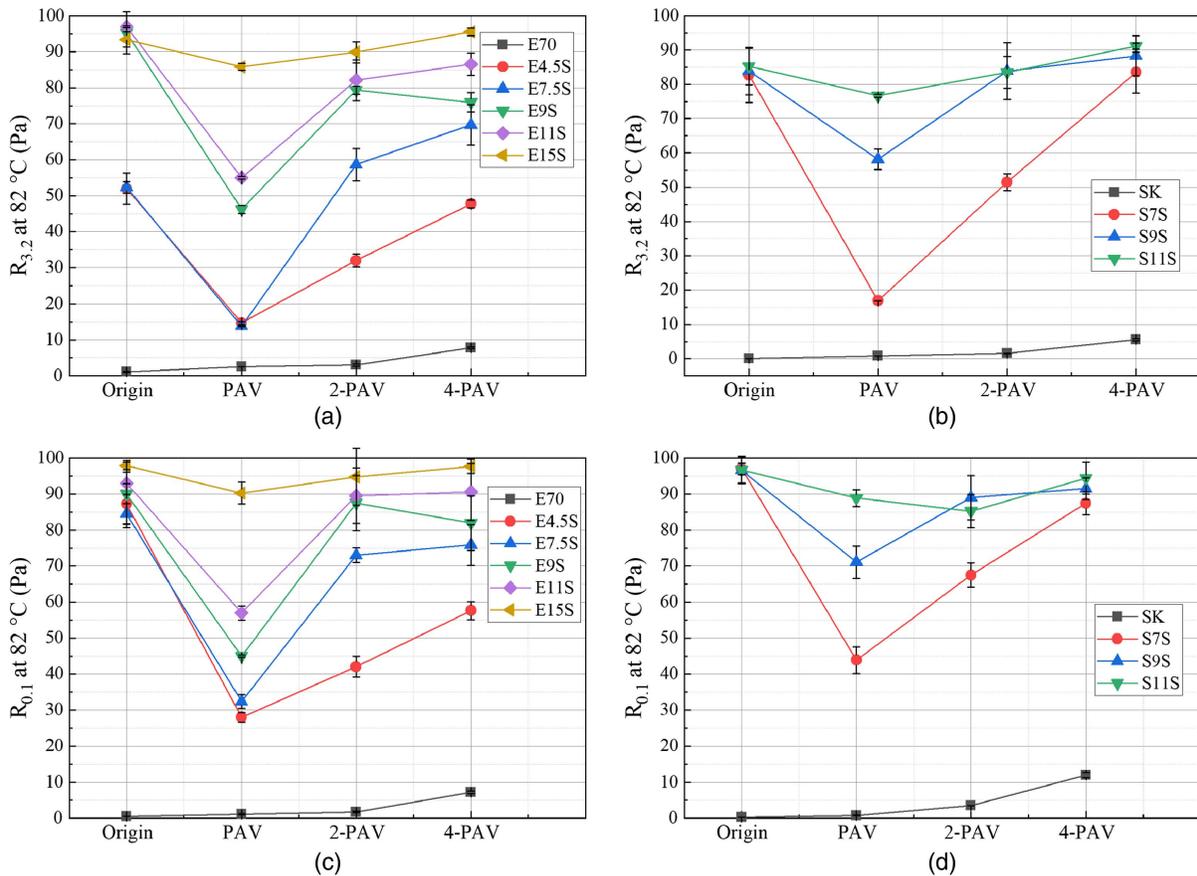
The  $R_{3,2}$  and  $R_{0,1}$  percentage recovery of base asphalt binders was lower than 10%, indicating that the base asphalt binder mainly had a viscous response at  $82^\circ\text{C}$  (Fig. 5). For HCPMA, the addition of



**Fig. 3.** Rutting parameter of HCPMA at different PAV aging periods: (a) HCPMA based on Esso asphalt; and (b) HCPMA based on SK asphalt.



**Fig. 4.** Nonrecoverable creep compliance of HCPMA at different PAV aging periods: (a and c) HCPMA based on Esso asphalt; and (b and d) HCPMA based on SK asphalt.



**Fig. 5.** Percentage recovery of HCPMA at different PAV aging periods: (a and c) HCPMA based on Esso asphalt; and (b and d) HCPMA based on SK asphalt.

SBS led to a noticeable increase of percentage recovery in the original state. The percentage recovery of HCPMA binders decreased before 1-PAV and increased afterward. These results indicate that the degradation of the polymer network is the reaction before PAV, and the hardening of the base binder played the main role afterward. Furthermore, percentage recovery at a higher stress level (3.2 kPa) had an improved differentiation degree. The  $R_{3,2}$  in the original state and the 4-PAV aging state increased with the increase of SBS content [Figs. 5(a and b)]. However,  $R_{0,1}$  was nearly the same in original state and at 4-PAV [Figs. 5(c and d)].

