Asphalt Modified by Styrene-Butadiene-Styrene Triblock Copolymer: Morphology and Model

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Abstract: The styrene-butadiene-styrene (SBS) triblock copolymer was used to modify the asphalt binder. The morphology and engineering properties of the binders were investigated using transmission electron microscopy (TEM), rotational viscometer, and dynamic shear rheometer. The morphology of polymer-modified asphalt was described by the SBS concentration and the presence of microstructure of the copolymer. When the SBS concentration increased, the copolymer gradually became the dominant phase, and the transition was followed by a change in engineering properties of SBS-modified asphalt. Results from TEM showed that depending on the asphalt and copolymer source, a variety of morphology can be found. The SBS-modified binders might show a continuous asphalt phase with dispersed SBS particles, a continuous polymer phase with dispersed asphalt globules, or two interlocked continuous phases. The optimum SBS content was determined based on the formation of the critical network between asphalt and polymer. Because of this network formation, the binders showed a large increase in the complex modulus that indicates resistance to rutting. At low SBS concentrations, the Kerner model was found to be appropriate to estimate the rheological properties of SBS-modified asphalt. An adapted Kerner equation was proposed in this study to predict the complex modulus of modified asphalt at high SBS concentrations.

Introduction

Increased traffic factors such as heavier loads, higher traffic volume, and higher tire pressure demand higher performance pavements. A high performance pavement requires asphalt cement that is less susceptible to high temperature rutting or low temperature cracking. Asphalt exposed to a wide range of load and weather conditions, however, does not have good engineering properties, because it is soft in a hot environment and brittle in cold weather. Therefore, asphalt is usually reinforced by polymers to improve its mechanical properties. Mixing asphalt with polymers that are practically immiscible has become very important, because an inhomogeneous material can be attained to meet the performance demand. In describing the microstructure interacting between asphalt and polymer, the term ''morphology'' is often used.

A limited number of polymers have been employed to mix with asphalt, including thermoplastics—ethylene-vinyl acetate (EVA), low density polyethylene (LDPE), high density polyethylene (HDPE), ethylene-propylene-diene (EPDM)—and elastomers—styrene-butadiene-styrene (SBS), styrene-butadiene random copolymers (SBR), and styrene-isoprene-styrene (SIS).

Among these, the most common one is poly-butadiene-base material, due to its excellent engineering properties and relatively low cost (Blanco et al. 1995, 1996; Brule 1996; Bahia et al. 1998; Lesueur et al. 1998) The wide range of properties attainable with these systems were either impossible to obtain from an individual polymer or would involve costly development of new polymers. To have a new material with good performance, it is required to understand the fundamental properties of polymer-modified asphalt (PMA). For this reason, a great deal of work has been focused on PMA (Bandyopadhya et al. 1997; Isacsson and Lu 1999; Gahvari 1997; King et al. 1992; Kraus 1982; Lee and Demirel 1987; Lewandowski 1994; Little et al. 1987) PMA needs to be engineered by choosing the right binder for application and making sure any additive used is compatible with the asphalt. Thus, this study tries to analyze mechanical properties of PMA based on the morphological structure of asphalt and polymer.

To improve the engineering properties of paving grade asphalt cement, SBS triblock copolymers were used in this study. The PMA generally shows enhanced properties at temperatures tested. However, no theory is available to explain why polymers are good to modify asphalt. More specifically, it is not clear how the properties of the polymer additives should be optimized to get better performances. The reinforcement mechanisms associated with the presence of polymers in asphalt are not well understood. Micromechanical models are shown to be able to predict fundamental properties of a composite based on the properties of individual constituents (Kerner 1956; Nielsen 1978; Christensen 1979; Buttlar et al. 1999) The understanding of the role SBS and asphalt play in the overall behavior provides the key by which PMA can be properly selected for the optimal combination. By understanding the various reinforcement mechanisms, it is also possible to set quality control limits for polymer-modified asphalt. This paper presents a new method for modeling the mechanical behavior of PMA. The accuracy of the proposed model is demonstrated by means of morphological observations.

