

# Use of Rheological Compatibility Criteria to Study SBS Modified Asphalts

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**ABSTRACT:** Polymer-modified asphalts (PMAs) were prepared using Bachaquero asphalt and styrene-butadiene-styrene (SBS) type copolymers. Their rheological behavior was compared to that of unmodified asphalt and of a compatible commercial PMA. Materials were submitted to frequency sweeps between  $10^{-1}$  and  $10^2$  rad/s from 0 to 50°C. Storage stability tests were performed for 72 h at 160°C. Ring and ball softening points from the top and the bottom of the blends were compared and were used along with fluorescence microscopy to evaluate stability. Samples prepared with styrene-ethylene-butylene-styrene (SEBS) showed improved compatibility and stability as compared with SBS-modified asphalts, probably because of a higher stability to thermal degradation from the absence of double bonds. An

additional improvement in stability and compatibility was observed for SEBS functionalized with maleic anhydride (SEBS-g-MAH)-modified blends. Better compatibility, however, did not improve rheological behavior at low temperatures. The systems studied are so complex from a chemical point of view that the rheological criteria normally used to predict compatibility of polyblends did not give enough information regarding the compatibility of the modified asphalts. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1772–1782, 2003

**Key words:** polymer modified asphalts; compatibility; rheology; SBS; blends

## INTRODUCTION

Asphalts have been used in different applications, but they are mostly used in the paving industry. Pavement tends to have several problems, among which high-temperature permanent deformation, or rutting, low-temperature thermal cracking, load-associated fatigue cracking, and chemical aging or hardening are the most common.<sup>1</sup> Growing traffic and higher axial loads of cars speed road damage. Furthermore, for practical and money-saving reasons, maintenance costs have to be reduced.<sup>2</sup> To address these problems, polymer-modified asphalts (PMAs) have been studied for the last 30 years.

Pavement is composed of stone aggregates surrounded by an asphaltic binder matrix (ca. 5% in weight). The performance of such pavement depends

on its binder properties, as it constitutes the continuous matrix and is the only component of the system that can be deformed.<sup>1,2</sup> Therefore, it is extremely important to study the behavior of the binder in order to predict or improve the properties of the resulting pavement. The rheological behavior of asphalt-polymer blends is of great interest because mechanical properties of the binder are closely related to the performance of pavements.<sup>4–6</sup>

Chemicals as asphalts are complex materials, the properties of which depend not only on the crude oil used to obtain the asphalt, but also on the refining process itself. Furthermore, the addition of a polymer dramatically changes the rheological properties of the asphalt,<sup>7</sup> in part because of its high molecular weight. Therefore, the formation of a homogeneous system is not easy, and incompatibility problems arise. Good compatibility is necessary in order to assure that the properties of both materials are adequately transferred to the final product to assure good performance by the system in the pavement.<sup>8</sup>

SBS copolymers have been widely used to modify asphalts. However, they do not produce thermodynamically stable blends, and phase separation is commonly observed during asphalt storing conditions (160°C).<sup>9</sup> One of the several approaches that have been

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TABLE I  
Characteristics of Polymers Employed to Modify the Asphalt

Commercial name	Polymer	Characteristics
Vector™ 2518 (Dexco Polymers)	Linear SBS	31 wt % styrene Content of diblock polymer: less than 1%
Kraton G1652 (Shell Chemical)	SEBS	30% styrene
Kraton FG1921X (Shell Chemical)	SEBS functionalized with maleic anhydride (MAH)	30% styrene 1.0% MAH
Kraton FG1901X (Shell Chemical)	SEBS functionalized with maleic anhydride	30% styrene 1.7% MAH

used to address the compatibility problem is chemical modification of the polymer in order to create some interactions between the polymer and the asphalt.<sup>9–15</sup>

The aim of this work was to study the compatibility of asphalts modified by triblock copolymers such as styrene–butadiene–styrene (SBS). Therefore, a low-penetration asphalt was modified with SBS, styrene–ethylene–butylene–styrene (SEBS), and SEBS grafted with maleic anhydride (SEBS-*g*-MAH). These blends were compared with the unmodified asphalt and with a commercially available compatible PMA. The study aimed to establish if the rheological criteria commonly used to predict the compatibility of polyblends could be used to study these polymer-modified asphalts.

## EXPERIMENTAL

### Materials

SBS, SEBS, and SEBS-*g*-MAH, listed in Table I, were used to modify a low-penetration-grade asphalt (Bachaquero 60/70). Table II shows the composition of the asphalt, which has a colloidal instability index (Ic) of 0.28.<sup>1</sup> A low-penetration asphalt was chosen to stress the low-temperature behavior differences of the different binders. Finally, a compatible PMA based on a proprietary technology from Citgo Asphalt was used as a reference for a compatible PMA with a good performance as paving material. This commercial polymer-modified asphalt is based on a 60/70 Boscan asphalt and has been modified with SBS, but its compatibilization technology is unknown.

### Preparation of Blends

PMAs were prepared by blending 4 wt % of each of the polymers with Bachaquero asphalt. In addition, blends with 1 wt % SBS and 1 wt % SEBS-*g*-MAH-2, respectively, were prepared. The different formulations are shown in Table III.

<sup>1</sup>The Ic provides information on the stability of the polymer–asphalt system. In general, an Ic higher than 0.28 predicts compatibility problems (phase separation) between the asphalt and the SBS.

Asphalt was softened in an oven for 16 h at 100°C and further heated to 165°C under constant mixing with a paddle mixer. Then the asphalt was changed to an LART high-shear Silverson mixer with a square hole high-shear screen at 4500 rpm and 170°C. The polymer was slowly added, and the mixing rate was increased to 6000 rpm and kept there for 4 h to ensure good mixing. At this point, the samples were taken for rheological testing, microscopy, and stability tests. The unmodified asphalt and the commercial PMA were also preheated for 16 h at 100°C but were not blended.

