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Changing Regularity of SBS in the Aging Process of Polymer Modified Asphalt Binder Based on GPC Analysis

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Abstract: The investigation on aging mechanism of Styrene-Butadiene-Styrene block copolymer (SBS) in polymer modified asphalt binder (PMA) is helpful to the application of PMA and the selection of anti-aging technology. However, it is very complex because of the various chemical molecular structures of SBS and asphalt binder, as well as the complicated physical and chemical reaction between the two components. In order to study the reaction mechanism of SBS in the preparation and service life of PMA, the molecular changes of SBS were studied through gel permeation chromatography (GPC) analysis before and after the rolling thin film oven (RTFO) test and pressure aging vessel (PAV) test of SBS modified asphalt binders. The results showed that the crosslink of SBS was the main reaction in the preparation of PMA with the increasing of molecular weight. The degradation of SBS was a minor reaction in the RTFO aging, and SBS still had enough effect to modify the performance of asphalt binder after RTFO aging. SBS had significant degradation and lost the capability of modifying the performance of asphalt binder because of the decline of molecular weight after PAV aging. The conclusions prove that the GPC method can explain the crosslink and degradation mechanism of SBS. The degradation of linear SBS and radial SBS in PMA is slightly different. The degradation of pure SBS is more serious when it was aged in the PAV test alone (no blending with asphalt binder), compared with the SBS in PMA. The reason is that the SBS in PMA is covered by asphalt binder and has less contact with oxygen.

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***Key words**: Aging; Degradation; GPC; Reaction mechanism; SBS modified asphalt.*

Introduction

Polymer modified asphalt binder (PMA) has been widely used in flexible pavements because of its perceived superior performance compared to base asphalt binder. Styrene-Butadiene-Styrene (SBS) block copolymer is the most widely used polymer to modify asphalt binder [1-5]. SBS exhibits a two-phase morphology, the polystyrene blocks with a glass transition (T_g) around 100℃, and the polybutadiene blocks with a glass transition around -80℃. The polystyrene block provides the strength of the material, while the polybutadiene block contributes to the elasticity [6, 7]. When asphalt binder and SBS are blended, the elastomeric phase swells and absorbs the maltene fraction of asphalt binder. At the same time, a three-dimensional polymer network is formed throughout the asphalt matrix at a suitable SBS concentration, normally between 3% and 5% [8]. SBS can contribute to asphalt binder strength and elastic properties in a wide temperature range [4, 5]. As a result, it can improve various aspects of asphalt mixture performance, such as resistance to rutting, thermal cracking, fatigue damage, and temperature susceptibility.

During the production and service life of the pavement, polymer modified asphalt binder will become aged. The degradation of SBS occurs because of heat, oxygen, light, and other effects, resulting in the decrease in molecular size of SBS [9-16]. This can also reduce its effectiveness in improving the asphalt binder performance and shorten the service life of asphalt pavement. The aging mechanism of SBS in modified asphalt binder is very complex because of the various physicochemical reactions between SBS and asphalt binder, especially with the aid of a stabilizer [8]. The study on the aging mechanism of SBS is helpful to the application of polymer modified asphalt and the selection of anti-aging measures [17-20]. It is not enough to study the performance change of polymer modified asphalt binder and the chemical reaction of asphalt binder only [9, 12]. However, the characterization of the chemical reaction behavior of SBS is rarely reported during the life cycle of PMA, which contains the preparation of PMA, the production of polymer modified asphalt mixture, and whole service life of the asphalt pavement [11-13, 15].

In this study, the degradation behavior of SBS in the preparation and aging process of SBS modified asphalt binder was investigated by gel permeation chromatography (GPC) analysis and PMA performance testing. The polymer modified asphalt binder with SBS copolymers of different architecture were prepared, then both the rolling thin film oven (RTFO) test and pressure aging vessel (PAV) test were used to simulate the short-term aging in the production of asphalt pavement and the long-term aging in service life of asphalt pavement. The physical properties of PMA were measured including penetration, softening point, ductility, viscosity, and visco-elasticity. SBS copolymer was also aged by PAV. The molecular weight and its distribution of SBS copolymers were measured by GPC in five conditions, including original SBS, SBS in original PMA, SBS in PMA after RTFO, SBS in PMA after PAV, and SBS aged by PAV alone, to determine the reaction effect of SBS on the performance of polymer modified asphalt binder.

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Table 1. Base Asphalt Technique Indexes.

