

## Reological behavior of modified asphalt by SBEBS copolymers

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### Abstract

Structural groups of SBS with 10% vinyl content were selectively hydrogenated, and the resulting compounds (SBEBS) were characterized by  $^1\text{H}$ NMR and gel permeation chromatography (GPC). Blends with asphalt were obtained after mixing with the hydrogenated polymer, followed by storage heat tests. The blends were characterized by rheometry. Partial hydrogenation of the polybutadiene block in SBS produces improved asphalt properties, as compared with SBS-asphalt blends (without hydrogenation), because of an improved stability, solubility with asphalt and resistance to thermal degradation brought about by lesser number of double bonds.

### Introduction

By adding specific polymers to paving-grade asphalt cements, an improvement in the mechanical and thermal properties and in the oxidative resistance of the material is observed. Additives usually considered are styrenic copolymers, such as SBS. The resulting blend possesses improved thermal and mechanical properties above those of asphalts<sup>1-6</sup>.

These conventional block copolymers tend to degrade in processing and/or over time because they have unsaturated sites that are reactive enough to combine with by free radicals created by oxidation, UV light or mechanical action<sup>3,6</sup>. This is especially true in regions experiencing elevated temperatures. For this reason, when the modified asphalt is subjected to drastic conditions, is necessary that the rubber be thermally, mechanically and oxidatively stable<sup>1-3</sup>. The blends with SEBS enhance considerably the thermal and oxidative stability of the compounds, together with increased processability at higher temperatures, by virtue of its poly (ethylene-co-1-butylene) centre block.

This work analyzes the modification of asphalt with hydrogenated poly (styrene-butadiene-styrene) copolymer containing different amounts of butadiene and ethylene-co-butylene.

### Experimental

#### Materials

SBS was synthesized via “living” sequential anionic polymerization<sup>7,8</sup>. Homogeneous catalytic hydrogenation of unsaturated polymer is a post-polymerization process intended to change the chemical and physical properties of the parent polymer, SBS. A number of hydrogenated polymers were synthesized in situ<sup>7</sup> with different degree of saturation, after they were characterized

by  $^1\text{H}$ NMR (SBEBS-22, SBEBS-52 and SBEBS-77) and gel permeation chromatography (GPC).

AC-20 (Salamanca, Mexico) paving asphalt had the following physical properties: penetration: 46 dmm (25°C, ASTM-D5); softening point: 56°C (ASTM-D36); viscosity: 395 Pa.s (135°C, ASTM-D4402). The asphalt contains 20 wt % asphaltene and 80 wt % maltene (ASTM D3279-90).

200 g of asphalt were heated to 180°C in a small container up to the softening point. A given amount of polymer (8 wt %) was mixed under stirring (500 rpm) for 4 h. The mixer was purged before loading with nitrogen to avoid degradation and crosslinking of the polymer, and oxidation of the asphalt and the blending was done under a nitrogen blanket. The storage stability of asphalt binders (PMA) was evaluated, after the samples were characterized by reometry.

Linear viscoelastic properties of asphalt and the PMA systems were measured in a strain-controlled rheometer AR-1000N using the parallel plate fixture (1 mm gap and 25 mm diameter). Frequency sweeps were applied from 0.1 to 100 rad/s at a strain amplitude within the linear viscoelastic range for a given temperature (-5, 15, 25, 40, 60, 75 and 100 °C). Temperature sweeps (-5 to 120 °C with 2 °C/min increments) were performed at a fixed frequency (1 rad/s).

### Results and discussion

The characteristics of the precursor polymer and partially hydrogenated moieties are given in Table 1. GPC data suggest no significant change in the chain length of the polymer upon hydrogenation with narrow polydispersity (D).