### PMA Stability

Asphalts were poured into a cigar tube and placed in a vertical position in a Blue M oven for 72 h at 160°C ± 1°C. Once cooled, the tubes were cut in three sections, and samples were taken from the top and the bottom portions and reheated at 150°C to take samples for microscopy and ring and ball (R&B) softening point tests.

R&B softening points were determined according to ASTM Standard D 36. The microstructure of the samples was studied by total reflection optical fluorescence microscopy under a Zeiss Axioskop microscope with a UV light source. Micrographs were taken with an MC100 camera with a Zeiss automatic counter. The Micrographs had a 600X magnification.

### Rheology

Rheological testing was performed on an RDA II Rheometrics dynamic rheometer using parallel plate geometry. A nitrogen atmosphere was used to cool

TABLE II  
Chemical Composition of Bachaquero 60/70 Asphalt

Component	Content (%)
Asphaltenes	8.7
Resins	25.9
Saturates	13.0
Aromatics	52.4

TABLE III  
Nomenclature Used to Identify Different Asphalts Tested

Material	Formulation
Unmodified asphalt	Bachaquero 60/70
Asphalt + 1% SBS	Bachaquero 60/70 + 1% Vector™ 2518
Asphalt + 4% SBS	Bachaquero 60/70 + 4% Vector™ 2518
Asphalt + 4% SEBS	Bachaquero 60/70 + 4% Kraton FG1924
Asphalt + 4% SEBS-g-MAH-1	Bachaquero 60/70 + 4% Kraton FG1921X
Asphalt + 1% SEBS-g-MAH-2	Bachaquero 60/70 + 1% Kraton FG1901X
Asphalt + 4% SEBS-g-MAH-2	Bachaquero 60/70 + 4% Kraton FG1901X
Commercial asphalt	Citgoflex®

samples below 20°C. Plate diameters were 8, 25, 40, or 50 mm, depending on 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 between 2% and 100% (at 30°C) and between 0.1% and 5% (at 0°C) 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 just below the LVR at 0°C, 5°C, 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, 40°C, 45°C, and 50°C.

## RESULTS AND DISCUSSION

### Compatibility and Stability

A minimum compatibility between the polymer and the asphalt is necessary to avoid separation during storing, pumping, and applying the asphalt and to achieve the expected properties in the pavement. Stability tests can establish whether the interactions created between the asphalt and the polymers during mixing are strong enough to resist a separation of the polymer in the conditions in which it is stored.

Two approaches have been accepted to find out if phase separation occurs during the stability test: phase compatibility and softening point variation.<sup>14</sup> Softening points between the top and the bottom of the samples after the stability test should not be higher than 4°C to show there is no substantial phase separation (storage stability). Samples are also compared by optical reflection fluorescence microscopy. When asphalts are irradiated with UV light, oils swelling the polymer reemit a fluorescent yellow or green light, whereas asphalt and asphalt components not contributing to the swelling remain dark under the optical microscope. For true stability the top portion of the blend should have the same continuous phase as the bottom portion.

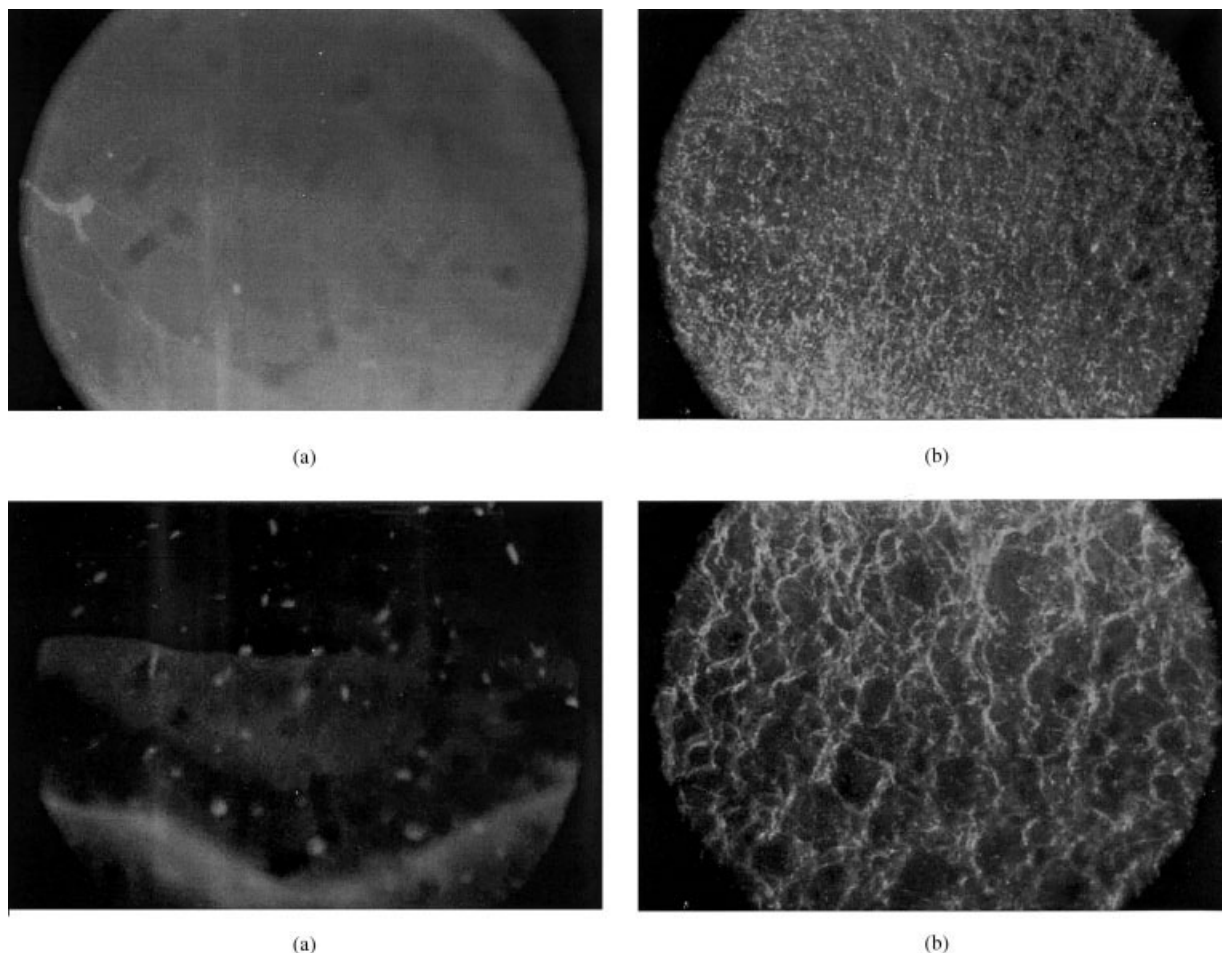
The morphology of PMAs depends mainly on the concentration and chemical structure of the polymer and the composition of the asphalt. Blends that have a

