

Comparative Study of the Effect of Sulfur on the Morphology and Rheological Properties of SB- and SBS-Modified Asphalt

Abigail Martínez-Estrada, A. Enrique Chávez-Castellanos, Margarita Herrera-Alonso, Rafael Herrera-Nájera

Departamento de Ingeniería Química, Facultad de Química, Universidad Nacional Autónoma de México, Distrito Federal 04510, México

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ABSTRACT: The modification of asphalt with styrene-butadiene block copolymers and sulfur was studied to elucidate the effect of the molecular characteristics of the polymer, polymer content, and sulfur/polymer ratio on the physical properties of modified asphalts. Two types of styrene-butadiene copolymers were used (SB and SBS), which differed considerably in terms of their chain architecture, average molecular weights, and size and distribution of their polybutadiene and polystyrene blocks, as shown by gel permeation chromatography, infrared spectroscopy, nuclear magnetic resonance, and differential scanning calorimetry. Sulfur/polymer/asphalt blends were prepared by a hot mixing process and characterized by conventional tests, fluorescence microscopy, and rheology. The results revealed that the morphology of the blends is strongly dependent on polymer concentration and sulfur/polymer ratio. In-depth rheological characterization showed that the thermomechanical

properties changed considerably upon addition of small amounts of sulfur. Collectively, these results suggest that sulfur increases the compatibility between polymer and asphalt by crosslinking polymer chains. Interestingly, the rheological behavior of blends prepared with a combination of SB and sulfur was similar to that exhibited by blends prepared with SBS either in the presence or absence of sulfur. This is explained by assuming that the addition of small amounts of sulfur to SB-modified asphalt facilitates the formation of an elastomeric network that resembles the one found in SBS-modified asphalt, effectively contributing to asphalt reinforcement. Nonetheless, the exact dosage of sulfur must be carefully controlled to prevent gel formation. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3409–3422, 2010

Key words: block copolymers; modified asphalt; rheology; viscoelastic properties; vulcanization; blends

INTRODUCTION

Asphalt is a heterogeneous material comprised of immiscible phases of asphaltenes and maltenes: asphaltenes are polyatomic hydrocarbons of relatively high molecular weight; maltenes are a mixture of resins, waxes, aliphatic and aromatic compounds.^{1,2} According to the asphalt emulsion model, asphaltene micelles, stabilized by resins and aliphatic compounds—are distributed within a continuous maltene phase.^{3–7} The exact composition of each phase depends on the source and extraction process. Asphalt is commonly used as a construction binder for roads and roofing as it is fairly inexpen-

sive and compatible with these construction materials, but more importantly, asphalt is able to dissipate mechanical stress, thereby preventing hard surface fracture. Nevertheless, neat asphalt (NA) is relatively temperature-sensitive: at low temperature (–30 to 0°C) it is brittle and undergoes low-thermal cracking, whereas at high temperature (40–65°C) it flows and suffers from rutting.⁸ This shortcoming is critical for road construction due to increased traffic volume, heavier vehicles, and higher tire pressure.⁹

Polymer-modified asphalts (PMAs) are composite materials that overcome the limitations of NA as a result of the addition of polymer. Examples of polymers used in the production of PMAs include natural rubber,^{10,11} copolymers of ethylene-vinyl acetate,^{12–14} polypropylene,^{15,16} styrene-ethylene-butadiene-styrene copolymers,^{17–19} and styrene-butadiene copolymers.^{20–25} PMAs consist of a binary system of polymer-rich and asphalt-rich phases, the characteristics of which result from selective interactions between asphalt components and polymer.²⁶

Poly(styrene-*b*-butadiene)-modified asphalts (SB-MAs) and poly(styrene-*b*-butadiene-*b*-styrene)-modified asphalts (SBS-MAs) are interesting materials in

Correspondence to: R. Herrera-Nájera (rherrern@servidor.unam.mx).

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that each of the blocks comprising the copolymers contributes to broaden the thermomechanical stability of PMAs.²⁷ The polybutadiene (PB) block, which selectively interacts with nonpolar components associated with maltenes,¹⁰ provides low-temperature ($\sim -100^\circ\text{C}$) break resistance; the polystyrene (PS) component prevents high-temperature ($\sim 100^\circ\text{C}$) deformation.²⁸ SB- and SBS-MAs consist of two phases: (i) a polymer-rich phase formed by maltenes-swollen polymer and (ii) an asphalt-rich phase composed of resin-stabilized asphaltenes distributed within a continuous maltenes matrix. The polymer-rich phase of asphalts modified with styrene-butadiene copolymers is a network of PB regions "tied" through PS nodes.^{20,21} The presence of polymer alters the composition of the asphalt phase, hence the morphology of a PMA (i.e., whether the polymer-rich phase is either the continuous or disperse phase) will strongly depend on polymer concentration.^{29,30} The molecular architecture of a polymer also has an important effect on the properties of PMAs, as observed when comparing sulfur-containing SB-PMAs and SBS-MAs.³¹ Changes in mechanical properties and morphology have been ascribed to the formation of an elastomeric network in the polymer-rich phase,^{20,21} either through physical entanglements in SBS-MAs or chemical crosslinks in sulfur-containing SB-MAs and SBS-MAs.³²⁻³⁴

SB-MAs and SBS-MAs are unstable under high-temperature storage conditions because of the incompatibility of their components.^{33,35} Polymer-rich and asphalt-rich phases separate denoting differences in solubility parameters, molecular weight, densities, and viscosities. This is an important shortcoming as exposure to elevated temperatures with minimum stirring is common during the production of PMAs. On occasions, phase separation is difficult to prevent because the exposure time to high temperatures and the time required for phase separation are comparable. A number of additives have been used to improve the compatibility between polymer and asphalt, including phosphorous-based compounds,^{36,37} sulfur-based additives,^{32,33,38,39} and maleic anhydride.^{23,40} It is generally believed that sulfur compounds modify asphalt by crosslinking polymer chains and grafting polymer chains with asphalt components.^{32,33,41-44} Despite substantial research in this area, vulcanized PMA blends have not been comprehensively characterized, and the role of elemental sulfur or organic sulfur compounds on the improvement of storage stability remains unknown.

This article presents a study on a series of PMAs produced with two styrene-butadiene copolymers, both in the presence and absence of sulfur. The effects of polymer concentration, polymer molecular architecture, and sulfur/polymer ratio on PMA properties were studied in terms of morphology and

rheological behavior. Additionally, the effect of sulfur on hot storage stability is discussed.

EXPERIMENTAL

Materials

Mexican asphalt (Salamanca, Mexico) was a donation from PEMEX. Sulfur (99%) and deuterated chloroform were purchased from Sigma Aldrich. Styrene-butadiene copolymers, Solprene S1205 and Solprene S416, were a donation from Dynasol Elastómeros de México.

Procedures

Polymer-modified asphalts

A high-temperature mixing process was used to produce the PMAs. Asphalt (c.a., 150 g) was added to a stainless steel vessel (100 mL) and heated by immersion in an oil bath equilibrated at 180°C (this results in a heating rate of $\sim 10^\circ\text{C}/\text{min}$). Sample temperature and heating rate were monitored by a thermocouple, immersed in the sample. Mechanical stirring (with a high shear rotor mixer, Euromix 33/300P) was started once the sample had reached 100°C ; stirring velocity was adjusted to 500 rpm. When the sample reached 180°C the desired amount of copolymer (5 or 12 wt %) was slowly added at constant stirring velocity and temperature. Blends prepared without sulfur were stirred for 5.5 h to ensure pseudo-equilibrium conditions. Blends containing sulfur were stirred for 4 h, then the desired amount of sulfur was slowly added; stirring continued for an additional 90 min. PMA samples were immediately quenched by immersion in ice and maintained at -10°C for further analysis.

The nomenclature used throughout the text is as follows. The first number indicates the polymer content of the PMA (5 or 12 wt %), followed by the type of polymer (SB or SBS). Samples containing sulfur are then denoted by the concentration of elemental sulfur in phr (parts of sulfur per hundred parts of polymer) followed by the letter "S" (for sulfur). For example, 12SB-3S represents a blend prepared with 12 wt % of SB and 3 phr of elemental sulfur. PMAs prepared with either SB or SBS are referred to as SB-MA and SBS-MA, respectively.

