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

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**Abstract:** The most common polymer–based modifier for asphalt binders is the styrene-butadiene-styrene (SBS), which owns superior mechanical characteristics to asphalt, such as increased toughness and resistance against permanent deformation. These properties improved further when higher amounts of SBS are incorporated in asphalt. Although this type of asphalt binders, named high content polymer modified asphalt (HCPMA) binders are used mainly for porous pavements, limited research on their ageing performance has been conducted. In this paper, Gel Permeation Chromatography (GPC), Fourier Transform Infrared (FTIR) and Dynamic shear rheology (DSR) were used to explore the evolution of chemical and rheological properties of HCPMA along with the ageing process and to comprehend factors affecting ageing. Firstly, this study identified that the ageing of HCPMA was a combination of oxidation of base asphalt and degradation of SBS polymer leading to an increase and a decrease of elasticity, respectively. The degradation of SBS happened mostly at the beginning and slowed down after ageing in Pressure Ageing Vessel (PAV)for 20 hours, which resulted in worst rutting resistance for HCPMA. The second finding is that, when SBS content was higher than 7.5%, more than half of SBS polymer remained even after 80 hours of PAV ageing. Although the molecular weight of SBS decreased from 230,000 to 70,000 due to the degradation, its modification effect was still significant. Thirdly, highly modification of SBS can retard the oxidation and hardening of base asphalt, especially from origin to first PAV aging state. Finally, Principal Component Analysis showed ten parameters used in this study could be explained by two principals: SBS content and asphalt ageing level. Based on PCA results, the complex modulus (G*) or phase angle (δ) of HCPMA can be well fitted ($R^2$>0.7) by the exponential function of SBS content and ageing index.

*Keywords:* high content polymer modified asphalt, long-term ageing, rheological characterization, chemical characterization

## 1 INTRODUCTION

Oxidative ageing of asphalt binders is one of main defects that causes embrittlement of asphalt and subsequently contributes to the total in-service deterioration of asphalt pavements. From the chemical point of view, through the ageing process of asphalt binders, oxygen reacts with certain molecules leading to the formation of polar functional groups, named carbonyls and sulfoxides. From the mechanistic point of view, this chemical process influences the flexibility and the stiffness of material (i.e., decrease of phase angle and increase of complex modulus) having also negative effect on the adhesion characteristics of asphalt.

Nowadays, due to the acceleration of the total deterioration of the pavement structures made by asphalt binders by the continuously increasing traffic and the more aggressive environmental conditions (e.g., high temperatures), the incorporation of polymer modifiers in asphalt binders is more and more important. Additionally, in modern societies such as the Netherlands or China (Van Rooijen, Turral, and Wade Biggs 2005; Jia et al. 2017), in where the requirements for having easy-maintained pavements of high permeability, skid resistance and sound absorption, the open-graded asphalt pavements attract increasing attention. The internal structure of open-graded pavements is of high amount of air-voids, and for this reason they are more vulnerable to the environmental effects, making the option of polymer modifiers of high importance as well. Polymers such as the styrene–butadiene-styrene block copolymers (SBS) are widely used as modifiers producing the ordinary SBS modified asphalt (<5%) (SBSMA) able to improve the ultimate performance of asphalt pavements(Polacco et al. 2015; Zhu, Birgisson, and Kringos 2014).

In addition to SBSMA, high content polymer modified asphalts (HCPMA) are prepared by the addition of high content of SBS (>6%) showing improved toughness and thus increased resistance against raveling (i.e., loss of aggregates from the surface of pavements)(Habbouche et al. 2018; Alvarez, Martin, and Estakhri 2011; Liang et al. 2017; Geng, Li, and Han 2016; Xu et al. 2016; Griebel et al. 2016; F. Zhang and Hu 2017). Therefore, these asphaltic materials are ideal for open-graded (porous) asphalt pavements, and have been applied in a number of pavement structures all over the world. Nevertheless, the primary challenge faced by many researchers on applying HCPMA in porous pavements is the ageing. Firstly, because of the open gradation of porous pavement, plenty of oxygen is introduced, which results in severe ageing. Meanwhile, owing to the high viscosities of HCPMA, they usually have higher mixing (180~190℃) and paving (170~180℃) temperatures. Furthermore, due to the unsaturated double carbon bond (C=C) SBS possess, this polymer is sensitive to oxygen and thus to oxidative ageing damage(H. Zhang et al. 2017; Lee et al. 2011; Y. Wang, Sun, and Qin 2015). Although the aging mechanism of SBS modified bitumen is quite complex, including the oxidation of base bitumen, chain scission of polybutadiene segment in SBS polymer, cross-linking or branching reaction between polymers, as well as grafting reaction between SBS polymer and bitumen component. The chain scission reaction occurs at polybutadiene segment play the main role, which lead to a significant decrease of molecular weight SBS polymer and a dramatic decrease of modification effect. (Ouyang et al. 2006; Pospíšil et al. 1999; Cortizo et al. 2004; Y. Wang, Sun, and Qin 2015). Considering the high content SBS used in HCPMA, the degradation of SBS polymer will cause severe performance deterioration in asphalt pavements.

