

Fundamental Characterization of SBS-Modified Asphalt Mixed with Sulfur

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ABSTRACT: The purpose of this study was to characterize the mechanical behavior of asphalt modified by styrene-butadiene-styrene (SBS) and sulfur. Viscosity, microscopy, and rheological tests were conducted to understand the engineering properties of the polymer-modified asphalt (PMA). Without the addition of sulfur, the polymer-modified asphalt was microheterogeneous and was made up of two distinct finely interlocked phases, especially at high SBS concentrations. After the addition of sulfur, the PMA was observed to have smaller asphalt domains and a fairly homogeneous dispersion of the asphalt in the SBS matrix. The compatibility between polymer and asphalt produced an elastic network into the asphalt. The addition of sulfur resulted in an excellent elastic system and substantially

increased the rheological properties of the PMA. Because of the colloidal nature of asphalt cements, their engineering properties were greatly improved because of the reinforcement of the SBS polymer and the physical-chemical interaction between SBS and asphalt. The difference in the softening point between the top and bottom layers decreased significantly, and elastic recovery increased when sulfur was present. A viscoelastic model was examined and shown to be appropriate for predicting the rheological properties of the asphalt-SBS blend mixed with sulfur. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2817–2825, 2007

Key words: compatibility; phase separation; strength; TEM

INTRODUCTION

About 96% of all paved roads and streets in the world are surfaced with asphalt binders. On average, the hot-mix asphalt (HMA) industry produces and places approximately 1200 million tons of HMA annually, valued at some \$27 billion. Asphalt used as a binder in HMA is a major byproduct of the refining industry.¹ About 50 million tons per year are produced for use primarily in road construction and repair worldwide. As pavement serves the public for transportation purposes, an important factor in road life is pavement distress. An ever-increasing number of heavy vehicles with super single tire and increased axle loads take their heavy toll on pavement performance. Polymer-modified asphalt (PMA) has been used in flexible pavements to reduce distress such as permanent deformation and cracking.^{2–4} There exists a wide variety of polymers that can be mixed with asphalt. Of these, styrene-butadiene-styrene (SBS) is probably the most frequently used polymer in asphalt modification; it is usually added as a percentage ranging from 3% to 6% by weight of the asphalt phase.^{5–8} The main

advantage of this modifying technology is that styrene and butadiene polymers are immiscible with each other. SBS has a two-phase morphology consisting of glassy microdomains made of polystyrene (PS) connected to rubber polybutadiene (PB) segments; therefore, SBS exhibits crosslinked elastomer network behavior. Allowing polystyrene domains to maintain a morphological structure originally makes SBS a good asphalt modifier because of its partial solubility. This thermoplastic elastomer behavior allows 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.^{9–12}

Storage stability, however, remains one of the most critical issues when SBS is mixed with asphalt. It is very common in the paving industry for the polymer to be blended with the asphalt and stored for weeks at a time. When the polymer is unsaturated as in the case of SBS, polymer degradation will occur. The consequences of the multiphase nature of asphalt-SBS blends is their thermodynamic instability and their tendency to macroscopically separate during storage, especially at high temperatures and in the absence of stirring. As a result, the operating conditions for the mixing procedure have to be properly chosen in order to attain a stable material that adequately balances mechanical properties and storage stability.

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TABLE I
Engineering and Chemical Properties of Base Asphalts

| Grade | Penetration 25°C (dmm) | Softening point (°C) | Viscosity 60°C (poise) | Asphaltenes (%) | Resins (%) | Aromatics (%) | Saturates (%) |
|-------|---------------------------|-------------------------|---------------------------|--------------------|---------------|------------------|------------------|
| AC-10 | 96 | 38 | 987 | 11.7 | 17.3 | 58.8 | 11.4 |
| AC-20 | 68 | 50 | 2098 | 12.2 | 17.7 | 57.1 | 12.1 |

The storage stability of SBS-modified asphalt is usually poor at elevated temperatures because of the incompatibility between the SBS and the asphalt. The addition of sulfur has been reported to improve the stability of polymer-modified asphalt. Welborn and Babashak 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.¹³ Maldonado et al. proposed a process of mixing asphalt with SBS via the addition of sulfur. This product was not practical in the paving industry because of excessive viscosity.¹⁴ Since then, methods for preparing storage-stable SBS-modified asphalt have been developed.^{15–19} Previous studies have been focused on the preparation processes and compositions of PMA. Little work has been done on the fundamental characteristics of PMA in the presence of sulfur.

Polymeric blends are viscoelastic in nature, and hence their mechanical behavior is dependent on time, temperature, and frequency in addition to blend morphology. More is required in modeling the mechanical behavior of PMA and in understanding the effect of sulfur on the engineering properties of PMA. However, no theory is available to explain the mechanism of sulfur reacting with polymer-modified asphalt. More specifically, it is not clear how the properties of SBS and sulfur additives could be optimized to obtain better performance. Understanding the role that SBS and sulfur play in the overall behavior is key to adequately selecting PMA for an optimal combination. This article presents a theoretical approach based on the micromechanical model and highlights the parameters governing the viscoelastic properties of PMA.

