The Influence of Styrene–Butadiene Diblock Copolymer on Styrene–Butadiene–Styrene Triblock Copolymer Viscoelastic Properties and Product Performance*

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SYNOPSIS

The effects of the styrene–butadiene (SB) diblock copolymer on the viscoelastic properties of styrene–butadiene–styrene (SBS) triblock copolymers were examined in both in the neat state and within specific product applications. The addition of the SB diblock copolymer into a pure SBS triblock copolymer resulted in a significant decrease in the plateau storage modulus and a quantitative linear rise in tan delta. In a pure triblock, in which all endblocks are anchored in polystyrene domains, all entanglements are physically trapped. The SB diblock embodies untrapped polybutadiene endblocks that are able to relax stress by chain reptation through the rubbery polybutadiene matrix. The SB diblock copolymer quantitatively lowered the microphase separation temperature (MST) of the SBS triblock copolymer. These changes in linear viscoelastic behavior manifest themselves into a reduction in the efficiency and performance of the SBS triblock copolymer in asphalt pavement binders and hot-melt adhesive blends. Specifically, the SB diblock diminished the complex shear modulus and elasticity of a polymer-modified asphalt, which translated into lower predicted rutting specification values. The increase in diblock content altered the viscoelastic response of the hot-melt adhesive blend, translating into a reduction in the shear holding power and shear adhesion failure temperature. The lack of network participation, coupled with the relaxation of the polybutadiene endblocks, accounts for the lower strength and greater temperature susceptibility of the diblock-containing systems. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The viscoelastic properties of styrene-butadiene-styrene (SBS) block copolymers were measured and modeled across actual application temperatures and in the high-temperature order–disorder transition region.[1–10] Styrenic triblock copolymers exhibit a two-phase morphology consisting of glassy polystyrene domains connected together by the rubbery polybutadiene segments. At temperatures between the polybutadiene and polystyrene glass transition temperatures, the triblock copolymer exhibits crosslinked elastomer network behavior, which is observed as a plateau in the shear storage modulus.

Above the polystyrene glass transition temperature, the styrene domains soften and the SBS triblock copolymer becomes melt-processable. This thermoplastic elastomer behavior has allowed the SBS triblock copolymer to become used extensively in adhesive and asphalt-modification applications.

SBS triblock copolymers are prepared by anionic polymerization, which allows strict control over block structure and molecular weight.[11–13] The chemistry related to the three basic anionic methods (sequential, difunctional, and coupling) of producing styrenic block copolymers has been reviewed.[11,12] Sequential-initiated and difunctional-initiated polymerizations produce triblock copolymers with pure block-polystyrene/block-polybutadiene/block-polystyrene structure. A third process, coupling technology, first prepares the styrene–butadiene (SB) diblock copolymer sequentially. The reactive ends of the SB diblock copolymers are coupled chemically

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to form the SBS triblock copolymer. Inefficiency in the coupling reaction results in the presence of residual SB diblock copolymer in the triblock copolymer.

A predominant amount of the published research on SBS block copolymers has been performed on samples which contain 10–25 wt % residual uncoupled SB diblock copolymer.[1,3,6–9] The SB diblock copolymers lack a second styrene endblock and disrupt the ideal network behavior of the pure triblock. Several authors have ignored the presence of the residual diblock copolymer in their interpretations of experimental data, while others have discussed the effects of a diblock on the tan delta on a qualitative basis. Cohen and Tschoegl described the influence of untrapped diblock on the loss tangent at intermediate reduced frequencies, but the diblock molecules did not have the molecular characteristics of residual uncoupled diblock.[3] Recently, Berglund and McKay showed quantitatively that the presence of the styrene–isoprene (SI) diblock copolymer in the styrene–isoprene–styrene (SIS) triblock copolymer results in a linear increase in the loss tangent (decrease in elasticity) and is responsible for the order–disorder transition occurring below the polymer decomposition temperature.[10]

Asphalt is a common binder in the construction sector for paving, roofing, and waterproofing applications. Asphalt consists of a wide range of molecules of different aromaticity and polarity. The current asphalt morphological model divides the many different asphalt molecules into two classes: polar and nonpolar.[14] The polar molecules associate through polar interactions or hydrogen bonding, thereby forming weak networks within the nonpolar medium. The weak network bonds dissociate under an increase in heat or loading. The nonpolar molecules act as the matrix for the polar network and predominately affect the low-temperature stiffness. Thus, asphalt behaves as a hard brittle solid at low temperatures, becoming Newtonian fluidlike at elevated temperatures. SBS block copolymers have been shown to increase the stiffness and elasticity of asphalt at higher temperatures.[15,16] Block copolymers form a continuous network within asphalt at polymer concentrations as low as 5 wt %. This improvement in hardness and elasticity decreases the asphalt pavement binder susceptibility to permanent deformation (rutting). The Strategic Highway Research Program (SHRP) proposed linear viscoelastic testing of asphalt pavement binders to correlate resistance to high-temperature rutting and low-temperature fatigue. These linear viscoelastic tests provide more thorough information than does the conventional, discrete, isothermal penetration (ASTM D-

5) and the isochronal softening point (ASTM D-36) tests currently used in the asphalt industry.

The SBS triblock copolymer provides the majority of the strength and elastic response required in hot-melt adhesive applications. Tackifier resins and oil are formulated with the block copolymer to optimize the viscosity, tack, and adhesive strength. The SBS molecular weight and styrene content required to optimize performance in hot-melt adhesives have been addressed.[17,18] Several authors correlated linear viscoelastic behavior with adhesive test properties for SIS and SBS block copolymers in pressure-sensitive adhesives.[19–23] In addition, it was shown that an increase in diblock content from 20 to 40% lowered the connectivity between styrene domains in SIS pressure-sensitive adhesives.[21]

The viscoelastic properties of pure SBS triblock copolymers and prepared SBS/SB blends have been measured in the neat state, in polymer/asphalt blends, and in hot-melt assembly adhesives. First, the influence of the SB diblock is quantitatively defined in the loss tangent and order–disorder transition of the neat copolymer. We then explain how alteration in neat viscoelastic behavior extends into the SBS/asphalt blend and SBS adhesive viscoelastic behavior and, ultimately, the product performance.