Based on the current literature, most of the researches have been focused on the impact of the ageing of ordinary SBS modified asphalts on their physical, chemical and rheological properties(Tang, Huang, and Xiao 2016; Z. Wang, Wang, and Ai 2014). However, there is a significant difference between HCPMA and ordinary SBSMA binders, and limited available data about the properties of HCPMAs. Therefore, this paper aims to explore the evolution of chemical and rheological properties of HCPMA during the ageing process and to comprehend its influential factors. Two types of base asphalt (i.e., Esso and SK asphalt binders) and various SBS dosages ranged from 4.5% to 15% were used. Rolling Thin Film Oven Ageing (RTFOT) and Pressure Ageing Vessel (PAV) of different time periods were applied to simulate different ageing levels in the laboratory. It is worth noting that the long-term aging is simulated with 20 hours of PAV aging. However, the aging degree of HCPMA in the field porous pavement is much more serious. The relationship between

The rheological and chemical changes during ageing are tracked with gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy and dynamic shear rheometer (DSR). For further comprehension of the relationship between performance- and component-related parameters, Principal Component Analysis (PCA) and regression analysis were employed.

## 2 MATERIALS AND METHODS

### 2.1 Materials

As mentioned before, two types of base asphalt were used to prepare the HCPMA. The explicit description of the base asphalt is shown in **Table 1**. Previous literature indicates that the constitution of base asphalt has a significant influence on the polymer-asphalt compatibility(Zhu, Birgisson, and Kringos 2014; Habbouche et al. 2018). As shown in **Table 1**, Esso asphalt has a relatively higher content of aromatic and asphaltenes fractions compared with SK asphalt. However, the saturate and resin fractions of Esso asphalt are relatively less.

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

| Asphalt | Esso | SK | Test specification |
|---|---|---|---|
| Saturates (%) | 7.8 | 13.2 | - |
| Aromatic (%) | 54.6 | 45.7 | - |
| Resin (%) | 18.5 | 24.6 | - |
| Asphaltene (%) | 19.1 | 16.5 | - |
| Softening (℃) | 50.9 | 46.6 | ASTM D36 |
| Penetration (25℃ 0.1 mm) | 64 | 71 | ASTM D113 |
| Viscosity(135 ℃, Pa·s) | 0.428 | 0.472 | ASTM D5 |

| | | | |
|---|---|---|---|
| Ductility(15 ℃, 0.1 cm) | >150 | >150 | ASTM D4124 |

Radial SBS of 230,000 g/mol average molecular weight (Mw) was chosen as the modifier (30wt% of styrene). For the preparation of HCPMA, the added content of SBS modifier was from 4.5% to 15% by the weight of base asphalt. In China, 4.5wt% and 7.5wt% of SBS are the typical dosages for dense and porous asphalt pavements, respectively. The specific description of samples can be seen in **Table 2**. To enhance the compatibility between asphalt and SBS polymer, a particular type of resin and 0.15wt% of sulfur used as agent able to form crosslinks between polymers were added, which enhanced the storage stability to the HCPMA. All samples have passed the segregation test (ASTM D5976) to ensure the uniformity of the asphalt.

**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 |

To simulate the short- and the long-term ageing, all HCPMA samples were aged in RTFOT ageing at 163 °C (ASSHTO T 240) and in PAV (ASSHTO R28), respectively. Also, PAV of different durations (20h, 40h, and 80h, named as 1PAV, 2-PAV and 4-PAV, respectively) were conducted after RTFOT ageing to evaluate the chemo-mechanical changes of HCPMA during ageing.