Hot storage test

Thermal stability of selected samples was examined by a hot storage test according to ASTM D 5892. For this, a magnesium cylinder (2 cm diameter, 15 cm height) was filled with freshly prepared PMA and stored in a vertical position for 48 h at 163°C . The sample was quenched by immersion in ice, stored at

TABLE I
Physical Properties of Neat Asphalt (NA)

Property (units)	Standard test used	Value
Composition (wt % asphaltenes)	ASTM D 3279-90, solubility in <i>n</i> -heptane	20
Penetration (dmm)	ASTM D 5 (25°C, 100 g, 5 s)	46
Softening point (°C)	ASTM D 36	65
Brookfield viscosity (Pa s)	ASTM D 4402-87 (135°C)	395

−10°C for 24 h, and cut into three equal parts. Top and bottom parts were used to evaluate the sample's storage stability according to a softening point criterion (ASTM D 5892); when the difference in softening point is less than 2.5°C the blend is considered to be stable.

Characterization

Molecular weights were determined by gel permeation chromatography (GPC) using an HP1090 HPLC equipped with a PL-gel column (5 μm). Tetrahydrofuran was used as an eluant at a flow rate of 1 mL/min; all measurements were carried out at 35°C. The average molecular weights are referred to PS standards. Block copolymer composition and the isomeric composition of the PB block were determined by infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). Polymer solutions (in CS₂, 10 mg/mL) were analyzed on a Perkin Elmer 1605 spectrophotometer. Signals at 800, 910, and 967 cm^{−1} were used to determine the relative amounts of styrene, 1,2-vinyl, and 1,4-trans butadiene isomers, respectively. A sample of SB of known isomeric composition was used as reference. High-resolution ¹H NMR spectra of copolymers were obtained using a Varian (Unity Inova) 300 MHz spectrometer in CDCl₃. Peak assignments and calculations (styrene content, PB isomeric composition, block/tapered ratio) were done according to Sardelis et al.⁴⁵ Glass transition temperatures (*T*_g) were measured on a DuPont 910 differential scanning calorimeter (DSC) under nitrogen (ultra-high purity). Each sample was subjected to three heating cycles. Temperature sweeps ranged from −130 to 130°C with a heating rate of 10°C/min. Results correspond to the second heating cycle. Conventional physical properties, reported in asphalt studies,^{20,21} of SB-MA and SBS-MA were determined according to standard methods: penetration (ASTM D 5, 25°C, 100 g, 5 s), softening point (ASTM D 36), and Brookfield viscosity (ASTM D 4402-87, 135, 160, and 180°C). Fluorescence microscopy was conducted on a Carl-Zeiss KS300 microscope equipped with a lamp of λ = 390–450 nm and 20× lens. Relative amounts of polymer-rich and asphaltene-rich phases were estimated using an image analyzer program. Rheological analysis was performed on a TA Instruments AR-200 with

parallel-plate geometry (25 mm diameter). Storage (*G'*) and loss (*G''*) moduli were determined under small oscillatory shear flow by two methods: (i) isothermal (40, 60, 80, 100, 120, 160, and 180°C) frequency sweep (0.01 < ω < 250 rad/s) and (ii) temperature sweep (40–180°C) with a heating rate of 5°C/min at constant amplitude (10 μm) and frequency (1 and 10 rad/s). Measurements were carried out within the linear viscoelastic region to preserve the structure of the sample. The results of the rheological characterization are presented in the form of master curves.

RESULTS

Neat materials

Conventional properties of neat asphalt (NA), this meaning penetration, softening point, and Brookfield viscosity, are presented in Table I. Rheological behavior of NA is presented in Figures 4, 6, and 8–12. This data are relevant, as it will be used as reference. Table II presents the molecular characteristics of the polymers used throughout this work. The data show that the SB and SBS differed considerably from each other in terms of their chain architecture, average molecular weights, and size and distribution of their PB and PS blocks.

Conventional properties

Samples of NA and freshly prepared PMAs were characterized in terms of their conventional properties, and the results are presented in Table III. The results show that all PMAs, regardless of the type of polymer and polymer/sulfur content, exhibited shorter penetration depths, higher softening temperatures, and higher Brookfield viscosity compared with NA. The difference, however, is dependent on polymer concentration, suggesting that the addition of polymer results in enhanced thermomechanical resistance of NA. These results are in agreement with previously reported data.^{20,21,27,28} When comparing the properties of PMAs prepared with the same polymer concentration or polymer/sulfur ratio (Table III, entries 3 vs. 9, 6 vs. 12, and 7 vs. 13), it is clear that those blends prepared with SBS exhibited higher thermomechanical resistance than those prepared with SB. Furthermore, this difference is

TABLE II
Properties of SB and SBS Copolymers Used in the Preparation of PMAs

Property	SB	SBS
Chain architecture	Linear	4-arm star
Composition (wt % styrene) ^a	22	30
Styrene distribution (% block/% tapered interface) ^a	81/19	97/3
Molecular weight (g/mol) ^b	130,000	216,000
Stereoisomeric composition of polybutadiene ^c		
(% 1,2-vinyl)	9	8
(% 1,4-trans)	34.4	36.4
(% 1,4-cis)	56.6	55.6
Stereoisomeric composition of polybutadiene ^a		
(% 1,2-vinyl)	9	13
(% 1,4-trans and -cis)	91	87
Glass transition temperature, T_g (°C) ^d	-85.7	-85.9

^a Estimated from ¹H-NMR data according to Sardelis et al.⁴⁵

^b Measured by GPC using polystyrene standards.

^c Determined from FTIR analysis.

^d Determined from DSC analysis.

greater when sulfur is included in the formulation. In general, addition of a relatively small amount of sulfur (1.0 phr) increases the thermomechanical resistance of PMAs; however, its exact composition in the blend must be carefully adjusted because slight excess will lead to gel formation. This balance is more delicate for the SBS-based blends. Interestingly, the properties of blends prepared with SBS can be closely matched to those of blends prepared with SB and particular amounts of sulfur, as seen when comparing entries 4 vs. 9, 5 vs. 10, and 7 vs. 12 in Table III.

Morphology

The term “morphology” herein refers to the shape and distribution of the polymer-rich phase as determined by fluorescence microscopy. Figures 1 and 2

present the morphology of fresh PMAs, and Figure 3 corresponds to a PMA sample subjected to the hot storage test. The pale regions of the images correspond to the polymer-rich phase; the dark areas represent the asphalt-rich phase consisting of asphaltenes and maltenes, neither of which produced detectable fluorescence radiation. The images show that all blends were heterogeneous systems comprised of polymer-rich and asphalt-rich phases. It is also evident that in all PMAs the area attributed to the polymer-rich phase is larger than its corresponding weight percentage (Table III). This difference is larger for PMAs containing sulfur. These results have been explained before considering that the polymer swells by absorbing maltenes, thus forming a bulky polymer-rich phase. Nonetheless, the morphology of low-polymer PMAs without sulfur shows

TABLE III
Conventional Properties of Neat Asphalt (NA) and Polymer-Modified Asphalts

Sample	T_s^a (°C)	Penetration (dmm)	Brookfield viscosity (cp)			Volume fraction (%)	T_s^b (°C)	
			135°C	160°C	177°C		Top	Bottom
NA	58	44	650	199	105	–	58	58
NA-20S	62	34.2	721	217	113	–	62	62
5SB-0S	65	42.3	1579	513	275	39	62	73
5SB-3S	67	27.8	2092	642	346	50	78	70
5SB-5S	72	29.2	3429	1092	567	55	71	73
12SB-0S	71	32.3	4583	1838	1029	60.4	69	75
12SB-1S	88	28	15,700	4583	3325	71.2	87	89
12SB-3S	90	22.3	–	–	–	72	95	95
5SBS-0S	67	25.8	1846	596	321	33	65	70
5SBS-1.5S	74	25.7	3030	950	479	33	72	73
5SBS-2S	77	25.6	3200	971	500	33	76	76
12SBS-0S	90	17	11,234	3254	2083	60.2	88	100
12SBS-1S	104	13.8	15,070	4541	2895	61.4	102	104
12SBS-2S	120	15.3	–	–	–	62	118	119

^a Softening temperature of a freshly prepared sample.