EXPERIMENTAL

Materials

The SBS triblock copolymers were prepared by a sequential anionic polymerization process that does not result in the presence of residual uncoupled SB diblock copolymer. Table I lists the styrene content and molecular weights of two pure SBS triblock copolymers: SBS-28 and SBS-30. Two separate SB diblock copolymers were prepared in a laboratory reactor. The diblock was polymerized to duplicate the molecular architecture of residual, uncoupled diblock copolymer. Each diblock copolymer has equivalent styrene content and half the molecular weight of the corresponding SBS triblock copolymer.

Table I   Neat SBS and SB Copolymer Properties

Sample I.D.	Styrene Content	Molecular Weight
SBS-28	28	68,000
SBS-30	30	100,000
SB-28	28	34,000
SB-30	30	50,000

SBS triblock/SB diblock copolymer blends were prepared by solution-blending the two copolymers in toluene. The solution blends were vacuum-oven-dried to obtain the polymer samples. The triblock and diblock weight fractions of each SBS/SB blend are shown in Table II.

Asphalt and Adhesive Sample Preparation

The SBS-30 triblock and SBS/SB blends were evaluated in an Exxon Baytown AC-10 asphalt. The AC-10 asphalt was placed into a metal can and oven preheated to 160°C. The can was placed below a Silverson L4R mixer and the mixing head lowered into the viscous asphalt. The appropriate amount of the polymer was added slowly into the asphalt at a mix speed of 3000-4000 rpm. Mixing continued under high shear for 30 min at 170°C. Next, the sample was transferred to a paddle-type stirrer and continuously mixed for an additional 60 min at 170°C. After the mixing procedure was completed, the polymer/asphalt blend was poured into storage tins.

The hot-melt adhesives were prepared by solution-blending the SBS-28 triblock copolymer or SBS/SB polymer blend and the other formulation ingredients with toluene in a glass jar. The 50% solids solution was shaker stirred for 16 h to promote sample homogeneity. Next, the solution was cast onto a 2 mil Mylar backing by using a 5 mil drawdown bar. The adhesive film was dried in an 80°C vacuum oven to remove the toluene solvent. In-house investigations have shown that solution-blending and melt-mixing methods produce adhesive blends with similar properties.

Formulation:

SBS or SBS/SB block copolymer	9.1 g
Tackifier (Aromatic modified aliphatic resin)	20.0 g
White paraffinic mineral plasticizer oil	7.3 g
Antioxidant	0.1 g

Test Procedures

The rheological measurements were performed on a Rheometrics dynamic mechanical spectrometer, RDS-II. The RDS-II is equipped with a force-rebalance transducer and a nitrogen-padded environmental chamber. Temperature sweeps were measured between −100 and 150°C at an oscillatory rate of 1 rad/s and applied strain autoadjusted within the linear viscoelastic region to maintain proper torque response. The frequency sweeps were measured over a range of an oscillatory rate of 0.1-100

Table II   SBS/SB Triblock/Diblock Blends

Sample I.D.	Wt % SBS-30	Wt % SB-30
Asphalt SBS/SB blend series		
SBS-30	100	0
SBS-30/SB1	95	5
SBS-30/SB2	90	10
SBS-30/SB3	85	15
SBS-30/SB4	75	25
SBS-30/SB5	50	50

Sample I.D.	Wt % SBS-28	Wt % SB-28
Adhesive SBS/SB blend series		
SBS-28	100	0
SBS-28/SB1	92	8
SBS-28/SB2	85	15
SBS-28/2B3	70	30

rad/s at applied strains within the linear viscoelastic region.

Neat SBS polymer and SBS/SB polymer blends were compression-molded into 25 mm-diameter disks. The SBS/asphalt blends were prepared using the SHRP test protocol. A sample piece of asphalt blend was placed in a silicon mold and heated to 120°C. By melting and reconditioning the asphalt, the preexisting structure is destroyed. The sample mold was cooled to assist removal of the asphalt sample from the mold. Next, the sample disk was loaded between the rheometer parallel plates. Adhesive blends were sectioned and loaded between rheometer test plates. The adhesives were evaluated for shear adhesion failure temperature (SAFT) and shear hold. Both tests were performed on adhesive bonds using a Mylar backing and a stainless-steel substrate. In the SAFT test, the 25.4 × 25.4 mm adhesive bond was exposed to a temperature ramp of 10°F/15 min and the temperature at bond failure recorded.[18] The shear hold test is an isothermal test run at 35°C that measures the time to bond failure. The shear hold test procedures are outlined in ASTM D-3654.

RESULTS AND DISCUSSION

Viscoelastic Behavior of Neat Block Copolymers

The influence of the SB diblock copolymer on the SBS triblock linear viscoelastic properties was investigated by preparing a series of triblock/diblock blends. Figure 1 plots G' as a function of temperature for the pure triblock copolymer and its blends with four different levels of the SB diblock. G' decreases
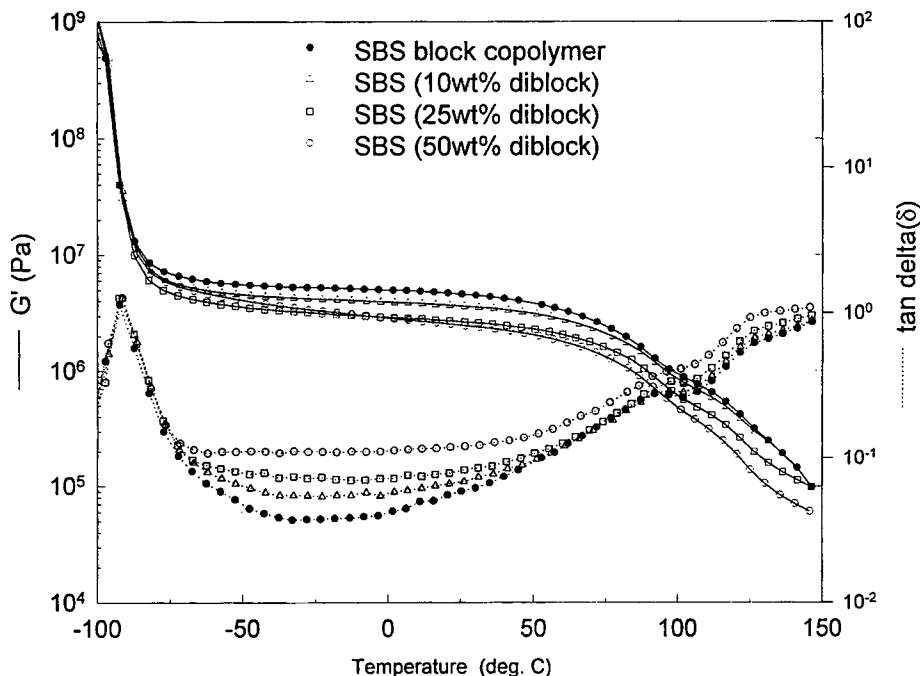
Figure 1 G' and tan delta vs. temperature at 1.0 rad/s for pure SBS triblock and three blends with SB diblock.

