

Vulcanization Characteristics of Asphalt/SBS Blends in the Presence of Sulfur

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ABSTRACT: The vulcanization of asphalt/styrene–butadiene–styrene (SBS) triblock copolymer blends in the presence of elemental sulfur was followed with a strain-controlled rheometer. The vulcanization of the blends took place at temperatures greater than 140°C. From 150 to 180°C, the curing rate of the blends increased significantly with increasing temperature, and the apparent activation energy of vulcanization was 45.2 kJ mol⁻¹. A suitable processing temperature for good mechanical and thermally stable properties was between 170 and 180°C. Both the structure of SBS and the sulfur level had important effects on the vulcanization of the blends. A plot of the electric current versus time showed the process of the dynamic vulcanization of the blends. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 989–996, 2001

Key words: modified asphalt; styrene–butadiene–styrene (SBS); vulcanization; dynamic vulcanization

INTRODUCTION

The use of styrene–butadiene–styrene (SBS) triblock copolymer as an asphalt modifier was originally developed by Shell Chemical Co.^{1,2} It has been recognized that the physical and mechanical properties and rheological behavior of conventional asphalt compositions can be improved with the addition of SBS.³ SBS exhibits a two-phase morphology consisting of glassy polystyrene (PS) domains connected to rubber polybutadiene (PB) segments at temperatures between the glass-transition temperatures of PB and PS, so SBS exhibits crosslinked elastomer network behavior. Above the glass-transition

temperature of PS, the PS domains soften, and SBS becomes melt-processable. This thermoplastic elastomer behavior has allowed SBS to become usable for extensive applications in asphalt modification. With the modification of asphalt by SBS, the high-temperature rutting resistance and temperature susceptibility of asphalt, as well as its low-temperature flexibility properties, are effectively improved.⁴

Because of the poor compatibility of SBS and asphalt, however, the storage stability of SBS-modified asphalt is usually poor at elevated temperatures. It has been reported that the stability of polymer-modified asphalt (PMA) can be improved by the addition of sulfur, frequently in the form of elemental sulfur. In 1958, Welborn and Babashak⁵ reported that the storage stability of natural and/or synthetic rubbers or their latex-modified asphalts can be improved significantly by the addition of sulfur. Maldonado et al.⁶ disclosed a process for preparing storage-stable SBS-

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modified asphalt via the addition of sulfur. However, because of the excessive viscosity, the product could not be industrially used. In 1990, storage-stable PMA with the addition of sulfur was prepared for and applied to practical road paving.⁷ Since then, some methods for preparing practical storage-stable SBS-modified asphalt have been developed.^{8–10} It is commonly believed that sulfur chemically crosslinks the polymer molecules and chemically couples the polymer and asphalt through sulfide and/or polysulfide bonds. Most studies have been focused on the preparation processes, compositions, and performance of PMA with the addition of sulfur. Few publications are concerned with studies on the vulcanization characteristics of PMA in the presence of sulfur and on the evaluation of the processability of the blend so far.

In our opinion, the preparation of storage-stable PMA with sulfur is dominated by the process of dynamic vulcanization, and so this concept can be applied to the process. Dynamic vulcanization,¹¹ which is widely used in rubber/plastic blends, is a route to produce new thermoplastic elastomers that have properties (e.g., ultimate mechanical properties and stability of phase morphology in the melt) as good or even, in some cases, better than those of elastomeric block copolymers. Dynamic vulcanization can be described as follows. After sufficient melt mixing of rubber and plastic, for example, in an internal mixer or a compounding extruder (to form a well-mixed blend), vulcanizing agents are added. Vulcanization then occurs as the mixing continues. Finely vulcanized rubber particles, formed by shearing and shattering, are dispersed homogeneously into the continuous plastic phase. As for the processing procedure, the preparation of PMA with sulfur is similar to the dynamic vulcanization of rubber/plastic blends.