low polymer content, as were those studied here, show polymer domains dispersed in asphalt. These polymer domains consist of polymer particles swollen by the solvating phase of the asphalt. In SBS-modified asphalts, polybutadiene is swollen by maltenes whereas polystyrene domains remain pure and associate between them.<sup>1</sup> According to microscopy evaluation of the samples after blending (not shown here), all blends were compatible, except the 4% SBS-modified asphalt.

Because of a greater difference in viscosity between the asphalt and the polymer than between the two polymers being blended, the separation process between polymers and asphalt occurred much faster than in a polyblend submitted to the same heating treatment.<sup>16</sup> Figure 1 shows micrographs of the top and bottom parts of selected blends after the stability test. The continuous phase of the top of the SBS-asphalt blend corresponds to the polymer and the continuous phase of the bottom to the asphalt [Fig. 1(a)], indicating that this blend is "unstable." Furthermore, the top and bottom of this blend show a 27°C difference in their softening points, as can be seen in Table IV. Blends of asphalt and 4% SEBS-g-MAH-1 [Fig. 1(b)], asphalt and SEBS, and asphalt and 4% SEBS-g-MAH-2 (not shown here) can be considered to be stable according to their micrographs and the difference in the R&B softening points. The small differences in softening points should be considered to be within experimental error.

According to their morphologies, SEBS-g-MAH blends seemed to be more stable and compatible than SEBS-based blends, indicating that the presence of functional groups in the polymer contributes to improve the stability of these polymer-modified asphalts. To withstand separation for 72 h at 160°C, there have to be strong interactions between the polymer and the asphalt or a chemical reaction had to have taken place to form covalent bonds, which are sufficiently resistant to the time and temperature conditions of the stability test.

Specifically, for the SEBS-g-MAH-modified asphalts, there is a chance that specific interactions occurred between the asphalt and the polymers, such as



**Figure 1** Fluorescence micrographs for: (a) asphalt + 4% SBS, after the stability test. Upper micrograph: top of the sample; lower micrograph: bottom of the sample. (b) asphalt + 4% SEBS, after the stability test. Upper micrograph: top of the sample; lower micrograph: bottom of the sample.

hydrogen bonding between the carbonyl groups of the maleic anhydride and the nitrogen of the amide in asphaltenes, or of the nitrogen of the amine in the asphaltenes or resins. Further, it is highly probable that the maleic anhydride group suffered hydrolysis in the presence of environmental moisture, creating additional opportunities for hydrogen bonding. Supplementary studies are necessary to estimate the dissociation energies of these interactions and to predict

whether they would be capable to resist the conditions of the stability test.

When functionalized polymers are blended, reactive or chemical compatibilization can occur, giving place to the formation of *in situ* copolymers because of the chemical reaction during processing. Several conditions have to be met for this compatibilization to take place.<sup>17</sup> Similarly, when predicting a compatibilization process between asphalt and polymers, the

**TABLE IV**  
Difference in R&B Softening Points Between Top and Bottom of the Blends after Stability Test at 160°C for 72 h

Material	R&B softening point (°C)		Difference (°C)	Comments
	TOP	BOTTOM		
Asphalt + 4% SBS	84.1	57.7	26.7	unstable
Asphalt + 4% SEBS	69.6	66.7	2.9	stable
Asphalt + 4% SEBS-g-MAH-1	70.3	70.4	0.1	stable
Asphalt + 4% SEBS-g-MAH-2	67.8	66.8	1.0	stable
Commercial PMA	68.1	69.4	1.3	stable

same factors are expected to hold. Blends were prepared under high shear at 170°C, favoring dispersion of the polymer in the asphalt; blends prepared with SEBS-*g*-MAH had reactive functional groups; residence time in the mixing equipment was long enough (4 hs) to allow the possible reactions to proceed; the only further processing needed by the asphalts was high temperature storing, and stability tests performed suggest that the samples prepared with the functionalized polymers were stable. Some chemical reactions could have taken place between the functional groups of the components of the polymer-asphalt blends.