across the plateau region with increasing diblock content. This reduction does not necessarily reflect a change in the effective volume fraction of polystyrene domains. In a pure triblock, in which all endblocks are anchored in polystyrene domains, all entanglements are physically trapped. When the diblock copolymer is added to the triblock copolymer, the network is no longer ideal. The untrapped polybutadiene endblock is able to relax, allowing G' to become time- and temperature-dependent. Previously, Kraus and Rollman attempted to quantitatively model the entanglement plateau modulus of a triblock copolymer in the presence of tackifier resin or process oil diluents. They showed that the addition of a diluent resulted in a reduction of the measured plateau modulus of a triblock copolymer.[24] The effects imparted by the diblock are analogous to adding a diluent to the triblock polymer, with the polybutadiene segment behaving as the diluent, since the polystyrene segment remains embedded in a glassy styrene domain.

The influence of the SB diblock on the SBS triblock copolymer viscoelastic properties may be further described by analyzing the loss data. Figure 1 plots tan delta vs. temperature, measured at a rate of 1.0 rad/s, for the neat SBS-30 triblock and triblock/diblock blends. We observe an increase in the loss tangent between −75 and 50°C, as a direct consequence of increasing the diblock content. Berglund and McKay previously demonstrated that an in-

crease in mechanical loss of an SIS triblock copolymer was initiated through the incorporation of an SI diblock copolymer.[10] On the time scale of the rheological experiment, relaxation of the midblock polymer segment is very limited, since both polystyrene endblocks are embedded within the glassy styrene domains. This lack of an efficient relaxation mechanism accounts for the plateau in the dynamic storage modulus, G'.
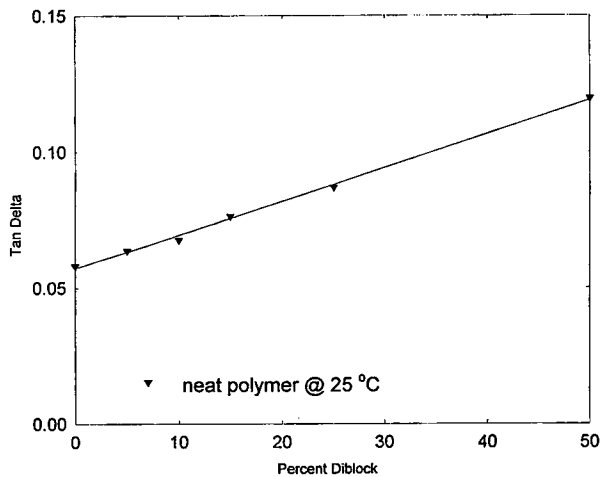
It has been shown that uncrosslinked polymer

Figure 2 Tan delta vs. SB diblock content for pure SBS-30 triblock and five blends with diblock. Tan delta was measured at 25°C and 1.0 rad/s.

chain segments exhibit long relaxation times within covalently bonded elastomer networks.[25] Lacking a second styrene endblock, the SB diblock contains an untethered polybutadiene endblock which essentially behaves as a dangling chain end. Relaxation is free to occur via reptation of the dangling chain end inside the rubbery matrix. This loss in elastic response is quantitatively described in Figure 2, where tan delta is plotted vs. the SB diblock content in the triblock/diblock blends. The loss tangent increases linearly with rising diblock content, as the inherent elastic response of the triblock copolymer network is diminished. The relaxation time does not fluctuate with the diblock level, since the molecular weight and molecular weight distribution of the diblock copolymer remain consistent. The untethered polybutadiene endblock on the SB diblock copolymer imparts an imperfection within the SBS triblock thermoplastic elastomer network.

Order–Disorder Transition of SBS Block Copolymers

Above the styrene glass transition temperature, the rheological properties in the melt region remain a function of the block copolymer morphology, where the morphology can be separated into two classes: the ordered, microphase-separated state and a single-phase, homogeneous state. The transition between these two thermodynamic states is referred to as the order–disorder transition or microphase separation temperature (MST). We implemented two separate experimental methods to detect the order–disorder temperature of SBS-28. The higher molecular weight, 30 wt % styrene SBS-30 triblock exhibited severe thermooxidative degradation at the higher temperatures (> 275°C) required to detect its MST. In the first method, the order–disorder transition is determined as a discontinuity in isochronal plots of G' or complex viscosity vs. temperature.[26–28] As the MST is traversed, the elasticity of the resin declines discontinuously and the complex viscosity will approach Newtonian behavior at low frequencies. Figure 3 presents G' as a function of temperature over several frequencies for the 28 wt % styrene SBS-28 triblock. The MST is identified by the discontinuity observed in G' near 230°C at the lower test frequencies.

The second method is based upon the concept that block copolymers exhibit thermorheologically simple behavior at temperatures that exceed the order–disorder transition temperature. Successive plots of G' vs. G'' will thus become independent of temperature.[6] Figure 4 plots G' vs. G'' for SBS-28 over the same range in temperature. In this method,
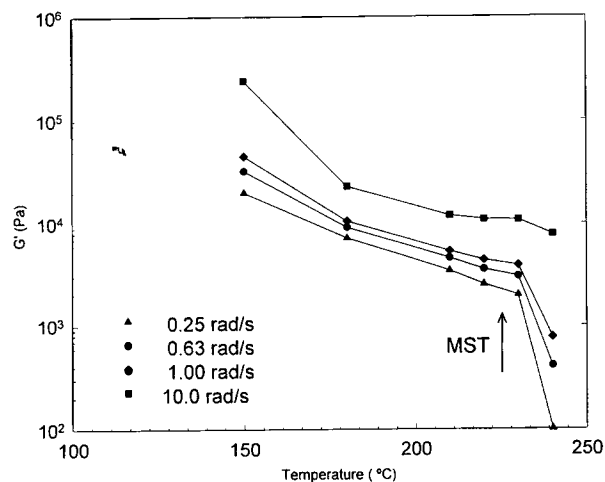
Figure 3 G' vs. temperature for SBS-28 at several different temperatures.

the MST is detected when the loci of points overlap at successively higher temperatures and the polymeric system becomes a thermorheological simple fluid. The thermorheological simple method detects an MST at 240°C for triblock SBS-28.