## 2.2 Experimental Methods

### *2.2.1 Dynamic shear rheometer (DSR)*

*Frequency sweep test*

The dynamic oscillatory test was performed on a TA DSR AR1500ex to obtain the complex modulus, phase angle and rutting factor of HCPMA. As the PG high-temperature grade 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 25-mm plate with a 1-mm gap (AASHTO T 315). Two replicates were performed for each asphalt sample, and the average value was recorded.

*Multiple stress creep and recovery (MSCR) test*

The MSCR test can be used to evaluate the viscoelastic properties of polymer modified asphalt(J. A. D’Angelo 2009; J. D’Angelo and Dongré 2009; Huang and Tang 2015). In this paper, the MSCR test was performed in the same DSR device described above to obtain non-recoverable creep compliance ($J_{nr}$) and percent recovery (R) at 0.1 kPa and 3.2 kPa (AASHTO 350). Two replicates were performed for each asphalt sample, and the average value was recorded.

*2.2.2 Fourier transform infrared (FT-IR) spectroscopy*

The infrared spectra values were collected using a Bruker TENSOR FT-IR spectrometer equipped with a reflection diamond 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 asphalt samples were conducted, and the average value was recorded. The $AR_{\tilde{v}}$ values were normalized to the total sum of all band areas ($\sum AR_{\tilde{v}}$), and the indexes are calculated as follows:

Carbonyl index: $$I_{CO} = AR_{1700}/\sum AR_{\tilde{v}} \quad (1)$$

Sulfoxide index: $$I_{SO} = AR_{1030}/\sum AR_{\tilde{v}} \quad (2)$$

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

where $\sum AR_{\tilde{v}}$ is given by:

$$\sum AR_{\tilde{v}} = AR_{1700} + AR_{1600} + AR_{1460} + AR_{1310} + AR_{1030} + AR_{965} + AR_{864} + AR_{814} + AR_{743} + AR_{725} + AR_{700} \quad (4)$$

Carbonyl and sulfoxide are the most commonly used indicator to measure the chemical oxidation of bitumen binder and the absorbance values of polybutadiene and polystyrene are generally 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 level of base asphalt and a polymer damage index ($I_{B/S}$) was used to reveal the degradation of SBS polymer. SBS consists of polybutadiene (PB) and polystyrene (PS), in which the PS segment possesses a corresponding peak at 699 $cm^{-1}$and PB segment possess a peak at 965 $cm^{-1}$(Lin et al. 2018, 2017; Lamontagne et al. 2001; Yut and Zofka 2011). As the unsaturated C=C bond on the PB segment is an easy target for oxygen, it can be aged and subsequently degraded. PS is relatively stable and exhibited much smaller change after ageing. 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, Huang, and Tang 2017; Yan et al. 2018).

*2.2.3 Gel permeation chromatography (GPC)*

In this study, the GPC device was used to characterise the molecular weight distribution of HCPMA for different ageing time periods in PAV. Before the GPC test, a 20 mg asphalt sample was dissolved with tetrahydrofuran (THF) in a 10 mL volumetric flask for 24 hours. The solution was filtered through a 0.45-µm PTFE filter and collected in a 0.5 mL centrifugal tube for GPC test. Waters 1515 High-Pressure Liquid Chromatography (HPLC) Pump and Waters 2414 Refractive Index (RI) detector were used for conducting the GPC test. The calibration curve was built with Shodex® Polystyrene Standards to convert the retention time to molecular weight. Two replicates were performed for each sample, and the average value was recorded.

## 3 RESULT AND DISCUSSION

### 3.1 Rheological Characteristics

*3.1.1 Complex modulus*

As illustrated in **Table 2**, the high-temperature performance grade (PG) of HCPMA ranges from 76 to 88 °C. As a result, 82 °C was chosen as the test temperature for the DSR test for fully distinguishing the high-temperature properties of HCPMA. As shown in **Figure 1**, the evolution of the modulus of base asphalt (Esso and SK) raised significantly along with the increase of ageing duration. As for E4.5S, the modulus still increased, while the increasing rate was lower than that of Esso asphalt. When SBS dosage reached 15%, the modulus even decreased after PAV ageing, due to the fact that the ageing of HCPMA consisted of two counterparts. One the one hand, the oxidation of 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 cause modulus decrease. When SBS dosage is less than 7.5%, the oxidative aging of base asphalt played the dominant role and the modulus increased. While, when the SBS dosage was more than 7.5%, the degradation of SBS played a more significant role, which led to modulus decrease before 20 hours of PAV aging. From this perspective, the with the increase of SBS content not only have a modification effect, but also have the function of retarding the oxidation of base bitumen, especially when SBS content is more than 7.5%.