However, these possible reactions would not explain the substantial improvement in the stability for the SEBS-modified asphalt, compared with the SBS-modified asphalt. The double bonds of SBS are the main difference between SBS and SEBS; therefore, thermal degradation is likely to occur through these unsaturations. Actually, crosslinking of polybutadiene has been reported to occur above 150°C.<sup>18</sup> Further, Kraus et al.<sup>19</sup> indicate that high asphalt mixing temperatures (175–205°C) favor thermo-oxidative and shear degradation of the polydienic block: first, a chain scission occurs, and in the final mixing steps crosslinking proceeds, giving place to polymer separation from the asphalt. On the other hand, it has also been proposed that SBS separates from asphalt as a result of competition between the modifier and the asphaltenes for maltene absorption.<sup>20</sup>

### Time-temperature superposition

Although some researchers consider that time-temperature superposition (TTS) holds for unmodified asphalts,<sup>6,21,22</sup> and some have found the same behavior for PMA,<sup>23–26</sup> others have reported that TTS holds neither for unmodified<sup>22,28</sup> nor for modified asphalt.<sup>29</sup>

### Master curves

Although the systems are very complex chemically, according to the frequency sweep master curves, all asphalts tested seem to have obeyed a TTS principle, as can be seen in Figure 2(a) for a compatible blend (asphalt + 4% SEBS-*g*-MAH-1) and Figure 2(b) for an incompatible blend (asphalt + 4% SBS). The remaining materials showed the same behavior. Moreover, single frequency sweep master curves were obtained regardless of the compatibility of the PMA.

The basic assumption of the TTS is that all relaxation times should show the same thermal dependence. Accordingly, the result in this study was rather unexpected because no factor seemed to contribute to the unification of the relaxation mechanisms of the phases. Although for heterogeneous systems TTS also holds when the disperse phase shows no relaxation

mode within the testing temperature range,<sup>29,30</sup> this explanation did not hold here. As can be seen by the lack of superposition according to other criteria listed later in the discussion, these master curves seem not to be sensitive enough to morphology or differences in compatibility for the materials employed here.

An important difference between the evaluated materials was in the crossover frequency,  $\omega_c$ . In general, as shown in Table V, the crossover frequency for the more compatible materials occurred at lower frequencies than for the less compatible materials, indicating a more elastic behavior under these circumstances. Ideally, at low temperatures a paving-grade asphalt should have a high crossover frequency, as can be seen for the commercial PMA, in order to extend the range of frequencies at which the material shows essentially the most dissipative behavior possible. No conclusions can be drawn regarding the influence of the degree of functionalization of the modifier on the viscoelastic balance of the blends.

For polymers, shifting factors fit better to Williams-Landel-Ferry (WLF) equations at the glass-transition temperatures or higher than to Arrhenius-type relationships. However, there has been some controversy regarding the relationship better describing the behavior of asphalts. Although some researchers consider the shifting factors to be better suited to a WLF equation,<sup>31</sup> others have written that they are better fitted to an Arrhenius-type equation.<sup>23,25,32</sup>

For the PMAs prepared in this study, shifting factors fit better to an Arrhenius-type function at temperatures between  $T_g$  and  $T_g + 100^\circ\text{C}$ , as can be seen in Table VI. This behavior has been reported for natural and synthetic asphalts,<sup>22</sup> for PEAD- and PEAD/EPDM-modified asphalts,<sup>25</sup> and for SBS- and SBR-modified asphalts.<sup>24</sup>

### Cole-Cole plots

Cole-Cole diagrams<sup>33</sup> can also be used to study the effect of the addition of polymer on the rheological behavior of asphalt. Cole-Cole diagrams consist of representations of the complex viscosity components ( $\eta^* = \eta' - i\eta''$ ) in the complex plane ( $\eta' \cdot \eta''$ ),<sup>23</sup> Aiji and Utracki<sup>17</sup> found that Cole-Cole plots are more sensitive to phase separation than are modulus or viscosity curves. Therefore, these plots have been used widely to study compatibility in polyblends. The occurrence of symmetrical parabolas has been considered proof of compatibility, and deviation from this symmetry has been related to incompatibility for polyblends, as well as for polymer-modified asphalts.<sup>17,23</sup>

Figure 3(a,b) shows normalized Cole-Cole plots for the different materials at 5°C and 40°C. Normalization was performed using zero shear viscosity estimated by adjusting the frequency sweeps to the Carreau-Yasuda model. Similar results were obtained when using zero