In the ordered melt state, both the polystyrene and polybutadiene domains remain intact and complete relaxation of the triblock copolymer requires at least two separate relaxation mechanisms. To establish a zero-stress configuration, the styrene endblocks must first diffuse out of the styrene domain, which then allows the entire polymer chain to diffuse through the entanglement network of the polybutadiene matrix. Above the MST, the triblock copolymer exhibits a simple terminal relaxation that can be associated with the flow of a homogeneous polymer melt. Several authors have shown that the two rheological methods detect vastly different temperatures (> 30°C) for the onset of the order–disorder transition in low styrene content SIS triblock copolymers.[10,27] Berglund and McKay proposed that the appearance of low-shear Newtonian viscosity behavior and the discontinuity in G' do not imply loss of the domain structure in SIS block copolymers, but are observed due to the differences between characteristic relaxation times of the two separate relaxation mechanisms in the triblock copolymer.[10] In contrast, we observe very close proximity for the MSTs detected by the two rheological methods for SBS-28. This close agreement between detection methods is likely a function of the SBS-28 molecular architecture. The lower molecular weight and cylindrical styrene domain morphology of SBS-28 offer unique thermodynamic phase behavior and characteristic relaxation times relative to the high mo-
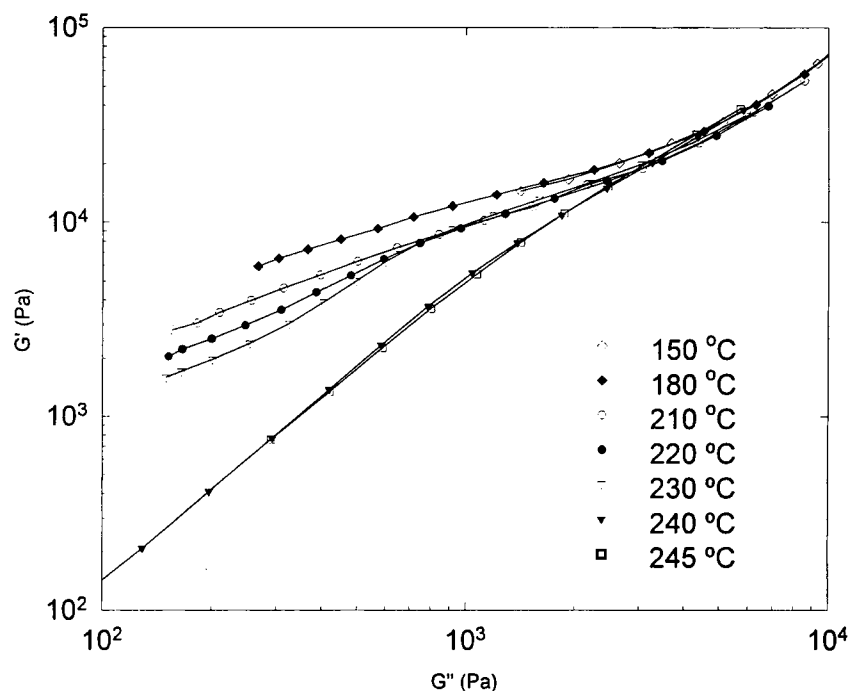
Figure 4 G' vs. G'' for SBS-28 at several different temperatures.

lecular weight, spherical styrene domain morphology, SIS triblock copolymer.

The focal point of this article has been to isolate the effects of SB diblock copolymer on the viscoelastic behavior of SBS triblock copolymers. The data in Figure 5 show that each incremental addition in diblock content results in a subsequent reduction in the MST. Linear regression analysis of the data points indicates a linear function of the MST with diblock content ($r^2 = .99$). Other authors have shown similar diblock-dependent behavior in a 14 wt % styrene SIS triblock copolymer and a hydrogenated
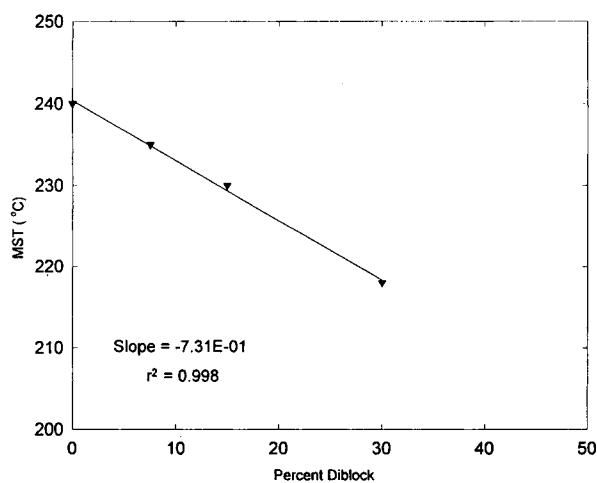

Figure 5   Order–disorder transition temperature for SBS-28 triblock and three blends with SB diblock.

1,4-polyiosprene–1,2-polybutadiene–1,4-polyisoprene (PI–PB–PI) triblock copolymer.[10,28] The pure SIS triblock copolymer retained its spherical domain structure over the entire temperature range investigated and did not exhibit an order–disorder transition. However, a 42 wt % diblock, SI/SIS copolymer blend showed a lower MST of 240°C. Gehlsen et al. suggested that the decrease in MST with rising diblock content in a PI/PI–PB–PI blend was in reasonable agreement with mean-field theories. The higher MST observed in the pure triblock was a result of the decrease in configuration entropy associated with a pure triblock in the ordered state.[28] The rubbery midblock must conform to configurations which allow both endblocks to position themselves at the domain interface. In our case, the SB diblock copolymer, unable to bridge two styrene domains, lessens the connectivity between domains in the triblock elastomer network, thereby increasing the entropic contribution and inducing a reduction in the microphase-separation temperature.