As ageing proceeds, the modulus of all HCPMA samples increased from PAV ageing condition to 4-PAV ageing condition. It indicates the degradation rate of SBS polymer slowed down in the following ageing duration. As for the HCPMA based on SK asphalt, the modulus evolution was similar to that of HCPMA based on Esso asphalt, rendering base asphalt had little influence on the modulus.

*3.1.2 Phase angle*

From **Figure 2 (a)**, the phase angle of Esso asphalt decreased about 10 degrees after

RTFOT ageing and 80 hours of PAV (4-PAV) ageing process. As for SK asphalt in **Figure 2 (b)**, the phase angle decreased about 14 degrees after ageing. The oxidation of base asphalt during the ageing process can result in a decrease of phase angle.

As for HCPMA, with the rise of SBS dosage, the phase angle in the original state decreased significantly from 90 degrees to about 42 degrees (E15S). The reason why phase angle decreased is that the addition of SBS polymer modifier can enhance the elasticity of HCPMA. The phase angle of HCPMA first increased and reached after PAV ageing, and then decreased significantly from PAV ageing condition to 4-PAV ageing condition. It suggests that SBS polymer degraded severely during RTFOT and PAV ageing process, and the polymer degradation reduced the effect of modification. However, after PAV ageing, the oxidation of base asphalt played the primary role, and the phase angle decreased instead. However, when SBS dosage is more than 11%, the ungraded SBS polymer still kept a considerable modification effect. Thus, the phase angle of HCPMA with 11% or 15% content of SBS polymer hardly increased from original ageing state to PAV ageing state.

*3.1.3 Rutting factor*

It can be seen in **Figure 3**, the evolution of rutting factor of HCPMA was very similar to that of the G*. It was because the modulus changed more significantly compared with phase angle, and thus rutting factor was mainly determined by modulus. Due to the "point-to-point" contact mode between aggregates in porous asphalt pavement, the high-temperature performance requirement of the asphalt is stricter. When SBS content is higher, the rutting factor reached its lowest point at PAV ageing state. Thus, to ensure improved high-temperature performance of HCPMA, rutting factor in ageing state needs to be considered.

*3.1.4 Non-recoverable creep compliance ($J_{nr}$)*

To fully distinguish the high-temperature properties of HCPMA with different base asphalt and SBS content, the MSCR tests were also conducted at 82 °C. According to **Figure 4**, the HCPMA showed highest $J_{nr}$ values (at 3.2kPa and 0.1kPa) at PAV ageing state. This phenomenon coincided with the evolution of the phase angle, which shows the highest phase angle. As mentioned before, the ageing of HCPMA consists of oxidation of base asphalt and degradation of SBS polymer. From the original state to PAV ageing state, the degradation of SBS polymer played the primary role, which led to an increase of $J_{nr}$. As the ageing process continued, the degradation of SBS slowed down and the oxidation of base asphalt played the dominant role. It should be noticed that, for the HCPMA with high SBS content (>9%), the increase of $J_{nr}$ was not so dramatic. It was due to the undegraded SBS polymer still had a considerable modification effect.

*3.1.5 Percentage recovery ($R_{3.2}$)*

According to **Figure 5**, $R_{3.2}$ and $R_{0.1}$ of base asphalt were lower than 10%, indicating base asphalt mainly showed the viscous response at 82 °C. As for HCPMA, the addition of SBS led to a noticeable increase of percent recovery in the original state. Similar to the evolution of $J_{nr3.2}$, the percent recovery of HCPMA shows the lowest value at PAV ageing state. These results also showed the ageing HCPMA consisted of oxidation of base asphalt and the degradation of SBS polymer. Furthermore, percent recovery at a higher stress level (3.2kPa) shows improved differentiation degree. As seen in **Figure 5(a)** and **(b)**, $R_{3.2}$ in original state and 4-PAV ageing state increased along with the rise of SBS content. However, $R_{0.1}$ in **Figure 5(c)** and **(d)** was nearly the same in original state and 4-PAV ageing state.