## Chemical Analysis

### Chemical Compositional Changes

The primary reaction of base asphalt binder during aging is oxidation, in which carbonyl and sulfoxide compounds are formed. Thus, the indexes of carbonyl ( $I_{co}$ ) and sulfoxide ( $I_{so}$ ) commonly are used to evaluate the aging extent of the base binder. The polymer damage index ( $I_{B/S}$ ) is used to characterize the degradation level of polymer, to avoid the influence of SBS concentration and the lack of scanning depth of the FTIR instrument.

In the specification, 20 h of PAV conditioning (1-PAV) is used to simulate the long-term aging. However, the aging extent of HCPMA in porous asphalt pavements is much more severe than that of the 1-PAV-aged HCPMA samples in the laboratory. For verification, in-field cores were collected from a 4-cm-thick porous asphalt pavement which had been in service for 8 years. To investigate the variation of aging extent with the depth, a layer of the in-field samples from the surface and from the bottom were collected, named surface and deep, respectively. To establish the link between in-field and laboratory aging of HCPMA designed for porous asphalt pavements, E7S (Esso asphalt base binder with 7% SBS content) was chosen as the benchmark. In the laboratory, E7S was subjected to short-term aging in a RTFOT and long-term aging in a PAV for different times (i.e., 20, 40, and 80 h) (Fig. 6). The sulfoxide peaks ( $1,030\text{ cm}^{-1}$ ) increased significantly with the increase of laboratory aging. The reaction product of in-field aging was slightly different from that of the laboratory aging. The peaks ( $1,030\text{ cm}^{-1}$ ) became wider, probably because the in-field aging included the influence of water and sunlight, and other chemical products were produced. The peaks of carbonyls ( $1,700\text{ cm}^{-1}$ ) also

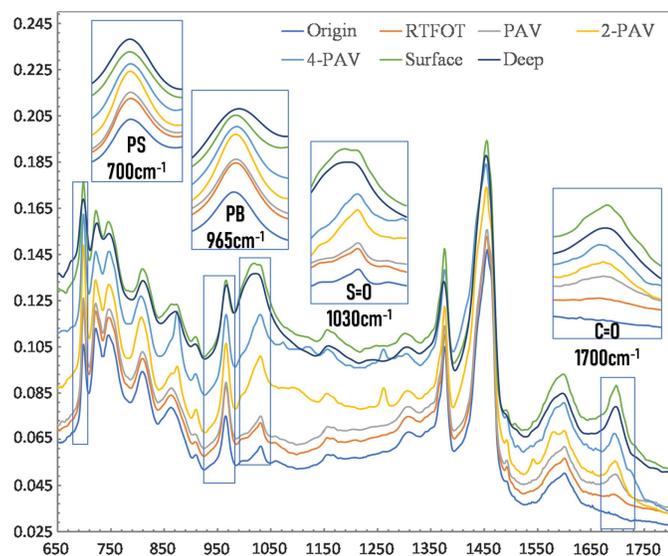


Fig. 6. Infrared spectra of laboratory and field aging.

increased significantly during the laboratory aging. The carbonyl peak area of 4-PAV was similar to that of in-field aging, indicating that the aging extent of both was close. There was almost no difference in the infrared spectra of surface and deep samples, which indicates that the aging degree of asphalt obtained from the surface and the 4-cm depth of pavement was almost the same.

To determine the effect of SBS content and base binder type on the aging of HCPMA, the carbonyl ( $I_{co}$ ) and sulfoxide ( $I_{so}$ ) indexes are illustrated in Fig. 7. SBS content had a minimal influence on the carbonyl formation [Fig. 7(a)]. The carbonyl index of HCPMA binders with lower SBS content was relatively high after 1-PAV. However, after 4-PAV, the carbonyl index of HCPMA with different SBS content was almost the same. This was mainly because with the increase of SBS content, the viscosity of HCPMA binders increased significantly and oxygen entered relatively more slowly. However, oxygen had sufficient time to penetrate HCPMA binders, so the carbonyl index was almost the same after 4-PAV. Regarding the influence of the type of base asphalt binder, the carbonyl index of HCPMA binders prepared with the Esso binder was relatively higher than that of HCPMAs prepared with the SK binders. The difference in the carbonyl index was not apparent after 1-PAV, whereas after 4-PAV, the difference was much more significant. The

