Variation in Chemical Properties of Two Kinds of Polymer Modified Asphalts during Thermal Degradation.

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ABSTRACT: Variations in the chemical characteristics of asphalt constituents and SBS in the second type of polymer modified asphalt (MT) and during thermal degradation process are compared with those of the H type of polymer modified asphalt (MH) from the yields of four constituents in both MT and MH separated by solvent extraction, the average molecular weight of four constituents in MT and MH, the molecular weight distribution of styrene –butadiene –styrene triblock copolymer (SBS) in MT and MH, physical properties (softening point and penetration), and concentration of radicals in MT and MH. As a result, the findings are as follows.
During thermal degradation of both MT and MH, the decomposed SBS molecules combined with the asphalt constituents, which resulted the increases of resin yields. Irrespective of term of thermal degradation within 10 days at 190 °C, the softening points of MH were higher than those of MT. During thermal degradation process of MH, the content of radicals in MH was lower than that of MT due to incorporation of most of the asphalt constituents into the SBS molecules. As a result, in comparison with MT, decomposition of the SBS molecules and the increases of the yield and the average molecular weight of ASP were suppressed with the increase of term of thermal degradation of MH.

KEY WORDS: Polymer modified asphalt, Thermal degradation, Chemical properties, Styrene –butadiene –styrene triblock copolymer, Content of radicals.

1 INTRODUCTION

It is well known that the polymer modified asphalt (MA) has superior properties, 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, asphalt pavement makes up 90% of paved road. In Tokyo, MA pavement makes up 80% of the asphalt paved road. In Japan, about 85% of MA was produced by modification of straight asphalt (SA) with styrene –butadiene –styrene triblock copolymer (SBS). On the other hand, recycle of pavement materials is obligated by law in Japan. In order to establish recycle process and lengthen of life of MA, degradation mechanism of MA must be clarified.

It was clarified that the rheological properties of the aged polymer modified bitumen were dependent on a combined effect of bitumen oxidation and SBS degradation (Lu and Isacsson 1998, 2000).   During ageing of MA, relation between thermal degradation of SBS and the physical and rheological properties of MA was discussed (Cortizo et al. 2004).   During the oxidative ageing of MA, it was revealed that the changes in the chemical structures of several kinds of polymer modifiers affected degradation of asphalt constituent in MA (Ruan et al. 2003a, 2004b).   They also discussed the changes in the rheological properties of several kinds of MA during long-term (2 -18 months) oxidation (Ruan et al. 2004b).   However, degradation mechanism of MA has not been fully reported from the variation on the chemical properties of MA.

Two kinds of MA, such as second type of MA (MT) and H type of MA (MH) are widely used in the pavement.   The softening point, ductility at 15°C, and toughness value at 25°C of MT are over 56.0°C, 30 cm, and 8.0 Nm, respectively.   On the other hand, those of MH are over 80.0°C, 50 cm, and 20 Nm, respectively (Japan Modified Asphalt Association, 2007). MT is superior in fluidity-resistant and abrasion-resistant, while MH is superior in fluidity-resistant and draining property.   Therefore, MT and MH are used as pavement at heavy traffic road, while MH is also used at an expressway and a drainage paved road.   The contents of SBS in MT and MH are 5% and 9%, respectively.   The microstructure of MT and MH is different due to the content of SBS.   Therefore, degradation mechanism of MT and MH might be different.   The authors have already reported variations in the chemical characteristics of asphalt constituents and SBS in MA during thermal degradation process (Sugano et al. 2009).   On the other hand, degradation of MA by oxidation is different from thermal degradation.

Degradation of asphalt consists of four terms, such as storage before shipment, mixing with aggregates, construct to road, and usage as pavement.   Thermal degradation is the most important factor for degradation of asphalt because thermal degradation participates in these four terms.   Thermal degradation is the only factor during the storage term of asphalt.

Therefore, in this study, variations in the chemical characteristics of asphalt constituents and SBS in MT during thermal degradation process are compared with those of MH from the yields of four constituents in both MT and MH separated by solvent extraction, the average molecular weight of four constituents in MT and MH, the molecular weight distribution of SBS in MT and MH, physical properties (softening point and penetration), and concentration of radicals in MT and MH.