## 3.2 Chemical Characterization

### *3.2.1 Chemical compositional changes*

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

In the specification, 20h of PAV aging is used to simulate the long-term aging. However, the aging degree of HCPMA in the field porous pavement is much more serious than the HCPMA sample aged with 20h of PAV in the laboratory. To prove this point of view, the in-field ageing degree of HCPMA in a real surface porous asphalt pavement, in-field samples were collected from a 4-cm thick asphalt pavement which was in service for eight years. To investigate the variation of ageing level along with the depth, a layer of the in-field samples from the surface and the bottom were collected, named as Surface and Deep, respectively. In order to establish the link between in-field and in-lab ageing of HCPMA designed for porous asphalt pavements, E7S (base asphalt is Esso asphalt, SBS content is 7%) was chosen as the benchmark. In the laboratory, E7S was conducted short-term ageing in RTFOT and long-term ageing in PAV of different length of time (i.e., 20, 40 and 80 hours) and the results is shown in **Figure 6**. The sulfoxide peaks (1030 $cm^{-1}$) increased significantly along with the deepening of in-lab ageing. However, the reaction product of in-field ageing is a little different from the in-lab ageing. The peaks (1030 $cm^{-1}$) became wider, probably because the in-field ageing contains water and sunlight, and other sulfoxide products were produced. The peaks of carbonyl (1700 $cm^{-1}$) also increased significantly with the time during the in-lab ageing. As shown in **Figure 6**, the carbonyl peak of 4-PAV is similar to those of in-field ageing, indicating the ageing degree of both is close. Meanwhile, there was nearly no difference between the infrared spectrum of Shallow and Deep, which indicates that the ageing degrees of asphalt obtained from the surface and in 4-cm depth of pavement was almost the same

To reveal the effect of SBS content and base asphalt type on the ageing of HCPMA, carbonyl ($I_{co}$) and sulfoxide ($I_{so}$) index were illustrated in **Figure 7**. From **Figure 7(a)**, SBS content had a minimal influence on the carbonyl formation. Under the PAV ageing, the carbonyl index HCPMA with lower SBS content is relatively high. However, under 4-PAV ageing, the carbonyl index of HCPMA with different SBS content was almost the same. Similar phenomena occurred in HCPMA prepared with base asphalts. It was mainly because with the increase of SBS content, the viscosity of HCPMA increased significantly and oxygen enters relatively slower. However, when the ageing level came to 4 times PAV (i.e., 80 hours), oxygen had sufficient time to penetrate HCPMA, so that the carbonyl index was almost the same. As for the influence of the type of base asphalt, the carbonyl index of HPCMA prepared with Esso asphalt was relatively higher than that of HPCMA prepared with SK asphalt. The difference in carbonyl index was not apparently in PAV ageing, whereas in the 4-PAV, the difference was significant. The most likely causes were the different composition of these two base asphalt binders.

As illustrated in **Figure 7 (b)**, the evolution of sulfoxide index was similar to that of carbonyl index. The SBS content also had no significant effect on the formation of sulfoxide, and HCPMA prepared with Esso produced more sulfoxide. The difference between sulfoxide and carbonyl is that sulfoxide is present at original state, increased rapidly at first and slowly later. While there was nearly no carbonyl in the original state and the increasing rate was relatively stable.

For the description of the evolution of SBS polymer during the long-term ageing, polymer damage index ($I_{B/S}$) of HCPMA was demonstrated in **Figure 8.** It can be observed that, SBS dosage nearly did not have a noticeable influence on the $I_{B/S}$, indicating that damage ratio of SBS polymer was relatively stable. However, with the increase of SBS content, the absolute content of residual SBS polymer increased. As shown in **Figure 8**, the degradation speed of SBS polymer was very quickly at the beginning of ageing process, and then slowed down. Most of the degradation occurred before 2-PAV ageing state. Furthermore, base asphalt type also influenced the degradation of the polymer. In original state, the $I_{B/S}$ was almost the same, mainly due to the fact that$I_{B/S}$ was depended on the butadiene/styrene ratio of SBS produced from the factory. However, $I_{B/S}$ of HCPMA prepared with SK asphalt was higher than that prepared with Esso asphalt. The most likely causes of lower $I_{B/S}$ is the difference in the particle distribution of SBS polymer in base asphalt, which will be explained in detail in the following parts.