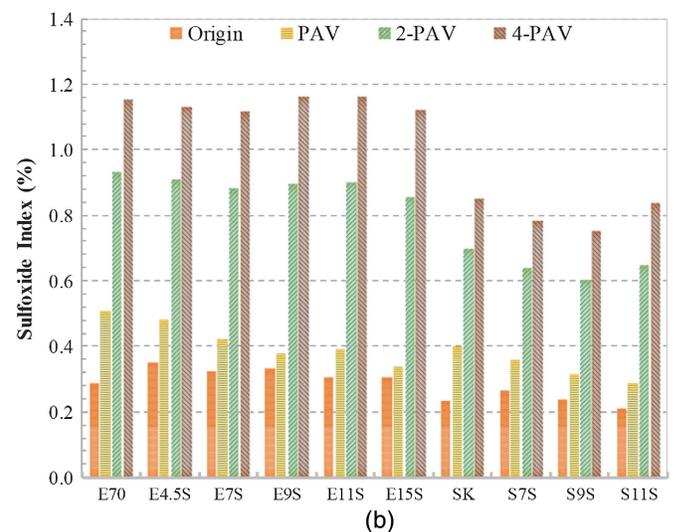
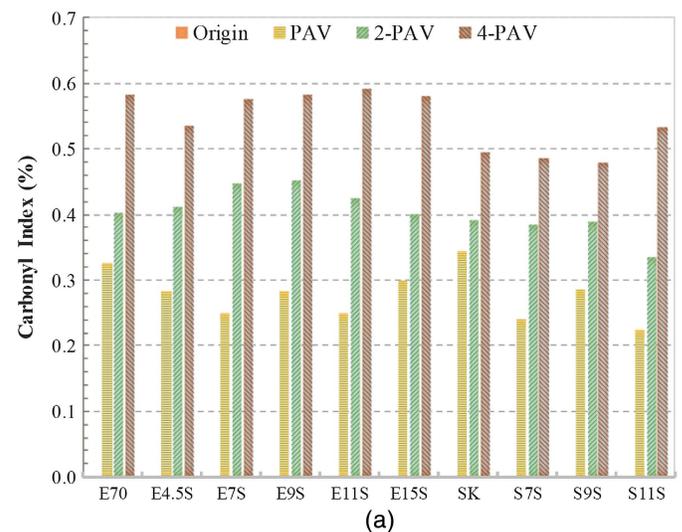


Fig. 7. Evolution of indexes during long-term aging: (a) carbonyl index; and (b) sulfoxide index.

most likely reason was the different compositions of these two base asphalt binders.

The evolution of the sulfoxide index was similar to that of the carbonyl index [Fig. 7(b)]. The SBS content also had no significant effect on the formation of sulfoxide, and HCPMA binders prepared with Esso produced more sulfoxide. The difference between sulfoxide and carbonyl compounds was that sulfoxides were present in the original state, and increased rapidly at first and slowly later, whereas there were almost no carbonyl compounds in the original state, and the rate of increasing was relatively stable.

To describe the evolution of SBS polymer during the long-term aging, the polymer damage index ( $I_{B/S}$ ) of HCPMA is shown in Fig. 8. The SBS dosage had almost no noticeable influence on  $I_{B/S}$ , indicating that the damage ratio of SBS polymer was relatively stable. However, with the increase of SBS content, the entire content of residual SBS polymer increased. The degradation of the SBS polymer occurred very quickly at the beginning of aging, and then slowed (Fig. 8). Most of the degradation occurred before the 2-PAV state. Furthermore, the base asphalt type also influenced the degradation of the polymer. In the original state, the  $I_{B/S}$  was almost the same; therefore  $I_{B/S}$  depended on the butadiene/styrene ratio of SBS produced in the factory. However, the  $I_{B/S}$  of HCPMA

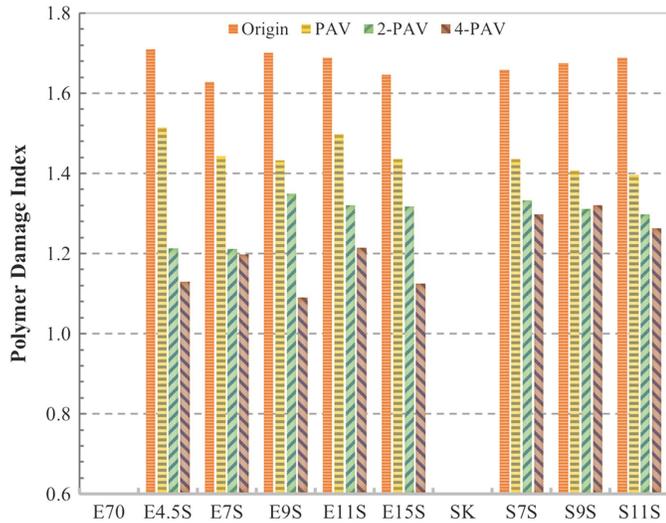


Fig. 8. Evolution of polymer damage index during PAV aging.

