

## Thermal degradation mechanism of polymer modified asphalt

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The effects of the period of thermal degradation of polymer modified asphalt (MA), and the content of asphaltene constituent in MA were discussed. By mixing the straight asphalt and styrene-butadiene-styrene triblock copolymer (SBS) at 190 °C for 6h, MA was produced. After that MA was thermally degraded at 190 °C for 5 -12 days. During the thermal degradation of MA, the yield of polar constituent (asphaltene) increased gradually with the decomposition of SBS. However, the decomposition of SBS was inhibited by MA of high asphaltene content.

### 1. Introduction

It is well known that the polymer modified asphalt (MA) has the superior property, such as fluidity-resistant, abrasion-resistant, and draining property, as binder in the pavement. Therefore, the output of MA increases every year, and exceeds 430 kt per year in Japan. In Japan, about 85% of MA was produced by the modification of straight asphalt (SA) with styrene-butadiene-styrene triblock copolymer (SBS). On the other hand, the recycle and lengthen of life of MA are required because the recycle of pavement materials is obligated by law in Japan. In order to establish the recycle process and lengthen of life of MA, the degradation mechanism of MA must be clarified. Lu and Isacson (1998, 2000) clarified that the rheological properties of the aged polymer modified bitumen were dependent on a combined effect of bitumen oxidation and SBS degradation. During the ageing of MA, Cortizo et al. (2004) discussed the relation between the thermal degradation of SBS and the physical and rheological properties of MA. During the oxidative ageing of MA, Ruan et al. (2003a) revealed that the changes in the chemical structures of several kinds of polymer modifiers affected the degradation of asphalt constituent in MA. They also discussed the changes in the rheological properties of several kinds of MA during the long-term (2 -18 months) oxidation (Ruan, et al., 2003b). However, the degradation mechanism of MA has not been fully reported from the variation on the chemical properties of MA. Therefore, in this study, the thermal degradation mechanism of MA was discussed from

the molecular weight distribution of SBS, thermogravimetry and the yields of four constituents separated by solvent extraction. Further, the effect of the difference in the yield of four constituents in raw SA was also discussed from the thermal degradation of two kinds of MA.

## **2. Experimental**

### **2.1 Sample preparation and the thermal degradation of samples**

Three kinds of SA, such as SAA, SAB and SAC, were used in this study. Three kinds of MA, such as MAA, MAB and MAC, were prepared by mixing SBS and the corresponding SA (SBS: SA = 1:9) at 190 °C for 6 h. The thermal degraded samples of MAA were prepared by heating MAA at 190 °C for 5 and 12 days, respectively. The thermal degraded samples of SA, MAB and MAC were prepared as same as MAA.

### **2.2 Separation of samples into four constituents**

After each sample was extracted with n-hexane under an ultrasonic irradiation, the slurry was filtered to separate residue and filtrate. The n-hexane insoluble (asphaltene) material was prepared from the residue by drying for 3 h under vacuum at 60 °C. On the other hand, after n-hexane was evaporated from the filtrate, the n-hexane soluble (maltene) material was prepared by drying for 3 h under vacuum at 60 °C. After each maltene was placed at the top of activated alumina (75 g) filled in the glass column with n-hexane, 300 ml of n-hexane, 300 ml of toluene, and 260 ml of mixture of methanol and toluene (80 ml of methanol, 80 ml of toluene and 100 ml of methanol) were successively flowed into the glass column. After each eluate was obtained, each fraction was obtained by the solvent evaporation from the eluate. The fractions from the eluates of n-hexane, toluene, and methanol+ toluene+ methanol were referred as saturates, aromatics and resins.