Viscoelastic Behavior of Polymer-modified Asphalt Blends

Linear viscoelastic measurements of asphalt and polymer/asphalt blends are experimentally difficult to perform. The data in Figure 6 illustrate how the complex shear modulus of the Baytown AC-10 asphalt decreases nearly 8 decades in magnitude over
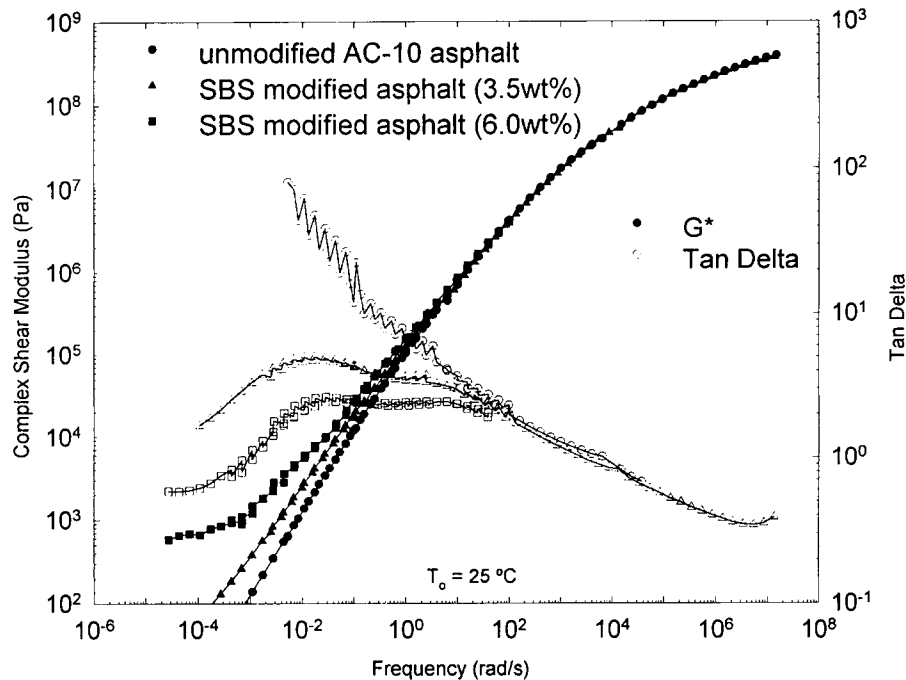
Figure 6 G^* and tan delta vs. reduced shear rate for neat AC-10 asphalt, 3.5 wt % SBS-30 in AC-10 asphalt, and 6.0 wt % SBS-30 in AC-10 asphalt. Reference temperature is 25°C.

a 70°C increase in temperature. While SBS triblock copolymers are thermorheologically complex materials, asphalt binders and polymer/asphalt blends behave as thermorheological simple fluids. Through time–temperature superposition principles, a series of frequency sweeps are shifted to a reference curve measured at 25°C, creating a rheological master curve.

We focus our analysis on two important temperature-dependent viscoelastic parameters: the complex shear modulus, G^*, and tan delta. G^* provides a measure of stiffness, and tan delta, a measure of elasticity. Neat AC-10 asphalt time–temperature superposition plots of G^* and tan delta are shown in Figure 6. Remember that the mirror image of the frequency axis is a temperature axis. At high shear rates or low temperature, G^* approaches the glassy state, which is related to local molecular motions of the asphalt carbon–carbon backbone. A gradual transition from glasslike behavior toward Newtonian fluid behavior occurs with decreasing shear rates. The asphalt eventually exhibits Newtonian fluid behavior as the weak polar network interactions dissociate at higher temperatures and the binder may fail via permanent deformation of the pavement. The monotonic increase in tan delta, with decreasing frequency, suggests that neat asphalt offers little elastic response at higher temperatures.

The data in Figure 6 also illustrate that incre-

mental addition of the SBS triblock copolymer into asphalt improves both the shear hardness and elastic response. The 3.5 wt % SBS triblock/asphalt blend shows improved complex shear hardness and elastic response at low reduced frequencies or high temperatures. Upon addition of 6 wt % SBS into the asphalt, we observe the emergence of a well-defined plateau in G^* and a further decrease in tan delta in the lower-frequency region. The existence of a plateau modulus provides evidence that SBS triblock chain entanglements or networks have formed. Although the triblock constitutes a weight fraction of only 6% in the asphalt blend, the association of the triblock with compatible asphalt fractions extends the volume fraction of the polymer enough to establish a network. This continuous polymer network is confirmed by the existence of a transition zone crossover modulus shown in Figure 7. In pure polymer systems, the crossover of $G' > G''$ provides mechanical confirmation of polymer chain entanglement or the formation of permanent polymer chain crosslinks. The formation of the SBS network within the asphalt provides nearly a threefold increase in asphalt stiffness and elasticity and thus improves pavement binder resistance to permanent deformation.

The presence of residual, uncoupled diblock alters the viscoelastic response of the polymer/asphalt blend. Figure 8 presents an isochronal plot of tan
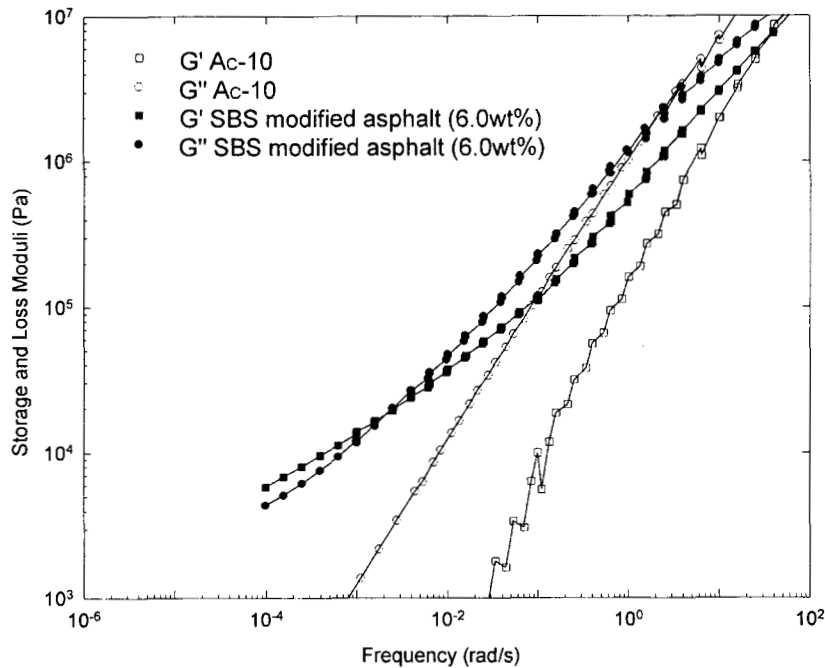
Figure 7 G' and G'' vs. shear rate for neat AC-10 asphalt and 6.0 wt % SBS-30 in AC-10 asphalt. Reference temperature is 25°C.