MATERIALS AND METHODS

Materials

AC-10 and AC-20 asphalt binders were mixed with two types of SBS (SBS-l, SBS-r) with four polymer contents. Table I lists the basic properties of asphalts provided by the China Petroleum Cooperation. The

molecular weight of the asphalt ranged from 1100 to 1200. Asphalt is traditionally regarded as a colloidal system and can be separated into four groups: asphaltenes, resins, aromatics, and saturates. The average asphaltene content was 11.9%, whereas resins, aromatics, and saturates made up 17.5%, 57.9%, and 12.7%, respectively. Such a composition has the potential for desirable compatibility with polymers. An SBS was supplied in the form of porous pellets by the Chie-Mei Enterprise Ltd. (Tainan, Taiwan). The polymer was a high-molecular-weight random block copolymer consisting of about 30% styrene and 70% butadiene in a mole-to-mole ratio. Two types of SBS copolymers were used in this study as listed in Table II. Sulfur is an industrial-grade product made by the Formosa Petrochemical Co. Ltd. The sulfur was mixed with SBS-modified asphalt at three different levels.

Sample preparation

SBS-modified asphalt was prepared by melt blending. The SBS copolymer was mixed with asphalt binders using a preparation method developed in the laboratory in order to maximize the rheological properties and to minimize asphalt degradation. The mixer, an Eyel 4 model produced by the Tokyo Kikakikae Company, could apply a constant mixing speed to ensure no voids were created in the mixtures. A propeller with an X shape was used in order to stir the polymer-modified asphalt. The mixing bath and the temperature control unit were manufactured by the Glas-Col Laboratory Products. The SBS was supplied by the manufacturer in the form of a fine uniform powder, which was suitable for mixing with asphalt because of the high surface area of the particles. The SBS was 1, 3, 5, or 7 wt % of the blend. The mixing temperature was kept constant at 170°C during the 60-min mixing process. Then sulfur was added to the blend, and the stirring continued at the same temperature for another 60 min in order to ensure homogeneous mixtures. Sulfur was 1, 3, or 5 wt % of the SBS.

TABLE II
Properties of SBS Copolymer

| Structure | Styrene–butadiene ratio | Specific gravity | Volatile matter (%) | Number average, M_n | Molecular weight, M_n |
|-----------------|----------------------------|---------------------|------------------------|--------------------------|----------------------------|
| SBS-l linear | 31 : 69 | 0.94 | 0.6 | 170,000 | 200,000 |
| SBS-r radial | 30 : 70 | 0.95 | 0.6 | 320,000 | 460,000 |

After completion, the asphalt–SBS blend mixed with sulfur was removed from the flask and divided into small containers. The blend was cooled to room temperature, sealed with aluminum foil, and stored for further testing. Note that the asphalt–SBS blends without sulfur were mixed for an additional 60 min in order to have a fair comparison.

Transmission electron microscopy

The morphology of the asphalt–SBS blend mixed with sulfur was observed with a transmission electron microscope (Zeiss 10C analytical machine). The samples were prepared by dissolving PMA in toluene (Baker, reactive grade), putting on a copper grid coated with Formvar, and evaporating the solvent to produce a film with a thickness of around 0.07 μm . This technique enabled the microstructural differences between the SBS and the asphalt in the PMA to be studied.

Stability test

The asphalt–SBS blend mixed with sulfur was poured into a toothpaste-shaped aluminum tube with a diameter of 25.4 mm (1 in) and a length 139.7 mm (5.5 in) according to ASTM D 5892. The specimen was placed vertically in an oven for 48 h at 163°C. Once cooled, the tubes were cut into three sections, and samples were taken from the top, middle, and bottom portions and reheated at 150°C to take samples for the ring-and-ball (R&B) softening point and penetration tests. The R&B softening point ($T_{\text{R\&B}}$) was determined according to ASTM D 36 and the penetration test according to ASTM D 5. The purpose of conducting the softening point test was to determine the temperature at which a consistency change occurred in the binder. PMA stability was assessed by the difference in softening point between the top and bottom samples.

Elastic recovery

In addition to conventional tests, a test of the elastic recovery of PMA was conducted to evaluate the percentage of recovery strain, measured after elongation during a conventional ductility test. The apparatus was manufactured according to ASTM D 6084. This test method is useful for confirming that sulfur has been added to the asphalt–SBS blend in order for it to have a basic elastomeric characteristic. In this test a 3-cm-long test specimen was elongated to 10 cm at a speed of 5 cm/min at 25°C and then cut in half. Elastic recovery was measured after 1 h and calculated by:

$$\text{Recovery, \%} = \frac{A - B}{A} \times 100$$

where A is the original elongation of the specimen (cm) and B is the elongation of the specimen with severed ends just touching (cm).

Rheological measurement

Rheological testing was performed on a TA-AR 2000 dynamic shear rheometer (DSR) using parallel plate geometry according to the Superpave test procedure. Plate diameter was 8, 25, or 40 mm, depending on the torque generated by the materials. The gap between the plates ranged between 0.8 and 1.9 mm and did not affect repeatability. All tests were carried out at least twice in order to assure repeatability of the results. Strain sweeps were carried out to establish the linear viscoelasticity range (LVR) of all samples. Viscoelastic behavior was considered linear if the modulus had not deviated more than 5% from its initial value. Samples were also submitted to frequency sweeps between 10^{-1} and 10^2 rad/s at a strain below the LVR. The complex modulus (G^*) and phase angle (δ) were measured with the DSR. G^* is a measure of the total resistance of a material to deformation when repeatedly sheared. Phase angle is an indicator of the relative amount of viscous (unrecoverable) to elastic (recovery) deformation.

