

Laboratory evaluation of the effects of long-term aging on high content polymer modified asphalt binder

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

3

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37 **Abstract:** The most common polymer-based modifier for asphalt binders is the
38 styrene-butadiene-styrene (SBS), which owns superior mechanical characteristics to
39 asphalt, such as increased toughness and resistance against permanent deformation.
40 These properties improved further when higher amounts of SBS are incorporated in
41 asphalt. Although this type of asphalt binders, named high content polymer modified
42 asphalt (HCPMA) binders are used mainly for porous pavements, limited research on

43 their ageing performance has been conducted. In this paper, Gel Permeation
44 Chromatography (GPC), Fourier Transform Infrared (FTIR) and Dynamic shear
45 rheology (DSR) were used to explore the evolution of chemical and rheological
46 properties of HCPMA along with the ageing process and to comprehend factors
47 affecting ageing. Firstly, this study identified that the ageing of HCPMA was a
48 combination of oxidation of base asphalt and degradation of SBS polymer leading to
49 an increase and a decrease of elasticity, respectively. The degradation of SBS happened
50 mostly at the beginning and slowed down after ageing in Pressure Ageing Vessel
51 (PAV) for 20 hours, which resulted in worst rutting resistance for HCPMA. The second
52 finding is that, when SBS content was higher than 7.5%, more than half of SBS polymer
53 remained even after 80 hours of PAV ageing. Although the molecular weight of SBS
54 decreased from 230,000 to 70,000 due to the degradation, its modification effect was
55 still significant. Thirdly, highly modification of SBS can retard the oxidation and
56 hardening of base asphalt, especially from origin to first PAV aging state. Finally,
57 Principal Component Analysis showed ten parameters used in this study could be
58 explained by two principals: SBS content and asphalt ageing level. Based on PCA
59 results, the complex modulus (G^*) or phase angle (δ) of HCPMA can be well fitted
60 ($R^2 > 0.7$) by the exponential function of SBS content and ageing index.

61

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

64

65 1 INTRODUCTION

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

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

88 In addition to SBSMA, high content polymer modified asphalts (HCPMA) are
89 prepared by the addition of high content of SBS (>6%) showing improved toughness
90 and thus increased resistance against raveling (i.e., loss of aggregates from the surface
91 of pavements) (Habbouche et al. 2018; Alvarez, Martin, and Estakhri 2011; Liang et al.
92 2017; Geng, Li, and Han 2016; Xu et al. 2016; Griebel et al. 2016; F. Zhang and Hu
93 2017). Therefore, these asphaltic materials are ideal for open-graded (porous) asphalt
94 pavements, and have been applied in a number of pavement structures all over the world.
95 Nevertheless, the primary challenge faced by many researchers on applying HCPMA
96 in porous pavements is the ageing. Firstly, because of the open gradation of porous
97 pavement, plenty of oxygen is introduced, which results in severe ageing. Meanwhile,
98 owing to the high viscosities of HCPMA, they usually have higher mixing (180~190°C)
99 and paving (170~180°C) temperatures. Furthermore, due to the unsaturated double
100 carbon bond (C=C) SBS possess, this polymer is sensitive to oxygen and thus to
101 oxidative ageing damage (H. Zhang et al. 2017; Lee et al. 2011; Y. Wang, Sun, and Qin
102 2015). Although the aging mechanism of SBS modified bitumen is quite complex,
103 including the oxidation of base bitumen, chain scission of polybutadiene segment in
104 SBS polymer, cross-linking or branching reaction between polymers, as well as grafting
105 reaction between SBS polymer and bitumen component. The chain scission reaction
106 occurs at polybutadiene segment play the main role, which lead to a significant decrease

107 of molecular weight SBS polymer and a dramatic decrease of modification effect.
 108 (Ouyang et al. 2006; Pospíšil et al. 1999; Cortizo et al. 2004; Y. Wang, Sun, and Qin
 109 2015). Considering the high content SBS used in HCPMA, the degradation of SBS
 110 polymer will cause severe performance deterioration in asphalt pavements.