2 EXPERIMENTAL

2.1 Sample preparation and degradation of samples

Two kinds of MA, such as MT and MH, were prepared by mixing SBS and SA at 190 °C for 6 h.   The thermal degradations of MT and MH were carried out at 190 °C for 5 or 10 days in nitrogen gas.

2.2 Separation of samples into four constituents

The experimental scheme for separation of samples into four constituents is summarized in Figure 1.   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; ASP) 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 the extract for 3 h under vacuum at 60 °C. After each maltene was placed at the top of activated alumna (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 (SAT), aromatics (ARO) and resins (RE).
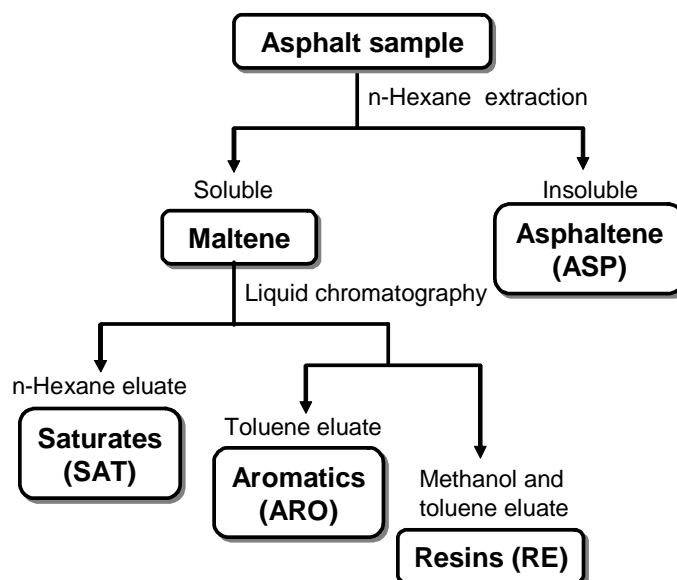
Figure 1: Experimental scheme for separation of samples into four constituents.

2.3 Gel permeation chromatography (GPC)

The average molecular weights of four constituents in SA, MT and MH, and the molecular weight distributions of SBS in SA, MT and MH were obtained by GPC. The 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. In the analysis, 1 mg of sample in 1 ml of tetrahydrofuran (THF) solution was prepared and 20µl of sample solution was injected into the column at 40 °C. The rate of the THF mobile phase was fixed at 1 ml/ min.

2.4 Electron spin resonance (ESR)

The contents of free radicals in SA, MT and MH as an indicator of degradation of asphalt were quantified by ESR. ESR measurements of asphalts were obtained with a JEOL JES-RE2X electron spin resonance spectrometer at 25 °C. The Mn^{2+}/MgO standard was used for g-value calibration. ESR spectra were recorded on a JEOL ES-EDX4 electron nuclear double resonance spectrometer.

2.5 Penetration at 25°C

The penetration test was conducted in accordance with JIS K 2530 (100 g weight, 5 s penetration, and 25°C temperature). An average of three measurements was recorded for each sample.

2.6 Softening point

Softening point was measured by the ring and ball method in accordance with JIS K 2531. An average of three values was recorded for each sample.

2.7 Thermogravimetry (TG)

The extents of decrease in weight of four constituents in MT and MH with the increase of temperature were analyzed by TG. A TG curve of each sample was measured with thermogravimetry/ differential thermal analysis (TG/DTA) instrument (Shimadzu, DTG-50). A weighed sample (2 mg) was heated at the rate of 20 °C /min up to 600 °C in a nitrogen atmosphere (Sugano et al., 2007).

3 RESULTS AND DISCUSSION

3.1 Physical properties of MT and MH

Softening Point and Penetration at 25°C before or after thermal degradation of SA, MT and MH are shown in Figure 2 (a) and (b), respectively. Softening Point of SA was smaller than those of MT and MH. Softening point of MT increased after 5 days degradation, however it decreased after 10 days degradation. On the other hand, variation in softening points of SA and MH with the increase of term of thermal degradation was negligible. Therefore, it was considered that thermal degradation mechanism of MT was different from that of MH.