State	Penetration at 25°C (0.1mm)	Softening Point (°C)	Ductility at 15°C (cm)	Penetration Index	Viscosity at 135°C(Pa·s)
Original	72	46	＞100	-1.3	0.4
RTFOT	49	51	78	-0.9	0.5
PAV	27	58	5.6	0.2	0.9

Table 2. Change of Molecular Weight of SBS in PMA.

Sample	Index	Original SBS	Unaged PMA	RTFO PMA	PAV PMA
SBS-1	M_n	1.48×10^5	2.23×10^5	1.66×10^5	7.22×10^4
	M_w	1.71×10^5	2.76×10^5	2.31×10^5	1.14×10^5
SBS-2	M_n	1.42×10^5	1.87×10^5	1.40×10^5	8.99×10^4
	M_w	1.86×10^5	2.99×10^5	2.24×10^5	1.25×10^5

Experimental Program

Materials

Asphalt binder from China (Penetration-grade 70#) was used as the base asphalt for preparation of polymer modified asphalt binder. The physical performance indexes of base asphalt binder are shown in Table 1. Two types of SBS (SBS-1 and SBS-2) produced in China were used as asphalt modifying agents in the study. The structures of SBS copolymer of SBS-1 and SBS-2 were linear and radial respectively. The content of SBS in the polymer modified asphalt binder was 4% by weight.

Preparation of SBS Modified Asphalt

Asphalt binders and SBS were blended at 170°C---180°C by a high-speed shearing mixer. To resolve the problem of separation of SBS from asphalt binder, solubilizer and stabilizer were added into the SBS modified asphalt binder. The shear impeller speed ranged from 5000 rpm–6000 rpm, and mixing duration was 60 minutes. Then the blend processing of SBS and asphalt continued in a swelling time of 30 minutes under the condition of 150°C. SBS-1 and SBS-2 modified base asphalt binders were numbered PMA-1 and PMA-2 respectively.

Aging Procedure

The aging procedure of the SBS modified asphalt binder samples was performed using two methods. 1) The rolling thin film oven (RTFO) test (ASTM D2872): the samples of SBS modified asphalt binders were aged at 163°C for 75 min using P877 rotary thin film oven to simulate the short-term aging of asphalt in the production of asphalt mixture and paving process of pavement. 2) The pressure aging vessel (PAV) test (ASTM D6521): SBS modified asphalt binders (after RTFO aging) were aged for 20 h under the condition of 100 °C and 2.1 MPa of air using PR9300 pressure aging instrument, to simulate the long-term aging of asphalt pavement equal to about 5 years.

The oxidative aging of pure SBS copolymer was performed as well. The two types of pure SBS (SBS-1 and SBS-2), which were not blended with base asphalt binder, underwent PAV aging alone.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) analysis can be used to test the molecular weight and molecular weight distribution of polymer [17, 18]. The test method can separate polymer molecule according to molecular size when the polymer solution flows through the special composition of the porous column. The GPC analysis of SBS modified asphalt binder can be used to obtain SBS molecular weight distribution curve.

PL-GPC50 gel permeation chromatography was used with three columns and the UV absorption detector in this paper. The mobile phase was tetrahydrofuran (THF), and its flow rate was l.0 mL/min. The sample concentration was 2.0 mg/mL, and 100 μL of the sample was injected into the columns.

Dynamic Mechanical Analysis

Dynamic shear properties of asphalt binder were measured with a dynamic shear rheometer (DSR). The temperature sweeps with 3°C increments were carried out at 10 rad/s in temperature ranges of 50–90°C in dynamic mechanical analysis (DMA). The parallel plates with a diameter of 25.0 mm and a gap width of 1.0 mm were applied. The actual torque was measured and the complex modulus (G^*) and phase angle (δ) were calculated respectively in the test.

Results and Discussion

Results of GPC and DMA

The molecular weight distribution of SBS was analyzed in order to ascertain the change of SBS in the preparation and aging process of PMA. The molecular weight (number-average molecular weight M_n and weight-average molecular weight M_w) and molecular weight distribution curves of SBS after the preparation process are shown in Table 2 and Figs. 1 and 2. The molecular weight distribution curves of SBS in PMA after RTFO and PAV are shown in Figs. 3 and 4. In the figures, the relative molecular weight of SBS is on the value of the abscissa and the corresponding content is on the ordinate. The total area under the curve is 1.0.