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

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

129

130 2 MATERIALS AND METHODS

131

132 2.1 Materials

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

140 **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 (°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
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141

142 Radial SBS of 230,000 g/mol average molecular weight (Mw) was chosen as
 143 the modifier (30wt% of styrene). For the preparation of HCPMA, the added content of
 144 SBS modifier was from 4.5% to 15% by the weight of base asphalt. In China, 4.5wt%
 145 and 7.5wt% of SBS are the typical dosages for dense and porous asphalt pavements,
 146 respectively. The specific description of samples can be seen in **Table 2**. To enhance
 147 the compatibility between asphalt and SBS polymer, a particular type of resin and
 148 0.15wt% of sulfur used as agent able to form crosslinks between polymers were added,
 149 which enhanced the storage stability to the HCPMA. All samples have passed the
 150 segregation test (ASTM D5976) to ensure the uniformity of the asphalt.

151 **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

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

157

158 2.2 Experimental Methods

159

160 2.2.1 Dynamic shear rheometer (DSR)

161

162 Frequency sweep test

163 The dynamic oscillatory test was performed on a TA DSR AR1500ex to obtain the
 164 complex modulus, phase angle and rutting factor of HCPMA. As the PG high-
 165 temperature grade of HCPMA is from 82 °C to 88 °C, the dynamic oscillatory test was
 166 employed at 82 °C. The test was conducted at 10 rad/s using 25-mm plate with a 1-mm
 167 gap (AASHTO T 315). Two replicates were performed for each asphalt sample, and the

168 average value was recorded.

169

170 *Multiple stress creep and recovery (MSCR) test*

171 The MSCR test can be used to evaluate the viscoelastic properties of polymer modified
172 asphalt(J. A. D'Angelo 2009; J. D'Angelo and Dongré 2009; Huang and Tang 2015).

173 In this paper, the MSCR test was performed in the same DSR device described above
174 to obtain non-recoverable creep compliance (J_{nr}) and percent recovery (R) at 0.1 kPa
175 and 3.2 kPa (AASHTO 350). Two replicates were performed for each asphalt sample,
176 and the average value was recorded.

177

178 *2.2.2 Fourier transform infrared (FT-IR) spectroscopy*

179 The infrared spectra values were collected using a Bruker TENSOR FT-IR spectrometer
180 equipped with a reflection diamond ATR accessory. To quantify the oxidation-related
181 change in IR absorption, band areas rather than peak absorbance values were used and
182 the functional groups of interest were identified. Three replicates of each asphalt
183 samples were conducted, and the average value was recorded. The $AR_{\tilde{\nu}}$ values were
184 normalized to the total sum of all band areas ($\sum AR_{\tilde{\nu}}$), and the indexes are calculated
185 as follows:

186

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

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

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

187

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

189

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

190

191 Carbonyl and sulfoxide are the most commonly used indicator to measure the chemical
192 oxidation of bitumen binder and the absorbance values of polybutadiene and
193 polystyrene are generally considered to reflect the degradation of mechanical properties
194 of the polymers. Therefore, in this study, the carbonyl index (I_{co}) and sulfoxide index
195 (I_{so}) were employed to evaluate the oxidation level of base asphalt and a polymer
196 damage index ($I_{B/S}$) was used to reveal the degradation of SBS polymer. SBS consists
197 of polybutadiene (PB) and polystyrene (PS), in which the PS segment possesses a
198 corresponding peak at 699 cm^{-1} and PB segment possess a peak at 965 cm^{-1} (Lin et al.
199 2018, 2017; Lamontagne et al. 2001; Yut and Zofka 2011). As the unsaturated C=C
200 bond on the PB segment is an easy target for oxygen, it can be aged and subsequently
201 degraded. PS is relatively stable and exhibited much smaller change after ageing. Thus,
202 the newly proposed $I_{B/S}$ was employed to evaluate the damage level of SBS in PMA,
203 which is not influenced by the SBS concentration and the scanning depth (Yan, Huang,

204 and Tang 2017; Yan et al. 2018).