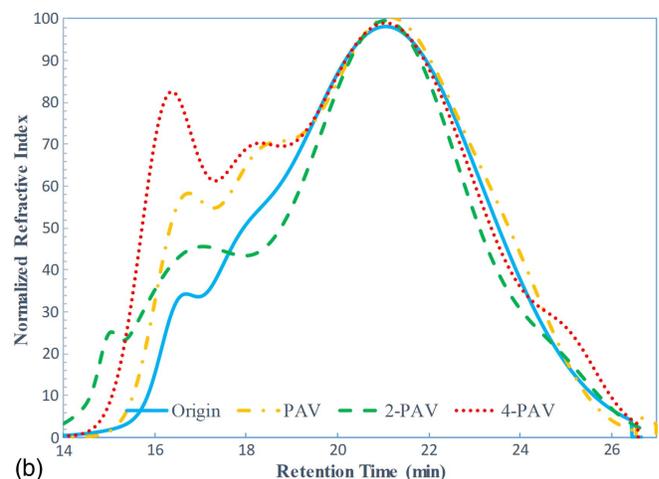
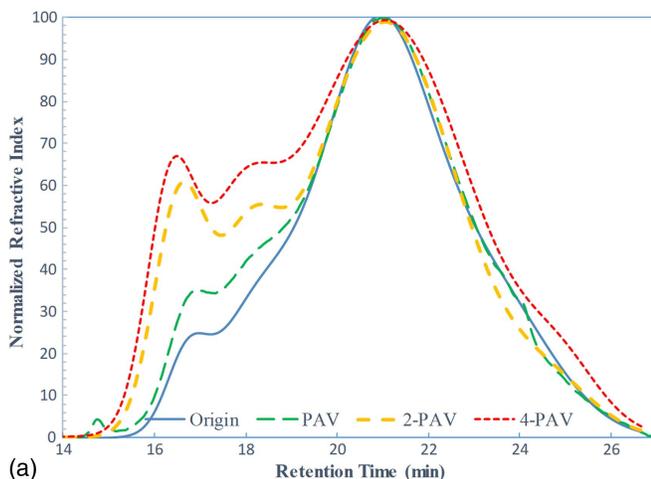


Fig. 9. Normalized chromatogram of base asphalt at different PAV aging periods: (a) Esso asphalt; and (b) SK asphalt.

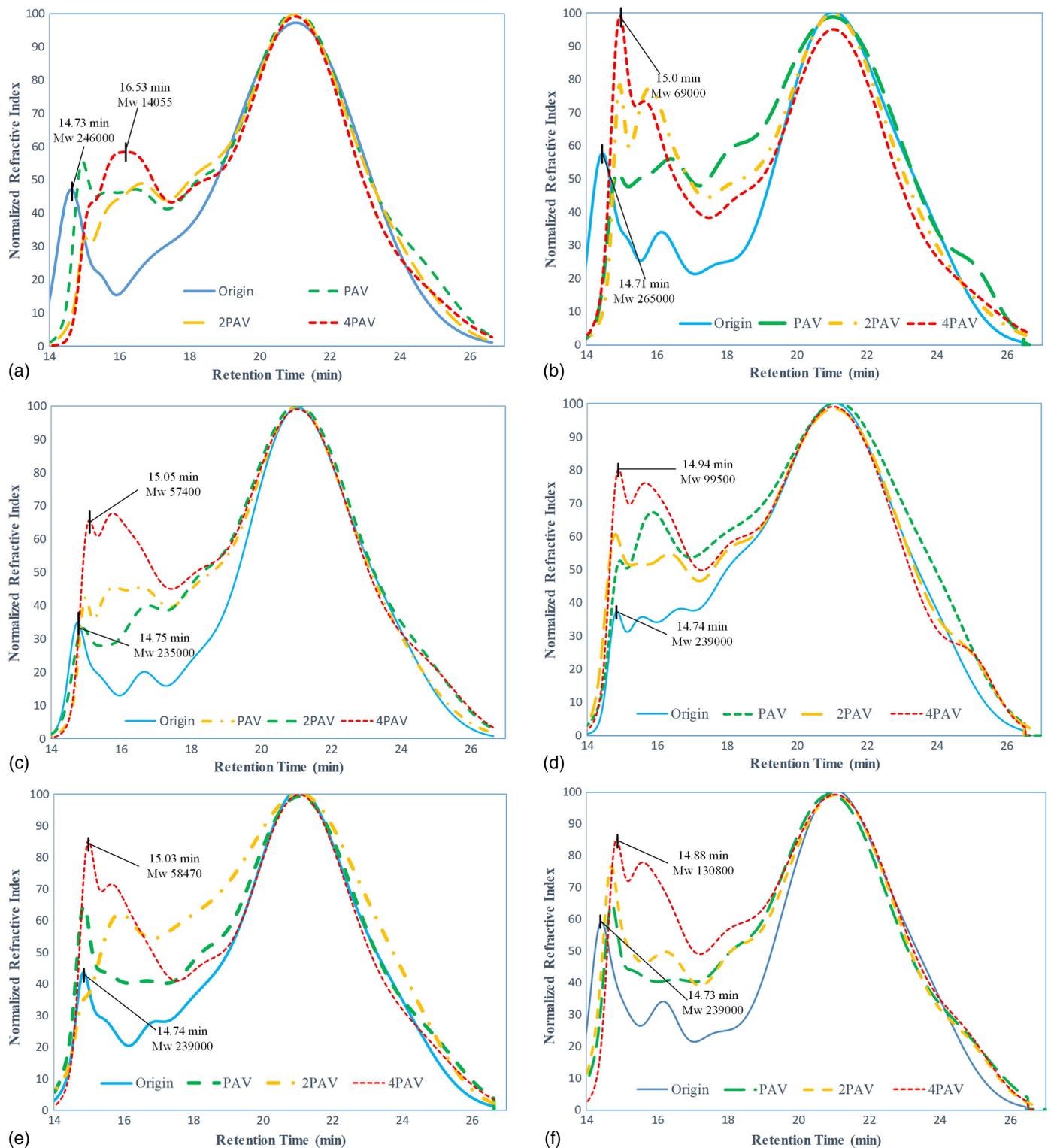
binders prepared with SK asphalt was higher than that prepared with Esso asphalt. The most likely cause of the lower  $I_{B/S}$  was the difference in the particle distribution of SBS polymer in the base asphalt, which is explained in detail in the following sections.