^b Softening temperatures of the top and bottom sample portions after storage.

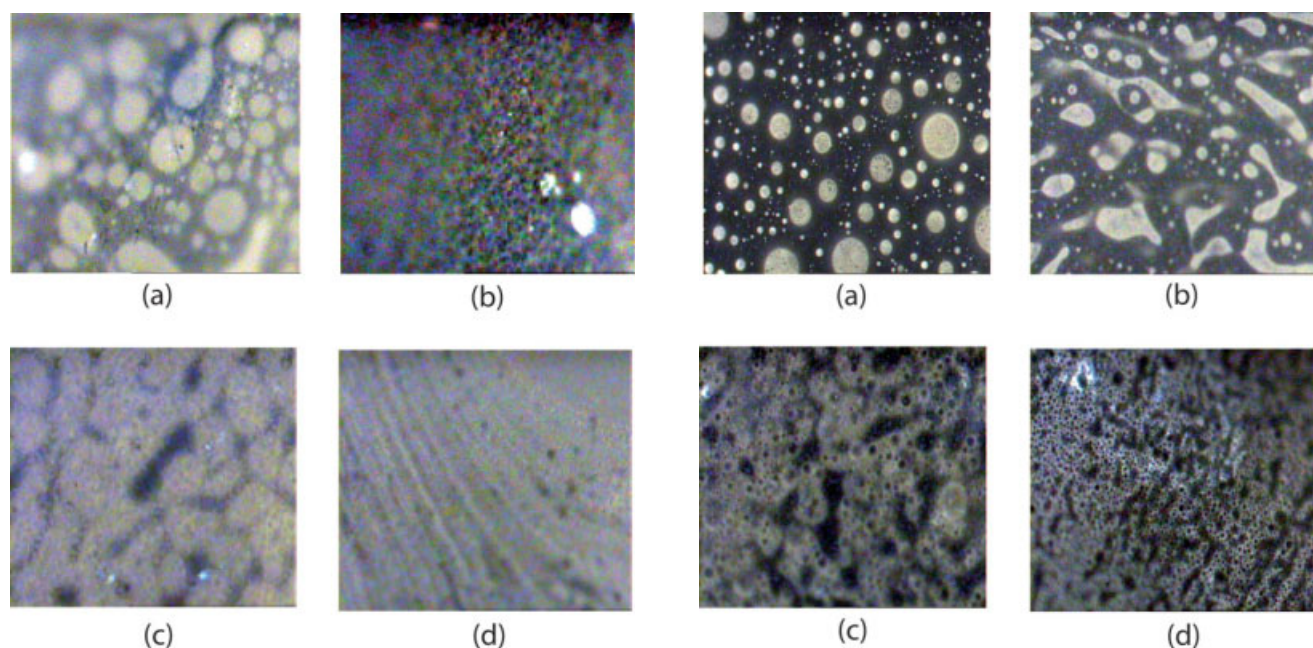


Figure 1 Fluorescence microscopy images ($\times 20$ magnification) of SB-MAs. Polymer-rich phase appears pale and asphalt-rich phase appears dark. Images (a) and (c) are nonvulcanized blends prepared with 5 or 12 wt % SB, respectively. Images (b) and (d) correspond to vulcanized blends (3 phr sulfur) containing 5 or 12 wt % SB, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 2 Fluorescence microscopy images ($\times 20$ magnification) of SBS-MAs. Polymer-rich phase appears pale and asphalt-rich phase appears dark. Images (a) and (c) are nonvulcanized blends prepared with 5 or 12 wt % SBS, respectively. Images (b) and (d) correspond to vulcanized blends (1.5 phr sulfur) containing 5 or 12 wt % SBS, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

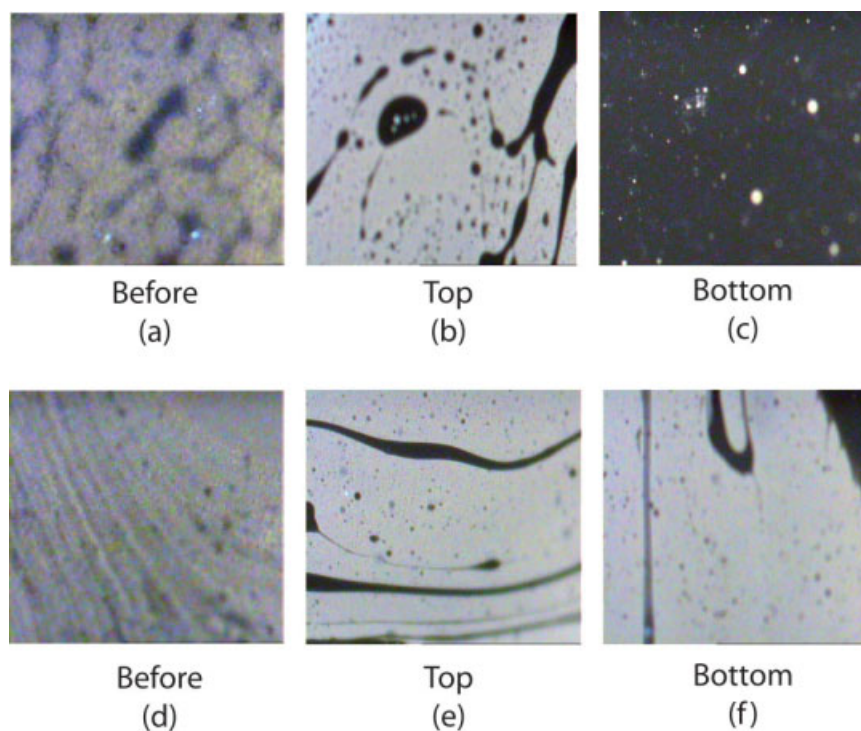


Figure 3 Fluorescence microscopy images ($\times 20$ magnification) of SB-MAs prepared with 12 wt % SB before and after the high-temperature storage test (HTST). Images (a) and (d) correspond to freshly prepared nonvulcanized and vulcanized (3 phr sulfur) samples, respectively. Images (b) and (c) correspond to the top and bottom parts of the nonvulcanized sample before HTST, respectively. Images (e) and (f) correspond to the top and bottom parts of the nonvulcanized sample after HTST, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

a polymer-rich phase embedded in the asphalt-rich phase [Figs. 1(a) and 2(a)]. Conversely, low-polymer blends containing sulfur displayed a continuous polymer-rich phase with relatively small asphalt-rich inclusions [Figs. 1(b) and 2(b)]. This phase inversion suggests that maltenes are distilled from asphalt toward the polymer. These results also suggest that at the start of the mixing process sulfur acts as a plasticizer, increasing the dispersion of the polymer and facilitating polymer swelling. Afterward, sulfur promotes crosslinking reactions. This phenomenon is also observed in high polymer blends with and without sulfur [Figs. 1(d)–2(d) and 1(c)–2(c), respectively].

Data correlating the morphology (Figs. 1–3) and volume fraction (Table III) of the polymer-rich phase of PMAs show that samples prepared with SB exhibit a larger polymer-rich phase than those prepared with SBS. Similar results were obtained for blends containing sulfur, suggesting that the interaction between asphalt and SB is different from that with SBS. It is important to point out that maltenes have a more favorable interaction with the PB block compared with the PS block, because maltenes swell PB but not PS. Asphaltene, on the other hand, are incompatible with both PB and PS. Also, SB is a linear diblock copolymer, whereas SBS is a triblock consisting of four equivalent diblock arms emanating from a silicon-based core with PS free ends; it is considered a triblock because two PS blocks flank a central PB block. Both the PB and the PS blocks of SB are shorter than those of SBS. Consequently, asphalt–polymer interactions are more favorable in SB because it has only one PS block preventing such interaction, compared to the four PS end blocks of SBS.