205

206 *2.2.3 Gel permeation chromatography (GPC)*

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

216

217 **3 RESULT AND DISCUSSION**

218

219 **3.1 Rheological Characteristics**

220

221 *3.1.1 Complex modulus*

222 As illustrated in **Table 2**, the high-temperature performance grade (PG) of HCPMA
223 ranges from 76 to 88 °C. As a result, 82 °C was chosen as the test temperature for the
224 DSR test for fully distinguishing the high-temperature properties of HCPMA. As shown
225 in **Figure 1**, the evolution of the modulus of base asphalt (Esso and SK) raised
226 significantly along with the increase of ageing duration. As for E4.5S, the modulus still
227 increased, while the increasing rate was lower than that of Esso asphalt. When SBS
228 dosage reached 15%, the modulus even decreased after PAV ageing, due to the fact that
229 the ageing of HCPMA consisted of two counterparts. On the one hand, the oxidation
230 of base asphalt led to an increase of modulus. On the other hand, the severe degradation
231 of SBS polymer had a softening effect on HCPMA, which cause modulus decrease.
232 When SBS dosage is less than 7.5%, the oxidative aging of base asphalt played the
233 dominant role and the modulus increased. While, when the SBS dosage was more than
234 7.5%, the degradation of SBS played a more significant role, which led to modulus
235 decrease before 20 hours of PAV aging. From this perspective, the with the increase of
236 SBS content not only have a modification effect, but also have the function of retarding
237 the oxidation of base bitumen, especially when SBS content is more than 7.5%.

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

243

244 *3.1.2 Phase angle*

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

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

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

261

262 3.1.3 Rutting factor

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

271

272 3.1.4 Non-recoverable creep compliance (J_{nr})

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

285

286 3.1.5 Percentage recovery ($R_{3.2}$)

287 According to **Figure 5**, $R_{3.2}$ and $R_{0.1}$ of base asphalt were lower than 10%, indicating

288 base asphalt mainly showed the viscous response at 82 °C. As for HCPMA, the addition
289 of SBS led to a noticeable increase of percent recovery in the original state. Similar to
290 the evolution of $J_{nr3.2}$, the percent recovery of HCPMA shows the lowest value at PAV
291 ageing state. These results also showed the ageing HCPMA consisted of oxidation of
292 base asphalt and the degradation of SBS polymer. Furthermore, percent recovery at a
293 higher stress level (3.2kPa) shows improved differentiation degree. As seen in **Figure**
294 **5(a)** and **(b)**, $R_{3.2}$ in original state and 4-PAV ageing state increased along with the rise
295 of SBS content. However, $R_{0.1}$ in **Figure 5(c)** and **(d)** was nearly the same in original
296 state and 4-PAV ageing state.

297

298 **3.2 Chemical Characterization**

299

300 *3.2.1 Chemical compositional changes*

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

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

329 To reveal the effect of SBS content and base asphalt type on the ageing of HCPMA,

330 carbonyl (I_{co}) and sulfoxide (I_{so}) index were illustrated in **Figure 7**. From **Figure 7(a)**,
331 SBS content had a minimal influence on the carbonyl formation. Under the PAV ageing,
332 the carbonyl index HCPMA with lower SBS content is relatively high. However, under
333 4-PAV ageing, the carbonyl index of HCPMA with different SBS content was almost
334 the same. Similar phenomena occurred in HCPMA prepared with base asphalts. It was
335 mainly because with the increase of SBS content, the viscosity of HCPMA increased
336 significantly and oxygen enters relatively slower. However, when the ageing level came
337 to 4 times PAV (i.e., 80 hours), oxygen had sufficient time to penetrate HCPMA, so that
338 the carbonyl index was almost the same. As for the influence of the type of base asphalt,
339 the carbonyl index of HCPMA prepared with Esso asphalt was relatively higher than
340 that of HCPMA prepared with SK asphalt. The difference in carbonyl index was not
341 apparently in PAV ageing, whereas in the 4-PAV, the difference was significant. The
342 most likely causes were the different composition of these two base asphalt binders.

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

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

363

364 3.2.2 Molecular weight changes

365 GPC tests were applied for component distribution analysis of base asphalt and
366 HCPMA in different ageing states (Canto et al. 2006; Wahhab H. I. Al-Abdul et al. 1999).
367 The order of elution is related to the molecular weight (Mw) of the studied components.
368 Firstly, high molecular weight species elute, followed by molecules with ever
369 decreasing molecular weight. For HCPMA asphalt, there were mainly three observable
370 peaks from left to the right, corresponding to the incorporated polymer (14~15 min),

371 asphaltenes (16~17 min) and maltenes (20~22 min). The normalised chromatogram of
372 base asphalt is illustrated in **Figure 9**, and the HCPMAs' was shown in **Figure 10**.