### **2.3 Analysis**

The gel permeation chromatography (GPC) system used was a Shimadzu LC-10ADVP pump equipped with a Shimadzu SPD-10ADVP UV-VIS spectrometer and two GPC columns, Shimadzu GPC-805 and GPC-804. A thermogravimetry (TG) curve of each sample was measured with TG/DTA instrument (Shimadzu, DTG-50) (Sugano, et al., 2007). The <sup>1</sup>H-NMR spectra of SAA and the four constituents were measured as a CDCl<sub>3</sub> solution with a JEOL JNM-EX90A (90 MHz, FT mode) spectrometer (Sugano, et al., 2006).

## **3. Results and Discussion**

### **3.1 Effects of polymer modification of asphalt on the thermal degradation**

The ultimate analyses and the average structural parameters of SAA and the four constituents are given in Table 1. The aromaticity index (fa) and the index of condensed aromatic ring (Haus/Caus) of the unit structure of SAA and the four constituents were calculated from the ultimate analysis and <sup>1</sup>H-NMR spectrum of the constituent according to the Brown and Ladner method (Brown and Ladner, 1960). The values of fa and the content of hetero atom increased in the order; saturates < aromatics < resins < asphaltene. The values of Haus/Caus and H/C decreased in the order; saturates >

Table 1 Ultimate analyses and the average structural parameters of SAA and the four constituents

	Ultimate analyses (wt%, dry basis)					Structural parameters	
	C	H	N	S+O <sup>1)</sup>	H/C	fa	Haus/Caus
<b>Straight asphalt</b>	<b>84.9</b>	<b>10.1</b>	<b>0.6</b>	<b>4.4</b>	<b>1.43</b>		
<b>Saturates</b>	<b>86.4</b>	<b>11.9</b>	<b>0.0</b>	<b>1.7</b>	<b>1.65</b>	<b>0.18</b>	<b>0.16</b>
<b>Aromatics</b>	<b>84.9</b>	<b>10.4</b>	<b>0.3</b>	<b>4.4</b>	<b>1.46</b>	<b>0.32</b>	<b>0.66</b>
<b>Resins</b>	<b>84.0</b>	<b>9.2</b>	<b>1.1</b>	<b>5.7</b>	<b>1.32</b>	<b>0.40</b>	<b>0.58</b>
<b>Asphaltene</b>	<b>83.7</b>	<b>7.7</b>	<b>1.2</b>	<b>7.4</b>	<b>1.11</b>	<b>0.52</b>	<b>0.51</b>

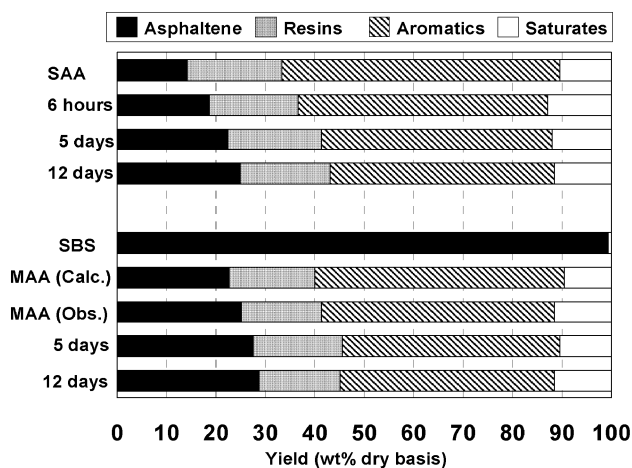


Figure 1 Yields of four constituents after the thermal degradation of SAA and MAA

aromatics > resins > asphaltene. Therefore, it was confirmed that the constituent of saturates was consisted of alkanes and aromatics attached to the long chain alkyl groups. On the other hand, the constituent of asphaltene was consisted of polynuclear aromatic compounds, which contained hetero atom and/ or attached to the oxygen containing functional groups. Estimating from the TG curves of the four constituents from SAA, the decomposition extent of four constituents increased in the order; asphaltene < resins < aromatics < saturates. The yields and the amounts of average molecular weight of four constituents after the thermal degradation of SAA and MAA are shown in Figures 1 and 2, respectively. From Figure 1, over 99% of SBS was classified into asphaltene constituent. The yield of MAA (Calc.) in Figure 1 indicates an arithmetic mean value using the yields of SAA and SBS, which means the yield of mixture of SAA and SBS (9:1) without thermal degradation. Compared with the calculated yield of MAA, the yield of asphaltene increased slightly since the thermal degradation between SAA and SBS occurred during the preparation of MAA with heat. During the thermal degradation of MAA, the increase of asphaltene yield and the decrease of aromatics yield were observed as same as the thermal degradation of SAA. From Figure 2, the molecular weight of asphaltene increased during the thermal