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Table 1. Properties of Base Asphalts

Grade	Penetration 25°C (dmm)	Softening point (°C)	Viscosity 60°C (poise)	Asphaltenes (%)	Oils (%)	Resins (%)	Weight average M_w
AC-10	91	32	962	12.1	70.1	17.8	1,300
AC-30	55	45	3,180	14.8	68.4	16.8	1,400

Materials and Methods

Materials

In this study, two paving grade asphalt binders (AC-10 and AC-30) were mixed with two types of SBS (SBS-1 and SBS-r). Five different polymer contents were prepared for tests. Table 1 lists the engineering and chemical properties of the base asphalts provided by the China Petroleum Corporation. Asphalt is a complex mixture of many different hydrocarbons made from crude petroleum, and its constituents are classified into three categories: (1) oils; (2) resins; and (3) asphaltenes. The average heptane-asphaltene content of the sample was 13.45%, while oils and resins were 69.25 and 17.3% of the sample, respectively. The SBS triblock copolymer is one of the most promising polymers for asphalt modification. The Chie-Mei Enterprise Ltd., Taiwan, supplied an SBS in the form of a graded ground crumb mixture with the maximum size of about 1-mm diameter. The polymer is a high molecular weight, random block copolymer consisting of about 30% styrene and 70% butadiene in mole ratio. Table 2 lists the basic properties of SBS copolymers used in this study.

Sample Preparation

SBS-modified asphalt was prepared by melt blending. The SBS copolymer was mixed with asphalt binders by using a preparation method developed in the laboratory to maximize the rheological properties and to minimize asphalt degradation. The mixer applied a constant mixing speed of 150 rpm to ensure no voids created in the mixtures. An "X" shaped propeller was used to stir the polymer-modified asphalt. The SBS samples, supplied by the manufacturer in the form of a fine uniform powder, were suitable for mixing with asphalt due to the high surface area of the particles. The SBS contents used were 3, 5, 6, 7, and 9% by weight of blend. In preparation, 600 g of the asphalt was heated to fluid condition and poured into a 2,000-mL spherical flask. Upon reaching 180°C, a weighed amount of polymer was slowly added to the asphalt. Mixing was then continued at 180°C for 2 h to produce homogeneous mixtures. After completion, the SBS-modified asphalt 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.

Rheological Measurements

Traditional tests, such as penetration and softening point, were first conducted for PMA samples. In accordance with the Superpave test procedure, the rheological properties of neat asphalt and SBS-modified asphalt were measured by a dynamic shear rheometer (DSR) over a broad range of temperatures. For tests at 40°C and higher, a 1-mm gap and a 25-mm diameter plate were used. For tests below 40°C, a 2-mm gap and an 8-mm diameter plate were used. Viscoelastic properties at different temperatures and frequencies were obtained. A specific strain level was determined at each testing temperature for each sample running a strain sweep at 100 rad/s prior to any frequency sweep. The strain was kept low enough so that all tests were performed within the linear viscoelastic range. In addition, the Brookfield apparatus is used to evaluate high temperature workability of PMA according to ASTM Method D 4402. High-temperature viscosity is measured to ensure that PMA is sufficiently fluid when pumping and mixing.

Transmission Electron Microscopy

Conventional techniques for determining the phase behavior of polymer-modified asphalt include optical and electron microscopy. Researchers found electron microscopy preferable, because it provides a clear view of a material in the raw state (Blanco et al. 1996; Michler 1996; Lesueur et al. 1998). The morphology of SBS-modified asphalt was observed by using a transmission electron microscopy (TEM)—model JEM-1200EX. 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 thickness of around 0.07 μm. This technique allows researchers to study the microstructure differences between SBS and asphalt in PMA.

Theoretical Background

For inhomogeneous materials like SBS-modified asphalt, the engineering properties are strongly influenced by the morphology of the composite. The microstructure of PMA is related to the characteristic of each constituent that forms the material. In this study, two models were used, because the morphology of the SBS-modified asphalt depends on the SBS concentration. When the copolymer concentration is relatively low, the Kerner (1956) model is used to model the engineering properties of PMA. As the SBS concentration is sufficiently high, a modified Kerner model is proposed in this study to describe the mechanical behavior of SBS-modified asphalt.