From Figure 2(b), penetration of MT was larger than those of SA and MH. With the increase of term of thermal degradation, penetration of SA, MT and MH decreased gradually.

3.2 Yields and TG curves of four constituents in MT and MH

Yields of four constituents before or after thermal degradation of SA, MT and MH are shown in Figure 3. Values in Figure 3 denote the average molecular weight of each
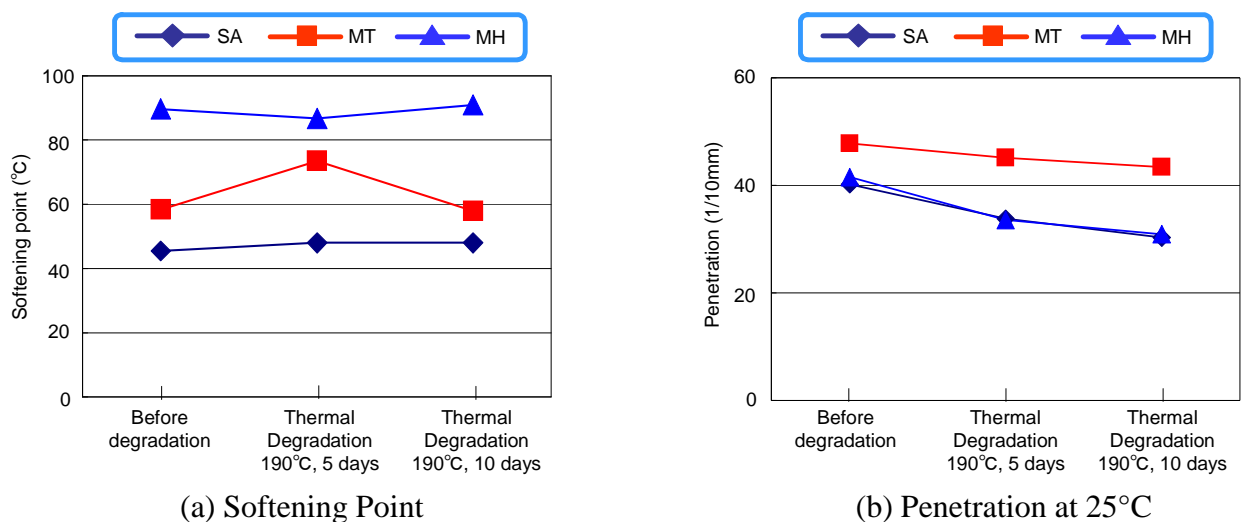

(a) Softening Point

(b) Penetration at 25°C

Figure 2: Softening Point and penetration at 25°C before or after thermal degradation of SA, MT and MH.

constituent. With the increase of term of thermal degradation, the yields of ASP in SA, MT and MH increased gradually. However, the SAT yield in SA and the RE yields in MT and MH increased gradually. On the other hand, increased yield of ASP in MH by thermal degradation was smaller than those of SA and MT.