Complex modulus and  $\tan(\delta)$  as a function of temperature at fixed frequency (1 rad/s) for the blends are shown in Figure 1. At higher temperatures, polymer modification leads to an

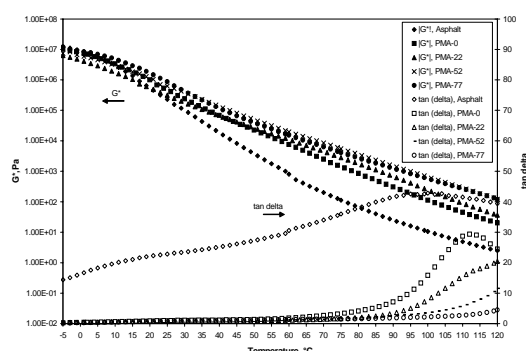
increase in the complex modulus and a decrease in the loss tangent. As the degree of hydrogenation increases, the blends become more elastic at high temperatures, leading to larger resistance to

Polymer	Vinyl (%)	Trans-cis (%)	Global Hyd. (%)	M <sub>w</sub> , g/mol	D
SBS0	9.0	91	0	132 000	1.07
SBEBS-22	6.0	72	22	134 000	1.07
SBEBS-52	0	48	52	137 000	1.07
SBEBS-77	0	23	77	131 000	1.02

permanent deformation in these systems.

**Table 1** Characteristics of SBS-0 and partially hydrogenated polymers. The polymers contain 30% of styrene.

The frequency-dependent modulus ( $G'$ ) behavior at fixed temperature (75°C) for asphalt and blends showed a decreasing slope of the curves in the low frequency region which is ascribed to rising level of entanglements and the formation of an elastic network (Figure 2). The elasticity of the blends increases with degree of saturation of the rubber.

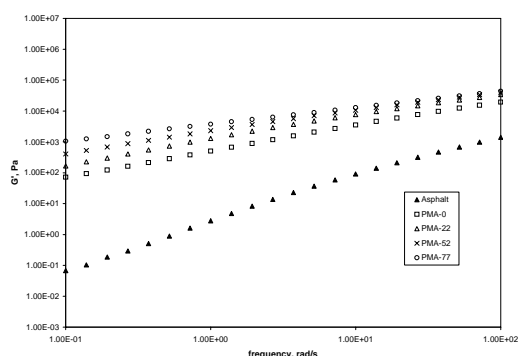


**Figure 1** Complex modulus and  $\tan \delta$  versus temperature for asphalt and blends, ( $\omega=1$  rad/s).

Storage stability was evaluated by means of the separation index<sup>9</sup>,  $I_s$ , according to

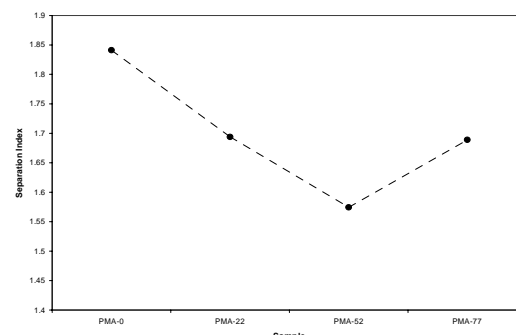
$$I_s = \log (|G^*|_{\text{bottom phase}}/|G^*|_{\text{top phase}}) \quad (1)$$

$I_s$  values were obtained at 25°C and 10 s<sup>-1</sup>. Modified asphalts show  $I_s$  values close to zero, corresponding to stable systems.



**Figure 2** Elastic Modulus versus frequency at 75°C for asphalt and blends.

As observed in Figure 3, the degree of phase separation depends on the nature of the polymer. Among the modified binders tested, PMA-52 is the most stable, as opposed to the PMA-0 binder.



**Figure 3** Separation index measured at 25 °C with constant frequency (10 rad/s) for blends.

## Conclusions

Asphalt blends with hydrogenated polymers possess improved stability at elevated temperatures with increasing elastic response. The increase in elasticity of the systems was evidenced by the behavior of the elastic modulus in the low frequency region, where the presence of entanglements leads to the formation of an elastic network. The behavior of the loss tangent at high temperatures is related to improvements of the resistance of the materials at high temperature, since the elasticity level of the blend remains as temperature increases. The blend that shows better improvements in the mechanical and rheological properties is the PMA-52 blend.

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