With this work, we aimed to establish methods for studying the vulcanization characteristics of SBS-modified asphalts in the presence of elemental sulfur and for evaluating their processability, to study the effect of the SBS structures and the sulfur level on the vulcanization characteristics of the blend, and to follow the dynamic vulcanization of PMA with sulfur.

MATERIALS AND MEASUREMENT

Materials

AH-90 paving asphalt was obtained from Zhongyou Xingneng Asphalt Factory (Jiangyin,

Jiangsu, China). The physical properties of the asphalt are as follows: penetration, 90 dmm (at 25°C; ASTM Standard D 5); softening point, 45.0°C (ASTM Standard D 36); and viscosity, 332 cP (135°C, ASTM Standard D 4402).

SBS 4303, 1301, and 1401 were produced by Yanshan Petrochemical Co., Ltd. (Beijing, China). SBS 4303 is a starlike polymer, containing 30 wt % styrene, and has a weight-average molecular weight (M_w) of 350,000. SBS 1301 and 1401 are linear polymers containing 30 and 40 wt % styrene, respectively; both have an M_w of approximately 110,000.

The sulfur was a commercial product (industrial grade) from Jinghai Chemical Co. (Shanghai, China).

Preparation of the Samples

Asphalt was heated to 160°C in a small container until it flowed fully. SBS (3.5 parts to 100 parts of asphalt) was mixed into the asphalt under high-speed stirring for 1 h, and the blend became essentially homogeneous. When the temperature of the SBS/asphalt blend was reduced below 120°C, a given level of sulfur was added into the blend, and the stirring was continued for 15 min at a low speed to ensure unreacted, homogeneous blends. Below 120°C, neither the reaction of the asphalt and sulfur nor the vulcanization of the SBS/sulfur blend could take place according to the literature.^{12,13}

Measurement of the Vulcanization Characteristics

We used a strain-controlled rheometer (Advanced Rheology Expanded System, Rheometric Scientific Co., Piscataway, NJ) with cup and plate geometry to determine the vulcanization characteristics of the blends. A sample (2.0 g) was placed in the lower shadow cup (30 mm in diameter). After the sample was heated to flow, the upper parallel plate (25 mm in diameter) was lowered for a tight fit with the sample. All the samples were held at a constant temperature of 80°C for 10 min, heated rapidly to a given temperature (120, 140, 150, 160, 170, 180, 210, or 230°C), and kept there for 1 h. The applied frequency and strain were 50 rad/s and 50%, respectively.

The vulcanization characteristics of the blends were determined in accordance with ASTM Standard D 2084-95. The maximum torque (M_H), minimum torque (M_L), t_0 , t_{50} , t_{90} , and curing rate ($1/t_{50}$) were obtained from the curing curves. t_0 is

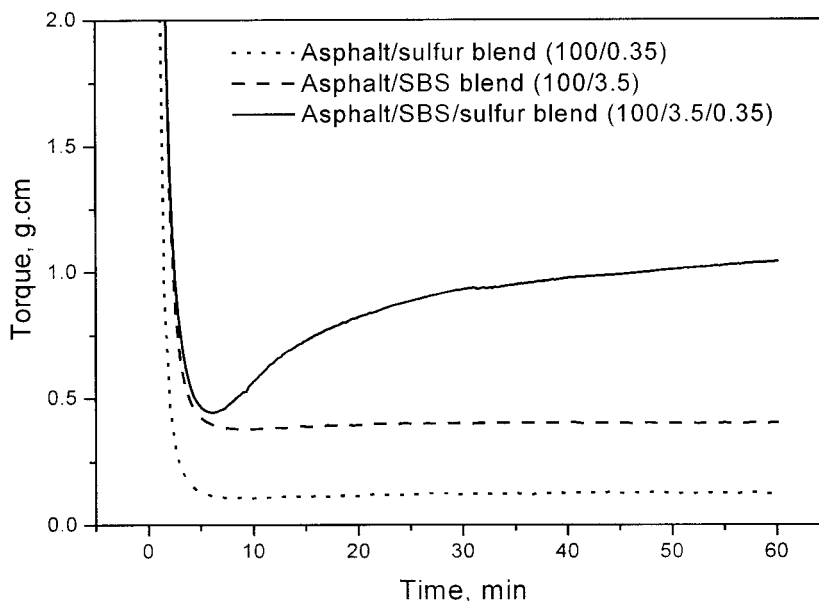


Figure 1 Control test for the vulcanization of the blend at the test temperature 180°C.