### Molecular Weight Changes

GPC tests were applied for molecular weight distribution analysis of base asphalt and HCPMA binders in different aging states (Canto et al. 2006; Wahhab et al. 1999). The order of elution is related to the molecular weight ( $M_w$ ) of the studied components. Firstly, high molecular weight species elute, followed by molecules with decreasing molecular weight. For HCPMA binder, there mainly were three observable peaks, corresponding to the incorporated polymer (14–15 min), asphaltenes (16–17 min), and maltenes (20–22 min). The normalized chromatogram of the base asphalt is illustrated in Fig. 9, and that of the HCPMA is shown in Fig. 10.

There was a dramatic increase of asphaltenes during aging, from 25 to 65 [Fig. 9(a)]. The peak of asphaltenes shifted from 16.80 to 16.65 min, indicating that the molecular weight of asphaltenes increased from 11,350 to 12,785. For the SK asphalt, the normalized refractive index increased even more, from 30 to 80. In addition, the peak of asphaltenes moved from 16.57 to 16.37 min, indicating that the molecular weight of asphaltene changed from 13,670 to 16,150. This indicates that the asphaltenes in the SK asphalt binder had a larger molecular weight than those in the Esso asphalt; concurrently, more asphaltenes were formed in SK during aging.

Regarding the HCPMA binders, the molecular weight distribution changed differently. The polymer peaks in the original state were at 246,000 and 265,000 [Figs. 10(a and b)], slightly higher than the molecular weight of SBS initially provided by the supplier ( $M_w = 230,000$ ). In the 4-PAV state, the polymer peak of E4.5S disappeared or was overlapped by the asphaltene peak ( $M_w = 14,055$ ), indicating a severe deterioration of SBS in E4.5S. For E15S, the polymer peak still existed, but changed to 15.0 min ( $M_w = 69,000$ ). This indicates that SBS polymer degraded into smaller molecules polymer during aging. At the same time, it is deduced that there was a grafting reaction between the degraded small polymer and the asphaltene molecules, which increased the peak and shifted it during the aging. With the increase of SBS polymer, this phenomenon was more evident, because the content of small-molecule polymers also increased. For a similar reason,  $J_{nr3,2}$  and the rutting factor of E15S at the 4-PAV state were much improved compared with that of E4.5S; the small molecules from degraded SBS polymer still had a significant modification effect.



**Fig. 10.** Normalized chromatogram of HCPMA at different aging stages: (a–c and e) HCPMA based on Esso asphalt; and (d and f) HCPMA based on SK asphalt.

Figs. 10(c–f) characterize the impact of base asphalt type on the aging. The molecular-weight polymer peak of S7S in the 4-PAV state was 99,500, which was higher than that of E7.5S (57,400). The 4-PAV-aged polymer peak of S11S also had a higher molecular weight (58,470) than that of E11S (130,800). This indicates that the degradation of SBS polymer in SK asphalt was not as severe as that in Esso asphalt. Thus,

the rheological properties of HCPMAs prepared with SK asphalt are expected to be better than those of HCPMAs prepared with Esso asphalt. Therefore, the rutting factor and  $J_{nr3.2}$  of HCPMAs in the 4-PAV state with different base binders were compared (Fig. 11). HCPMAs prepared with SK asphalt had better high-temperature properties compared with HCPMAs based on Esso asphalt at 4-PAV state.