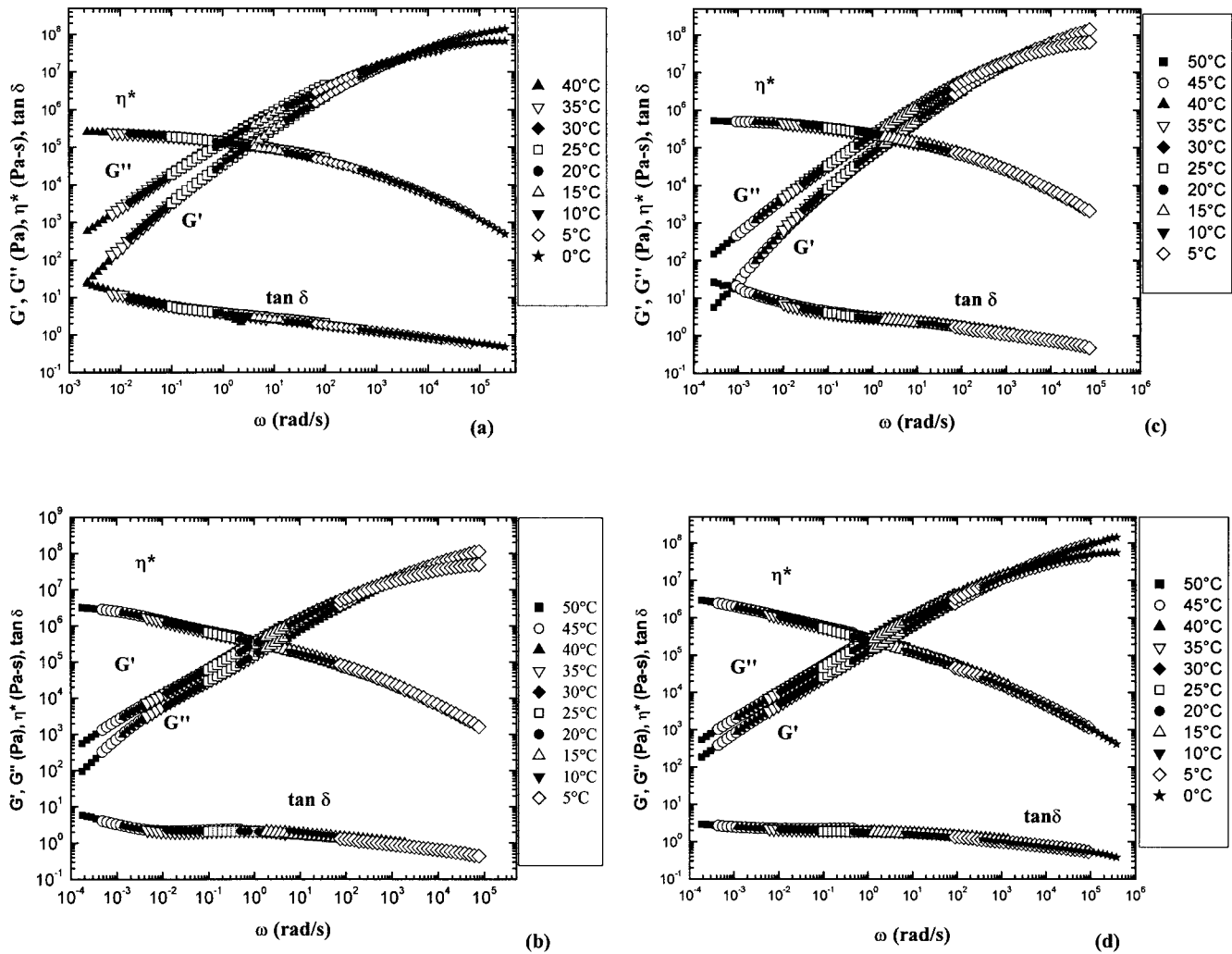


Figure 2 Master curves (reference temperature: 25°C) for: (a) neat asphalt; (b) asphalt + 4% SBS; (c) asphalt + 4% SEBS-g-MAH-1; (d) commercial asphalt.

shear viscosity estimated from the Ellis model. Except for the unmodified asphalt and the blends with 1% polymer content, the curves of the systems were restricted to the high-frequency region, providing information on the elasticity of the materials. The deformation mechanisms with the longest relaxation times are those that contrib-

ute more to the viscous deformations.<sup>34</sup> Curves limited to the left side of the Cole–Cole plots were essentially elastic at all temperatures from 0°C to 50°C, whereas those shifted to the right show a transition from an elastic behavior, at low temperatures, to a viscous behavior, at higher temperatures.

TABLE V  
Crossover Frequency of the Materials at Different Testing Temperatures (Experimental Data)

Material	$\omega_c$ (rad/s)			
	0°C	5°C	10°C	15°C
Neat asphalt	0.93	6.14	18.4	> 100
Asphalt + 1% SBS	0.33	3.52	24.8	97.4
Asphalt + 4% SBS	0.25	2.79	8.97	46.2
Asphalt + 4% SEBS	< 0.1	0.41	2.81	16.5
Asphalt + 4% SEBS-g-MAH-1	<sup>a</sup>	0.84	7.11	17.6
Asphalt + 1% SEBS-g-MAH-2	<sup>a</sup>	2.63	16.9	83.1
Asphalt + 4% SEBS-g-MAH-2	<sup>a</sup>	0.48	4.19	16.2
Commercial asphalt	0.31	3.40	25.4	> 100

<sup>a</sup> Could not be estimated because of compliance problems at the testing temperature.

TABLE VI  
WLF and Arrhenius Parameters for the Tested Materials (Reference Temperature: 25°C)

Material	WLF			Arrhenius	
	$C_1$	$C_2$	$r^2$	$Ea$ (kJ/mol)	$r^2$
Asphalt	11.7	84.4	0.6572	228.6	0.9850
Asphalt + 1% SBS	14.2	101.8	0.8243	209.3	0.9850
Asphalt + 4% SBS	26.2	196.0	0.2583	216.4	0.9970
Asphalt + 4% SEBS	11.4	95.0	0.7103	220.8	0.9921
Asphalt + 4% SEBS-g-MAH-1	14.6	122.6	0.4814	208.7	0.9928
Asphalt + 1% SEBS-g-MAH-2	15.1	127.3	0.8059	207.1	0.9974
Asphalt + 4% SEBS-g-MAH-2	15.6	122.9	0.8301	217.9	0.9967
Commercial asphalt	40.7	313.7	0.0912	217.2	0.9918

Asphalts are complex materials, composed of different types of compounds (asphaltenes, aromatics, resins, and paraffins). The presence of a polymer further increases the complexity of the system. In pure SBS the coupling between the blocks originates different relaxation mechanisms with different levels of thermal dependence.<sup>35</sup> Furthermore, interfacial phenomena can have a great effect on the viscoelastic properties of polymer blends. According to these characteristics, SBS-modified asphalts were expected to show a wide distribution of relaxation times as effectively seems to have happened.