The physical properties of SBS modified asphalt binder before and after aging are shown in Table 3. Although both PMA-1 and PMA-2 binders have been modified with linear SBS and radial SBS, only slight differences in penetration, softening point, ductility, and viscosity were observed before and after aging. However, the penetration of base asphalt binder decreased from 72 to 49 and 27

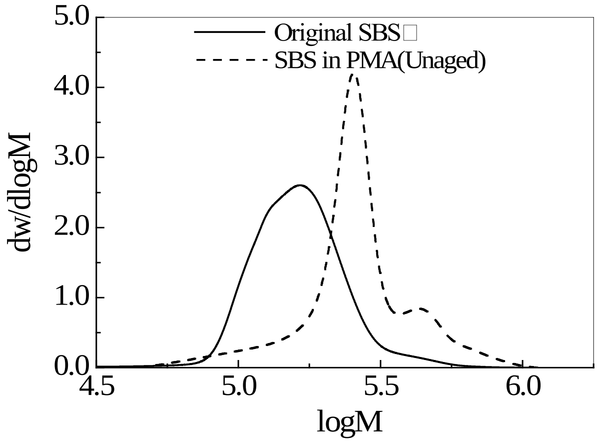

Fig. 1. GPC Result of SBS-1 after Preparation Process of PMA.

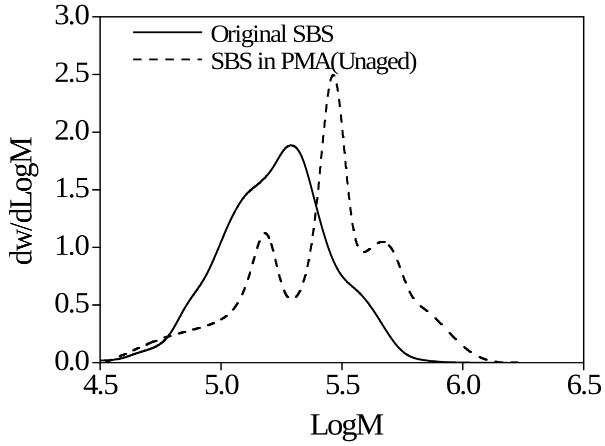

Fig. 2. GPC Result of SBS-2 after Preparation Process of PMA.

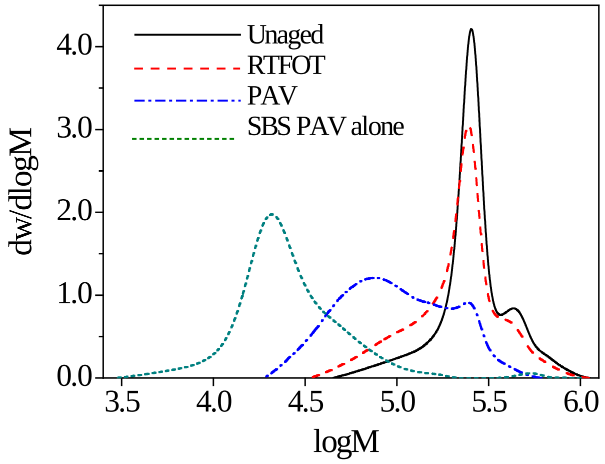

Fig. 3. GPC Result of SBS-1 in PMA after PAV Aging.

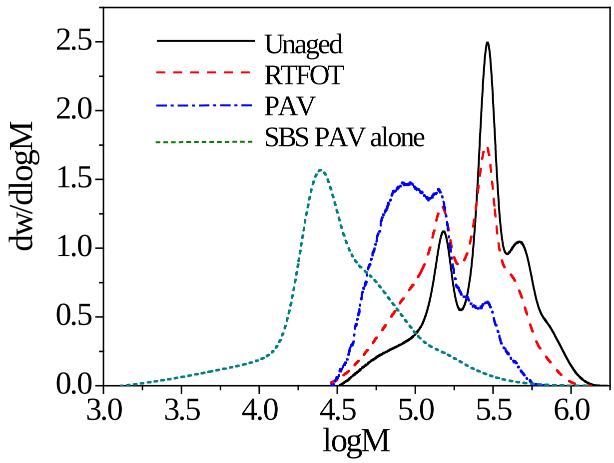

Fig. 4. GPC Result of SBS-2 in PMA after PAV Aging.

Table 3. SBS Modified Asphalt Technique Indexes.