Kerner Model

For a matrix containing nearly spherical inclusions, the Kerner (1956) model can be used to calculate the engineering properties of a composite (Nielsen 1978, Christensen 1979). The Kerner model is a self-consistent approximation model that derives its expression based on analysis of deformation and stress within a

Table 2. Properties of Styrene-Butadiene-Styrene (SBS) Copolymer

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	160,000
SBS-r	radial	30/70	0.95	0.6	320,000	460,000

composite. The PMA microstructure is modeled as a continuous medium where SBS particles are dispersed as the inclusion. Asphalt as the matrix then surrounds these SBS particles. The Kerner model provides an expression for shear modulus of the composite given by

$$\frac{G_c}{G_m} = \frac{(1-\phi_i)\cdot G_m + (\alpha+\phi_i)\cdot G_i}{(1+\alpha\phi_i)\cdot G_m + \alpha(1-\phi_i)\cdot G_i} \qquad (1)$$

$$\alpha = \frac{2(4-5\mu_m)}{(7-5\mu_m)} \qquad (2)$$

where G_c = shear modulus of a composite; G_m = shear modulus of the matrix; G_i = shear modulus of the inclusion; ϕ_i = concentration of inclusion; α = function of Poisson ratio of a composite; and μ_m = Poisson ratio of the matrix.

Modified Kerner Model

When the SBS concentration is sufficiently high, the dependence of modulus on polymer concentration is underestimated in the Kerner (1956) equation. Essentially, the Kerner model assumes that the concentration scale is compressed due to the limited volume fraction that can be occupied by SBS. However, for high SBS concentrations, it is appropriate to view asphalt immobilized at the surface of SBS that acts as a part of the matrix. A correction term was proposed in this study to consider the volume fraction effectively occupied by SBS in PMA. The Kerner equation can be modified if the volume fraction is replaced by an effective volume fraction, ϕ_{eff}, given as

$$\phi_{eff} = \phi_i + \frac{\phi_i^2 \cdot (1-\phi_{fm})}{\phi_{fm}^2} \qquad (3)$$

where ϕ_{fm} is the maximum packing fraction. An effective volume fraction is calculated from experimentally determined values of the composite modulus.

Results and Discussion

Morphology of Styrene-Butadiene-Styrene-Modified Asphalt

The morphology was studied by TEM to characterize the nature of the continuous phase and the fineness of the dispersion of the discontinuous phase. As shown in Figs. 1 and 2, blends of SBS polymers and asphalt exhibit a multiphase morphology. The light phase in the picture represents the swollen polymer, and the dark phase is the asphalt. SBS is dispersed as small particles in the asphalt. Note that the horizontal bar in these pictures stands for a length of 500 nm. When the miscibility of SBS is restricted, the polymer that appears in small proportion usually segregates into small regions. Secured in the continuous matrix formed by the asphalt, these small regions are called the discrete phase. The combination of these two constituent materials yields a PMA in which SBS and asphalt are combined to result in a material that has properties different from those of either constituent. In this way, it is possible to improve substantially the properties of asphalt and to obtain a novel material with engineering properties superior to those of the constituents.

Different types of SBS showed distinctively different morphologies as shown in Figs. 1 and 2. Because of differences in molecular weight, polarity, and structure, there exists the chemical dissimilarity between asphalt and SBS. The morphology is the
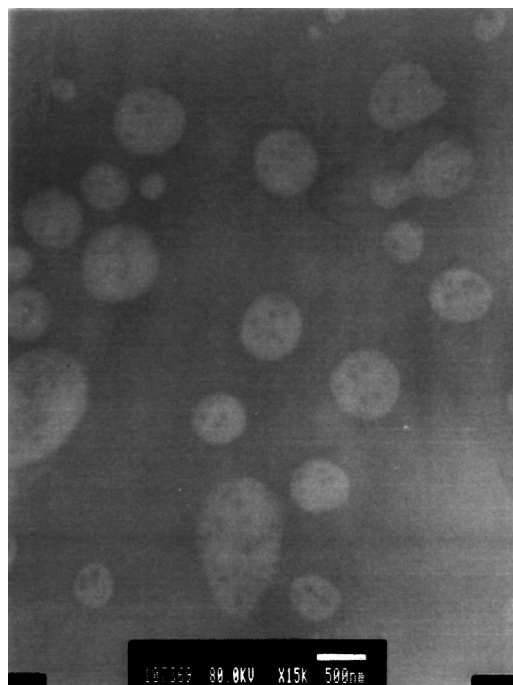

Fig. 1. Transmission electron microscopy of asphalt binder AC-30 modified with 3% by weight SBS-r

result of the mutual interaction of SBS and asphalt, and consequently is influenced by asphalt composition and polymer nature and content.