For the asphalts studied, the form of the curves seems not to be associated with the compatibility of the systems. Deviations from the parabola have been attributed to the presence of a second relaxation process<sup>36</sup> or to the superposition of different relaxation functions as a consequence of complex relaxation processes. Utracki and Sammut<sup>37</sup> stated that neither the absence of symmetry nor the bimodality in Cole–Cole plots can be taken as evidence of phase separation, only as an indication of a complex distribution of relaxation times. Cole–Cole plots provide information

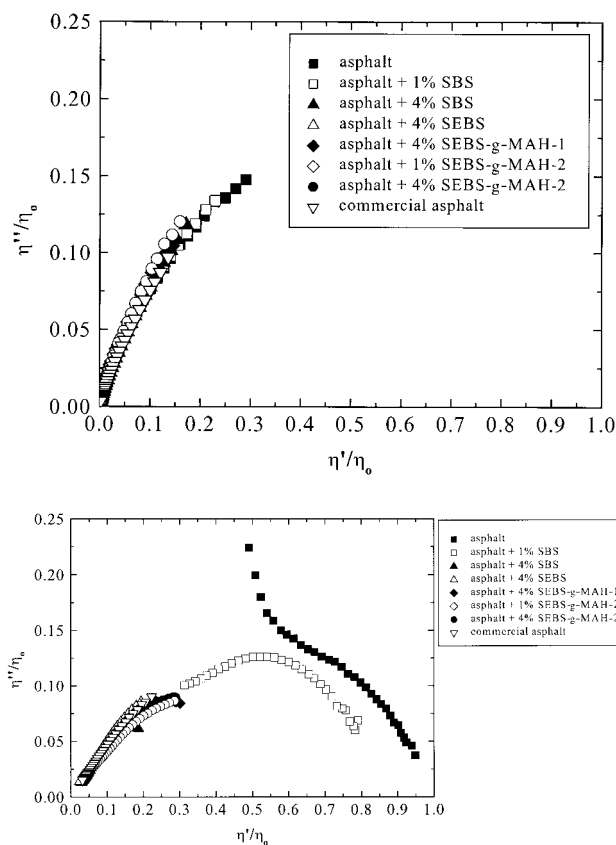


Figure 3 Normalized Cole-Cole plot at: (a) 5 °C ( $\eta_0$  from the Carreau model); (b) 40 °C ( $\eta_0$  from the Carreau model).

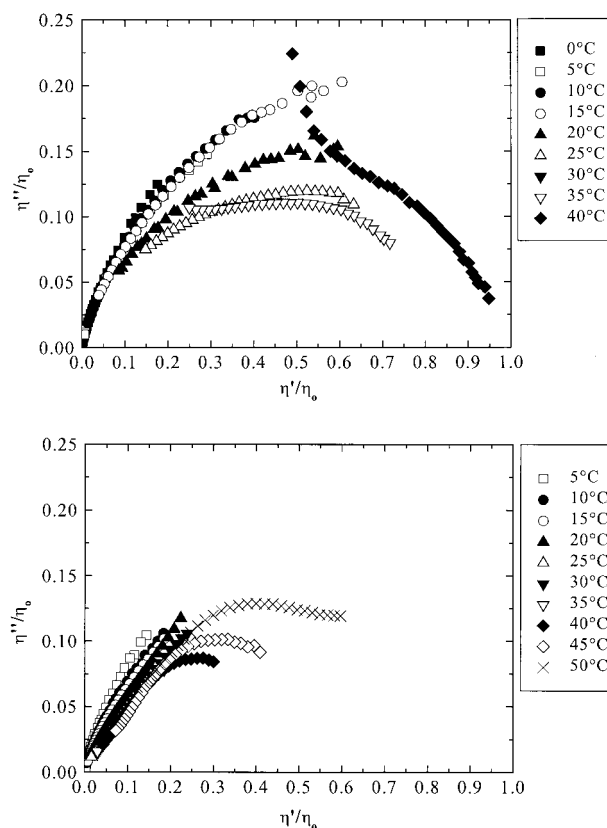
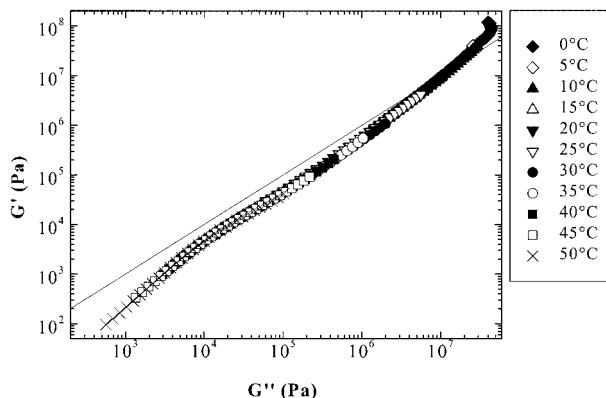


Figure 4 Normalized Cole-Cole plot at different temperatures for: (a) neat asphalt ( $\eta_0$  from the Carreau model); (b) asphalt + 4% SEBS-g-MAH-1 ( $\eta_0$  from the Carreau model).



**Figure 5** Han plots for the asphalt + 4% SBS at different temperatures.

regarding the relaxation occurring in polyblends, independently of whether they occur in two separate phases or in true solutions.<sup>38</sup>

In general, the behavior of the evaluated polymer asphalt blends seems to have been characterized by a broad distribution of relaxation times as a consequence of their structural complexity, making their curves depart from the expected symmetrical parabola behavior. However, to corroborate this, the relaxation and retardation spectra should be calculated.