State	Samples	Penetration at 25°C (0.1 mm)	Softening Point (°C)	Ductility at 5°C (cm)	Penetration Index	Viscosity at 135°C (Pa·s)
original	PMA-1	59	80	37	0	1.7
	PMA-2	55	86	42	0.1	1.6
RTFOT	PMA-1	43	68	17	0.2	2.1
	PMA-2	41	70	18	0.2	2.2
PAV	PMA-1	31	71	0	0.3	2.6
	PMA-2	30	74	3	0.4	2.8

after the RTFO and PAV aging, respectively, and the penetration of PMA-1 decreased from 59 to 43 and 31 after the RTFO and PAV aging, respectively. The results indicated that the anti-aging performance of PMA is superior to that of base asphalt binder from the penetration changes of asphalt binders after the aging test. The similar tendency can be obtained from the change of viscosity as shown in Table 1 and Table 3.

The dynamic mechanical analysis (DMA) results of polymer modified asphalt binders before and after aging are shown in Figs. 5 – 8. The micrograph of SBS in modified asphalt binder is shown in Fig. 9.

Properties Change of SBS during the Preparation of PMA

Figs. 1 and 2 are the molecular weight distribution of SBS-1 and SBS-2 respectively. The figures show that the molecular weight distribution curves of SBS in PMA move in the direction of high molecular weight. The content of large molecular SBS (the right side of the curves) in modified asphalt binder increased after the preparation process. As shown in Table 2, the average molecular weight (number-average molecular weight M_n and weight- average molecular weight M_w) of SBS increased after the preparation process. The small molecules of SBS are beyond the scope of the

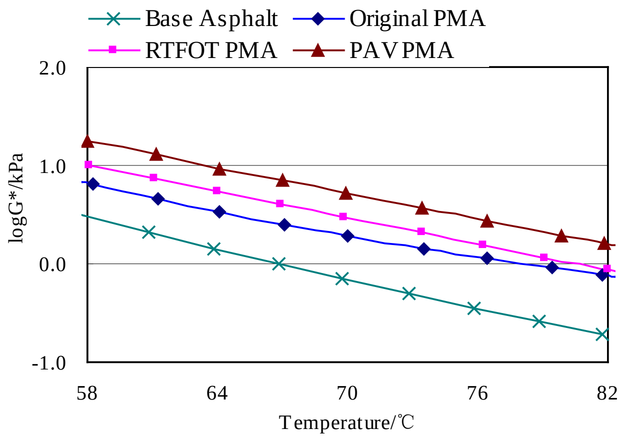

Fig. 5. Complex Modulus (G*) of PMA-1 before and after Aging.

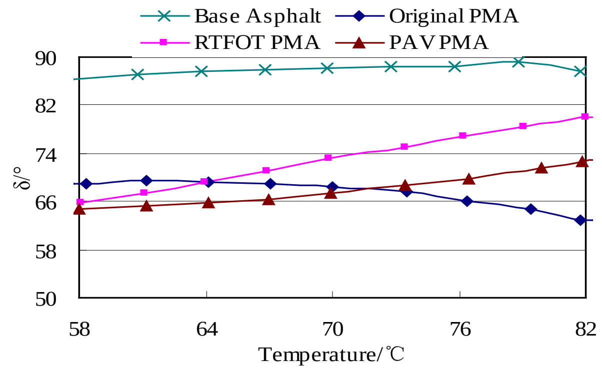

Fig. 6. Phase Angle (δ) of PMA-1 before and after Aging.

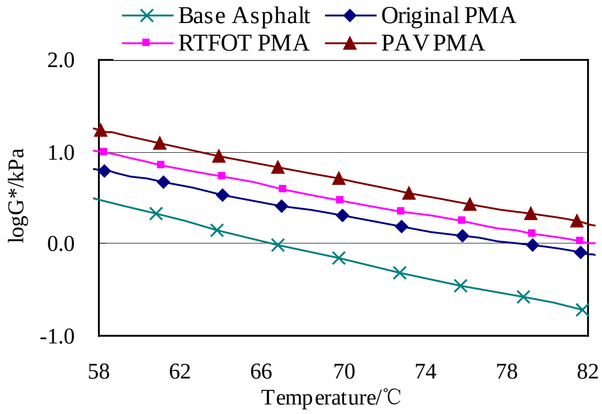

Fig. 7. Complex Modulus (G*) of PMA-2 before and after Aging.

original curve in the Figs. 1 and 2, indicating that the content of SBS with small molecule increased by a small amount. This occurred because trace amounts of SBS degraded. The crosslink and degradation reactions occurred simultaneously in the process of SBS modified asphalt binder. It was proven that the crosslink reaction was the main reaction in the modification process.