the time when the torque is equal to M_L ; t_{50} and t_{90} are the times when the torque is equal to $(M_H - M_L) \times 50\% + M_L$ and $(M_H - M_L) \times 90\% + M_L$, respectively.

We determined the activation energy of curing (E) by assuming that the dependence of $1/t_{50}$ on the cure temperature (T ; K) followed an Arrhenius relationship:

$$1/t_{50} = A \exp(-E/RT),$$

where A is the pre-exponential factor and R is the universal gas constant. E was obtained from the slope of a plot of $\log t_{50}$ versus $1/T$ from 150 to 180°C.

Dynamic Vulcanization

A digital amperometer was connected with a high-shear stirrer in series. After the asphalt was fully melted, 6.0 wt % SBS (1301) was added to the asphalt at 180°C and was stirred for 60 min; then, 5.0 wt % sulfur (based on the rubber content) was added and stirred for 90 min. The stirring speed was kept at 4000 rpm in the course of the vulcanization process. The electric current was recorded. A plot of the electric current versus time was used to describe the process of dynamic vulcanization.

RESULTS AND DISCUSSION

Reaction of Asphalt and Sulfur

It has been reported that sulfur (up to 50 wt % in asphalt) can improve the physical and mechanical properties of sulfur/asphalt mixtures.¹⁴ The improvement is related to a reaction of asphalt and sulfur, which occurs within the aromatic and naphthenic centers (Ar) in the asphalt molecules, giving rise to higher asphaltene/resin ratios and to the formation of sulfur structures such as Ar—SS—Ar and Ar—(S)_x—Ar.¹⁵ Besides the formation of the sulfur structures, the evolution of H₂S is also evidence of the reaction. That the reaction of asphalt and sulfur begins around 130°C was confirmed by Filippis et al.^{12,14}

In our experiment, to study the vulcanization characteristics of SBS-modified asphalt in the presence of sulfur, we kept all the asphalt blends at 180°C, and the variations in torque with time were compared among asphalt/sulfur (100/0.35), asphalt/SBS 4303 (100/3.5), and asphalt/SBS 4303/sulfur (100/3.5/0.35) blends, as shown in Figure 1. The torque of the asphalt/sulfur blend is the lowest, and the torque of the asphalt/SBS 4303/sulfur blend is the highest. There is little dependence of the torque on time for the asphalt/sulfur and asphalt/SBS 4303 blends, which indicates that the reaction of asphalt and sulfur has little effect on the torque of the asphalt/SBS 4303/