Figs. 1 and 2 demonstrate that the asphalt is the continuous phase of the system, and the SBS phase is homogeneously dispersed through it. The small SBS spheres appeared to be swollen by the oils in asphalt. Asphalt is a colloidal suspension of asphaltene particles in an oily continuous matrix containing resins. Oils
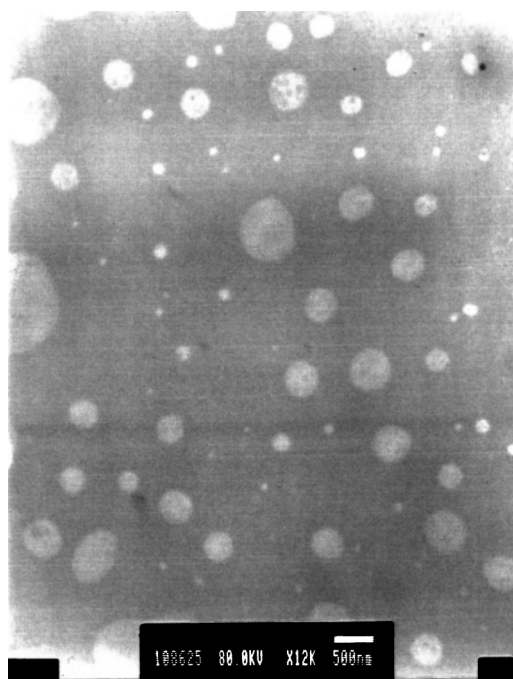

Fig. 2. Transmission electron microscopy of asphalt binder AC-30 modified with 3% by weight SBS-1
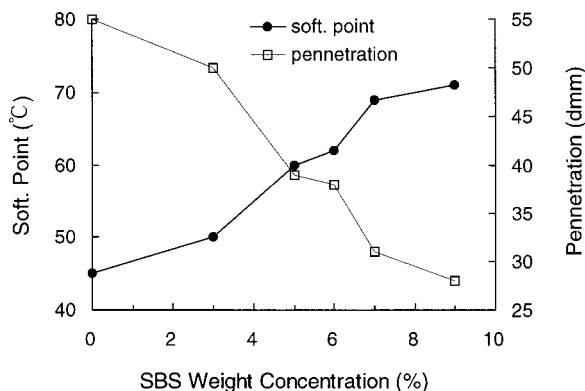
Fig. 3. Traditional properties of asphalt binder AC-30 modified with SBS-r

Fig. 4. Transmission electron microscopy of asphalt binder AC-30 modified with 5% by weight SBS-r

in asphalt have the lowest molecular weight (240–800 g/mol) and large number of saturated side chains and few rings that can be absorbed by the SBS copolymer. Resins are the intermediate molecular weight compounds (800–2,000 g/mol) that act as an interfacial part to prevent coalescence of the asphaltene. Asphaltenes are the highest molecular weight that contributes to the stiffness of the asphalt.

The swelling of SBS caused an increase in asphaltene content when compared to the initial composition of asphalt cement, leading to a hard matrix. Fig. 3 shows that both penetration and ring-and-ball softening point (T_{r+b}) of SBS-modified asphalt were enhanced as a result. The softening point and penetration are important performance criteria for PMA (Shuler et al. 1992; Lee et al. 1997). As illustrated in Fig. 3, T_{r+b} increases rapidly with addition of 3% SBS copolymer when the SBS becomes a dispersed phase in asphalt. As the concentration of SBS increases to 5%, both the polymer and asphalt phases become continuous; this is the composition region where inversion of the phases takes place. After 6% weight concentration, the increase in T_{r+b} becomes relatively flat. This suggests that a content that is slightly higher than the critical network formation content is the optimum content for SBS modification. The magnitude of the achievable increase in T_{r+b} is a function of polymer molecular weight. Similar trends can also be observed from the penetration curve.

Fig. 4 shows that the SBS concentration is around 5%, the dark phase represents the polymer, and the light phase is the asphalt. At this moment, the SBS phase gradually becomes the matrix of the system, and PMA starts the phase inversion. This phase inversion results from the SBS copolymer swollen by the oils and the asphalt enriched in asphaltenes containing virtually no polymer. The SBS copolymers represent a triblock structure in which polystrene is the thermoplastic end block, and polysbutadiene is the rubbery midblock. Within the polymer-rich phase, there are two microphases—swollen polybutadiene and essentially pure polystyrene domains, which act as physical crosslink sites to form a network. When the polymer-rich phase forms the continuum as shown in Fig. 4, the SBS-modified asphalt displays rubber-like elasticity.