High-polymer SB and SBS samples that contained sulfur exhibited phase inversion phenomena, denoted by a continuous polymer-rich phase with small asphalt-rich inclusions [Figs. 1(b,d) and 2(b,d)]. These results suggest that sulfur increases the compatibility between asphalt and the copolymers, promoting the formation of three-dimensional structures.

In regard to the thermal stability of the blends, Figure 3 shows the morphology of samples 12SB-0S and 12SB-3S subjected to the hot storage test. These results suggest that addition of a relatively small amount of sulfur (3 phr) is enough to prevent phase separation during hot storage. Nevertheless, further studies are necessary to elucidate the exact role of sulfur in these systems.

Rheology

The mechanical resistance of NA, PMAs, and sulfur/PMAs was determined by rheological analysis. Their rheological data are organized and discussed in terms of master curves. Storage (G') and loss (G'')

moduli were measured by small-amplitude oscillatory shear deformation within the linear viscoelastic regime, and from this data master curves of storage modulus $G'(\omega)$, complex viscosity $\eta^*(\omega)$, black diagram $\delta(G^*)$, and phase angle isocrones $\delta(T)$ were constructed applying the time-temperature superposition principle with 80°C as the reference temperature. As all PMAs were prepared following the same procedure and the rheological tests were essentially nondestructive, differences in their rheological behavior are attributed exclusively to their composition and molecular structure of the polymer modifier. Figures 4–12 summarize the rheological behavior of the two sets of PMAs; results of NA are also included for comparison.

Storage modulus

The elastic behavior of a sample is expressed in terms of the storage modulus [Fig. 4(a–d)] because it represents the completely recoverable part of the mechanical energy used during deformation. The general trend for all samples, including NA, is increased elastic behavior with increasing shear deformation frequency (ω) (i.e., decreasing temperature). However, the degree of elasticity is dependent on the amount of polymer and on the sulfur/polymer ratio. All PMAs are more elastic than NA. Under identical conditions (polymer concentration and sulfur/polymer ratio), samples prepared with SBS are more elastic than those prepared with SB. For example, plots a and b in Figure 4 show that the storage modulus of SBS-MA with 5 wt % copolymer (with or without sulfur) is approximately sevenfold that of SB-MA under the same conditions. This difference is more pronounced for PMAs formulated with higher polymer concentration [Fig. 4(c,d)]. Also, and in agreement with the results of conventional properties (Table III), the storage modulus profile of a given SBS-based blend is fairly well reproduced by a blend containing a combination of SB and sulfur. This similarity is exemplified in the storage modulus profiles of 12SB-1S vs. 12SBS-0S and 5SB-3S vs. 5SBS-0S, presented in Figure 5.

Complex viscosity

Complex viscosity η^* has been used to describe the viscoelastic character of composites, such as asphalt and PMA.^{46,47} Figures 6 and 7 present master curves of the complex viscosity of NA and PMAs. These results show that all samples exhibit a viscous liquid-like behavior at low shear stress, where the loss modulus clearly exceeds the storage modulus. PMAs formulated with high polymer concentrations or high sulfur/copolymer ratios plateau at lower frequency (i.e., higher temperature). Blends prepared

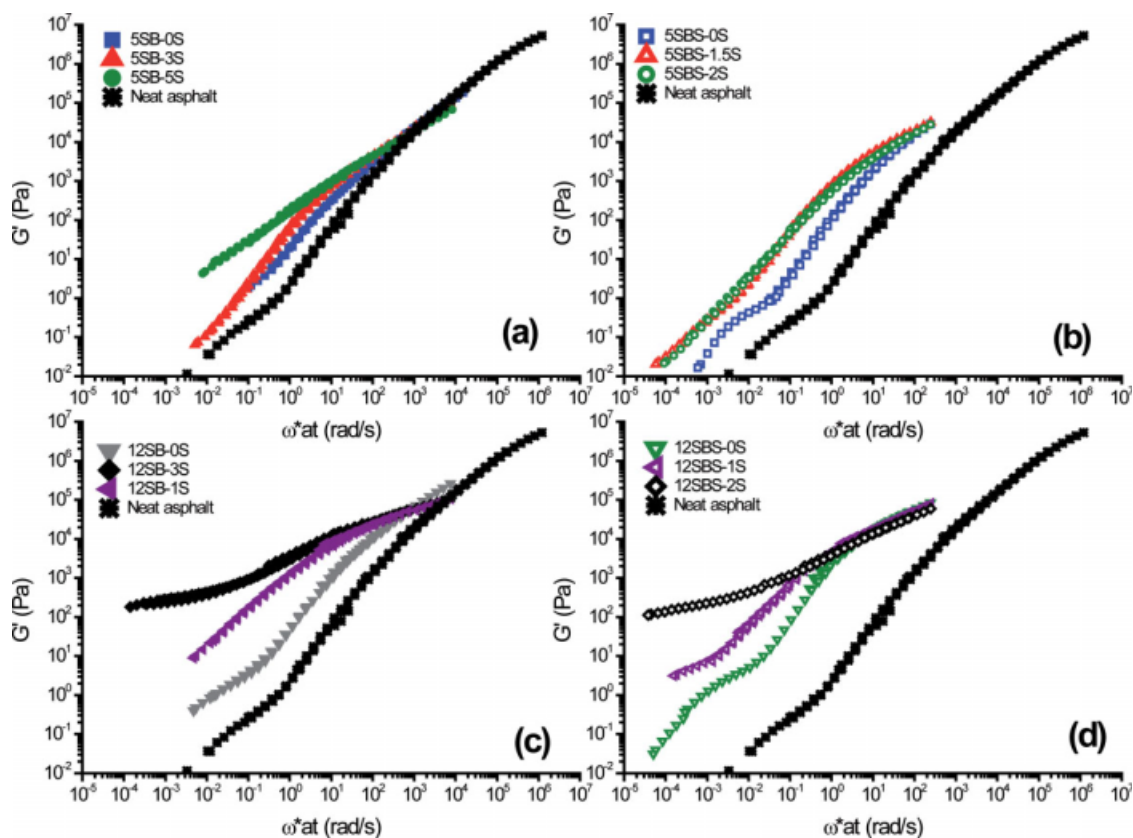


Figure 4 Master curves of storage modulus G' (G' as a function of reduced frequency ωa_T) of neat asphalt, nonvulcanized and vulcanized (with varying amounts of sulfur) SB-MAs and SBS-MAs. (a) SB-MAs containing 5 wt % SB; (b) SBS-MAs containing 5 wt % SBS; (c) SB-MAs containing 12 wt % SB; (d) SBS-MAs containing 12 wt % SBS. Guide: 5SB-3S corresponds to a PMA prepared with 5 wt % SB and 3 phr sulfur. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with SBS, regardless of sulfur content, exhibit greater resistance to flow compared with their SB analogs, since SBS-MAs exhibit higher complex viscosity and low-frequency limiting η^* . Addition of sulfur results in an increase of η^* and this effect is more evident for SBS-MA. It is also observed that the contribution of SBS to the $\eta^*(\omega)$ behavior of asphalt can be mimicked using a combination of SB and sulfur. The similarity of these PMAs is apparent when comparing the $\eta^*(\omega)$ profiles of 5SBS-0S vs. 5SB-3S and 12SBS-1S vs. 12SB-3S, as shown in Figure 7.