delta and the complex shear modulus vs. temperature for a series of 6 wt % SBS and SBS/SB polymer/asphalt blends. An increase in tan delta correlates to a decrease in elastic response or memory of the asphalt binder. The complex shear modulus exhibits a decrease in magnitude with increasing diblock content. More specifically, we observed that the presence of 10% SB diblock in the SB/SBS blend (sample SBS-30/SB1) results in a 26% reduction in the complex shear modulus of the polymer-modified
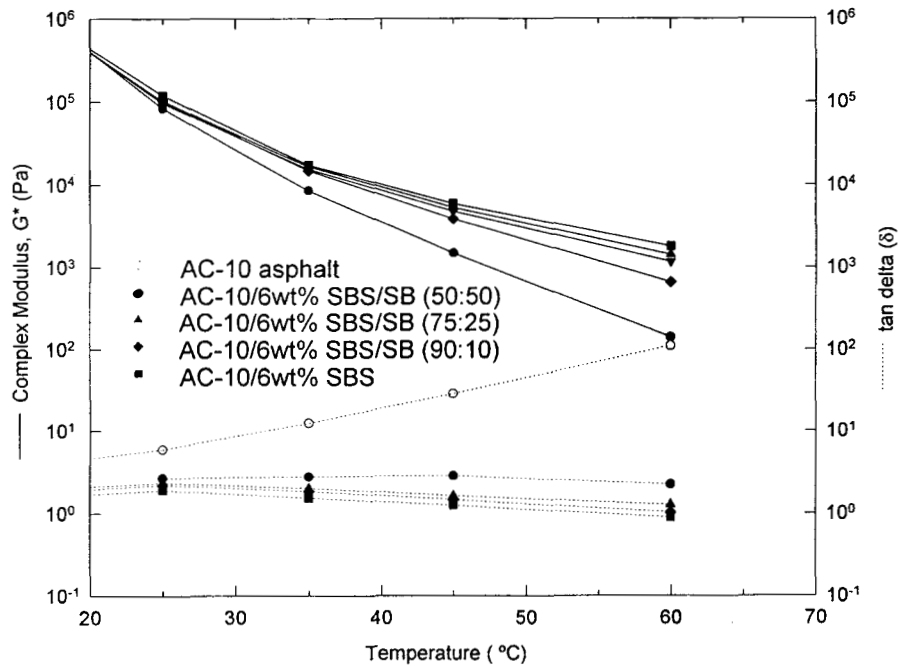

Figure 8 G^* and tan delta vs. temperature for neat AC-10 asphalt and four SBS/SB-modified AC-10 asphalt blends.

asphalt, with respect to the pure triblock-modified asphalt. The data in Figure 8 demonstrate that increasing the level of diblock concentration in the resin results in further declines in the complex shear modulus and elasticity of the polymer-modified asphalt blends, since the SB diblock copolymer promotes discontinuity in the continuous polymer network and diminishes the inherent integrity of the thermoplastic elastomer network.

SHRP has proposed a specification parameter, $G^*/\sin \delta$, to predict the resistance of an asphalt pavement binder to rutting.[29] This parameter is numerically equal to the inverse of the loss compliance, $1/J''$. A larger parameter value translates into a decrease in the asphalt binder's predicted susceptibility to permanent deformation under load. Reductions in the polymer/asphalt linear viscoelastic properties manifest themselves into lower SHRP rutting specification values (Fig. 9). Imperfections imparted by the presence of the SB diblock diminishes the ideal elastic nature of the SBS triblock copolymer network, thus decreasing copolymer performance efficiency within the asphalt.

SBS Hot-Melt Assembly Adhesives

SBS triblock copolymers are incorporated extensively into hot-melt adhesive (HMA) formulations where they provide the bulk of the required mechanical strength and elastic response. A generic HMA formulation was selected to illustrate the effects of tackifier resin and oil on the viscoelastic properties of the SBS-28 triblock copolymer and, more importantly, to serve as a foundation for the extension of the triblock/diblock blend study into an adhesive application. Tancrede and Diehl utilized this same HMA formulation to highlight the performance attributes of the pure triblock copolymer as a function of triblock molecular architecture.[17,18]

Dynamic viscoelastic measurements were used to understand the effects of SB diblock on SBS triblock hot-melt adhesives. The data in Figure 10 shows G' and tan delta plotted as a function of temperature, measured at 1.0 rad/s, for hot-melt adhesives prepared with the pure SBS-28 triblock copolymer and its blends with three different levels of SB diblock. Each incremental rise in SB diblock content is met with a reduction in G' across the plateau region. As expected, G' parallels the trends previously shown in Figure 1 for the neat SBS-30 triblock copolymer. The untethered polybutadiene endblocks are able to relax applied stress, disrupting the ideal nature of the SBS triblock copolymer network in a hot-melt adhesive formulation. As the test temperature approaches the modified polystyrene domain T_g, G' be-
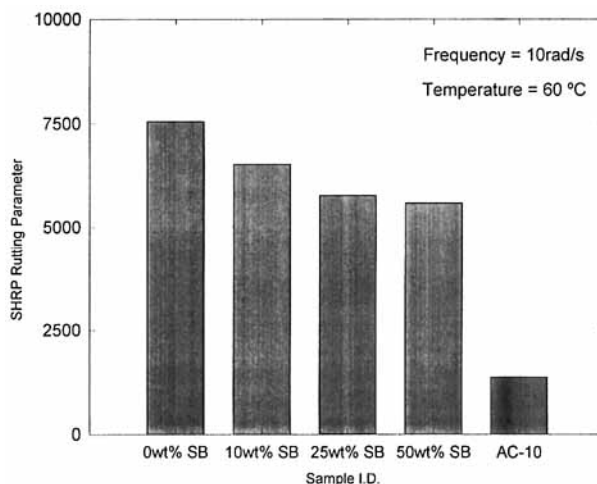