RESULTS AND DISCUSSION

Phase compatibility

Compatibility between polymer and asphalt is critical to the engineering properties of PMAs. Transmission electron microscopy was used to study the morphology in order to characterize the nature of the continuous phase and the fineness of the dispersion of the discontinuous phase. Figure 1(a) shows the original micrographs of the asphalt–SBS blend mixed with 0 wt % sulfur. Note that in these images all horizontal bars represent a length of 500 nm, the light phase represents SBS polymer, and the dark phase is asphalt. The particles of the SBS-modified asphalt appeared to coalesce and to be large in size, as shown in Figure 1(a). At 7 wt % SBS, the polymer-modified binder showed a continuous polymer phase with dispersed asphalt globules. The asphalt particles were dispersed in the white SBS matrix coarsely, indicating SBS was difficult to disperse in asphalt. In addition, the PMA started the phase inversion, in which the polymer became the dominant phase at 7 wt % SBS. This phase inversion resulted from the SBS copolymer swollen by the oils and the asphalt enriched in asphaltene containing virtually no polymer. Because of differences in intrinsic structural features and molecular weight, asphalt and SBS were chemically immiscible. Like SBS-1, SBS-r was also dispersed as small particles in

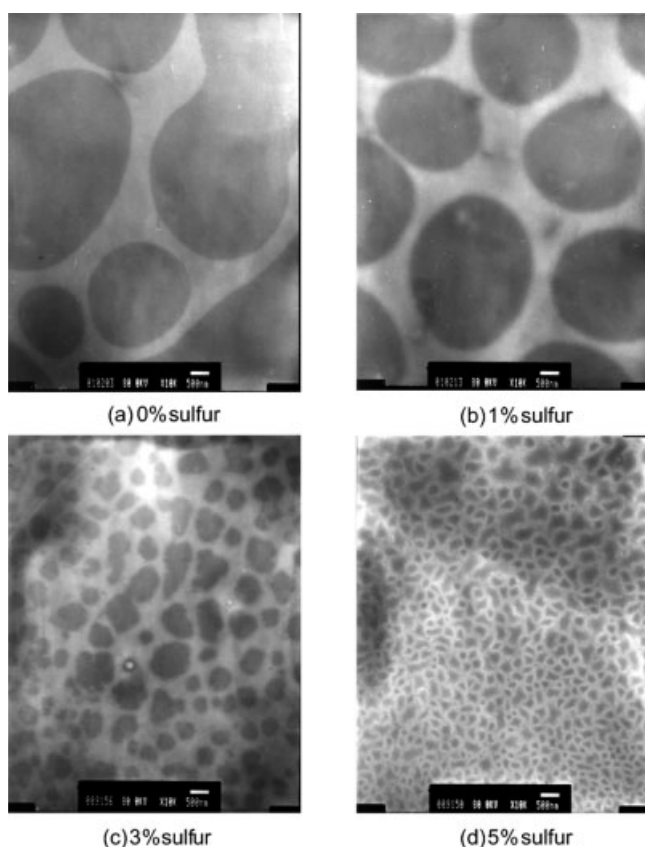


Figure 1 Micrographs of AC-10 asphalt mixed 7 wt % SBS-I blends with various sulfur contents.

the asphalt, resulting in an incompatible material. Because SBS-r is higher in molecular weight than SBS-l, SBS-r particles tended to be larger in the presence of asphalt. This incompatibility suggests that pure SBS-modified asphalt has poor storage stability.

The micrographs of the asphalt-SBS blends with 1, 3, or 5 wt % sulfur are shown in Figure 1(b–d), respectively. The asphalt particles became smaller with increasing sulfur, suggesting that sulfur promotes uniform dispersion of SBS in asphalt matrix. As the sulfur content increased, the asphalt particles decreased in diameter from approximately 1 to 0.01 μm . The decrease in polymer size meant compatibility had improved significantly through a process called vulcanization. Vulcanization is widely used in rubber/plastic blends so that the properties of a composite are as good as or, in some cases, better than those of the polymers. In PMA, vulcanization occurs when a vulcanizing agent—sulfur—is added to asphalt-SBS blends. These morphologies indicate asphalt-SBS blends mixed with sulfur would be more stable and more compatible than pure SBS-modified asphalt. The presence of sulfur improves the stability of PMA. A similar effect of vulcanization also was observed for AC-20 asphalt and SBS-r polymer.