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

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

397 The section below describes the influence of base asphalt on the ageing of HCPMA
398 and the results are illustrated in **Figure 10(c)-(f)**. The molecular weight polymer peak
399 of S7S in 4-PAV state was 99,500, which was higher than that of E7.5S (57,400).
400 Meanwhile, the 4-PAV aged polymer peak of S11S also had a higher molecular weight
401 (58,470) than that of E11S (130,800). It indicates the degradation of SBS polymer in
402 SK asphalt was not as severe as that in Esso asphalt. Thus, the rheological property of
403 HCPMAs prepared with SK asphalt is expected to be improved compared with
404 HCPMAs with Esso asphalt. So, the rutting factor and $J_{nr3.2}$ between HCPMAs in the
405 4-PAV ageing state with different base asphalt were compared, and the results were
406 revealed in **Figure 11**. It is evident that HCPMAs with SK asphalt performed better
407 with different SBS contents after 4-PAV ageing.

408

409 **3.3 Principal component analysis**

410 In this paper, ten types of different parameters were used to characterized 32 HCPMA
411 samples in different with different base bitumen, SBS dosage and aging state. For
412 further analysis of the relationship between these parameters, and afterwards, establish

413 the fitting equation between different parameters, principal component analysis was
 414 conducted.

415 Principal component analysis (PCA) is a statistical procedure that uses an
 416 orthogonal transformation to convert a set of observations of possibly correlated
 417 variables (entities each of which takes on various numerical values) into a set of values
 418 of linearly uncorrelated variables called principal components (K. Wang et al. 2018). In
 419 this paper, the PCA was conducted on 32 samples in different ageing state and ten
 420 parameters by using SPSS software. According the analysis report, the first and second
 421 principal components can explain more than 75% variance, indicating that the validity
 422 of PCA analysis. Therefore, the relationship between the asphalt samples and the
 423 studied variables is illustrated in **Figure 12**. The first principal mainly describes the
 424 ageing of asphalt, which is consisted of I_{so} , I_{co} , and $I_{so+I_{co}}$. It highlights that the ageing
 425 of the asphalt play a dominant role as first principal represents most variance level
 426 (47%). The content of SBS is positively correlated with the second principal, which can
 427 be associated with the active SBS content. Based on the results of this analysis, $R_{3.2}$ was
 428 positively correlated with the second principal, while $J_{nr3.2}$ and phase angle were
 429 negatively correlated. Thus, the ratio of viscosity and elasticity of HCPMAs were
 430 mainly determined by the SBS content and the SBS degradation. On the other hand, the
 431 rutting factor and the modulus were both positively correlated with the first and second
 432 principal, rendering both the ageing level of asphalt and the active SBS content had a
 433 significant influence on the rutting resistance of HCPMA.

434 According to the results of PCA, 10 types of characterization parameters can be
 435 attributed to oxidation degree and active polymer content. Meanwhile, the oxidation
 436 degree can be characterized with I_{co} , and the active SBS content can be characterized
 437 with SBS content (SBS%) and polymer damage index ($I_{B/S}$). Thinking from the opposite
 438 direction, every parameter can be described with these two principals. For example,
 439 complex modulus and phase angle, most commonly used parameters, can be described
 440 with these two principals with exponential functions. The exponential functions can be
 441 as follows
 442

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

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

443

444 In the equation:

445

446 K_1, K_4 : Coefficient of the volume occupied by SBS polymer after swelling,

447 SBS%: SBS content added in the fabrication of HCPMA,

448 $SBS\% \cdot I_{B/S}$: Effective SBS content considering degradation during ageing,

449 K_2, K_5 : Impact coefficient of base asphalt ageing,
450 K_3, K_6 : Impact coefficient of SBS polymer degradation.
451 $\delta_{Base\ asphalt}, G_{Base\ asphalt}^*$: Phase angle and complex modulus of base asphalt in
452 original state at 82 °C.
453 δ_{SBS}, G_{SBS}^* : Phase angle and complex modulus of SBS polymer at 82 °C.
454 According to DMA test results, $\delta_{SBS} = 11.2^\circ$ and $G_{SBS}^* = 106,000$
455 Pa.

456

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

469

470 **4 CONCLUSION**

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

474

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

- 491 • HCPMA prepared with Esso base asphalt are easier to suffer from ageing. It may
 492 be due to more aromatics in Esso asphalt, which leads to the presence of SBS as
 493 smaller particles and more natural to degrade.
- 494 • PCA showed that the 10 parameters of 32 asphalt samples could be explained by
 495 two principals: oxidation level of asphalt and SBS content. Based on PCA results,
 496 G^* or δ of HCPMA can be well fitted ($R^2 > 0.7$) by the exponential function of SBS
 497 content and ageing index. Thus, G^* or δ can be well predicted according to the
 498 fitting formula. Unfortunately, this fitting can only be used for HCPMA prepared
 499 with the same base asphalt.

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