English

Fundamental Characterization of SBS-Modified Asphalt Mixed with Sulfur J.S. Chen^{*}, and C.C. Huang

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Introduction

About 96% of all paved roads and streets in the world are surfaced with asphalt binders (EAPA 1998). Asphalt used as a binder in hot-mix asphalt (HMA) is a major by-product of the refining industry. As pavements serve public for transportation purposes, an important factor in road life is the pavement distress. Polymer-modified asphalt (PMA) has been used in flexible pavements to reduce distress such as permanent deformation and cracking. Of all these polymers,



styrene-butadiene-styrene (SBS) is probably the most frequently used polymer in asphalt modification; it is usually added in percentages ranging from 3% to 6% by weight with respect to the asphalt phase (Becker et al. 2003; McKay et al. 1995). The main advantage of this modifying technology is that styrene and butadiene polymers are immiscible to each other. With the modification of asphalt by SBS, the hightemperature rutting resistance and temperature susceptibility of asphalt, as well as its low-temperature flexibility properties, are effectively improved (Schuler et al. 1985).

Storage stability, however, remains one of the most critical issues when SBS mixing 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 contains unsaturation as in the case of SBS, polymer degradation will occur. The consequence of this multiphase nature of asphalt-SBS blends is that they are thermodynamically unstable and tend to macroscopically separate during storage, especially at high temperatures and in the absence of stirring. The storage stability of SBS-modified asphalt is usually poor at elevated temperatures due to incompatibility between SBS and asphalt. Pfeiffer and Van Doormaal (1936) 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.

More is required in modeling the mechanical behavior of PMA and 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 performances. The understanding of the role SBS and sulfur play in the overall behavior provides the key by which PMA can be adequately selected for optimal combination. This article presents a theoretical approach based on the micromechanical model and highlights the parameters governing the viscoelastic properties of PMA.

Phase Compatibility





The compatibility between polymer and asphalt is critical to the engineering properties of PMAs. The morphology was studied by using transmission electron microscopy (TEM) to characterize the nature of the continuous phase and the fineness of the dispersion of the discontinuous phase. Fig. 1(a) shows the original micrographs of the asphalt-SBS blend mixed with 0 wt% sulfur. The light phase in the picture represents the SBS polymer and the dark phase is the asphalt. The particles of the SBS-modified asphalt appear to coalescence and their size appears large, as shown in Fig. 1(a). At 7 wt% SBS, the polymer-modified binder shows a continuous polymer phase with dispersed asphalt globules. The asphalt particles are dispersed in the white SBS matrix coarsely, indicating that SBS is difficult to disperse into asphalt. This incompatibility implies that pure SBS-modified asphalt has poor storage stability.

The micrographs of the asphalt-SBS blends with 1, 3, 5 wt% sulfur are shown in Figs. 1(b) to 1(d), respectively. The size of asphalt particles becomes smaller with increasing sulfur, implying that sulfur promotes a uniform dispersion of SBS in asphalt matrix. As the sulfur content increases, the size of asphalt particles approximately decreases from 1 to $0.01 \ \Box$ m. The decrease in polymer size means the compatibility has been improved significantly through a process called vulcanization. According to these morphologies, the asphalt-SBS blends mixed with sulfur appear to be more stable and compatible than the pure SBS-modified asphalt. The presence of sulfur improves the stability of PMA.

Physical Properties and Storage Stability

The effect of sulfur content on the physical properties and storage stability of PMA is shown in Figs. 2 to 5. The ring-and-ball (R&B) softening point ($T_{R\&B}$) and the penetration value have been an important indicator of pavement performance. As illustrated in Fig. 2, R&B softening points increase with increasing SBS copolymer when SBS reinforces the asphalt phase. At the same time, $T_{R\&B}$ increases

with increasing sulfur content, which implies that the high-temperature properties of the asphalt-SBS blend are improved by sulfur. When the content of SBS is fixed at 3 wt%, the SBS-modified asphalt with

0 wt% sulfur shows a much lower softening point compared with the 5 wt% sulfur-modified asphalt having the same SBS content. Through vulcanization, the softening point of the SBS-modified asphalt is significantly promoted. Fig. 3 shows that, as the sulfur content increases, the penetration of polymermodified asphalt decreases. Fig. 4 shows that the elastic recovery of asphalt-SBS blends increases with increasing sulfur. The minimum requirement for the elastic recovery of SBS-modified asphalt is 60% according to ASTM specification D 5892. Adding at least 3 wt% sulfur seems to be necessary to meet the requirement of elastic recovery. Test results presented in Figs. 2, 3 and 4 illustrate that the addition of sulfur clearly enhances the engineering properties of asphalt-SBS blends. The improvement on the engineering properties appears to result from the enhanced compatibility, as demonstrated in Figs. 1(c) to 1(d).



Figure 2. Change in R&B softening point of AC-20 asphalt mixed with SBS-r under various sulfur contents



Figure 3. Change in 25 [] C penetration of AC-20 asphalt mixed with SBS-r under various sulfur contents

Fig. 5 shows that there exists a marked difference in 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 displays good stability. When SBS is added more than 5%, the difference in the R&B softening point becomes distinct. Softening points between the top and the bottom of PMAs after the stability test should not be higher than 5 \square to show there is no substantial phase separation. After the addition of more than 3 wt% sulfur, the T_{R&B} difference for the polymer-modified asphalt could be controlled within

 $2 \square C$. The storage stability of an asphalt-SBS blend is effectively improved with the addition of sulfur. The dispersed structure shown in Figs. 1(c) to 1(d) was found to be favorable to the resulting physical

properties of PMA.



Figure 4. Changes in 25 🛛 C elastic recovery at of AC-20 asphalt mixed with SBS-r under various sulfur contents



Figure 5. Effect of sulfur content on storage stability of AC-10 asphalt mixed with SBS-r

Conclusions

Micrographs obtained from a transmission electron microscope illustrated that the addition of sulfur significantly improves the storage stability of SBS-modified asphalt at high temperatures. After the addition of sulfur, PMA showed smaller asphalt domains and a fairly homogeneous dispersion of the asphalt in the SBS matrix. Appearance of a dispersed structure began at 3 to 5 wt% sulfur by weight of SBS. At high sulfur concentrations the compatibility of SBS-modified asphalt was enhanced. Because of the colloidal nature of asphalt cements, their engineering properties of asphalt were highly improved because of the reinforcement of the SBS polymer, and the physical-chemical interaction between SBS and asphalt.

References

Becker, M.Y., Muller, A.J., Rodriguez, Y.R. (2003). Use of Rheological Compatibility Criteria to Study SBS Modified Asphalt. *Journal of Applied Polymer Science*, Vol.90, pp.1772-1882.

European Asphalt Pavement Association (1998). Asphalt in Figures, The Netherlands, Breukele.

McKay, K.W., Gros, W.A., Diehl, C.F. (1995). The Influence of Styrene-Butadiene Diblock Copolymer on

Styrene-Butadiene Styrene Triblock Copolymer Viscoelastic Properties and Product Performance. *Journal of Applied Polymer Science*, Vol.56, pp.947-958.

Pfeiffer, J.P.H. and Van Doormaal, P.M. (1936). The Rheological Properties of Asphaltic Bitumen. *Journal of Institute of Petroleum*, Vol.22, pp.414-440.

Shuler, T.S., Collins, J. H. and Kirkpartick, J.P. (1985) Asphalt Rheology: Relationship to Mixture. *ASTM Special Technical Publication* 941, pp.82-95.

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