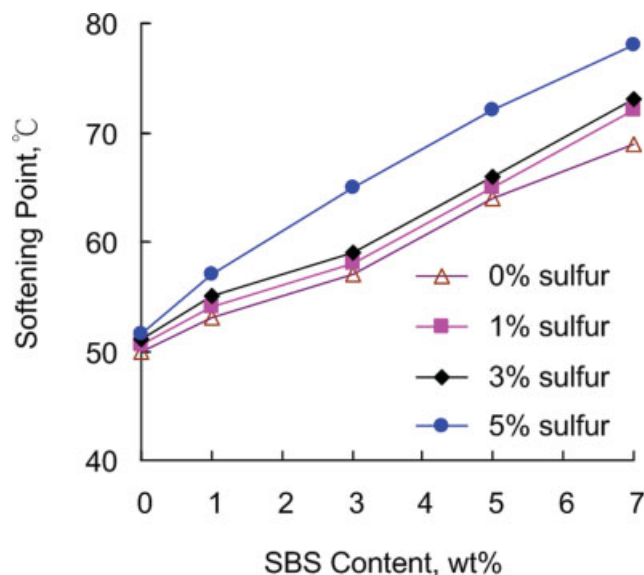


Figure 2 Changes in R&B softening point of AC-20 asphalt mixed with SBS-r with various sulfur contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Physical properties and storage stability

The effects of sulfur content on the physical properties and storage stability of PMA are shown in Figures 2–5. The ring-and-ball (R&B) softening point ($T_{R\&B}$) and penetration have been important indicators of pavement performance.²⁰ As illustrated in Figure 2, the R&B softening point increased with increasing SBS copolymer when SBS reinforced the asphalt phase. At the same time, the $T_{R\&B}$ increased

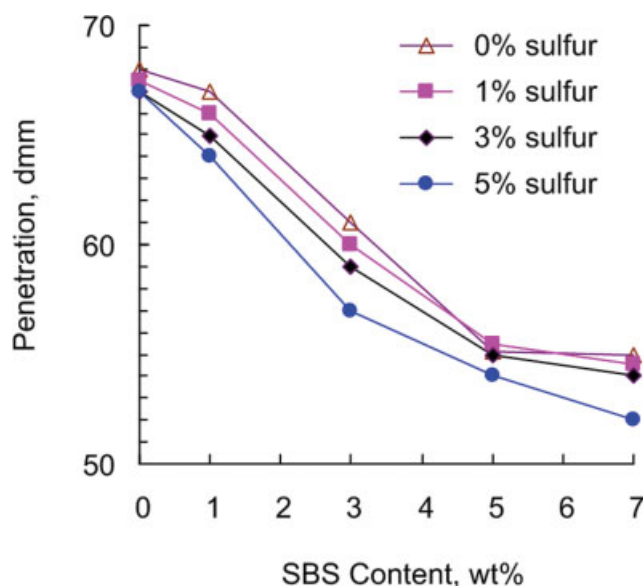


Figure 3 Change in 25°C penetration of AC-20 asphalt mixed with SBS-r with various sulfur contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

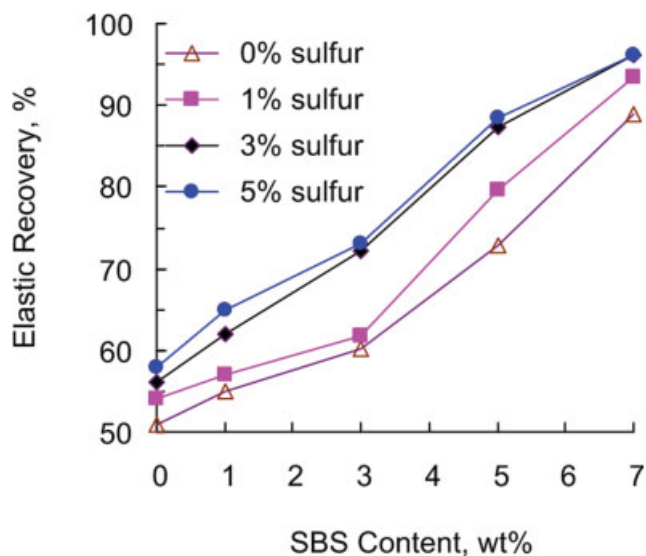


Figure 4 Changes in 25°C elastic recovery of AC-20 asphalt mixed with SBS-r with various sulfur contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with increasing sulfur content, which implies that the high-temperature properties of the asphalt-SBS blend were improved by sulfur. When the content of SBS was fixed at 3 wt %, the SBS-modified asphalt with 0 wt % sulfur showed a much lower softening point than the 5 wt % sulfur-modified asphalt having the same SBS content. Through vulcanization, the softening point of the SBS-modified asphalt was significantly promoted. Figure 3 shows that as sulfur content increased, penetration of the polymer-modified asphalt decreased. Figure 4 shows that the elastic recovery of the asphalt-SBS blends increased with increasing sulfur. The minimum requirement for elastic recovery of SBS-modified asphalt is 60% according to ASTM specification D 5892. Adding at least 3 wt % sulfur seems necessary to meet the requirement of elastic recovery. The test results shown in Figures 2–4 illustrate that the addition of sulfur clearly enhanced the engineering properties of the asphalt-SBS blends. The improvement in the engineering properties appears to have resulted from the enhanced compatibility, as demonstrated in Figure 1(c–d).