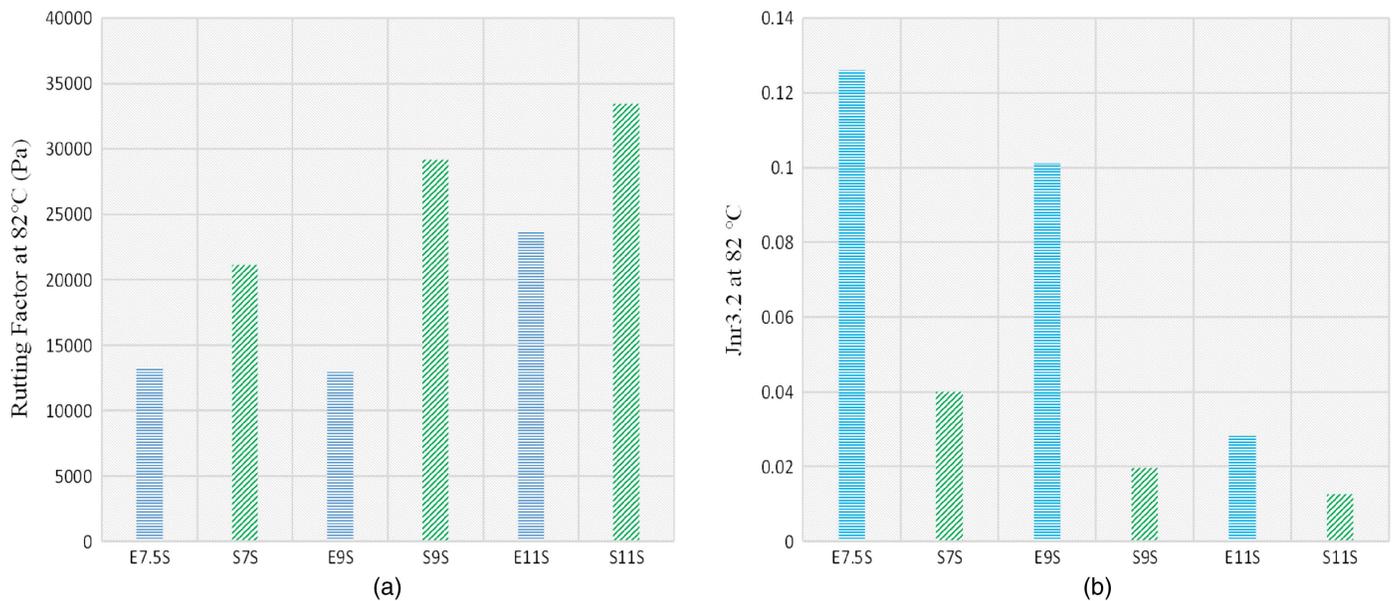


Fig. 11. HCPMA with different base asphalts at 4-PAV aging state: (a) rutting factor; and (b)  $J_{nr3.2}$ .

### Principal Component Analysis

In this research, 10 different types of parameters were used to characterize 32 HCPMA samples with different base bitumens, SBS dosages, and aging states. For further analysis of the relationship between these parameters, and to establish the fitting equation between different parameters, principal component analysis was conducted.

Principal component analysis is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables (entities which take on various numerical values) into a set of values of linearly uncorrelated

variables called principal components (Wang et al. 2018). In this paper, the PCA was conducted on 32 samples in different aging states and 10 parameters by using IBM SPSS statistics version 22 software. According to the analysis report, the first and second principal components explained more than 75% of the variance, indicating the validity of PCA analysis. The relationship between the asphalt samples and the studied variables is illustrated in Fig. 12. The first principal mainly described the aging of asphalt, which consisted of  $I_{so}$ ,  $I_{co}$ , and  $I_{so} + I_{co}$ . This highlights that the aging of the asphalt plays a dominant role, because first principal represents the highest variance level. The content of SBS is positively

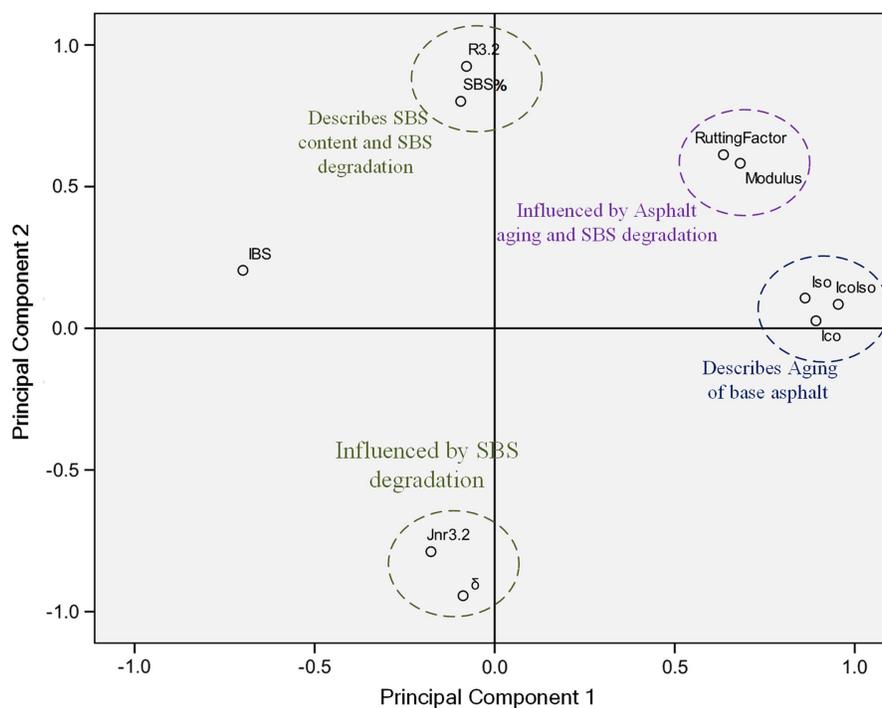


Fig. 12. Loading plot of PCA.

correlated with the second principal, which is associated with effective SBS content. Based on the results of this analysis,  $R_{3,2}$  was positively correlated with the second principal, whereas  $J_{nr3,2}$  and phase angle were negatively correlated. Thus, the ratio of viscosity and elasticity of HCPMAs was determined mainly by the SBS content and SBS degradation. On the other hand, the rutting factor and the modulus both were positively correlated with the first and second principals, indicating that both the aging level of asphalt and the active SBS content had a significant influence on the rutting resistance of HCPMA.