The average molecular weight of ASP before or after thermal degradation of SA, MT and MH are shown in Figure 4. With the increase of term of thermal degradation, the average molecular weight of ASP in SA and MT increased, however, the increased amount of the average molecular weight of ASP in SA was larger than that in MT. On the other hand, the average molecular weight of ASP in MH was almost constant. The TG curves of four constituents in MT and MH are shown in Figure 5. Decomposition extent of four constituents in both MT and MH increased in the order; ASP < RE < ARO < SAT.
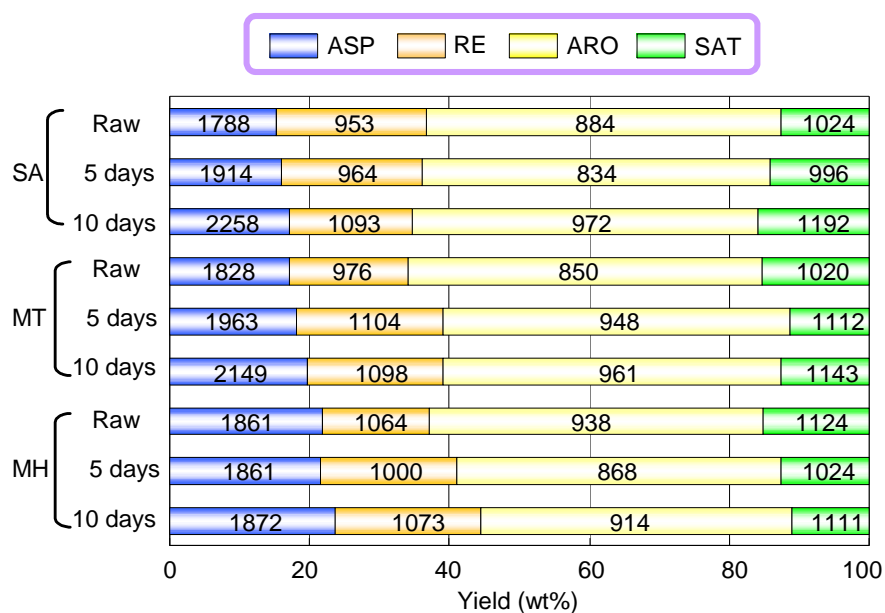
Values in the figure denote the average molecular weight of each constituent.

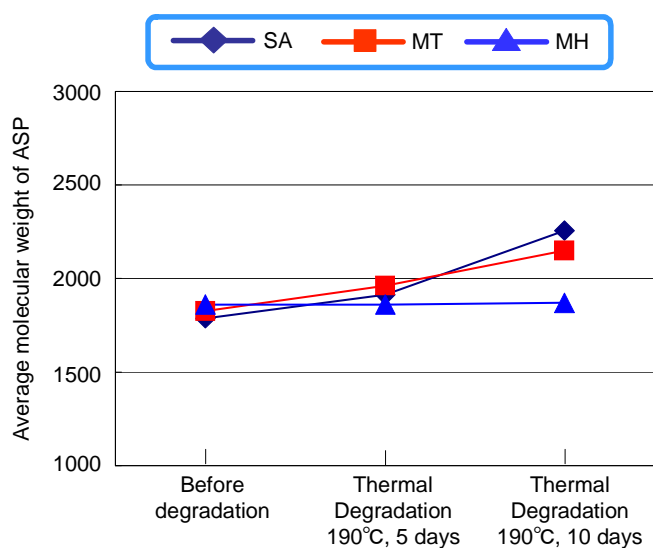Figure 3: Yields of four constituents before or after thermal degradation of SA, MT and MH.

Figure 4: Average molecular weight of ASP before or after thermal degradation of SA, MT and MH.

3.3 Molecular weight distribution of SBS in MT and MH

The molecular weight distributions (GPC profiles) of SBS before or after thermal degradation of MT and MH are shown in Figure 6. The molecular weight of two peaks ascribed to SBS copolymer are 180,000 (15 min.) and 90,000 (16 min.). In comparison with the height ratio of two peaks of raw SBS, those of SBS in both MT and MH increased. Therefore, it was clarified that decomposition of SBS occurred during preparation of MT and MH. The height ratio of SBS in both MT and MH increased with the increase of term of thermal degradation. The intensity of UV absorption of two peaks of SBS in both MT and MH decreased with the increase of term of thermal degradation. However, the increased amount of height ratio and the decreased intensity of UV absorption with the increase of term of thermal degradation of MH were lower than those of MT.
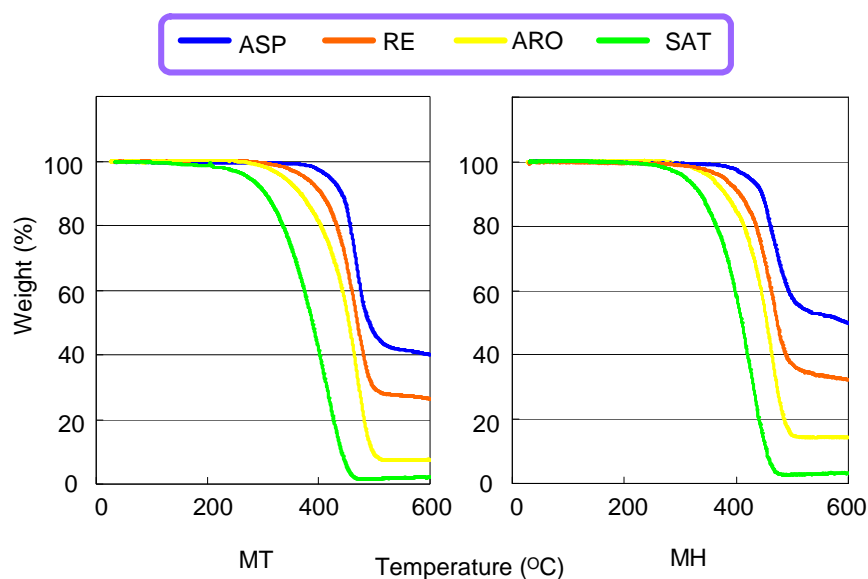
Figure 5: TG curves of four constituents in MT and MH.