Figure 5 shows a marked difference between the top and bottom sections of pure SBS-modified asphalt, indicated by 0% sulfur content. At a relatively low SBS concentration, the polymer-modified asphalt displayed good stability. When more than 5% SBS was added, the change in the R&B softening point became apparent. The difference in the softening point between the top and bottom of PMAs after the stability test should not have been greater than 5°C in order to show there was no substantial phase separation.³ After the addition of more than 3 wt % sulfur, the difference in the $T_{R\&B}$ for the polymer-modified

asphalt could be controlled within 2°C. The storage stability of the asphalt-SBS blends was effectively improved with the addition of sulfur. The dispersed structure shown in Figure 1(c,d) was found to be favorable to the resulting physical properties of the PMA.

Rheological properties of asphalt-SBS blends mixed with sulfur

The rheological properties of asphalt-SBS blends mixed with sulfur can be characterized by constructing master curves for complex moduli (G^*) at different loading times and test temperatures. The time-temperature superposition principle, also called the method of reduced variables, is generally used for constructing master curves.²¹ In constructing a master curve using the time-temperature superposition, data obtained from a DSR are first collected over a range of temperatures and loading times. A standard reference temperature must then be selected, which generally is 25°C. The data at all other temperatures are then shifted with respect to time until the curves merge into a single smooth function. The shifting may be done based on any of the viscoelastic functions; if the time-temperature superposition principle is valid, all the other viscoelastic functions will form continuous functions after shifting. A typical set of master curves for one of the systems, AC-20 asphalt mixed with SBS-r with various sulfur contents, is shown in Figure 6. With approximately 1000 data points together, plotting marks for every experimental point would appear clogged in Figure 6 and confuse readers. Thus, for clarity, individual data points were omitted, and

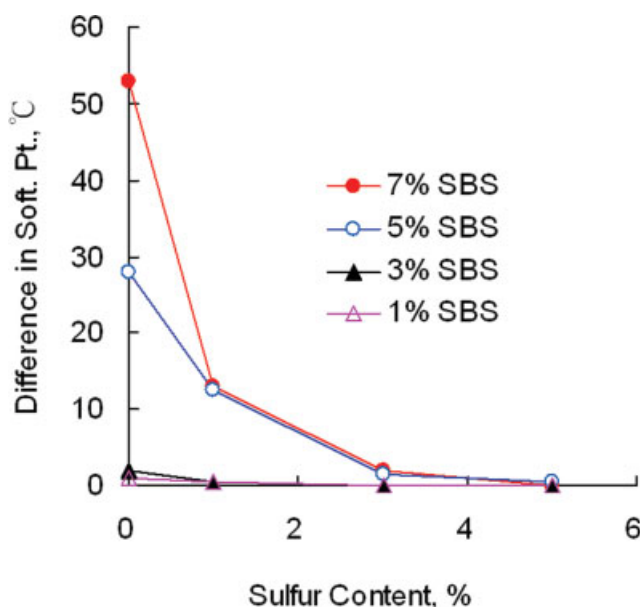


Figure 5 Effect of sulfur content on storage stability of AC-10 asphalt mixed with SBS-r. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

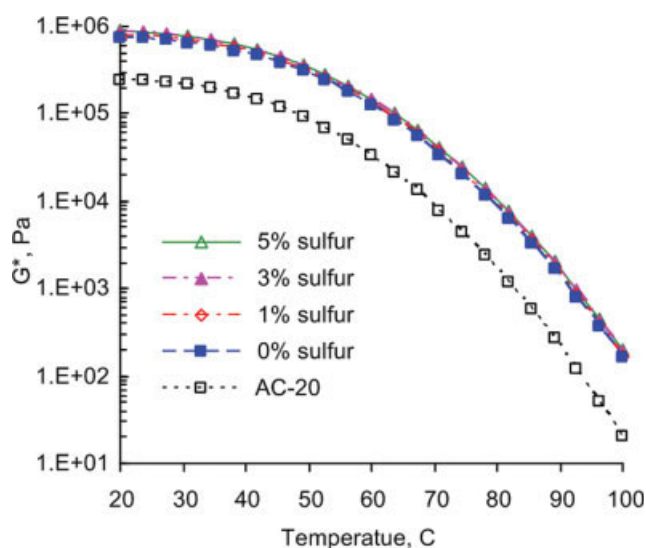


Figure 6 Complex modulus (G^*) of AC-20 asphalt mixed with 5 wt % SBS-r with various sulfur contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

master curves constructed from the time–temperature superposition principle are shown. It is indicated in Figure 6 that a smooth master curve can be formed for both pure asphalt and PMA.

The complex modulus of pure asphalt was lower than that of SBS-modified asphalt. Because the general shapes of both asphalt and PMA are similar, it is believed the viscoelastic trend of PMA was inherited from the asphalt binder; however, with the help of sulfur acting as a vulcanization agent, SBS shifted vertically up the master curve of PMA. Similar results were observed from the sets of master curves generated for other systems including AC-10 asphalt and SBS-1.

Asphalt binders are generally reinforced by adding polymers, as shown in Figure 6. Not only did the asphalt–SBS blends mixed with sulfur become harder, but the rheological type also changed, that is, the shape of the master curve for blends was different from that for pure asphalt. This subtle difference was discerned by calculating the complex modulus ratio of the blend to AC-20 asphalt, as shown in Figure 7.