Black diagram

The rheological behavior of PMAs was also analyzed in terms of their black diagram (phase angle δ as a function of the complex modulus G^*), allowing the analysis of raw experimental data at a variety of shear frequencies and temperatures. Before discussing the black diagrams, it is important to mention that the master curves of complex modulus as a function of shear frequency $G^*(\omega)$ of all samples were similar, in that G^* increased smoothly with

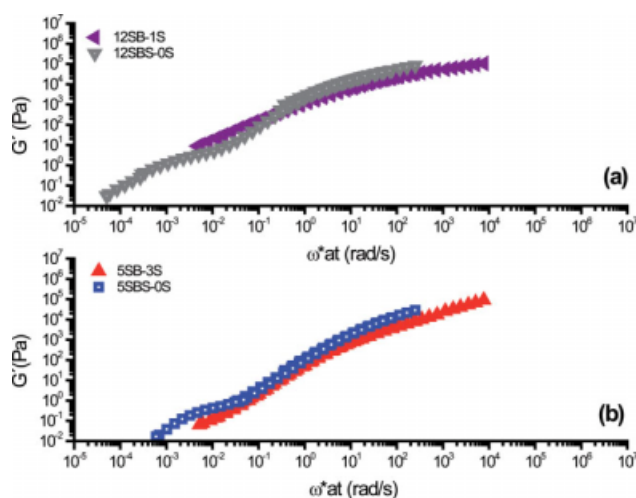


Figure 5 Master curves of storage modulus G' (G' as a function of reduced frequency ωa_T): (a) vulcanized SB-MA (1 phr sulfur) containing 12 wt % SB and nonvulcanized SB-MA containing 12 wt % SBS; and (b) vulcanized SB-MA (3 phr sulfur) containing 5 wt % SB and nonvulcanized SB-MA containing 5 wt % SBS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

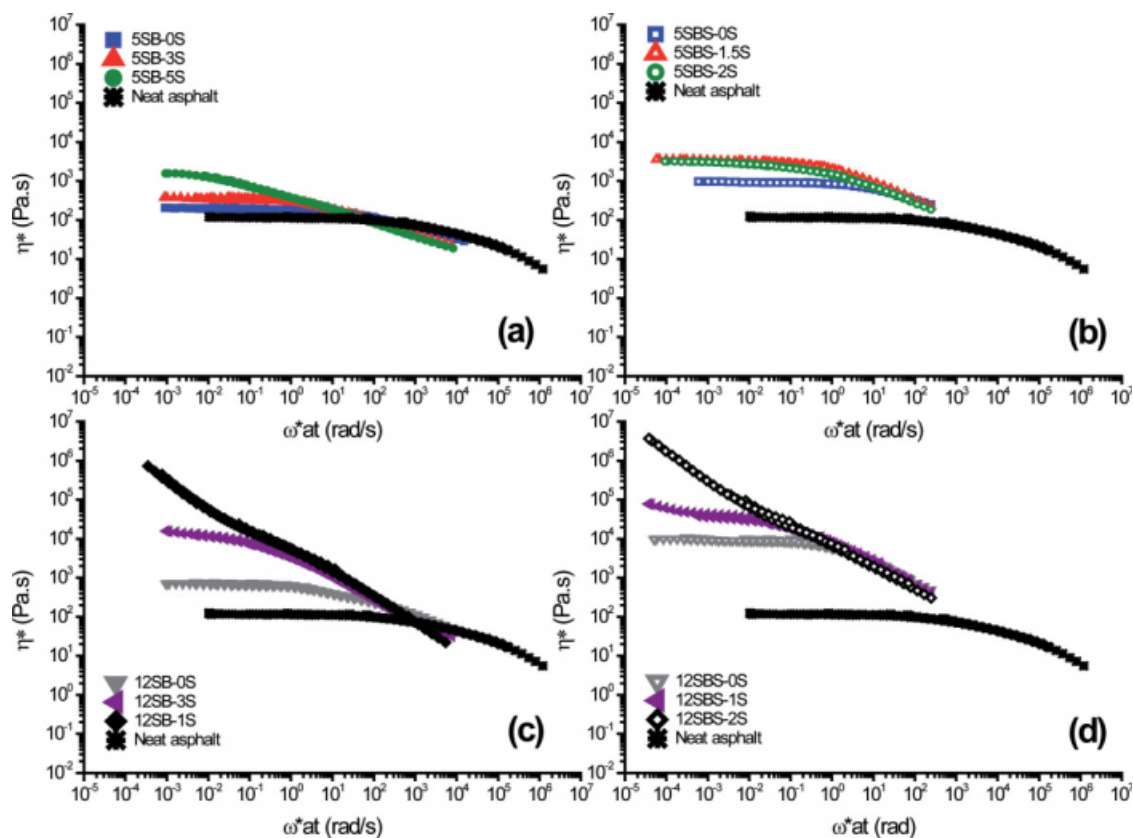


Figure 6 Master curves of complex viscosity η^* (η^* as a function of reduced frequency ωa_T) of nonvulcanized and vulcanized (with varying amounts of sulfur) SB-MAs and SBS-MAs. (a) SB-MAs containing 5 wt % SB; (b) SBS-MAs containing 5 wt % SBS; (c) SB-MAs containing 12 wt % SB; (d) SBS-MAs containing 12 wt % SBS. Guide: 5SB-3S corresponds to a PMA prepared with 5 wt % SB and 3 phr sulfur. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decreasing ω (data not shown); G^* also increased with the amount of copolymer or sulfur/copolymer ratio. Figure 8(a–d) shows the black diagram of NA and various PMAs. Slope changes in the $\delta(G^*)$ profiles of PMAs, indicative of an elastic-viscoelastic behavior that entails structural changes, are attributed to the presence of the copolymer as this behavior differs from that exhibited by NA. The type of copolymer and its concentration, as well as the sulfur/polymer ratio, strongly influence the shape of the $\delta(G^*)$ profiles [Fig. 9(a,b)]. Regardless of the type of polymer, addition of relatively small amounts of sulfur dramatically changes the elastic-viscoelastic character of PMAs [Fig. 9(a): 5SB vs. 5SB-3S and 5SBS vs. 5SBS-1.5S]. Again, black diagrams of SBS-MA and sulfur/SBS-MA are similar to those of blends produced using combinations of SB and sulfur, as observed in Figure 9 (5SBS vs. 5SB-3S and 12SBS vs. 12SB-1S). These results support the idea that the rheological behavior of a given SBS-MA or sulfur/SBS-MA can be fairly well reproduced using blends of sulfur and SB, simply by adjusting the sulfur/copolymer content.

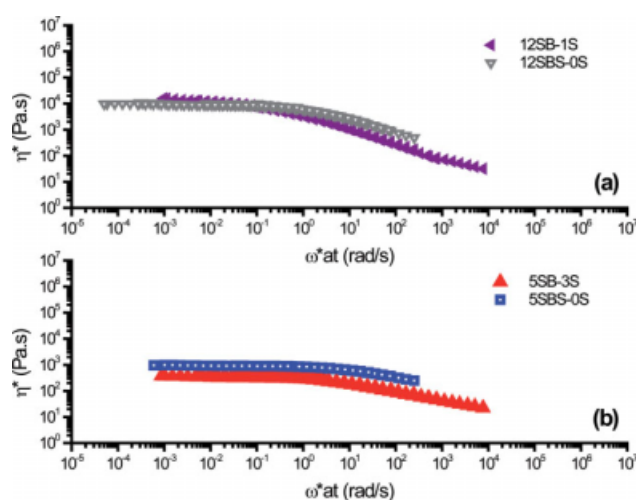


Figure 7 Master curves of complex viscosity η^* (η^* as a function of reduced frequency ωa_T): (a) vulcanized SB-MA (1 phr sulfur) containing 12 wt % SB and nonvulcanized SBS-MA containing 12 wt % SBS; and (b) vulcanized SB-MA (3 phr sulfur) containing 5 wt % SB and nonvulcanized SBS-MA containing 5 wt % SBS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