Engineering Properties of Styrene-Butadiene-Styrene-Modified Asphalt

Two asphalt binders (AC-10 and AC-30) were mixed with five SBS levels (3, 5, 6, 7, and 9%). The complex shear moduli of these bl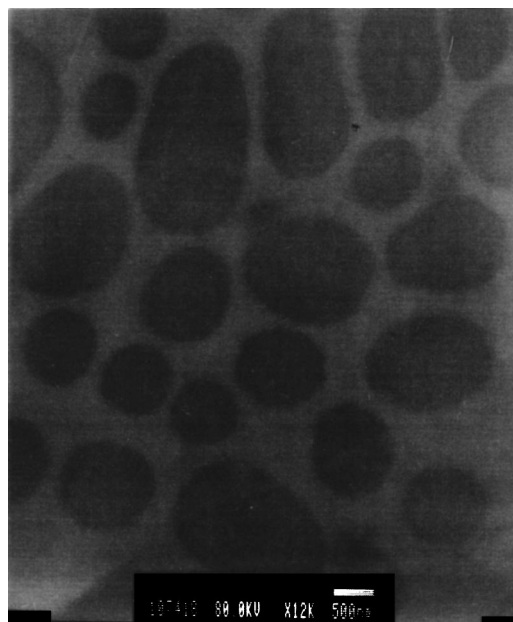ends were measured by the DSR. Fig. 5 illustrates the complex modulus for SBS-modified asphalt at different compositions. When the asphalt is modified by the SBS copolymer, the complex modulus increases as a function of the amount of SBS copolymer. This enhancement forms in two stages. At 3% SBS concentrations, local SBS networks begin to form. This localized networking can reinforce the asphalt binder. At 5% SBS concentration, the local networks begin to interact forming a critical network that leads to a sharp increase in the complex modulus. The complex modulus increases by a factor of 6 with just a 5% weight addition of the SBS. It is important that the critical content for network formation be exceeded; otherwise, the SBS does not show significant improvement over unmodified binders. However, once the critical networks begin to form, increases in polymer content are accompanied by less significant property increases as shown in Fig. 5. Note that this critical content may be dependent on asphalt and polymer source.

In Fig. 6 the Brookfield viscosity was plotted as a function of SBS weight concentration. It appears that at 3% weight concentration, the SBS forms a localized network structure. This network results in a twofold increase in the complex modulus. When the SBS content is greater than 3%, the local networks seem to interact forming a continuous network throughout the binder. The network acts as a support structure for the PMA. The result is a
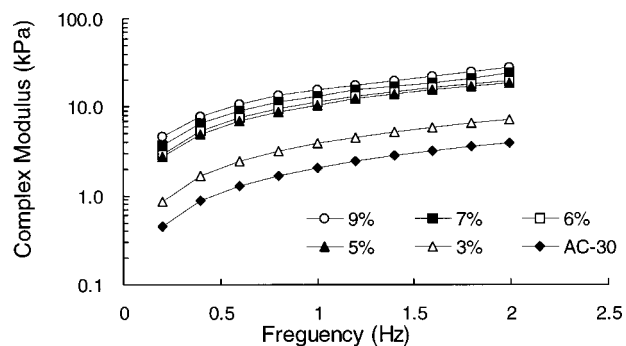

Fig. 5. Complex modulus of styrene-butadiene-styrene-modified asphalt at 60°C
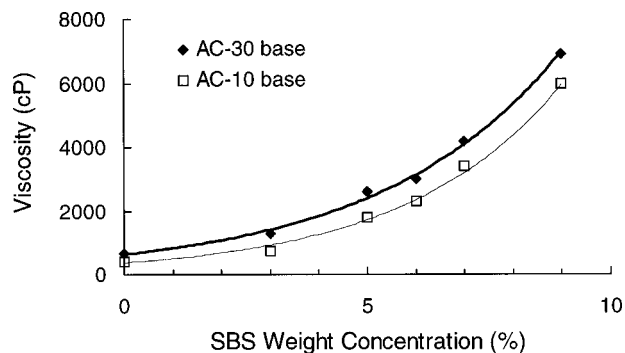
Fig. 6. Viscosity as function of composite composition at 135°C

curvilinear increase in the complex modulus with increasing SBS content. It should be noted that pumping PMA normally is not a problem, so long as the Brookfield viscosity is below 3,000 cP at 135°C. Fig. 6 shows that, when the SBS weight concentration is more than 6%, it may be difficult to handle PMA during transportation.