It can be seen in Figure 7 that effect of the addition of SBS and sulfur on the moduli was lower at lower temperatures and greater at higher temperatures. The higher the sulfur content, the higher was the modulus ratio. The modulus of asphalt binders was close to that of sulfur at low temperatures. Therefore, the effect of sulfur on asphalt cements was decreased at low temperatures. Stiffness ratios were observed to be higher at high temperatures because the difference in the modulus between asphalt and sulfur became larger. For example, asphalt became viscous in hot

weather, whereas sulfur remained relatively rigid. Taking the time–temperature superposition principle into considered suggests that the introduction of sulfur had little effect when the loading time was short but decreased the viscous component of the response when the loading time was long. As illustrated in Figure 7, high stiffness ratios at high temperatures imply the addition of sulfur could enhance the engineering properties of PMA to improve its ability to resist rutting on pavement during summer. In contrast, stiffness ratios at low temperatures remained unchanged, indicating PMA was still flexible enough to combat fatigue and low-temperature cracking after the addition of sulfur.

The test results presented in Figure 8 confirmed that the addition of sulfur resulted in smaller $\tan \delta$ values. The $\tan \delta$ value was maintained within a relatively stable range with decreasing frequency for asphalt mixed with sulfur, whereas conventional asphalt binders showed a dramatic increase. The addition of sulfur helped the polymer-modified asphalt to behave as an elastic network. Adding sulfur, thus, was beneficial to reducing the tendency toward rutting in hot weather. At the same time, the smaller phase angles suggest that the addition of sulfur could reduce the possibility of fatigue cracking on pavement.

The degree of stiffening effect was dependent on asphalt and SBS as well as sulfur. Figure 9 shows that for the two asphalts tested, AC-10 and AC-20, the relative increase was asphalt dependent. The stiffening effects had three possible causes: (1) the volume filling of the SBS polymer, (2) the physical–chemical interaction between asphalt and SBS, and (3) the dispersion function from sulfur.

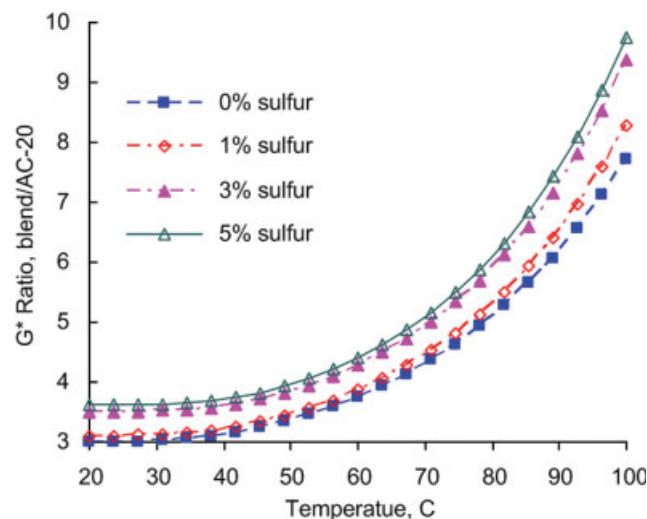


Figure 7 Complex modulus (G^*) ratio of AC-20 asphalt mixed with 5 wt % SBS-r with various sulfur contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

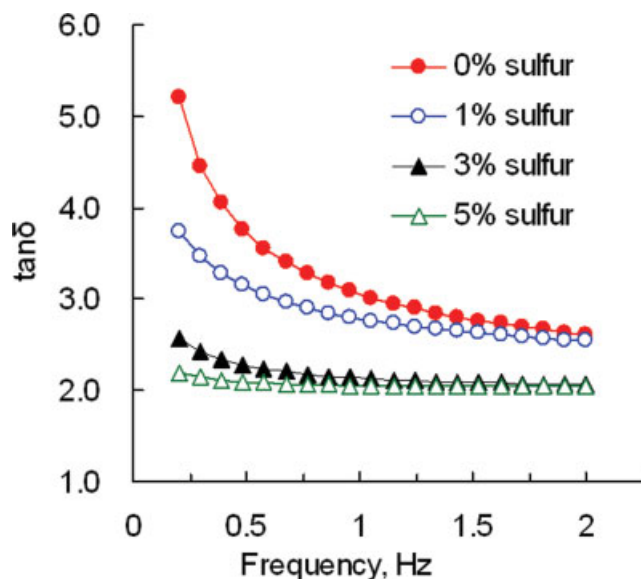


Figure 8 Effect of sulfur on $\tan \delta$ of AC-20 asphalt modified with 5 wt % SBS-r at 60°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Modeling rheological properties of asphalt-SBS blends mixed with sulfur

For inhomogeneous materials like an asphalt-SBS blend mixed with sulfur, the engineering properties of PMA were strongly influenced by the characteristics of each constituent that formed the material. When asphalt was mixed with SBS and sulfur, the resulting mastic was a composite in which the asphalt was the matrix and the SBS was the filler, whereas the sulfur was a dispersion agent. A micromechanical model allows an engineer to predict the properties of the composite, given the volume percentage and properties of the components. Several micromechanical models have been developed to calculate the viscosity or modulus of viscoelastic composites. Among them are those developed by Einstein, Mooney, Kerner, and Nielsen.^{22–25} These models all assume the relationship between stress and strain is linear. The theory of composite systems started with the equation developed by Einstein. His equation predicts the viscosity of a suspension of rigid spherical particles in a dilute fluid. It is applicable only for materials that have low concentrations of noninteractive filler and only provides steady-state viscosity. Mooney's equation expanded that of Einstein to cover a wider range of concentrations under perfect adhesion. However, when the matrix is a highly viscous material, the values for viscosity predicted by the Mooney equation are far too large.