3.4 Content of radicals in MT and MH

The contents of radicals of SA, MT and MH at 25 °C and 60 °C are shown in Figure 7. The contents of SA, MT and MH increased with the increase of temperature. Therefore, it is expected that the contents increase at the thermal degradation temperature (190 °C). With the increase of temperature, the content did not increase significantly for MA with small content of radicals. The contents of MT and MH were lower than that of SA. Therefore, it was considered that the contents of radicals of MT and MH were suppressed by addition of SBS. It was also estimated that the suppressive effect in MH was stronger than that in MT.

The contents of radicals before or after thermal degradation of SA, MT and MH are shown in Figure 8. The contents in SA, MT and MH increased with the increase of term of thermal degradation. However, the increased contents of radicals of MT and MH were lower than that of SA, and the suppressive effect in MH with the increase of term of thermal degradation was stronger than that in MT. Accordingly, with the increase of term of thermal degradation, it is considered that the content does not increase significantly for MA with small content of radicals.

3.5 Thermal degradation mechanisms of MT and MH

Comparison of thermal degradation mechanisms of MT and MH was considered as below. A scheme of this consideration is shown in Figure 9. It was reported that the asphalt constituents in MT and MH were swelled into SBS molecules due to the incorporation of 9 hold weight of the asphalt constituents, such as RE and ARO into the SBS molecule (Uesaka et al. 2005). Therefore, only a part of asphalt constituent was swelled by SBS molecule in MT because SBS content in MT is only 5%. As a result, it is well known that the asphalt constituents outside the SBS molecules in MT form a continuous