The molecular structures of SBS and asphalt binder are significantly different. SBS is spontaneously incompatible with asphalt binder [8]. And the preparation process of polymer modified asphalt binder requires high temperature and high speed shear

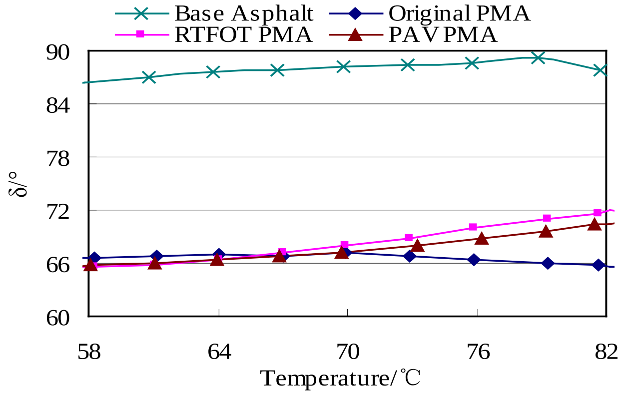

Fig. 8. Phase Angle (δ) of PMA-2 before and after Aging.

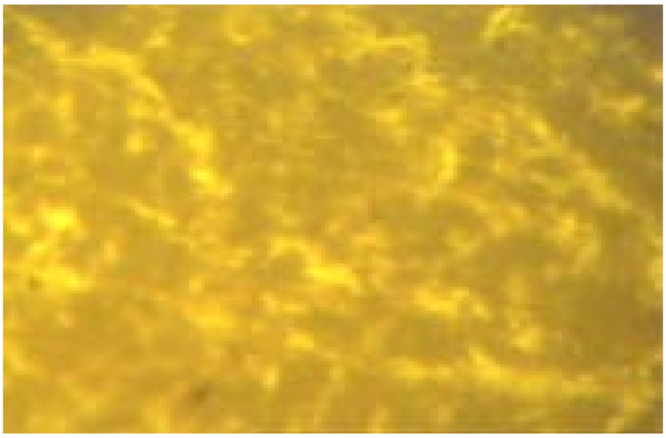

Fig. 9. Micrograph of SBS in Modified Asphalt.

conditions. The reaction process is as follows: SBS was dispersed into the asphalt binder in the situation of high temperature and shear strength. On the promotion of the stabilizer for cross-linking reaction, part of the SBS block opened and generated free radicals constantly. Then crosslink reaction occurred within asphalt binder or itself. The SBS with large molecular weight was produced and further formed into the continuous phase structure [4]. The bright part in Fig. 9 is the crosslink structure of SBS. This can improve the stability of SBS modified asphalt binder, and prevent the separation of SBS and asphalt binder, which is important to improve the performance of asphalt binder [2, 4]. This can increase the complex modulus and reduce the phase angle of PMA compared with base asphalt binder in Figs. 5 – 8.

Degradation of SBS during the Production of Pavement

The molecular weight distribution curves of SBS by GPC test after RTFO aging are shown in Figs. 3 and 4. Figs. 3 and 4 show that the content of small SBS molecular (the left side of the curves) in SBS modified asphalt binder increased after aging, while the content of large SBS molecular (the right side of the curves) decreased. As a result, the molecular weight for the whole SBS system decreased when subjected to aging. As shown in Table 2, the average molecular weight (M_w and M_n) of SBS after RTFO aging decreased. The reduction of the SBS peak indicates that the SBS crosslinked

(a) Original SBS (b) Aged SBS

Fig. 10. Picture of Original SBS and Aged SBS.

structure has a certain degree of degradation [10, 12, 15]. The SBS long strand breaks into fragments at the expense of generating low molecular weight substances [19, 20].

The average molecular weight of two kinds of SBS (linear structure SBS and radial structure SBS) has decreased after RTFO aging. The aging degradation took place in different types of SBS. However, the results show that the decrease degrees of average molecular weight of the two types of SBS are different. The ratio of M_n after aging and before aging of SBS-1 is 74.5%, and the ratio of SBS-2 is 74.7%. The two ratios are uniform. But the ratios of M_w of SBS-1 and SBS-2 are 83.6% and 74.8%, respectively. The results indicated that these two types of SBS had different aging speeds. The degradation of linear SBS is lower than radial SBS, but the difference is slight.