degradation of SAA, however, the value did not change during the thermal degradation of MAA.

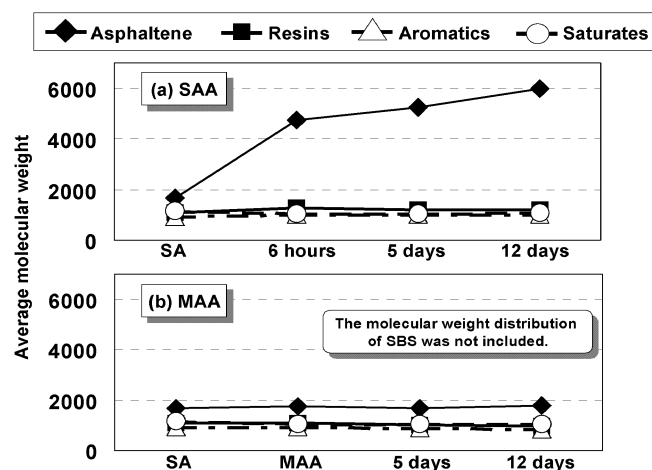


Figure 2 Average molecular weight of four constituents after the thermal degradation of (a) SAA and (b) MAA

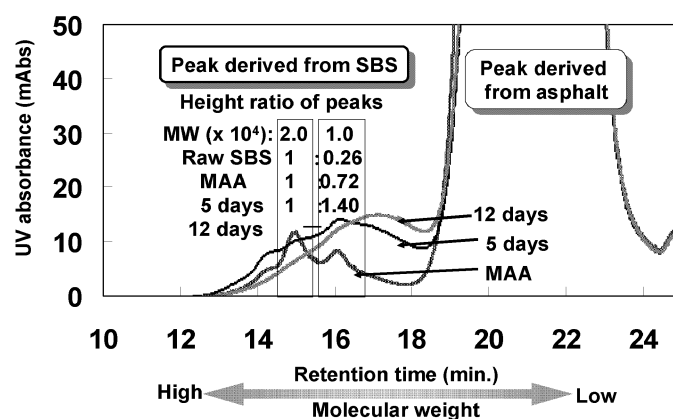


Figure 3 Molecular weight distributions (GPC profiles) of SBS after the thermal degradation of MAA

The variation in molecular weight (GPC profile) of SBS during the thermal degradation of MAA was shown in Figure 3. The height ratio of two peaks (200,000 and 100,000) of molecular weight was 1: 0.26 for the raw SBS. However, the peak height of 100,000 increased during the thermal degradation of MAA. Therefore, SBS in MAA was decomposed to the low molecular weight during the thermal degradation of MAA. As written above, the decomposition extent of four constituents in SAA increased in the order; asphaltene < resins < aromatics < saturates. Therefore, the decomposition of SBS progressed successively by the radicals formed from the constituents in maltene, which were decomposed at the relatively lower temperature. During the thermal degradation of MAA, the yield of asphaltene increased, however, the molecular weight of asphaltene

did not change as shown in Figures 1 and 2 because SBS, which classified in asphaltene,