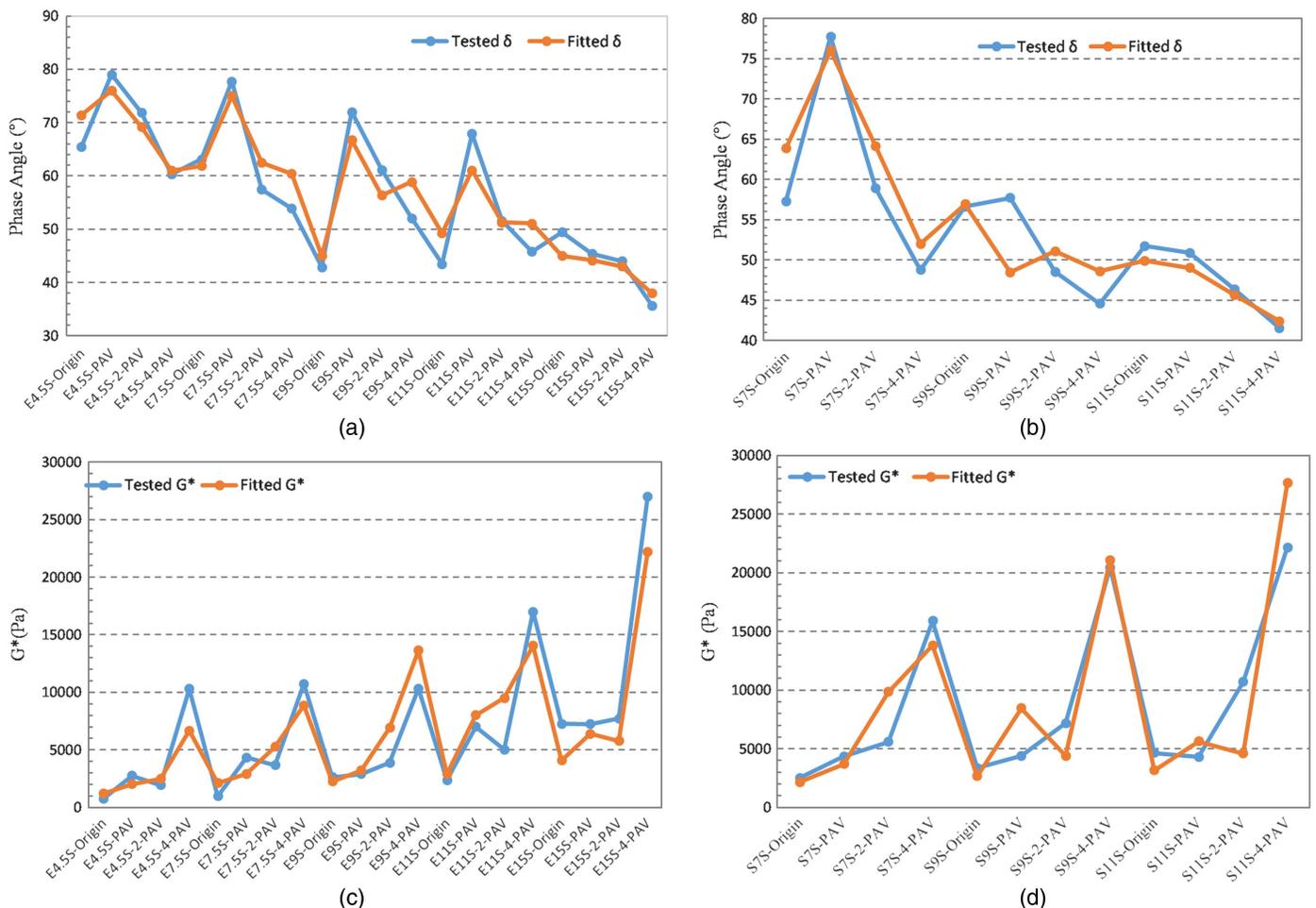
According to the results of PCA, 10 types of characterization parameters can be attributed to two aspects: oxidation degree and effective polymer content. The oxidation degree can be characterized with  $I_{co}$ , and the effective SBS content can be characterized by SBS content and polymer damage index ( $I_{B/S}$ ). For example, complex modulus and phase angle, the most commonly used parameters, are described with these two principals with exponential functions as