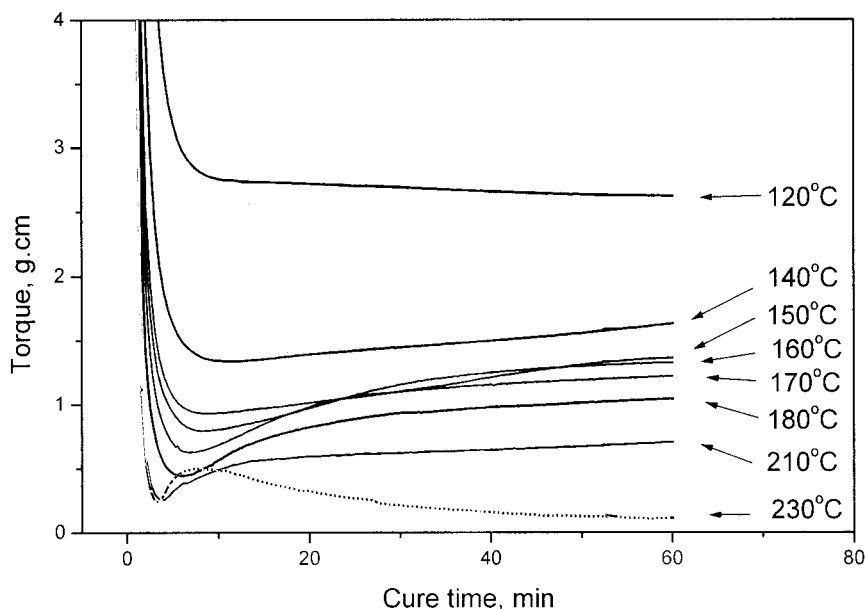


Figure 2 Effect of the temperature on the vulcanization of the asphalt/SBS 4303/sulfur (100/3.5/0.35) blend.

sulfur blend at a low level of sulfur. In our opinion, a great amount of sulfur can modify asphalt, but the small amount of sulfur used in this study cannot modify asphalt individually, and its obvious modification effect can only be realized through the reaction of sulfur and SBS. Moreover, the torque of the asphalt/SBS blend is higher than the torque of the asphalt/sulfur blend, and they remained unchanged with increasing time. This phenomenon coincides with our expectation and implies that the chemical reaction of asphalt and SBS is nearly impossible. The torque of the asphalt/SBS/sulfur blend increases significantly with increasing time, which reflects the process of the gradual formation of elastic crosslinking networks.

Vulcanization Characteristics of the Asphalt/SBS 4303/Sulfur Blend

The torque–time curves of the asphalt/SBS 4303/sulfur blends at different temperatures (120–230°C) are shown in Figure 2. The curves of the asphalt/SBS 4303/sulfur blends are similar to the curing curves of rubbers.¹⁶ The temperature of the blends increased from 80°C to a given elevated temperature between 140 and 210°C in a very short time, leading to a drop in torque to the lowest position of the curve. After that, the torque increased significantly with increasing time because of the vulcanization of the blends.

The vulcanization of the blends depends on temperature to a great extent. At 120°C, the torque changed little with time, implying that there was no vulcanization. The blends vulcanized normally from 140 to 210°C. At 230°C, degradation or decomposition of the blends took place and resulted in a decrease in torque, apparently after short-term vulcanization.

Some important parameters in the torque–time curves of Figure 2 from 150 to 180°C are given in Table I: M_H , M_L , t_0 , t_{50} , and t_{90} . As the temperature increased, M_H , M_L , t_0 , t_{50} , and t_{90} of the blends decreased, whereas the curing rate

Table I Vulcanization Parameters and E of Asphalt/SBS4303/Sulfur (100/3.5/0.35) Blend

	Temperature (°C)			
	150	160	170	180
M_H (g cm)	1.362	1.322	1.220	1.026
M_L (g cm)	0.932	0.793	0.627	0.444
$M_H - M_L$ (g cm)	0.430	0.529	0.593	0.582
t_0 (min)	12.0	8.3	6.6	6.0
t_{50} (min)	35.0	24.4	17.7	15.2
t_{90} (min)	51.6	43.9	42.0	42.0
Curing rate (100 min ⁻¹)	2.86	4.13	5.65	6.58
E (kJ mol)	45.2			