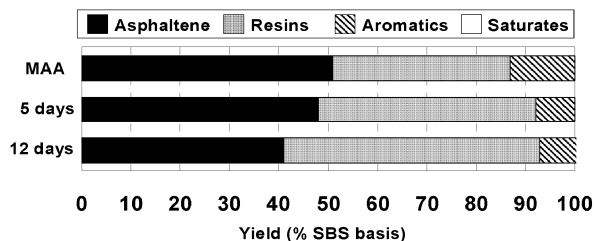


Figure 4 Yields of SBS classified to four constituents after the thermal degradation of MAA

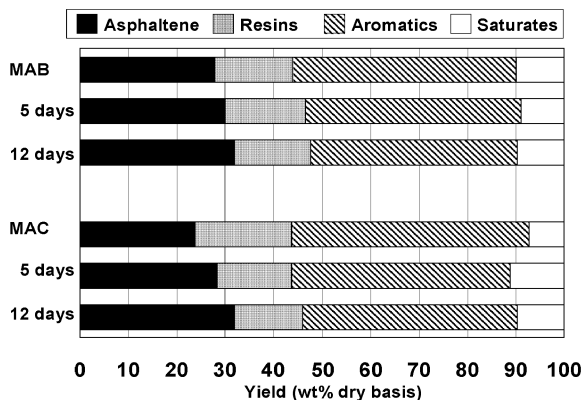


Figure 5 Yields of four constituents before and after the thermal degradation of MAB and MAC

combined with radicals from maltene and the combined maltene constituent was contained in asphaltene. Therefore, during the thermal degradation, MAA degraded by the decreases of both the maltene yield and the effect of SBS as a thermoplasticity elastomer. The yields of SBS classified to four constituents after the thermal degradation of MAA are shown in Figure 4. The yields of SBS were calculated from the proportion of peak area in each constituent ascribed to SBS. On the preparation of MAA, half of SBS was contained in asphaltene. During the thermal degradation of MAA, the content of SBS in resins increased in compensation for the decrease of SBS in asphaltene. As written above, during the thermal degradation of MAA, radicals formed from the decomposition of SBS were stabilized with the easily formed radicals formed from maltene. Therefore, it was considered that the stabilized molecules formed from SBS and maltene were mainly contained in both asphaltene and resins. Further, during the thermal degradation of MAA, it was anticipated that the amount of stabilized molecules in resins increased with the progress of the decomposition of SBS.

### **3.2 Effects of properties of asphalt substrate on the decomposition of SBS during the thermal degradation of two kinds of MA**

The yields of four constituents in two kinds of SA, such as SAB and SAC, are shown in Figure 5. The yields and the average molecular weight of asphaltene in SAB were larger than those in SAC. The values of average molecular weight of resins in SAB was also larger than that in SAC. Estimating from the TG curves of the four constituents in SAB and SAC, the decomposition extent of four constituents in SAB was higher than that in SAC. The yields of four constituents after the thermal degradation of MAB and MAC are also contained in Figure 5. The yield of asphaltene in MAB were higher than that in MAC, which was consistent with the yields of asphaltene in SAB and SAC. However, with the increase of period of the thermal degradation, the increasing yield of asphaltene in MAB were lower than that in MAC. During the thermal degradation of MAB and MAC, the peak height of 100,000 increased as well as MAA in Figure 3. However, the increasing amount of the peak height ratio on the thermal degradation of MAB was lower than that of MAC. In other words, compared with SBS in MAB, the decomposition of SBS to the low molecular weight was enhanced in MAC. Therefore, the decomposition of SBS was considered to be enhanced in MAC because the yield and molecular weight of asphaltene in MAC and the decomposition extent of MAC were lower than those in MAB. Accordingly, it was clarified that the decomposition of SBS was dependent on the properties of the asphalt substance.

## **4. Conclusions**

During the thermal degradation of MA, the yield of polar constituent (asphaltene) increased gradually with the decomposition of SBS. The stabilized molecules formed from SBS and maltene were mainly contained in both asphaltene and resins. With the progress of the decomposition of SBS, the amount of stabilized molecules in resins increased. On the other hand, the decomposition of SBS was inhibited by MA of high asphaltene content.

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