$$G_{HCPMA}^* = (1 - K_1 \cdot SBS\% \cdot I_{B/S}) \cdot G_{Base\ asphalt}^* \cdot e^{K_2 \cdot I_{co}} + K_1 \cdot SBS\% \cdot I_{B/S} \cdot G_{SBS}^* \cdot e^{K_3 \cdot I_{B/S}} \quad (5)$$

$$\delta_{HCPMA} = (1 - K_4 \cdot SBS\% \cdot I_{B/S}) \cdot \delta_{Base\ asphalt} \cdot e^{K_5 \cdot I_{co}} + K_4 \cdot SBS\% \cdot I_{B/S} \cdot \delta_{SBS} \cdot e^{K_6 \cdot I_{B/S}} \quad (6)$$

where  $K_1$  and  $K_4$  = coefficients of volume occupied by SBS polymer after swelling;  $SBS\%$  = SBS content added in the fabrication of HCPMA, and  $SBS\% \cdot I_{B/S}$  = effective SBS content considering degradation during aging;  $K_2$  and  $K_5$  = impact coefficient of base asphalt aging;  $K_3$  and  $K_6$  = impact coefficient of SBS polymer degradation;  $\delta_{Base\ asphalt}$  and  $G_{Base\ asphalt}^*$  = phase angle and complex modulus of base asphalt in original state at 82°C; and  $\delta_{SBS}$  and  $G_{SBS}^*$  = phase angle and complex modulus of SBS polymer at 82°C, and according to DMA test results,  $\delta_{SBS} = 11.2^\circ$ , and  $G_{SBS}^* = 106,000$  Pa.

The regression results and the fitted equation are presented in Fig. 13 and Table 3. The data were divided into two groups, one belonging to HCPMA prepared with Esso asphalt, and the other belonging to HCPMA with SK asphalt. All four fitting formula had a high  $R^2 (> 0.7)$ , indicating a good fit (Fig. 13). From this point of view, the evolution of rheological parameters along with the aging can be predicted with the results of FTIR tests and the fundamental rheological parameter of base asphalt and SBS polymer in the original state. Unfortunately, although the basic rheological parameters of base asphalt we considered in the fitting equation, the  $G^*$  or  $\delta$  of HCPMA with different base asphalts could not be predicted with only one equation. The main reason is that the swelling states of SBS polymers in Esso asphalt and SK asphalt are very different, and they further influence the degradation levels of SBS polymer.



**Fig. 13.** Regression results and fitted equations: (a and b) phase angle; and (c and d) complex modulus.

**Table 3.** Parameters in regression formula

Rheological parameters	Regression parameters	Esso	SK
Complex modulus	Base binder (Pa)	82	96
	SBS polymer modifier (Pa)	1,060,000	1,060,000
	$K_1$	1.202	4.209
	$K_2$	7.694	11.219
	$K_3$	-0.912	-1.599
	$R^2$	0.823	0.856
Phase angle	Base binder (degrees)	88	84
	SBS polymer modifier (degrees)	11.2	11.2
	$K_4$	3.228	2.190
	$K_5$	-0.170	-0.600
	$K_6$	0.521	-0.881
	$R^2$	0.723	0.768

## Conclusions

This study explored the chemical and rheological changes in high-content polymer-modified asphalt (HCPMA) during aging. Conclusions are drawn as follows:

- The aging of HCPMA is a combination of oxidation of base asphalt binder and degradation of SBS polymer, leading to an increase and decrease of elasticity, respectively. The oxidation of base binder goes on all the time, but the degradation of SBS was fast at the beginning and slowed after 20 h of PAV conditioning. As a result, HCPMA binders were viscous until the end of 20 h of PAV aging and then became more elastic until 80 h of PAV aging.
- When the SBS content was more than 7.5%, a considerable amount of SBS polymer remained even after 80 h of PAV conditioning. Its molecular weight was reduced from 230,000 to 70,000–130,000, but the modification effect still was efficient. Therefore, the most effective way to maintain considerable properties of HCPMA binders is to increase the content of SBS.
- The SBS modification of asphalt binders has significantly retarded the oxidation and hardening of base binders, especially after 20 h in a PAV, mainly due to the fact that the curing of the SBS polymers still was occurring at the early stage of aging, and the degradation of SBS polymer can retard the hardening of HCPMA binders as well.
- HCPMA binders prepared with Esso base binder were more vulnerable to oxidative aging, most possibly because of high aromatic content in the Esso binder, which leads to the presence of SBS polymer as smaller particles which more naturally degrade.
- PCA showed that the 10 parameters of 32 asphalt samples could be explained by 2 principals: oxidation level of asphalt, and SBS content. Based on PCA results,  $G^*$  or  $\delta$  of HCPMA can be well fitted ( $R^2 > 0.7$ ) by the exponential function of SBS content and aging index. Thus,  $G^*$  or  $\delta$  can be well predicted by the fitting formula. Unfortunately, this fitting can be used only for HCPMA prepared with the same base asphalt.

## Data Availability Statement

All data, models, or code generated or used during the study are available from the corresponding author by request.

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