Figure 9   SHRP rutting resistance parameter, $G^*/\sin$ delta, measured at 60°C and 10 rad/s for neat AC-10 asphalt and four SBS/SB-modified AC-10 asphalt blends.

gins to decline rapidly with increasing temperature as the physical network entanglements yield to the terminal relaxations of the triblock copolymer. This temperature diminishes slightly with rising SB diblock content; thus, the HMAs containing diblock copolymer soften at successively lower temperatures.

Also in Figure 10 we observe an increase in tan delta between 10 and 50°C, proportional to the diblock level. This loss in elastic response is described quantitatively in Figure 11, where the loss tangent measured at 25°C and 1 rad/s is plotted vs. the SB diblock content in the triblock/diblock blends for both the neat polymers and the hot-melt adhesives. The increase in tan delta with increasing diblock exhibits a strong linear correlation in both the neat state and within the hot-melt adhesive formulation. We believe that this loss is a direct result of the relaxation of the polybutadiene endblocks through the rubbery polybutadiene matrix. The influence of the SB diblock content is more conspicuous in the HMA, since the slope of tan delta plotted as a function of the SB diblock in Figure 11 is greater relative to the pure SBS triblock copolymer and its blends with the diblock. From a simplified perspective, we can view the HMA as a swollen polymer network.

Essentially, the tackifier resin and oil enlarge the triblock copolymer elastomer network, forcing an extension of the chain configuration of the polybutadiene midblocks. Several authors have demonstrated that upon dilution the concentration of entanglement loci diminishes within a chemically crosslinked network, resulting in faster terminal relaxation times.[30] In the hot-melt adhesive blend, the polybutadiene endblocks become less constrained in the rubbery matrix of the swollen polymer network
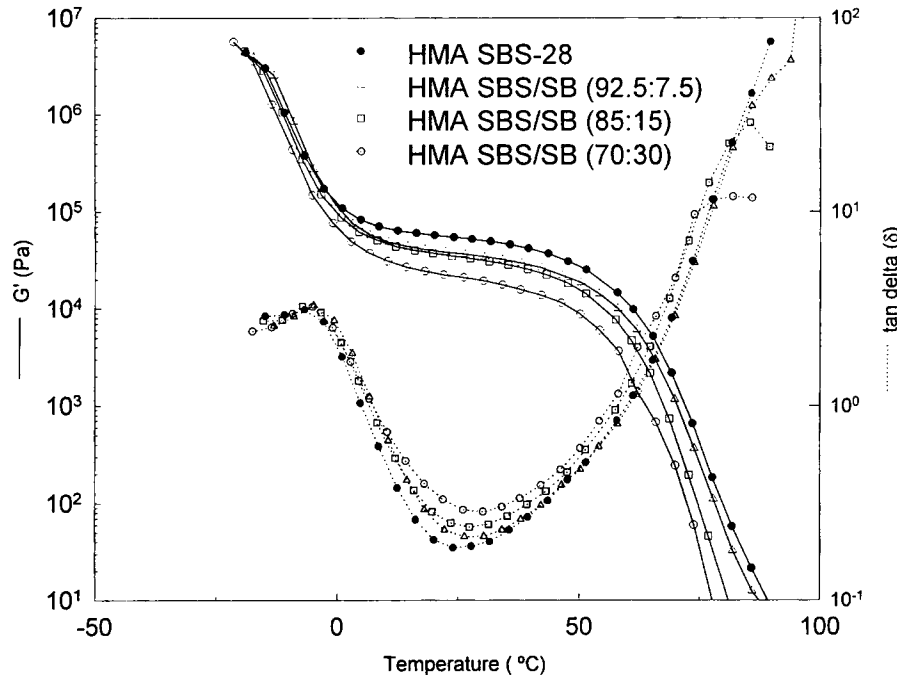
Figure 10 *G'* and tan delta vs. temperature at 1.0 rad/s for hot-melt adhesive blends containing pure SBS-28 triblock and three SBS/SB triblock/diblock blends.

and thus are able to relax applied stress faster and contribute to higher loss. In these highly extended systems, each polymer chain must participate completely to maximize the elastic response of the network. The presence of the SB diblock lowers the effective number of crosslinks present in the HMA elastomer network, reducing the efficiency of the SBS triblock copolymer within the hot-melt adhesive.
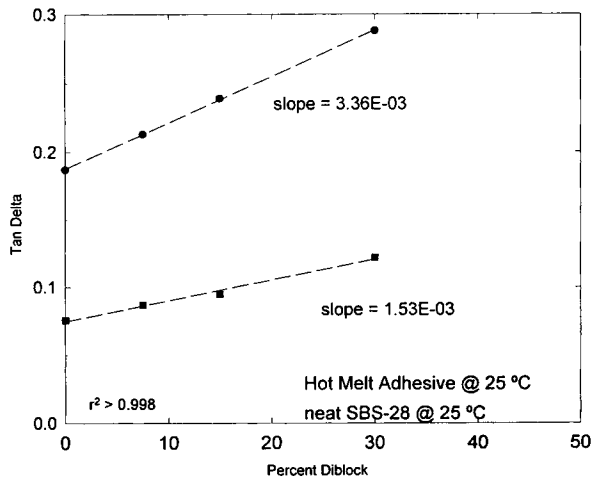
Traditional performance properties of hot-melt

Figure 11 Tan delta vs. SB diblock content for SBS-28 triblock and SBS-28/SB diblock blends and hot-melt adhesives made with these polymers.

adhesives include the process melt viscosity, adhesion to a substrate, and shear strength. The measured performance of a hot-melt adhesive is an intricate function of the type of polymer, tackifier resin, and oil and the concentration of each ingredient in the formulation. In practice, the SBS triblock copolymer principally provides the adhesive strength in the HMA, while the oil and tackifier resin are added to balance melt viscosity, tack, and peel adhesion with bond strength. Diehl and Tancrede demonstrated how these performance properties may be optimized as a function of block copolymer molecular weight and styrene content.[18] The scope of this article has been to address the impact of the SB diblock on the inherent network integrity of an SBS triblock network. Therefore, we focus on the shear hold and shear adhesion failure temperature (SAFT) tests that measure the internal bond strength of a hot-melt adhesive.