*3.2.2 Molecular weight changes*

GPC tests were applied for component distribution analysis of base asphalt and HCPMA in different ageing states(Canto et al. 2006; Wahhab H. I. Al-Abdul et al. 1999). The order of elution is related to the molecular weight (Mw) of the studied components. Firstly, high molecular weight species elute, followed by molecules with ever decreasing molecular weight. For HCPMA asphalt, there were mainly three observable peaks from left to the right, corresponding to the incorporated polymer (14~15 min), asphaltenes (16~17 min) and maltenes (20~22 min). The normalised chromatogram of base asphalt is illustrated in **Figure 9**, and the HCPMAs' was shown in **Figure 10**.

As shown **in Figure 9(a)**, what can be seen is a dramatic increase of asphaltenes along with the ageing process, from 25 to 65. Meanwhile, the peak of asphaltenes moved leftward from 16.80 min to 16.65 min, indicating the molecular weight of asphaltenes increased from 11,350 to 12,785. Regarding the SK asphalt, the normalised refractive index increased even higher, from 30 to 80. Also, the peak of asphaltenes moved from 16.57 min to 16.37 min, rendering the molecular weight of asphaltene moved from 13,670 to 16,150. This indicates that the asphaltenes in SK asphalt has larger molecular weight than that in Esso asphalt, at all ageing levels. Meanwhile, more asphaltenes were formed in SK during the ageing.

Regarding the HCPMA, the molecular weight distribution changed differently. As illustrated in **Figure 10(a)** and **(b)**, the polymer peak in the original state was at 246,000 and 265,000, which was slightly higher than the molecular weight on SBS originally provided by the supplier (Mw=230,000). While in the 4-PAV ageing state, the polymer peak of E4.5S disappeared or was overlapped by the asphaltenes peak (Mw=14,055), indicating a severe deterioration of SBS in E4.5S. As for E15S, the polymer peak still existed and moved rightward to 15.0 min (Mw=69,000). This indicated that SBS polymer degraded into smaller molecules polymer during ageing. At the same time, it is deduced that there is a grafting reaction between degraded small polymer and the asphaltene molecular, which made the peak higher and moved leftwards during the aging. Meanwhile, with the increase of SBS polymer, this phenomenon was more evident, as the content of small molecular polymer also increased. However, considering the $J_{nr3.2}$ and the rutting factor of E15S at the 4-PAV ageing state was much improved than that of E4.5S, these small molecules from degraded SBS polymer still had significant modification effect.

The section below describes the influence of base asphalt on the ageing of HCPMA and the results are illustrated in **Figure 10(c)-(f)**. The molecular weight polymer peak of S7S in 4-PAV state was 99,500, which was higher than that of E7.5S (57,400). Meanwhile, the 4-PAV aged polymer peak of S11S also had a higher molecular weight (58,470) than that of E11S (130,800). It indicates the degradation of SBS polymer in SK asphalt was not as severe as that in Esso asphalt. Thus, the rheological property of HCPMAs prepared with SK asphalt is expected to be improved compared with HCPMAs with Esso asphalt. So, the rutting factor and $J_{nr3.2}$ between HCPMAs in the 4-PAV ageing state with different base asphalt were compared, and the results were revealed in **Figure 11**. It is evident that HCPMAs with SK asphalt performed better with different SBS contents after 4-PAV ageing.

### 3.3 Principal component analysis

In this paper, ten types of different parameters were used to characterized 32 HCPMA samples in different with different base bitumen, SBS dosage and aging state. For further analysis of the relationship between these parameters, and afterwards, establish the fitting equation between different parameters, principal component analysis was conducted.