phase of straight asphalt. On the other hand, most part of the asphalt constituents in MH was swelled into the SBS molecules owing to the high content (9%) of SBS in MH. As a result, it is well known that the SBS molecules in MH form a continuous phase of SBS. Therefore, the softening point of MH was higher than those of SA and MT. During thermal degradation process of MH, it was estimated that the thermally stable SBS molecules protected the thermally unstable
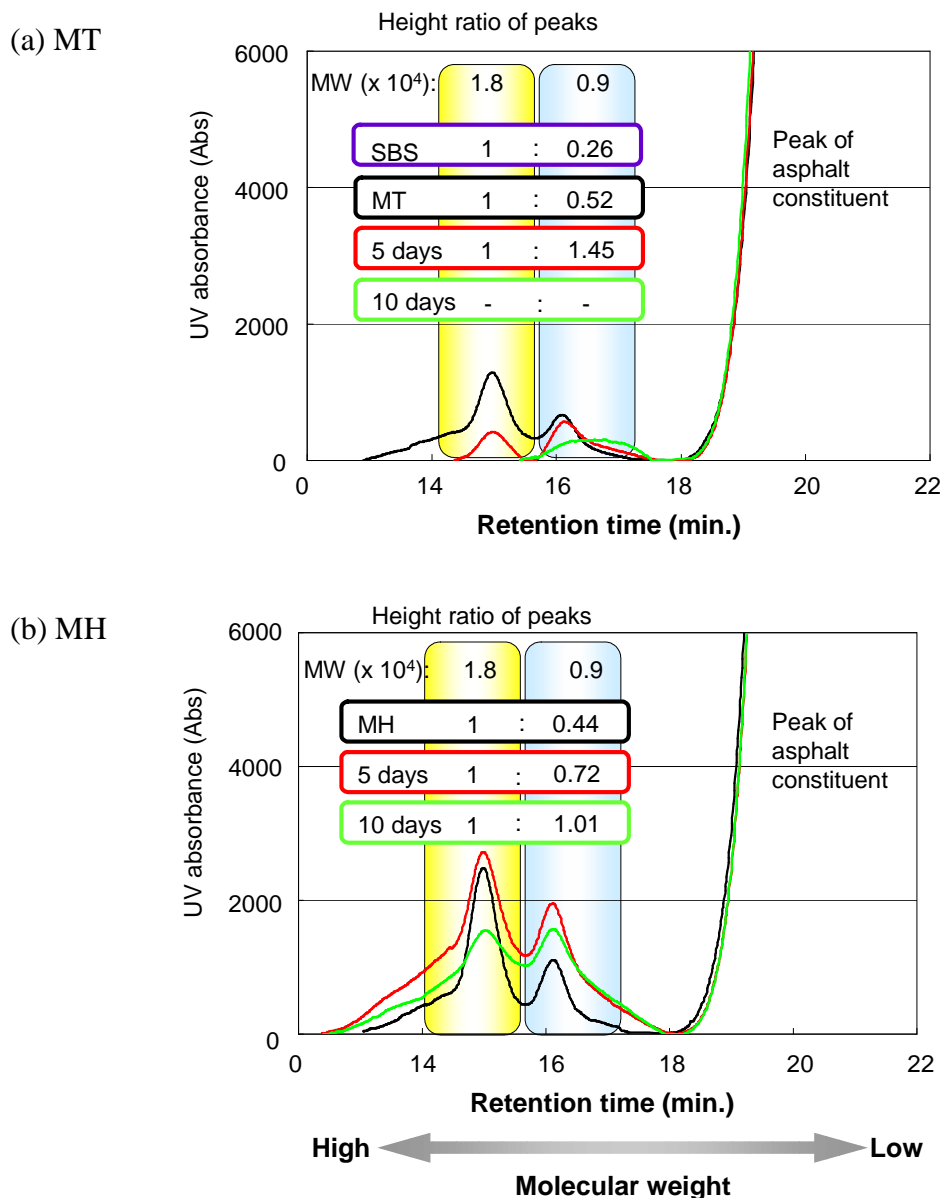

Figure 6: Molecular weight distributions (GPC profiles) of SBS before or after thermal degradation of (a) MT and (b) MH.

asphalt constituents in MH due to incorporation of the asphalt constituents into the SBS molecules.   Therefore, the content of radicals in MH was lower than those of SA and MT.

During thermal degradation process of MT, the content of radicals increased because the thermally unstable asphalt constituents, such as SAT and ARO, outside the SBS molecules decomposed.   It was considered that the radicals formed from the thermally unstable asphalt constituents polymerized with the SBS molecules and other asphalt constituents.   As a result, both decomposition of the SBS molecules and increases of polar constituents, such as ASP and RE, occurred during thermal degradation of MT.   Estimating from variation of the softening point of MT, increases of polar constituents and decomposition of the SBS molecules proceeded on the initial and final stages of thermal degradation process of MT, respectively.   Therefore, the increased content of radicals during thermal degradation of MT was higher than that of MH.   Accordingly, it was clarified that the continuous phase of straight asphalt and the dispersed SBS molecules decomposed simultaneously during thermal degradation process of MT.
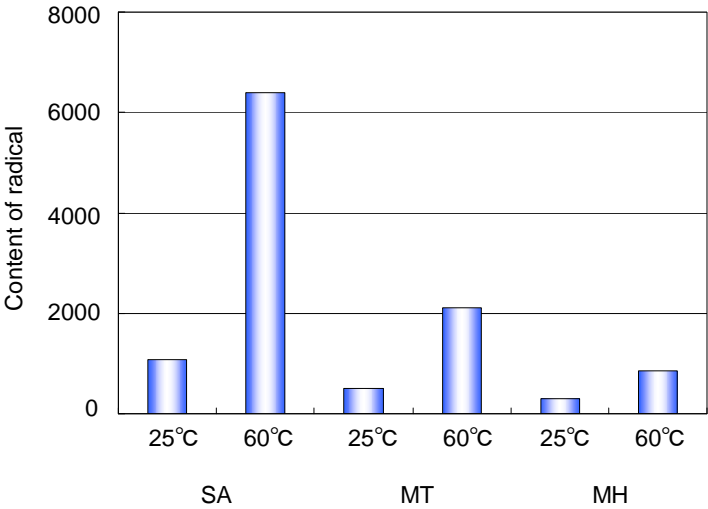