Figure 12 presents shear hold and SAFT data plotted for HMAs prepared with SBS-28 and its blends with three incremental levels of the SB diblock. Shear hold is an isothermal (35°C) test that measures the time to adhesive bond failure. The shear hold declines with rising diblock level. The HMA sample SBS-28/SB3, containing 30 wt % SB diblock, shows a reduction of 66% in shear hold relative to the pure SBS-28-based HMA. This suggests that the SB diblock does not contribute to internal bond strength in the adhesive bond.
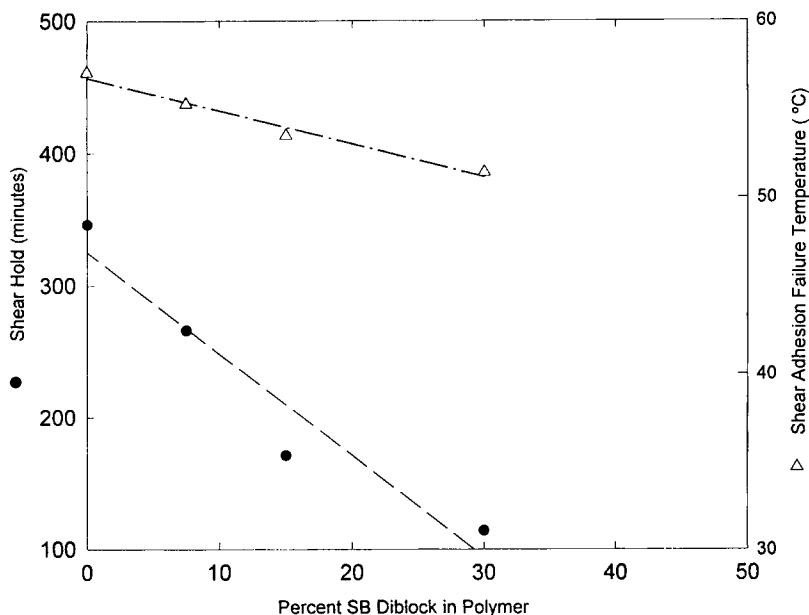
Figure 12   Shear hold and SAFT vs. SB diblock content for hot-melt adhesive blends containing SBS-28 triblock and blends with SB diblock.

High-temperature creep resistance of the adhesive bond is an additional important performance property in many HMA applications. In the SAFT test, a sample is subjected to a temperature ramp at the rate of 10°F/15 min and the temperature at bond failure is recorded. As seen in Figure 12, the HMA prepared with SBS-28/SB3 has a 7°C lower SAFT than that of the pure SBS-28-based HMA. Although the influence of the diblock is less dramatic than are the differences observed in the shear hold test, the SAFT temperature declines significantly with increasing diblock content. This decrease in SAFT with rising diblock level is in agreement with previous studies which observed a decrease in SAFT in pressure-sensitive adhesives prepared with an SIS triblock copolymer containing 20 and 40 wt % SI diblock.[21] More importantly, we demonstrate quantitatively that the SAFT properties are a linear function of diblock content over the range of composition listed in Table II.

Good agreement exists between the measured dynamic viscoelastic parameters and the traditional shear-resistance tests. The decline in shear holding power parallels the decrease observed in the plateau region of G'. Samples formulated with higher SB diblock levels show subsequently lower elastic strength and a gain in viscous loss due to relaxation of the uncoupled polybutadiene chain ends. In addition, the decrease in SAFT is predicted by the softening-point temperature of G' shown in Figure 10 and the decrease in the MST of the neat polymer shown in Figure 5. The lack of network participation, coupled with the relaxation of the polybutadiene endblocks, accounts for the lower adhesive strength and greater temperature susceptibility of the diblock-containing systems.

CONCLUSION

Styrene–butadiene (SB) diblock copolymers influence dramatically the viscoelastic properties of styrene–butadiene–styrene (SBS) triblock copolymers. The addition of the SB diblock copolymer into a pure SBS triblock copolymer resulted in a significant decrease in the storage modulus and a quantitative linear rise in tan delta across the viscoelastic plateau region. In a pure triblock, in which all endblocks are anchored in polystyrene domains, all entanglements are physically trapped. The SB diblock embodies untrapped polybutadiene endblocks that are able to relax stress by chain reptation through the rubbery polybutadiene matrix, reducing the elastic response of the physical network. The SB diblock copolymer also quantitatively lowered the microphase-separation temperature of the SBS triblock copolymer by diminishing the connectivity between domains and thus increasing the thermodynamic entropic contributions. These changes in the viscoelastic properties provide mechanical confirmation that the SB diblock copolymer does not contribute to the ideal nature of the thermoplastic elastomer network, behaving essentially as a dangling chain end in a thermoset network.

These changes in linear viscoelastic behavior manifest themselves into a reduction in the efficiency and performance of the SBS triblock copolymer in asphalt pavement binders and hot-melt adhesive blends. The SBS triblock copolymer behaves essentially as a swollen polymer network within the asphalt or adhesive formulation, where the polybutadiene endblocks of the SB diblock become less constrained in the rubbery matrix of the swollen polymer network and are able to relax applied stress faster and contribute to higher loss. An increase in the diblock content resulted in a measurable decline in the complex shear modulus and elasticity of the polymer-modified asphalt that translated into lower SHRP rutting specification values. A quantitative increase in mechanical loss and a subsequent reduction of the plateau storage modulus and softening point is observed in the SBS triblock hot-melt adhesive upon the addition of the SB diblock copolymer. These shifts in dynamic viscoelastic behavior translate into a reduction in the measured shear-holding power and shear-adhesion failure temperatures of the adhesive.

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