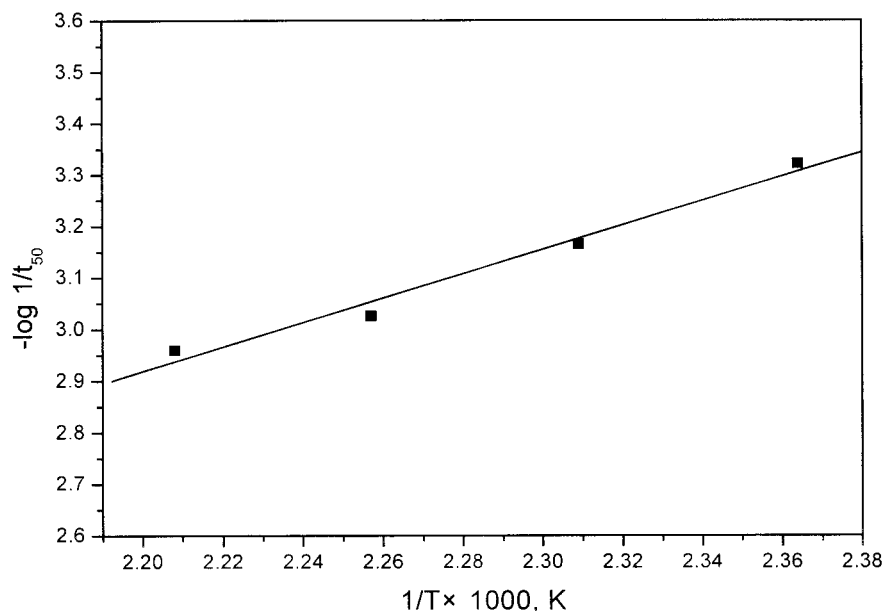


Figure 3 Plot of $\log 1/t_{50}$ versus $1/T$.

increased. However, the curing rate increased and t_0 decreased significantly at elevated temperatures of 170–180°C. Therefore, the blend containing sulfur should be processed at relatively high temperatures, such as 170–180°C. Moreover, as indicated by the curing curves, the processing of the blend was completed in 1 h. The apparent activation energy of the vulcanization of the blend (E) estimated from an Arrhenius plot,

as shown in Figure 3, was 45.2 kJ/mol, as given in Table I. The low E value represents the lower sensitivity of the vulcanization of the blend to the temperature.

Effect of the Sulfur Level

Figure 4 and Table II show the effect of the sulfur level on the vulcanization of the blends. With

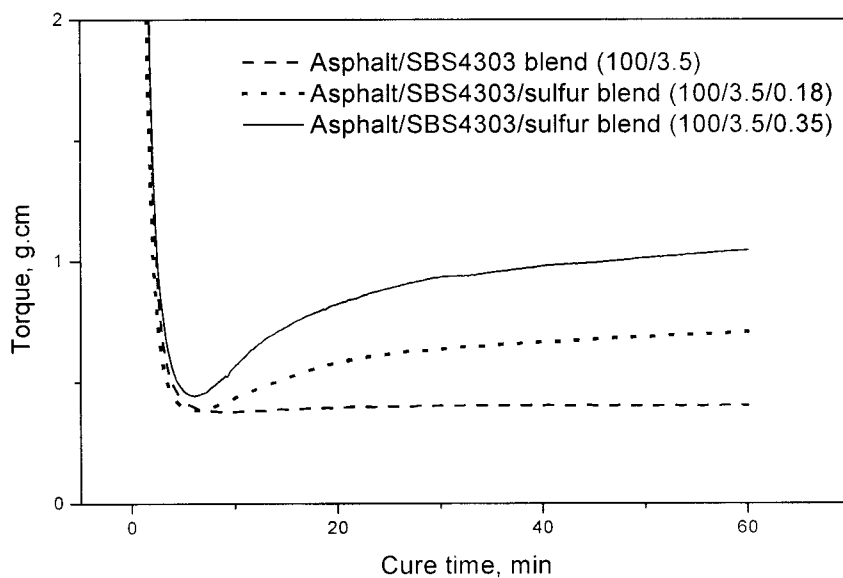


Figure 4 Effect of the sulfur level on the vulcanization of the asphalt/SBS/sulfur blend at 180°C.

Table II Effect of Sulfur Level on Vulcanization Characteristics of the Blends

	Sulfur Level (wt %)	
	5	10
M_H (g cm)	0.704	1.026
M_L (g cm)	0.384	0.444
$M_H - M_L$ (g cm)	0.320	0.582
t_0 (min)	6.6	6.0
t_{50} (min)	17.0	15.2
t_{90} (min)	44.6	42.0
Curing rate ($100/\text{min}^{-1}$)	5.88	6.58

increasing sulfur level, M_H and M_L increased significantly, and t_0 , t_{50} , and t_{90} decreased. The results show that with an increasing sulfur level, the vulcanization of the blends began early, and the curing rate of the blends increased in addition to the degree of vulcanization.