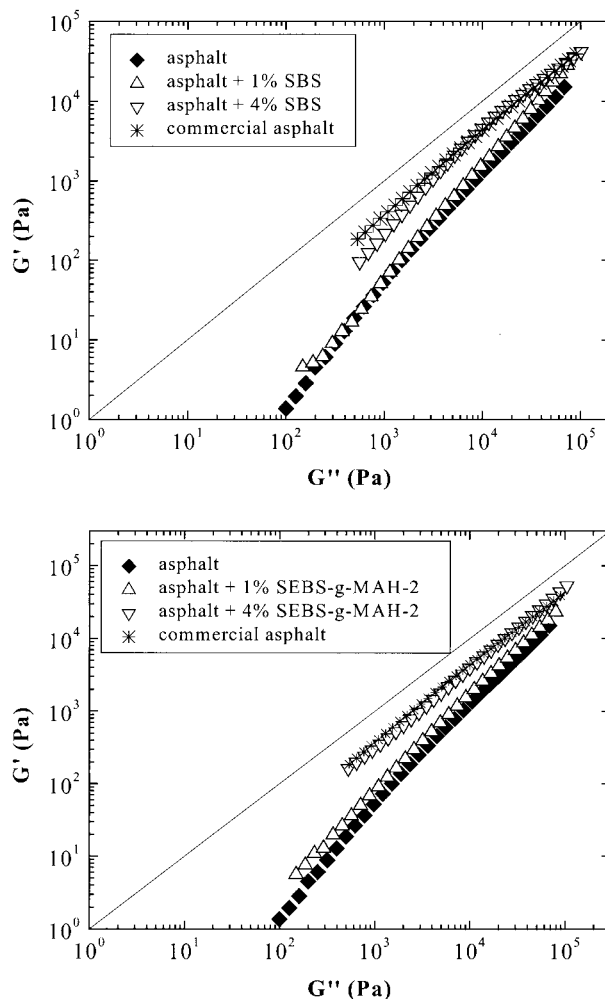
As can be seen in Figures 4(a,b) for unmodified asphalt and 4% SEBS-g-MAH-1, respectively, the form of the Cole–Cole plots changes with temperature. This behavior is more evident for the asphalt and the low-polymer-content blends and seems not to have been affected by the concentration of functional groups in the polymer. This may be explained in two ways. First, changes in the compatibility of the systems may occur with temperature. Some components of the blends might display UCST (upper critical solution temperature) behavior. Second, the materials might be showing various independent relaxation modes, the contribution of which could have changed with temperature. These modes might be associated with the different phases of the blends or with the interphases, which could show their own relaxation mechanisms.

As single master curves were obtained for the frequency sweeps, Cole–Cole plots were completed using data from these curves in order to cover a wider range of relaxation times and to see if symmetry of the parabolas could be attained in this way (not shown here). Still, no meaningful relationship between the plots and the compatibility of the different asphalts was found. For example, neat asphalt as well as blends with 1% polymer showed parabolas. The asphalt with 4% SBS (incompatible) showed complete parabolas, whereas none of the compatible blends showed parabolas. The blend with 4% SEBS-g-MAH-1 exhibited bimodality, indicating the possibility of two relaxation mechanisms. As stated by Wisniewski et al,<sup>39</sup> incom-

patibility induces strong local interactions that could have very long relaxation times, giving rise to a deviation in the low-frequency region of the Cole–Cole plots. However, this does not explain why the blend with 4% SEBS-g-MAH-1 showed a second relaxation mechanism.

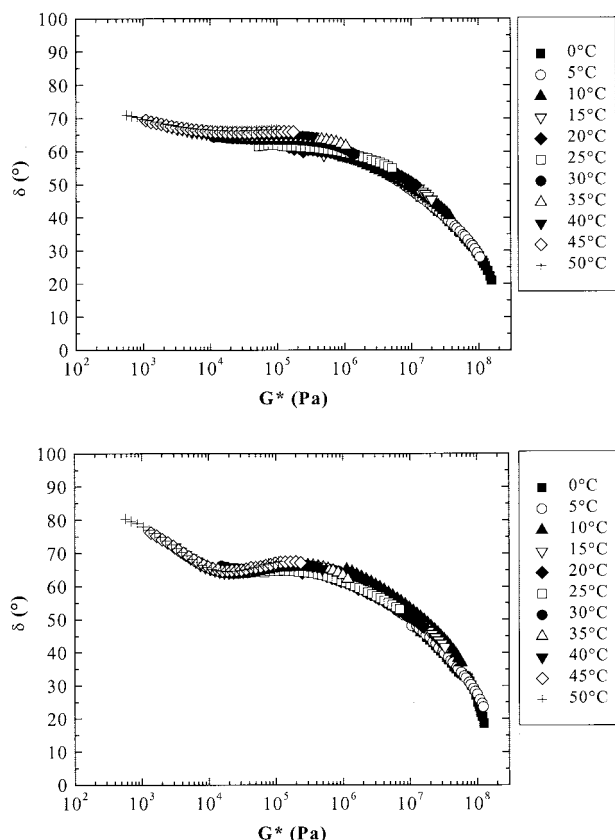
**Han diagrams**

Han, or modified Cole–Cole, plots consist of representations of the changes between the elastic and viscous components of the complex modulus.<sup>40</sup> Although frequency is not directly shown in the plots, the higher modulus values correspond to higher frequency conditions. If a straight line, corresponding to  $G' = G''$ , is drawn, its intercept with the Han curve represents the crossover frequency between  $G'$  and  $G''$ . Data on the right and under the straight line indicate a behavior dominated by the viscous or loss component of the modulus, that is, stress is dissipated by flow. Data on the left or above the equimodulus line indicate that the



**Figure 6** Han plots for: (a) SBS modified asphalt at 50 °C; (b) SEBS-g-MAH-2 modified asphalt at 50 °C.





**Figure 7** Black curves for (a) neat asphalt and (b) asphalt + 4% SBS.

elastic mechanisms dominate the behavior of the samples under the respective testing conditions.<sup>40</sup>

As expected, at high temperatures the asphalt polymer blends were predominantly viscous, while at low temperatures the materials showed crossover frequency, indicating a transition in the behavior of the blends, as could also be observed in the frequency sweeps. In addition to Han plots of the polyblends,<sup>41</sup> for the polymer-modified asphalts were temperature independent, regardless of whether compatible or incompatible blends were considered, as can be seen in Figure 5, which shows the Han plot for the incompatible 4% SBS blend. The same behavior was observed for all other materials tested.