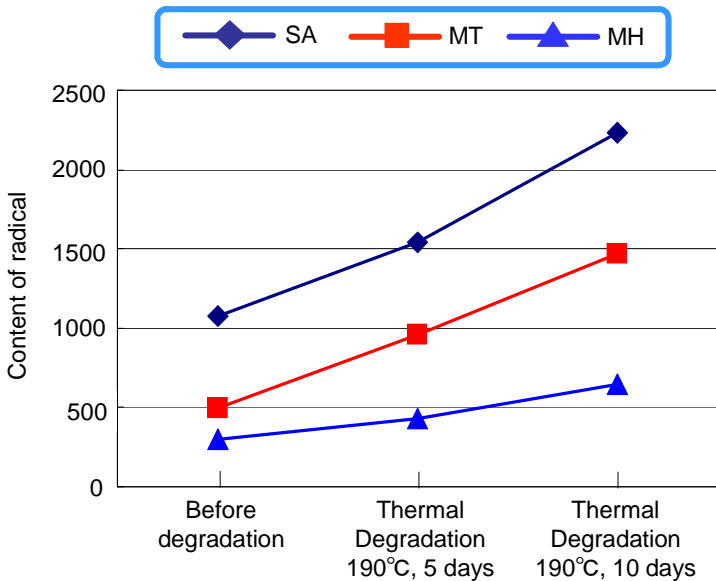Figure 7: Contents of radicals of SA, MT and MH at 25 °C and 60 °C.

Figure 8: Contents of radicals before or after thermal degradation of SA, MT and MH.

During thermal degradation process of MH, the average molecular weight of ASP did not increase significantly. Further, in comparison with the thermal degradation of MT, decomposition of the SBS molecules in MH was not enhanced due to suppression of the increase of radical content in MH. Accordingly, during thermal degradation process of MH, the continuous phase of SBS decomposed, however, the dispersed constituents of straight asphalt did not decompose significantly. Estimating from these discussions, it is clarified that thermal degradation mechanism of MH is different from that of MT.

3.6 Thermal degradation mechanisms of SBS in MT and MH

During thermal degradation of both MT and MH, it was considered that the decomposed SBS molecules combined with the asphalt constituents, which resulted the increases of RE yields. On the other hand, as written above, intensity of UV absorption of two peaks of SBS in both MT and MH decreased with the increase of term of thermal degradation. Therefore, elasticity of SBS in MT and MH decreased with decomposition of SBS, which resulted the decrease of penetration at 25°C with the increase of term of thermal degradation.
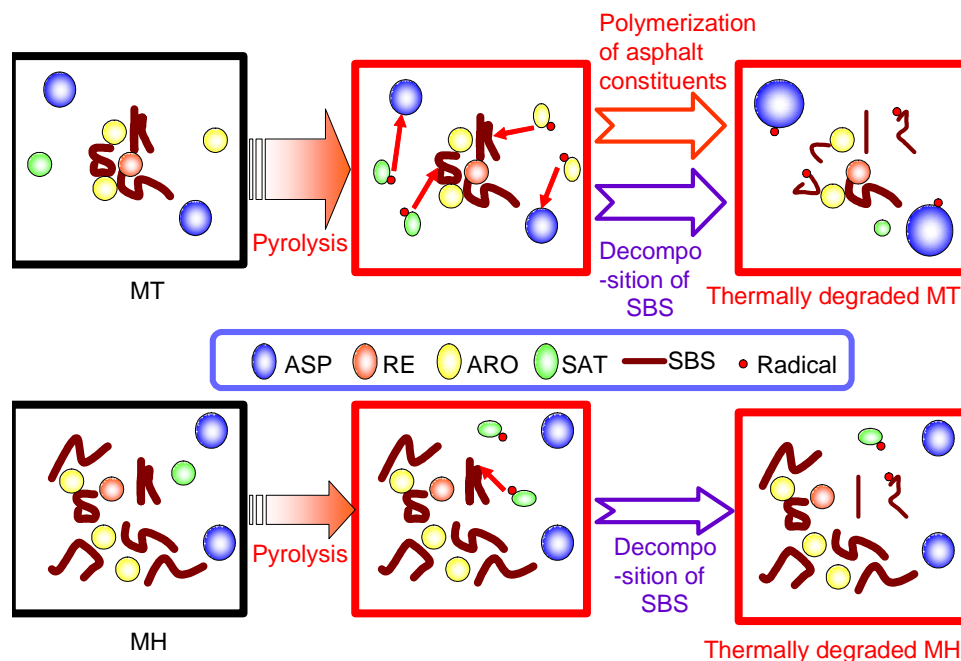