The molecular weight distribution curve in Figs. 3 and 4 shows that the molecular weight of SBS after aging changed less in the overall rate. The macromolecules in SBS whose molecular weight is more than 10^5 still account for a large portion, and only a small part of the SBS in modified asphalt binder has degraded. From the DMA curve in Figs. 5 and 6, the complex modulus (G^*) of PMA after RTFO aging increased in accordance with base asphalt binder. Unlike the base asphalt binder, the phase angle (δ) of PMA after RTFOT aging increased because of the degradation of SBS. However, the phase angle (δ) of PMA is lower than that of base asphalt binder. It is also proven that most of the cross-linked structure of SBS in PMA is unspoiled, which still has a good modification effect on asphalt binders.

Degradation of SBS during the Service Life of Pavement

Figs. 3 and 4 show that SBS molecular weight distribution curves tend to move in the direction of small molecular weight after PAV aging. Compared with RTFO aging, the overall curve changed by a big margin after PAV aging. The results in Table 2 show that the average molecular weight of SBS after PAV aging has a decreasing trend overall, and the average molecular weight drops to 50% of SBS before aging. It is proven that after construction, SBS modified asphalt binders continue to age in its service life, so that the SBS has further degradation, and the degradation is then more serious. The results from the integral curve of Figs. 3 and 4 show that the number of molecular level of nearly 50% SBS has dropped to 10^4 after PAV aging of PMA, which approaches the molecular weight of macromolecules in base asphalt binder. The modified effect on asphalt binder of SBS declines significantly in accord with the performance test conclusion of SBS modified asphalt binder listed in Table 3.

From the DMA curve in Figs.7 and 8, the complex modulus (G^*) of PMA after PAV aging increases in accord with the RTFO aging. Unlike the RTFO aging, the phase angle (δ) of PMA after PAV aging decreased. This is because of the synthetic action between the serious aging of base asphalt binder and the degradation of SBS.

The molecular weight of SBS-1 and SBS-2 in the same asphalt binder was all reduced after aging. However, the test results show that the degrees of aging are different. The ratio of number average molecular weight (M_n) after aging and M_n before aging of SBS-1 is 32.3%, and the ratio of SBS-2 is 48.0%. However, the ratios of M_w of SBS-1 and SBS-2 are uniform (41.3% and 41.8%, respectively), indicating that the aging levels of the two types of SBS are different. The degradation of linear SBS is more serious than radial SBS.

Degradation of SBS during the PAV Aging Alone

Fig. 10 shows the pictures of original SBS and PAV aged SBS. The color of SBS in Fig. 10(a) is white, but the color of SBS in Fig. 10(b) becomes a bit yellow. SBS becomes yellow and brittle after PAV aging alone (no blending with asphalt binder), which is consistent with the phenomenon of thermal oxidative aging of polymer. Figs. 3 and 4 show that the peak values of the curves present at different molecular weights, and the molecular weight corresponding to the peak value of pure SBS undergoing PAV aging alone is lower than that of the SBS in PMA. This indicated that the degradation of SBS is more serious when it was aged alone, compared with the SBS in PMA. In other words, the aging extent of SBS in PMA was lower. This is mainly due to the fact that SBS is covered by the asphalt binder and has a lower chance of contact with oxygen. Therefore, the SBS can be protected and result in less oxidation during aging. SBS and asphalt binder can protect each other. So the SBS and asphalt binder together aged less in the PMA system than they are aged alone.

Conclusions

The degradation process of SBS in the modified asphalt binders during the short-term aging process and the long-term aging process was investigated by testing its molecular weight and molecular weight distribution with GPC analysis in this paper, and the following conclusions were drawn:

1. In the production of SBS modified asphalt binders, the molecular mass of SBS increases, the crosslink structure of SBS forms, and a small quantity of SBS degrades.
2. A small part of the SBS in polymer modified asphalt binders degrades after RTFO aging, but it still has a good modification effect on the asphalt binders. It means that the degradation of SBS in the construction process of polymer modified asphalt binders has less negative influence on the performance of SBS modified asphalt binders.
3. The degradation of SBS in polymer modified asphalt binders is serious after PAV aging, and the average molecular weight of SBS decreases obviously. The number magnitude of molecular level of nearly 50% SBS has dropped to 10^4 after PAV aging, which is close to the molecular weight of

macromolecules of the asphalt binder. In addition, the modified effect on the performance of asphalt binder of SBS declined significantly.

4. The aging degree of SBS in PMA undergoing PAV testing is less than the pure SBS suffered in PAV testing alone. The reason is that the SBS in PMA is covered by asphalt binder and has less contact with oxygen, resulting in the decreased opportunity for oxidation.

Acknowledgements

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