Kerner developed an equation to calculate the shear modulus of a composite provided there is good adhesion between the two phases. However, Kerner's equa-

tion generally predicts a low modulus when the modulus of the filler is close to that of the matrix.

None of these equations are appropriate for predicting the modulus of SBS-modified asphalt because (1) they are used to calculate only the viscosity and (2) the values they predict for viscoelastic composites are unreliable when the modulus of the matrix is close to that of the filler.

Nielsen modified Kerner's equation to take into account the packing properties of the filler and the relative modulus of the two phases. Perfect adhesion between two phases is assumed. By averaging the stress across a plane orthogonal to the applied load, he developed equations as follows:

$$G_c(t, T) = G_m(t, T) \cdot \frac{1 + A \cdot B \cdot V_f}{1 - B \cdot \phi \cdot V_f} \quad (1)$$

$$\phi = 1 + \frac{1 - V_p}{V_p^2} \cdot V_f \quad (2)$$

where subscript c is the composite, subscript m is the matrix, subscript f is the filler, G is the complex modulus that is changing with time (t) and temperature (T), V_f is the volume fraction of the fillers (filler volume/composite volume), V_p is the maximum filler packing volume ratio (filler solid volume/apparent filler volume), ϕ is the function of the volume fraction of each component, A is the factor relating to the geometry of the filler and Poisson's ratio of the matrix, and B is the factor relating the relative stiffness of filler and matrix.

Factor A is the factor used to indicate the effect of filler shape and matrix Poisson ratio (ν) on the viscoelastic composite. Parameter A is related to the

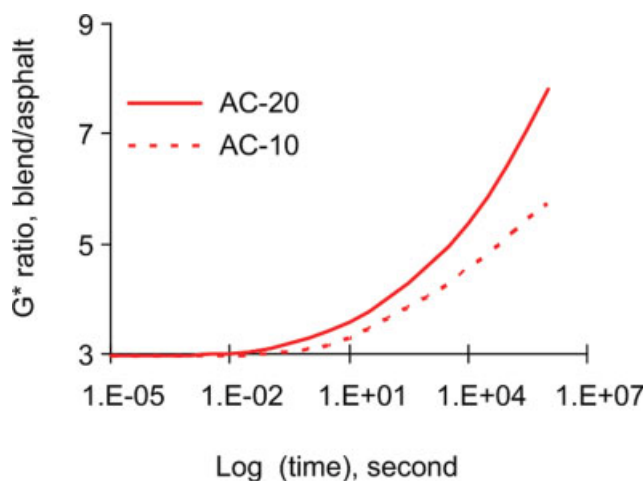


Figure 9 Complex modulus (G^*) ratio of asphalt mixed with 5 wt % SBS-I and 3 wt % sulfur. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

generalized Einstein coefficient, K_E , which is shown by $A = K_E - 1$. The other factor, B , is given by the following equation:

$$\frac{\frac{G_f}{G_m} - 1}{\frac{G_f}{G_m} + A}$$

where G_f ranges from 5 to 10^4 MPa depending on temperature and loading time. At the same test conditions, the value of G_f is distinctly larger than that of G_m . Note that parameter B approaches 1 when the ratio of G_f to G_m becomes significantly large.

This equation explains well what was discussed about the complex modulus ratio shown in Figure 7. When the modulus of asphalt is close to that of SBS at lower temperatures, the value of parameter B approaches zero. As a result, the ratio of G_c to G_m becomes smaller at low temperatures, as shown in eq. (1); thus, the modulus ratios with a short loading time is less than that with a long loading time according to the time-temperature superposition principle. The trend predicted by this equation corresponds to what can be observed in Figure 7. In addition, the equations have been successfully used to predict the modulus of various viscoelastic composites²⁶; thus, Nielsen's model was chosen to predict the rheological properties of the asphalt-SBS blend mixed with sulfur in this study.