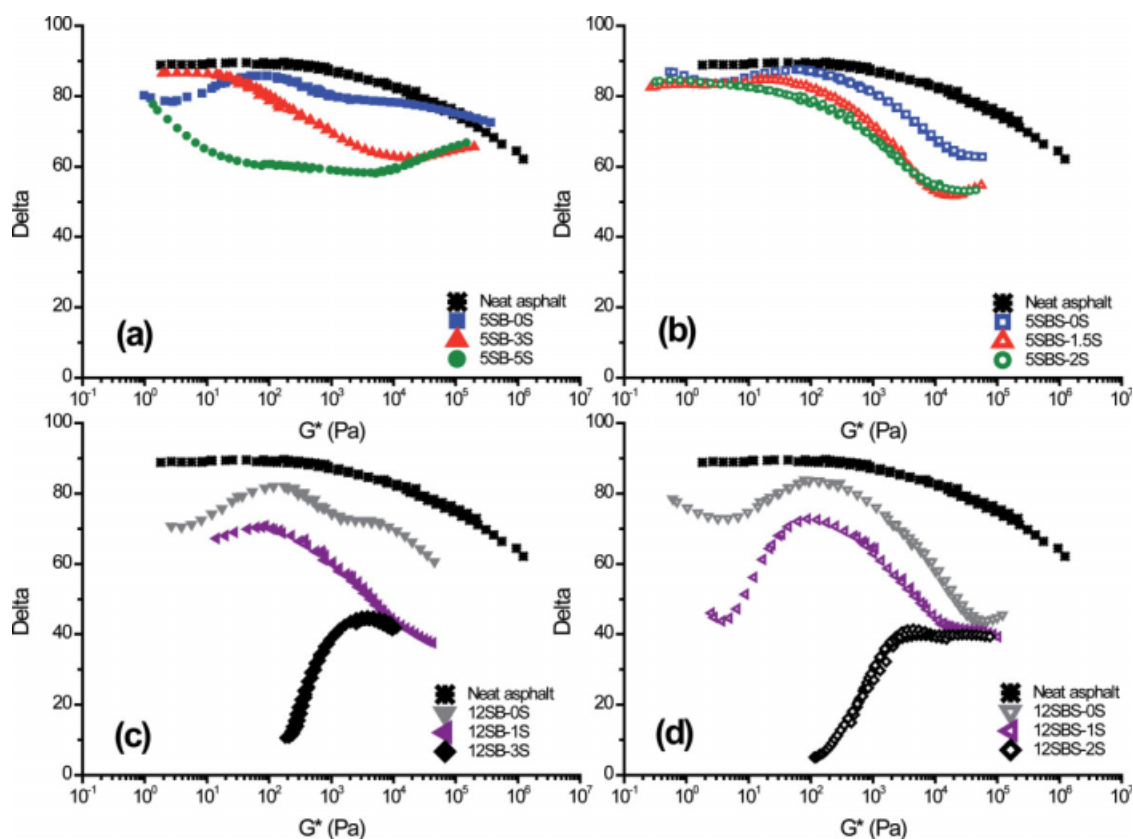


Figure 8 Master black diagrams (phase angle δ as a function of complex modulus G^*) of neat asphalt, nonvulcanized and vulcanized (with varying amounts of sulfur) SB-MAs and SBS-MAs. (a) SB-MAs containing 5 wt % SB; (b) SBS-MAs containing 5 wt % SBS; (c) SB-MAs containing 12 wt % SB; (d) SBS-MAs containing 12 wt % SBS. Guide: 5SB-3S corresponds to a PMA prepared with 5 wt % SB and 3 phr sulfur. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Isochronal plots

Phase angle isochrones have been used to characterize the elastic response of PMA⁴⁷ as δ is generally considered to be structure sensitive. Figures 10–12 present the isochronal plots $\delta(T)$ of NA and PMAs at frequencies of 1 (Fig. 10) and 10 rad/s (Fig. 11). The viscoelastic character of NA over the temperature range investigated is evident as its elastic character decreased with increasing temperature ($\delta = 67^\circ$ at $T = 60^\circ\text{C}$ to $\delta = 90^\circ$ at $T = 160^\circ\text{C}$). Although all PMAs follow the same trend as NA, the influence of the polymer-rich phase on their mechanical properties is reflected in higher elastic responses. It is also apparent that SBS-MAs exhibited higher elasticity than SB-MAs, and that the addition of sulfur increases the elastic response of PMAs. These effects are clearly observed at high temperatures ($T > 90^\circ\text{C}$) and for blends with high polymer concentration. As for the master curves previously discussed, the isochronal plots (Fig. 12) show the possibility of reproducing the rheological behavior of SBS-MA or sulfur/SBS-MA with sulfur/SB blends.

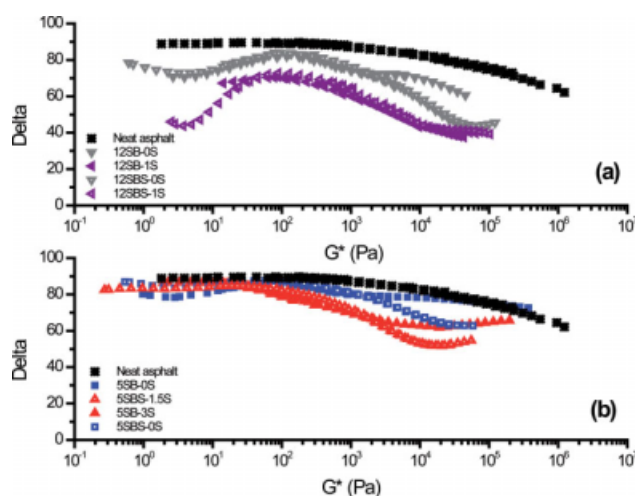


Figure 9 Master black diagrams (phase angle δ as a function of complex modulus G^*): (a) vulcanized SB-MA (1 phr sulfur) containing 12 wt % SB and nonvulcanized SBS-MA containing 12 wt % SBS; and (b) vulcanized SB-MA (3 phr sulfur) containing 5 wt % SB and nonvulcanized SBS-MA containing 5 wt % SBS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

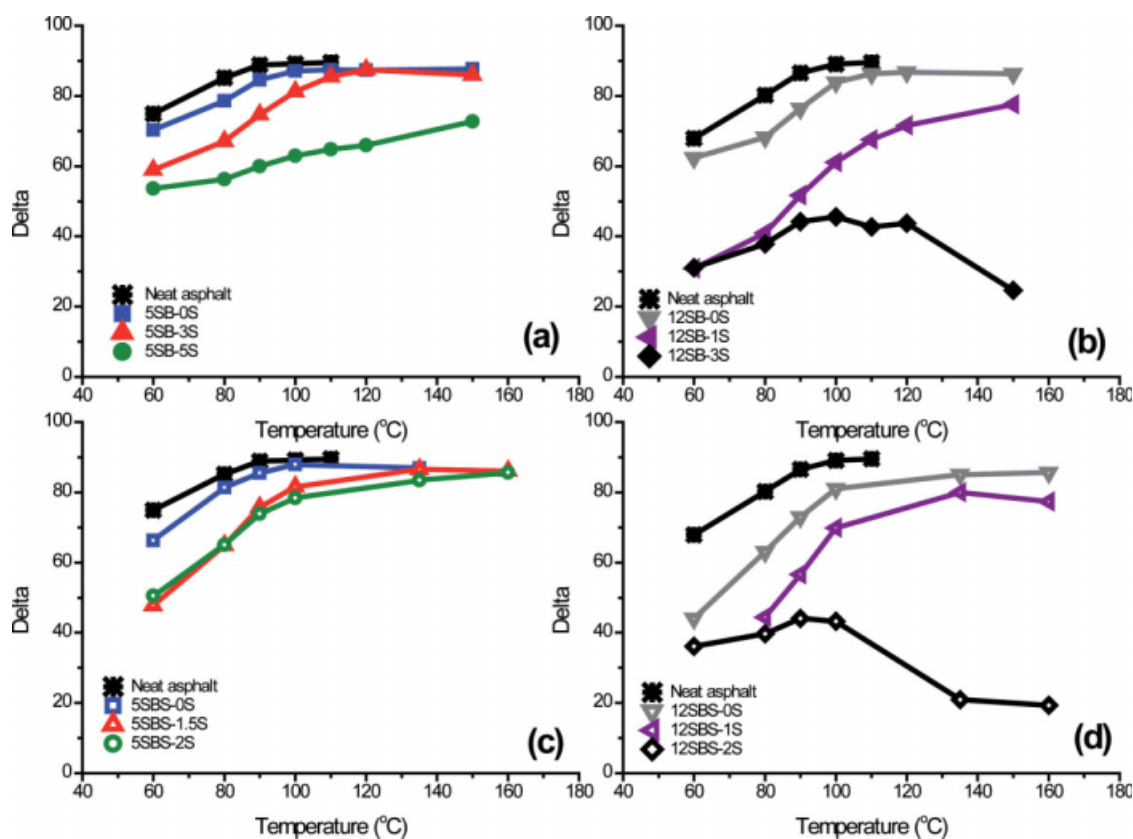


Figure 10 Isochronal ($\omega = 1$ rad/s) plots of phase angle δ as a function of temperature of neat asphalt, nonvulcanized (with varying amounts of sulfur) SB-MAs and SBS-MAs. (a) SB-MAs containing 5 wt % SB; (c) SBS-MAs containing 5 wt % SBS; (b) SB-MAs containing 12 wt % SB; (d) SBS-MAs containing 12 wt % SBS. Guide: 5SB-3S corresponds to a PMA prepared with 5 wt % SB and 3 phr sulfur. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In summary, these results clearly indicate that the rheological behavior of PMAs depends on their composition, particularly on the type and amount of polymer or sulfur/polymer ratio used in their preparation. Addition of relatively small amounts of sulfur dramatically affects the rheological behavior of SB- and SBS-based PMAs. The possibility of reproducing the rheological behavior of SBS-MA or sulfur/SBS-MA with sulfur/SB blends exists. Nonetheless, precise dosing of sulfur is particularly important as slight excess can lead to gel formation, especially in SBS-based PMAs.