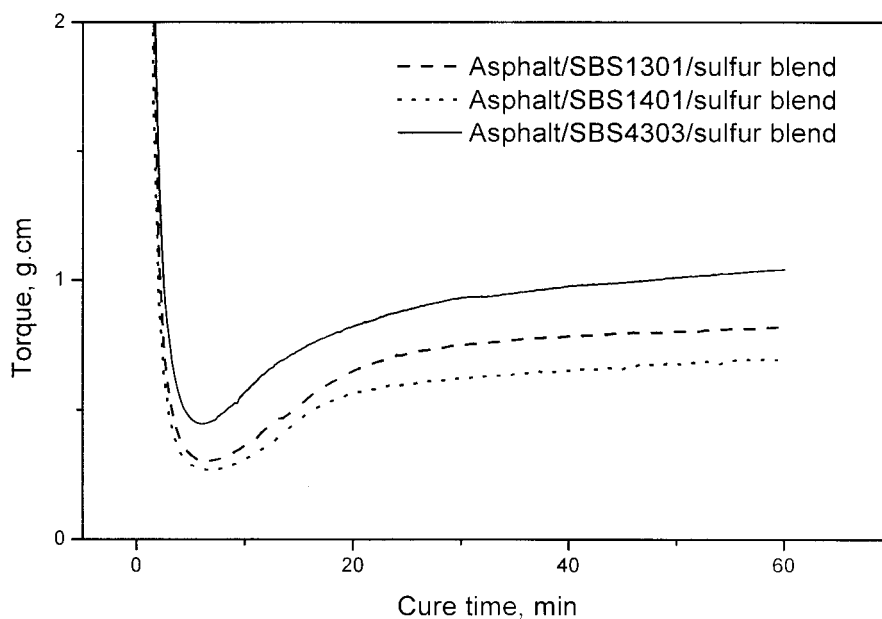
Effect of the SBS Structure

Besides the sulfur level, the SBS structure influences the vulcanization of asphalt/SBS blends significantly. Figure 5 shows the effect of the structure of SBS rubbers on the vulcanization of the blends. Under a given condition, the torque of the asphalt/SBS 4303/sulfur blend was higher than

Table III Effect of SBS Structures on the Vulcanization Characteristics of Asphalt/SBS/Sulfur Blends

	SBS Grade		
	4303	1301	1401
M_H (g cm)	1.026	0.818	0.695
M_L (g cm)	0.444	0.300	0.266
$M_H - M_L$ (g cm)	0.582	0.518	0.429
t_0 (min)	6.0	6.6	7.0
t_{50} (min)	15.2	16.2	15.9
t_{90} (min)	42.0	34.0	40.1
Curing rate ($100/\text{min}^{-1}$)	6.58	6.17	6.29

the torque of the asphalt/SBS 1301/sulfur and asphalt/SBS 1401/sulfur blends. The curing rate of asphalt/SBS 4303/sulfur was the highest, and the rates of the asphalt/SBS 1301/sulfur and asphalt/SBS 1401/sulfur blends were about the same. As also shown in Table III, the vulcanization of the blend with SBS 4303 began earlier than that of the blends with SBS 1301 and SBS 1401. The differences in the structures of SBS rubbers may be responsible. SBS 4303 is a star-like triblock copolymer with a high M_w of 350,000. SBS 1301 and SBS 1401 are linear triblock copolymers with M_w 's about one-third the M_w of SBS 4303.