The data shown in Figure 6 were fitted to eq. (1) to estimate the parameters. Nielsen's model was used to determine these parameters for each concentration using nonlinear regression analysis. To perform this task, the complex modulus was calculated according to the method of least squares. The pre-

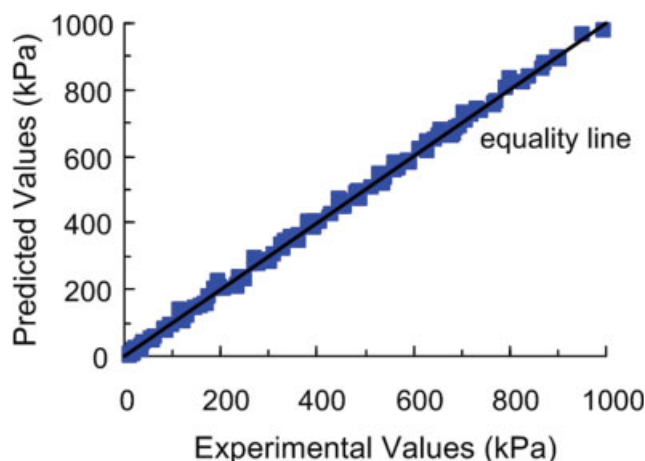


Figure 10 Comparison of measured values with predicted values. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

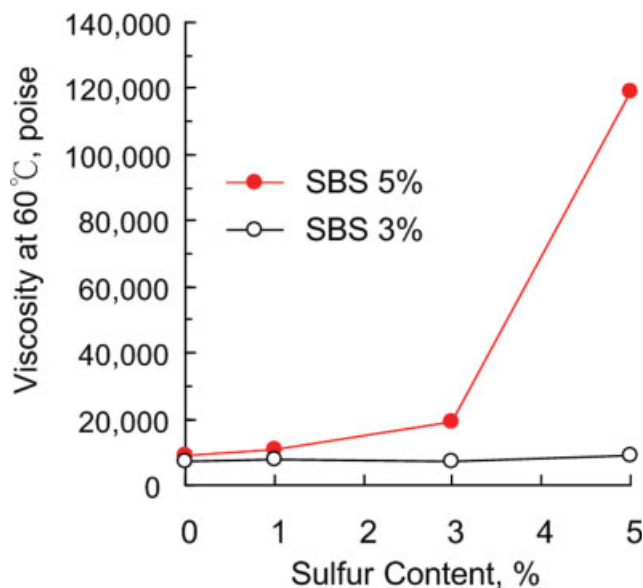


Figure 11 Effect of sulfur on 60°C viscosity for SBS-modified asphalt. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dicted values based on eqs. (1) and (2) matched well with the measured values, as shown in Figure 10.

Using such a procedure is consistent with our definition of parameters and also gives low variability in nonlinear curve fitting. For practical purposes, the effect of adding sulfur on the viscosity of SBS-modified asphalt is also shown in Figure 11. The addition of sulfur had limited influence on asphalt mixed with 3 wt % SBS. When the content of SBS was fixed at 5 wt %, the SBS-modified asphalt with 5 wt % sulfur showed a much larger viscosity than that with 3 wt % sulfur having the same SBS content. A PMA specification in Taiwan has called for a viscosity of at least 8000 poises for heavily trafficked highways. In this case, it seems that 5 wt % SBS and 3 wt % sulfur will be needed to achieve the required viscosity and stability when mixed with asphalt. By using the fundamental properties of each phase, the Nielsen model has been shown to be able to predict the rheological properties of asphalt-SBS blends mixed with sulfur. This suggests there is good adhesion among asphalt, SBS, and sulfur because this model assumes good adhesion among all the components. Again, this good-adhesion assumption corresponded to the storage stability of asphalt-SBS blends mixed with sulfur. The addition of sulfur resulted in smaller asphalt globules, as shown in Figure 1(b-d). The surface area of the smaller particles was much larger than that of the larger ones. In a situation with good adhesion, smaller particles have a higher interfacial area, thus increasing the potential adsorption and stiffening the composite system.

CONCLUSIONS

In the present study radial and linear styrene-butadiene-styrene (SBS-r and SBS-l) copolymers were blended with AC-10 and AC-20 asphalt binders to investigate the effect of sulfur on the polymer-modified asphalt (PMA). With a relatively low sulfur level, a continuous phase was present, and the composite behaved like asphalt with a moderately enhanced elastic response. The appearance of a dispersed structure began at 3–5 wt % sulfur by weight of SBS. At high sulfur concentrations the compatibility of SBS-modified asphalt was enhanced. Micrographs obtained from a transmission electron microscope illustrated that the addition of sulfur significantly improved the storage stability of SBS-modified asphalt at high temperatures. SBS-r exhibited larger particles in the presence of asphalt than did SBS-l. *In situ* chemical reactions resulting from sulfur could reduce the coarseness of SBS and enhance the solubility of the polymer in the asphalt. The storage stability of both SBS-l and SBS-r polymers mixed with asphalt was significantly improved after the addition of sulfur. Because of the colloidal nature of asphalt, the mechanical properties of asphalt-SBS-l and asphalt-SBS-r blends were enhanced for two reasons: (1) the presence of sulfur, and (2) the swelling of the polymer. Increasing sulfur levels led to an increase in the complex modulus ratio of SBS-modified asphalt to pure asphalt, and consequently the addition of sulfur changed the mechanical behavior of SBS-modified asphalt. The sulfur reinforcement became pronounced with long loading times. To better understand how the engineering properties of polymer-modified asphalt were influenced by the behavior of each individual component, a micromechanical model was presented to model the rheological properties of the asphalt-SBS blend mixed with sulfur. Future topics for the asphalt-polymer-stabilizer system include the kinetics and reaction mechanism and their effects on the engineering properties of PMA.

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