Modeling Engineering Properties of Styrene-Butadiene-Styrene-Modified Asphalt

At a relatively low concentration, the Kerner (1956) model appears to be adequate to describe the mechanical behavior of SBS-modified asphalt as shown in Fig. 7. The Kerner model fits the experiment data up to 15 kPa at which point the concentration of the SBS copolymer is in the range between 5 and 6%. The Kerner model is based on the assumption of spherical inclusions being randomly distributed in a soft matrix. The model can be calibrated by the corresponding complex moduli of both matrix and inclusion obtained from the rheological measurements. The effective volume fraction is based upon the added SBS weight and validated from the pictures taken from the transmission electron microscopy. From the TEM micrograph shown in Figs. 1 and 2, it is clear that the morphology of SBS-modified asphalt largely satisfies the assumption. The agreement between computed data and experimental results at low concentrations was thus explained.

As the polymer concentration increases, SBS is gradually swollen by the oily fraction of the asphalt and becomes the continuous phase. The value predicted by the Kerner model starts deviating from one measured by the experiment. Previous discussion has indicated that at 5% SBS concentration, there appears a
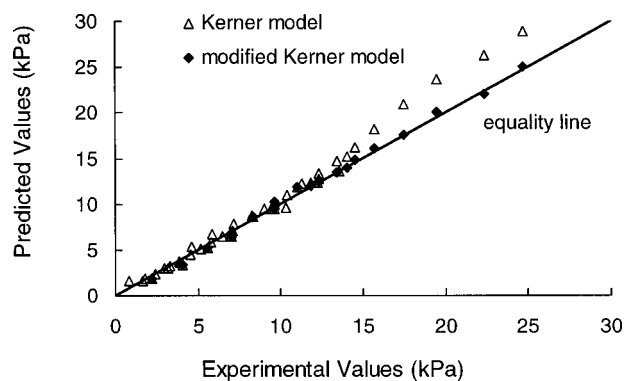

Fig. 7. Comparison of complex shear moduli obtained from experimental and prediction methods

phase inversion that changes drastically the morphology of SBS-modified asphalt. For concentrations lower than the phase inversion concentration ($\phi_{inverse}$), the SBS forms the discrete phase as discussed previously. On the other hand, for concentrations larger than $\phi_{inverse}$, the asphalt become the discrete phase with morphology different from the former case.

The modified Kerner model in Eq. (3) considers the phase inversion when one tries to predict the engineering properties of PMA. As illustrated in Fig. 7, the modified Kerner model corresponds well with the experiment points. It is implied that the microstructure of SBS-modified asphalt is extremely important. There exists a close relationship between the microstructure of modified asphalt and its physical properties. PMA with different polymer contents could have substantially different microstructures and properties. Because a modified binder consists of two distinct phases, both SBS and asphalt natures are important. The modified Kerner model was shown to be a powerful tool for predicting various reinforcing mechanisms in modified asphalt, including volume filling and phase inversion. In spite of limited systems studied, results indicated that this model could help establish target polymer contents for modified asphalt and could help set rational tolerance range for use during mixture production.

Conclusions

In this study SBS copolymer was blended with asphalt binders to investigate the effect of SBS modification on asphalt binder properties. Dynamic shear rheometer and TEM were shown to be excellent tools for determining the formation of physical networks. Based on the morphology of the material, analytical models were used to predict the mechanical behavior of SBS-modified asphalt. Because of the colloidal nature of asphalt cements, their mechanical properties were highly enhanced after SBS modification for two reasons: (1) the presence of the dispersed phase; and (2) the swelling of the polymer. For low copolymer concentrations, the Kerner model was used, and good agreement was obtained between the experimental data and the predicted value. Appearance of a continuous polymer structure was observed to begin at a SBS content of about 5%. The minimum percentage of polymer to ensure the formation of its continuous phase depends to a greater extent on the base asphalt and the polymer itself. A change of regime of the softening point and penetration profiles was observed at SBS weight concentration around 5%. The phase inversion appeared to occur when the SBS gradually became the continuous matrix phase. As the SBS became the continuous phase, the effective volume fraction changed accordingly. The adaptation of the Kerner equation could take into account the phase inversion for blends over 5% SBS. This suggests that a content that is slightly higher than the phase inversion content is the optimum content for SBS modification. The modified Kerner model proposed in this study was shown to well predict the engineering properties of SBS-modified asphalt after phase inversion.

Acknowledgments

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