The relationship between the stored and the dissipated energy during shear deformation should be independent of the composition of the blends as long as the molecular structure remains unchanged.<sup>41,42</sup> On the other hand, for polyblends with a well-differentiated interface when no interactions occur between the phases, slipping between the phases tends to occur,<sup>43</sup> originating different curves for incompatible blends. Therefore, compatible polymer blends have a composition independent of the relationships between  $G'$  and  $G''$ , whereas incompatible polyblends show concentration-dependent behavior.<sup>41</sup>

Han curves for the unmodified asphalt were compared with those of 1% and 4% polymer, both for blends with an incompatible polymer (SBS) and for blends with a compatible polymer (SBS-*g*-MAH-2), as can be seen in Figure 6. For each of these blends, a Han plot at 50°C is shown here as an example. The curves of the commercial asphalt were included only as a reference. As expected, the curves of the incompatible blend were clearly differentiated. However, the compatible system showed exactly the same behavior, that is, concentration-dependent curves. The higher the polymer content, the more the behavior of the blend departed from the behavior of the unmodified asphalt. This difference was present at all temperatures but was more noticeable when the temperature was higher, suggesting minor changes in miscibility with temperature.

These results suggest that Han plots may not be an adequate rheological criterion to predict compatibility of polymer-modified asphalts.

#### Black curves

Black diagrams are another useful method to represent rheological data without including frequency or temperature.<sup>28</sup> As the phase angle is approximately the derivative of the log  $G^*$  versus frequency curve at a constant temperature, these plots are very sensitive to morphology.<sup>44</sup> When plotting the phase angle against  $G^*$ , the effect of shifting the curves along the frequency axis is eliminated, and temperature-independent curves can be obtained when the material holds TTS.<sup>30</sup>

Polymer-modified asphalts can show Black curves that range between a curve for a more or less susceptible viscoelastic liquid to those of a viscoelastic solid with structure and properties close to those of a pure elastomer.<sup>28</sup> Any deviation from a single curve would mean the structure is changing under the effect of thermomechanical stresses.<sup>28,45</sup>

Figure 7 shows representative Black curves for neat asphalt, a compatible and an incompatible PMA tested in this study. All samples showed that TTS held quite well despite the complex structure of the blends, when compared with results for other systems (see curves for PVC homopolymer in Van Gurp and Palmen.<sup>30</sup> However, superposition was not perfect for any of the materials, not even for the commercial asphalt [Fig. 7(c)], indicating that this criterion does not seem to work for the compatibility prediction of these blends under these test conditions.

When comparing the behavior of diverse samples, the difference between the curves is not as pronounced as the difference in the normalized Cole-Cole plots but is more noticeable than that in the frequency sweep master curves. The form of a Black curve is related to the structure of the asphalt. Small

changes in the phase angle as a function of  $G^*$  correspond to broad relaxation spectra. In contrast, great variations in the phase angle originate in narrow relaxation spectra.<sup>28,45</sup> According to this, the commercial PMA [Fig. 7(c)] and the blend with 4% SEBS- $g$ -MAH-2 (not shown here) are the materials with the widest relaxation spectra, whereas the material with 1% SBS (not shown here) has the narrowest relaxation spectrum.

The presence of a polymer changes the behavior of the asphalt at high (left-hand side of the curves) as well as at intermediate temperatures (central region of the curves), as can be seen when comparing the different Black curves. For the neat asphalt (not shown here), the phase angle practically reached  $90^\circ$  at low frequencies or high temperatures, indicating an essentially viscous behavior under these conditions. This behavior remained practically unchanged when adding 1% polymer. Blends with 4% polymer and the commercial PMA showed lower phase angles, indicating a more elastic behavior,<sup>46</sup> corroborating results shown before. This higher elastic behavior could indicate the asphalts have a lower susceptibility to rutting. According to SHRP criteria,  $G^*/\sin \delta$  at 1.6 Hz were calculated at high temperatures to compare the different asphalt polymer blends (not shown here). The higher the polymer content in the blend, the lower was the rutting susceptibility; however, no significant trend could be observed regarding the relationship between the compatibility and the susceptibility to rutting.

At low temperatures (right-hand side of the curves), no discontinuities are shown in the curves for any of the materials, indicating that in this region their structure did not change with thermomechanical conditions. All the materials tested behaved essentially as elastic solids at low temperatures.

## CONCLUSIONS

The modification of a 60:70 Bachaquero asphalt with SEBS or SEBS functionalized with maleic anhydride produced compatible and stable blends. The improvement in compatibility and stability does not necessarily mean a system with improved rheological properties, as the lower crossover frequencies show. However, the use of a higher penetration grade of asphalt to prepare the blends could improve the low-temperature behavior of the PMA systems and should therefore be evaluated. Despite the chemical complexity of the systems examined, single master curves for frequency sweeps were obtained for all the materials evaluated. TTS also allowed plotting rather continuous Black curves. These curves provided information regarding the elastic character of the materials. The form of the Cole–Cole plots changed with temperature. This behavior can be attributed to changes in the compatibility of the blends when changing temperature or to the components of the asphalt–polymer

blends having different relaxation mechanisms with a different thermal dependence. For the systems studied, Han plots were independent of temperature but dependent on concentration for compatible, as well as for incompatible, PMAs. In general, blends with 4 wt % of polymer behaved the same way as the commercial compatible PMA. The systems studied are so complex from a chemical point of view that the rheological criteria normally used to predict compatibility of polyblends do not provide enough information regarding the compatibility of the modified asphalts. Several factors might have affected the results because there are five components in the blends plus the interphases between them.

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