Principal component analysis (PCA) is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables (entities each of which takes on various numerical values) into a set of values of linearly uncorrelated variables called principal components (K. Wang et al. 2018). In this paper, the PCA was conducted on 32 samples in different ageing state and ten parameters by using SPSS software. According the analysis report, the first and second principal components can explain more than 75% variance, indicating that the validity of PCA analysis. Therefore, the relationship between the asphalt samples and the studied variables is illustrated in **Figure 12**. The first principal mainly describes the ageing of asphalt, which is consisted of $I_{so}$, $I_{co}$, and $I_{so}+I_{co}$. It highlights that the ageing of the asphalt play a dominant role as first principal represents most variance level (47%). The content of SBS is positively correlated with the second principal, which can be associated with the active SBS content. Based on the results of this analysis, $R_{3.2}$ was positively correlated with the second principal, while $J_{nr3.2}$ and phase angle were negatively correlated. Thus, the ratio of viscosity and elasticity of HCPMAs were mainly determined by the SBS content and the SBS degradation. On the other hand, the rutting factor and the modulus were both positively correlated with the first and second principal, rendering both the ageing 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 oxidation degree and active polymer content. Meanwhile, the oxidation degree can be characterized with Ico, and the active SBS content can be characterized with SBS content (SBS%) and polymer damage index ($I_{B/S}$). Thinking from the opposite direction, every parameter can be described with these two principals. For example, complex modulus and phase angle, most commonly used parameters, can be described with these two principals with exponential functions. The exponential functions can are as follows

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

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

In the equation:

$K_1$,$K_4$: Coefficient of the volume occupied by SBS polymer after swelling,
SBS%: SBS content added in the fabrication of HCPMA,
$SBS\% \cdot I_{B/S}$: Effective SBS content considering degradation during ageing,

$K_2$, $K_5$: Impact coefficient of base asphalt ageing,

$K_3$, $K_6$: Impact coefficient of SBS polymer degradation.

$\delta_{Base\ asphalt}$, $G^*_{Base\ asphalt}$: Phase angle and complex modulus of base asphalt in original state at 82 °C.

$\delta_{SBS}$, $G^*_{SBS}$ : Phase angle and complex modulus of SBS polymer at 82 °C. According to DMA test results, $\delta_{SBS} = 11.2$ ° and $G^*_{SBS}$=106,000 Pa.

The regression results and fitted equation were presented in **Figure 13** and **Table 3**. The data has been divided into two groups, one belonging to HCPMA prepared with Esso asphalt, and the other belonging to HCPMA with SK asphalt. As shown in **Figure 13**, all four fitting formula had a high R2 (>0.7), indicating a good fit. From this point of view, the evolution of rheological parameters along with the ageing can be predicted with the results of FTIR test and the fundamental rheological parameter of base asphalt and SBS polymer in the original state. Unfortunately, though the basic rheological parameters of base asphalt have been considered in the fitting equation, the G* or δ of HCPMA with different base asphalt could not be predicted with only one equation. One main reason is that the swelling states of SBS polymer in Esso asphalt and SK asphalt are very different, and it further influences the degradation level of SBS polymer, as seen in GPC test result.

## 4 CONCLUSION

The presented study was designed to explore the evolution of chemical and rheological properties of high content polymer modified asphalt (HCPMA) along with the ageing process and to comprehend the influential factors of ageing. Conclusions are as follows:

- The ageing of HCPMA is a combination of oxidation of base asphalt and degradation of SBS polymer leading to increase and decrease of elasticity, respectively. The oxidation of base asphalt goes on all the time, but the degradation of SBS is fast at the beginning and slow down after 20 hours of PAV ageing. As a result, HCPMA becomes viscous at first until the end of the 20 hours PAV and then turns to be more elastic until the 80 hours PAV.
- When SBS content was more than 7.5%, a considerable amount of SBS polymer remained even after 80 hours of PAV ageing. Its molecular weight was reduced from 230,000 to 70,000~130,000, but the modification effect was still good. Therefore, the most effective way to maintain considerable properties of HCPMA is to increase the content of SBS.
- The modification of SBS polymer have a significant function of retarding the oxidation and hardening of asphalt binder, especially before the end of first PAV aging process. It is mainly because the curing of SBS polymer is still going on at the early stage of aging, and the degradation of SBS polymer can also retard the hardening of HCPMA.

- HCPMA prepared with Esso base asphalt are easier to suffer from ageing. It may be due to more aromatics in Esso asphalt, which leads to the presence of SBS as smaller particles and more natural to degrade.
- PCA showed that the 10 parameters of 32 asphalt samples could be explained by two principals: oxidation level of asphalt and SBS content. Based on PCA results, G* or δ of HCPMA can be well fitted ($R^2$>d0.7) by the exponential function of SBS content and ageing index. Thus, G* or δ can be well predicted according to the fitting formula. Unfortunately, this fitting can only be used for HCPMA prepared with the same base asphalt.

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