DISCUSSION

To explain these results, it is important to recall certain aspects regarding the composition of asphalt, the molecular characteristics of the polymers, and polymer-asphalt and sulfur-polymer-asphalt interactions taking place during the production and hot storage processes of PMAs. In this work, a sol-type asphalt was used, which according to the asphalt micellar model, is comprised of micelles of asphal-

tenes stabilized by maltenes (resins and aliphatic compounds) embedded in a maltenes matrix. The styrene-butadiene block copolymers tested were similar in terms of their overall monomer composition and isomeric composition of the PB block; however, they differed in block size and distribution. SB [poly(styrene-*b*-butadiene)] is a linear diblock copolymer. SBS [poly(styrene-*b*-butadiene-*b*-styrene)] consists of four equivalent diblock arms emanating from a silicon-based core with PS free ends; it is considered a triblock because two PS blocks flank a central PB block. These differences are important as the microstructure, hence mechanical properties, of particles (i.e., a collection of polymer chains) is determined by the molecular characteristics of the polymer.

Polymer particles are three-dimensional networks of microphase-segregated regions of PB and PS. The polymers studied have a styrene content between 25 and 30 wt %, resulting in discrete PS regions dispersed in a continuous PB phase. The flexible PB matrix ($T_g \sim -100^\circ\text{C}$) is fastened to glassy PS domains ($T_g \sim 100^\circ\text{C}$), thus at high temperature the particles behave as a thermoplastic and at ambient temperature they behave as crosslinked rubber.

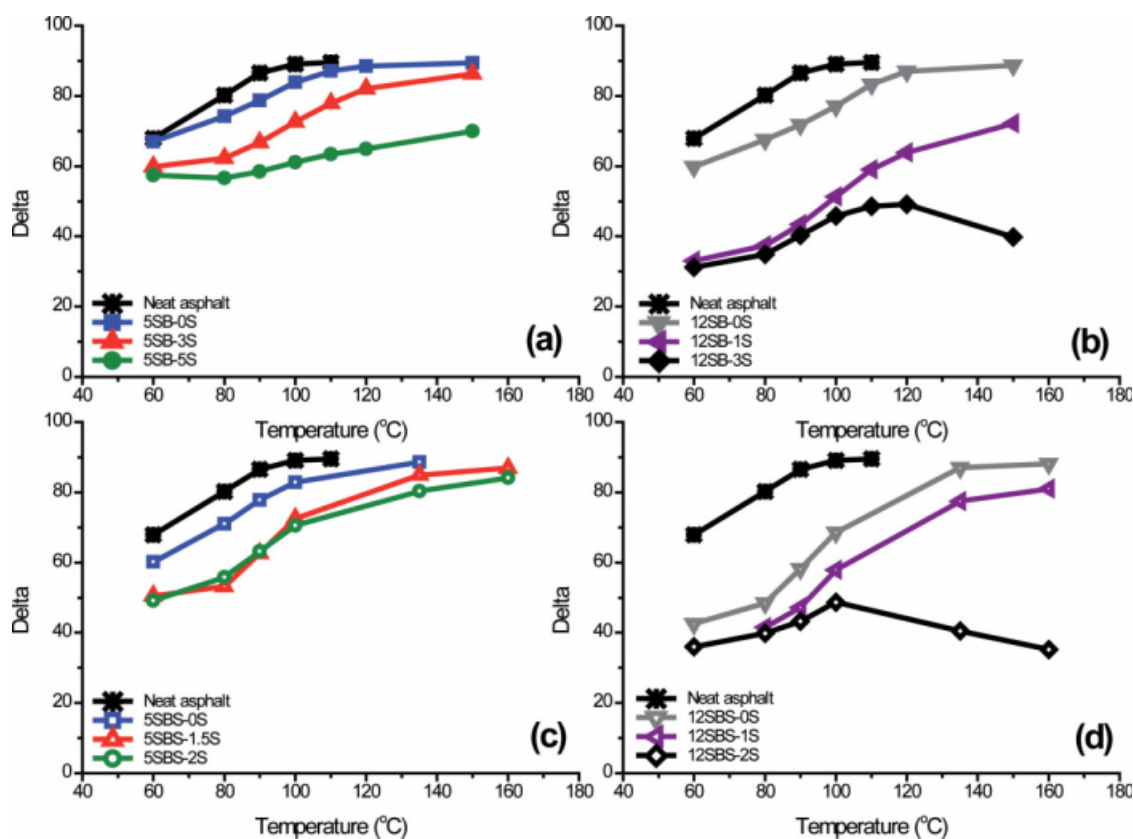


Figure 11 Isochronal ($\omega = 10$ rad/s) plots of phase angle δ as a function of temperature of neat asphalt, nonvulcanized and vulcanized (with varying amounts of sulfur) SB-MAs and SBS-MAs. (a) SB-MAs containing 5 wt % SB; (c) SBS-MAs containing 5 wt % SBS; (b) SB-MAs containing 12 wt % SB; (d) SBS-MAs containing 12 wt % SBS. Guide: 5SB-3S corresponds to a PMA prepared with 5 wt % SB and 3 phr sulfur. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Given the difference in molecular characteristics of the precursor copolymers, it is expected that the microstructure, and consequently mechanical behavior, of neat SB particles will differ from those of SBS.

In the preparation of PMAs, polymer particles interact with asphalt components: PB is preferentially swollen with maltenes, thus producing significant changes in particle microstructure and on the distribution of asphaltenes/maltenes. The result is a heterogeneous mixture composed of polymer-rich and asphaltenes-rich phases embedded in maltenes, the specific characteristics of which depend on asphalt composition, molecular characteristics of the polymer, polymer/asphalt ratio, and mixing conditions. The polymer-rich phase is presumed to be a three-dimensional network of microphase-segregated regions of PS and maltenes-swollen PB. The asphalt-rich phase is composed of micelles of asphaltenes stabilized with maltenes. The spatial arrangement and interactions of these macrophases, evidenced through their morphology and rheological behavior, will determine the properties of the PMAs. Consequently, the polymer-rich and asphalt-rich phases of SB-MA are different from those of SBS-MA, given

that the molecular characteristics of these two block copolymers are different.