Figure 9: Comparison of thermal degradation mechanisms of MT and MH.

4 CONCLUSIONS

Variations in the chemical characteristics of asphalt constituents and SBS in MT during thermal degradation process are compared with those of MH. Our conclusions are as follows.
1. The contents of radicals of both MT and MH were lower than that of SA because generation of radicals was suppressed by addition of SBS. The softening points of MT and MH were higher than that of SA due to addition of SBS.
2. During thermal degradation of both MT and MH, the decomposed SBS molecules combined with the asphalt constituents, which resulted the increases of RE yields.
3. Irrespective of term of thermal degradation within 10 days at 190 °C, the softening points

of MH were higher than those of MT.

4. During thermal degradation process of MH, the content of radicals in MH was lower than that of MT due to incorporation of most of the asphalt constituents into the SBS molecules. As a result, in comparison with MT, decomposition of the SBS molecules and the increases of the yield and the average molecular weight of ASP were suppressed with the increase of term of thermal degradation of MH.

REFERENCES

Cortizo, M. S., Larsen, D. O., Bianchetto, H., Alessandrini, J. L., 2004. *Effect of the thermal degradation of SBS copolymers during the ageing of modified asphalts*. Polym. Degrad. Stab., 86, 275-282.

Japan Modified Asphalt Association, 2007. *Quality and test methods of polymer modified asphalt for road pavement.* Japan Modified Asphalt Association Standard JMAAS-01.

Lu, X., Isacsson, U., 1998. *Chemical and rheological evaluation of ageing properties of SBS polymer modified bitumens*. Fuel, 77, 961-972.

Lu, X., Isacsson, U., 2000. *Artificial aging of polymer modified bitumens*. J Appl. Polym. Sci., 76, 1811-1824.

Ruan, Y., Davison, R. R., Glover, C. J., 2003a. *Oxidation and Viscosity Hardening of Polymer-Modified Asphalts*. Energy Fuels, 17, 991-998.

Ruan, Y., Davison, R. R., Glover, C. J., 2003b. *The effect of long-term oxidation on the rheological properties of polymer modified asphalts*. Fuel, 82, 1763-1773.

Sugano, M., Shimodaira, K., Hirano, K., Mashimo, K., 2007. *Additive effect of cobalt-exchanged coal on the liquefaction of subbituminous coal*. Fuel, 86, 2071-2075.

Sugano, M., Iwabuchi, Y., Watanabe, T., Kajita, J., Iwata, K., Hirano, K., 2009. *Thermal degradation mechanism of polymer modified asphalt*. Chemical Engineering Transactions, 18, 839-844.

Uesaka, K., Sugiura, M., Yamanokuchi, H., Maruyama, T., 2005. *Study on qualitative characteristics of high viscous polymer modified asphalt during manufacturing and storing process*. Journal of Pavement Engineering, JSCE, 10, 213-219.