**Figure 5** Effect of the SBS structures on the vulcanization of the asphalt/SBS/sulfur (100/3.5/0.35) blend at 180°C.

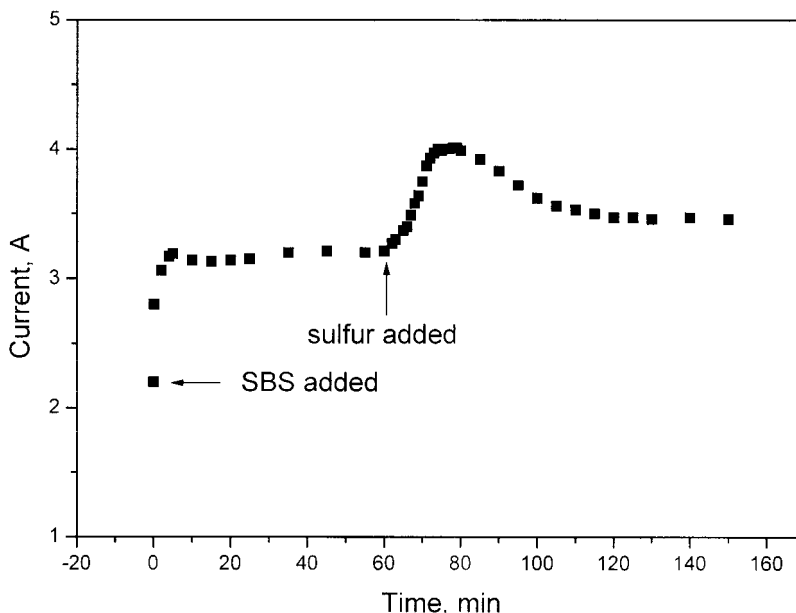


Figure 6 Dynamic vulcanization of the asphalt/SBS 1301/sulfur (100/6.0/0.30) blend at 4000 rpm and 180°C.

Dynamic Vulcanization of PMA with Sulfur

The dynamic vulcanization of PMA with sulfur was followed with a high-shearing mixer, as shown in Figure 6. Because asphalt is a Newton fluid at elevated temperatures, an open high-speed mixer is suitable equipment for the dynamic vulcanization of PMA. If the mixing speed is fixed, the torque is proportional to the electric current of the mixer. The distribution of SBS in asphalt, vulcanization, and other chemistry reactions of PMA will result in a change in the current. The dynamic vulcanization process of the asphalt/SBS 4303/sulfur (100/6/0.18) blend is shown in Figure 6. The addition of SBS to asphalt resulted in increased viscosity. One hour later, sulfur was added, and the electric current increased significantly because of the crosslinking reaction. Carbon-carbon double bonds of PB chains in SBS molecules were crosslinked by sulfur through a free-radical mechanism,¹⁷ which led to the formation of a network structure. After about 20 min, the crosslinked network of the blend was gradually destroyed by high-speed shearing and shattering, leading to a decrease in the current. The time duration was consistent with the duration in static vulcanization of the blend at the same processing temperature. As indicated by a final unchanged value of the current, it took about 45 min for the vulcanization and shearing and shattering of the blend to be

complete. However, this current was higher than that before sulfur was added; that is, the viscosity of the dynamically vulcanized blend was higher than that of the unvulcanized blend. Finely vulcanized rubber particles, formed by shearing and shattering, were dispersed homogeneously in a continuous asphalt phase. It is thought that fine SBS particles are wrapped by some aromatic components in asphalt through polysulfide or sulfide bonds, leading to improved compatibility with asphalt. Thus, storage-stable SBS-modified asphalt was obtained by dynamic vulcanization and can be used in practical applications.

CONCLUSIONS

The vulcanization of asphalt/SBS blends in the presence of elemental sulfur was followed with a strain-controlled rheometer with cup and plate geometry. The blends cured at temperatures greater than 140°C. From 150 to 180°C, the curing rate of the blends increased significantly with increasing temperature, and the apparent activation energy of vulcanization was 45.2 kJ mol⁻¹. The structure of SBS and the sulfur level had great effects on the vulcanization. A plot of the electric current versus time showed the process of the dynamic vulcanization of the blends.

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