When relatively small amounts of sulfur are added to freshly prepared PMAs, vulcanization occurs, producing smaller polymer-rich phases and changes in the rheological behavior. Vulcanization, which occurs through the PB block, results in increased number of covalent crosslinks, thus creating complex high-molecular-weight networks. In this sense, vulcanized SB resembles nonvulcanized SBS, as it too consists of styrene-butadiene chains chemically tethered through their PB block. Consequently, the vulcanized polymer-rich phase of SB-MAs is expected to mimic the polymer-rich phase of nonvulcanized SBS-MAs. Furthermore, vulcanization of SBS, which has a star-like architecture and higher molecular weight than SB, should result in the formation of an even more complex high-molecular-weight network. Evidently, addition of sulfur to SB-MA and SBS-MA will affect both the microstructure of the polymer-rich phase and the rheological behavior of vulcanized PMAs to a degree that depends on the extent of vulcanization. For the same degree of vulcanization, changes in the characteristics of SBS

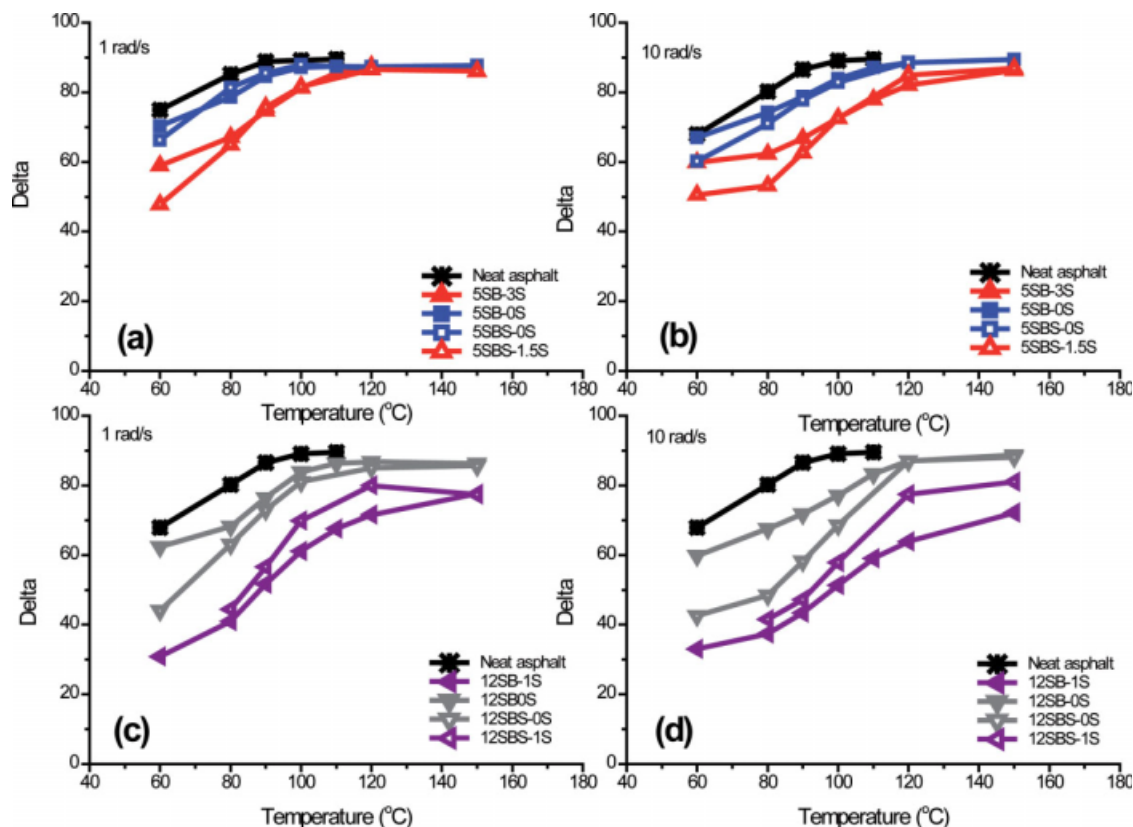


Figure 12 Isochronal plots of phase angle δ as a function of temperature of vulcanized SB-MAs and nonvulcanized SBS-MAs. (a) vulcanized SB-MA (3 phr sulfur) containing 5 wt % SB at 1 rad/s; (b) nonvulcanized SBS-MA containing 5 wt % SBS at 10 rad/s; (c) vulcanized SB-MA (1 phr sulfur) with 12 wt % SB at 1 rad/s; (d) nonvulcanized SBS-MA with 12 wt % SB at 10 rad/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and SBS-MAs will be more significant than those observed in SB and SB-MAs.

Fluorescence microscopy results revealed that PMAs containing the same amount of polymer or polymer/sulfur ratio exhibited similar morphology of the polymer-rich phase, regardless of the type of polymer used (SB or SBS). These results suggest that the molecular characteristics of the polymer have no appreciable influence over the morphology of the polymer-rich phase. On the other hand, the observed effect of sulfur is to promote polymer dispersion within the asphalt matrix as well as to increase blend stability during the hot storage process. Therefore, the spatial arrangement of the two phases present in PMAs is mainly determined by the amount of polymer and sulfur/polymer ratio.

Rheological characterization of PMAs was conducted under linear viscoelasticity conditions to preserve the blends' structure (i.e., macrophase characteristics). In contrast to fluorescence microscopy, rheology results indicate that under the same conditions of polymer concentration or sulfur/polymer ratio, PMAs prepared using SBS exhibited different viscoelastic properties than SB-containing blends. SBS-modified asphalts exhibited higher viscoelastic-

ity and elastic character than their SB analogs. These results are explained considering that SBS chains (having larger PS and PB blocks than SB, as well as an inherently three-dimensional architecture) are more readily well integrated to the three-dimensional network of the polymer-rich phase than those of SB chains.

As previously shown, PMAs prepared with a combination of sulfur and SB possessed characteristics (conventional properties, morphology, and rheological behavior) similar to those of PMAs prepared exclusively with SBS or SBS and very small amounts of sulfur. This is explained by assuming that sulfur promotes the dispersion of the polymer-rich phase in the asphalt matrix and affects chain crosslinking. The experimental similarity between the rheological behavior of vulcanized SB-MA and nonvulcanized (or less vulcanized) SBS-MA is explained by considering that the polymer-rich phase of these blends has comparable two-phase three-dimensional networks. Vulcanization of SB chains creates molecules that resemble the triblock structure of SBS with the elastomeric blocks acting as junction points between PS blocks. As mentioned previously, the higher sensitivity of SBS-MA for vulcanization is attributed to

its complex architecture and larger block molecular weight.

Lastly, results of the hot storage test reveal that addition of relatively small amounts of sulfur greatly increases the thermal stability of SB-MAs or SBS-MAs. These results are explained considering that polymer crosslinking promotes dispersion of the polymer-rich phase, observed as smaller particles, therefore preventing phase separation of the thermodynamically incompatible polymer-rich and asphalt-rich phases. Nonetheless, precise dosing of sulfur is extremely important as slight excess leads to gel formation. This balance is more delicate for SBS-MA because vulcanization of SBS molecules produces more complex networks with higher molecular weights, responsible for the increased elastic character of the PMAs. On the other hand, blends prepared with SB accept higher amounts of sulfur before becoming a gel because SB is a linear diblock with smaller block sizes than those of SBS. Thus, the formation of a three-dimensional network of micro-phase-segregated structures, hence the mechanical resistance of a PMA, is more easily tunable for SB-based systems.

Although the results presented here do not conclusively establish the relationship between the morphology and rheological properties, they show that the polymer-rich phase has an important influence on the rheological behavior of these types of blends. Further studies are required to better understand the specific role of each component on material properties.

CONCLUSIONS

This study was aimed at identifying the parameters that determine the mechanical and thermal stability of asphalt modified with styrene-butadiene copolymers and sulfur. The blends studied herein were prepared using two types of styrene-butadiene copolymers with and without sulfur to establish the effect of polymer concentration, molecular characteristics of the polymer, and sulfur/polymer ratio on the morphology and rheological properties of PMAs. Microscopy analyses of SB- and SBS-MAs revealed that the morphology of the polymer-rich phase was determined mainly by the concentration of polymer. The molecular characteristics of the polymers influenced the rheological properties of PMAs, as for the same polymer concentration, SBS-MAs were more elastic and had greater resistance to flow than SB-MAs.

Addition of small amounts of sulfur to PMAs produced dramatic changes in both the morphology of the polymer-rich phase as well as in their rheological behavior. Sulfur-containing PMAs had increased mechanical resistance, particularly SBS-MAs. Small

amounts of sulfur produce crosslinking and promote dispersion of the polymer-rich phase in asphalt, thus preventing phase separation during hot storage. The dosage of sulfur, however, should be carefully tuned to prevent gelation, especially for SBS-MAs as they are more susceptible to gel formation than SB-MAs.

Finally, we observed that the rheological behavior of SBS-MAs, with or without sulfur, is fairly well reproduced by blends of SB-modified asphalts with relatively small amounts of sulfur, suggesting that sulfur facilitates the formation of three-dimensional structures which effectively reinforce asphalt.

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