

# Rheology of asphalt and styrene–butadiene blends

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**Abstract** In recent years, many authors have researched polymer-modified asphalt blends and tried to better understand the rheological behavior of these materials. In this work, the thermomechanical response of an asphalt formulation was researched trying to find better asphalt-modified blends that allow for the construction of improved asphalt roads. The experimentation included several polymer–maltene formulations developed at different polymer concentrations and temperatures where the asphaltenes of the original asphalt were removed. Such separation was carried out because the maltene fraction represents the portion of the asphalt that chemically reacts with the polymer modifier. The rheological behavior of the blends was determined from oscillatory shear flow data. Analysis of the  $G'$ ,  $G''$ ,  $G^*$  moduli and phase angle ( $\delta$ ) as a function of oscillatory frequency for various temperatures led to the conclusion that the maltenes behaved as a pseudo-homogeneous viscoelastic material that could dissipate stress without presenting structural changes. Furthermore, all maltenes–polymer blends behaved more viscoelastically than the non-blended maltenes depending on the amount of the polymer contained in the formulation. The blend viscosity increased with polymer concentration, and this

increase was seen in both the viscous and elastic moduli. Furthermore, performance grade trials were also performed according to the AASHTO TP5 to determine the failing temperature. It was noticed that the limiting temperature increased with the modifier concentration with a  $\delta$  between 50° and 60°, indirect value of elasticity found to have industrial applications for asphalt pavements.

## Introduction

Asphalt has a short life cycle failing mainly due to temperature changes, traffic load, and UV solar radiation. One common way of increasing the performance of the bitumen is blending the asphalt with polymer modifiers (PMA). PMA has better mechanical properties and higher durability than the non-modified asphalt. The polymer is blended with the asphalt to improve its resistance to rutting, abrasion, fatigue, and aging at medium and high temperatures. The polymer in a PMA road should neither make it too viscous at high service temperatures (resulting in permanent deformation) or too brittle at low service temperatures (resulting in crack development). Furthermore, the chemical composition of the asphalt plays a key role because it depends on the asphalt source and the distillation method from which it is obtained [1, 2]. Consequently, the asphaltenes and maltenes may not only differ in amount but in composition as well; whereas the maltenes contain low molecular weight components, the asphaltenes are the dispersed phase with solid particles of high molecular weight [3, 4]. Polymer-modified asphalt (PMA) must have superior stability during storage and transportation in order to guarantee homogeneous mechanical properties during application and road service. One of the most important results that can be found in the literature is

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the demonstration that the thermomechanical behavior of an asphalt mixture is improved when the polymer modifier forms a network either from molecular interactions or chemical reactions between the asphalt and the polymer [5–8].

A commonly used asphalt modifier is the poly(styrene-*block*-butadiene-*block*-styrene-*block*) (SBS) whose styrene blocks provide the modified asphalt its durability and the butadiene elements its rubber properties [9]. The SBS is immiscible with the asphalt so that stability problems are prone to occur when not enough interactions between components take place; thus, asphalt–polymer microphase compatibility is highly desirable [7, 10–13]. Blend stability is vital because the paving process requires the elaboration, storage, and transport of the modified asphalt at temperatures around 180 °C from the asphalt modification facility to the location of the road pavement application. The whole process may take up to 3 days, enough time for either phase separation or segregation to occur in unstable mixtures. The classical tests applied for pure asphalt specification, like penetration, ring and ball temperature and viscosity are not satisfactory to well characterize a PMA.

Many authors [8–13] have suggested the use of rheological tests to predict the performance, stability, and elasticity of PMAs. These tests involve less destructive methods, where the sample dissolution is not necessary, giving more reliable information about the asphalt modification. In the rheological tests performed in the dynamic mode, data are taken concerning the range of deformation corresponding to the linear viscoelastic range [9, 14]. Thus, the shearing frequencies used in the sample characterization can be correlated to traffic conditions [15]. Linear viscoelastic properties provide relevant information about the PMA structure and its thermomechanical response. Additionally, the linear viscoelastic properties are strongly dependent on the changes in the composition, molecular weight distribution and, when considering multiphase systems, interface characteristics. In this way, these properties constitute useful tools to analyze the influence of different types of asphalt–SBS blend properties [2, 9].

From a different point of characterization, asphalt morphology has become a common way of analyzing phase separation through a fluorescence microscopy and linked to the tube separation test associated with the D-36 ASTM standard [7, 8, 10–14, 16, 17]. The fluorescence images show the phase morphology of immiscible blends; the system usually starts with the asphalt as the continuous phase but after processing, it may become dispersed in a polymer network. It is generally accepted as a SBS stable system, a blend where the polymer modifier somehow becomes the continuous phase [9, 18]. The immiscibility of the SBS is an advantage over other polymer modifiers [9, 18] since the chemistry can be modified to improve the

blend stability. For example, the linear SBS is more compatible than the ramified one [11, 17]; the increased compatibility tends to improve stability, which is in turn related to the rheological properties of the material and the polymer as the continuous phase.

Isacsson and Lu [7] and Lu and Isacsson [8] observed phase inversion in a polymer concentration higher than 6% (w/w), which has been a controversial value because many authors have reported different results at the onset of the inversion. If the asphalt used contains a relatively low fraction of asphaltenes and a high amount of aromatics, the mixture tends to be more stable. Materials that are more stable than the SBS have been found in the poly(styrene-*block* [(butadiene)<sub>1-x</sub>-(ethylene-co-butylene)<sub>x</sub>]-*block*-styrene-*block*) (SBEBS) produced by hydrogenation of the SBS, a less polar modifier with lower susceptibility to oxidation [8, 9, 13]. The SEBS performance has been improved by functionalizing it with maleic anhydride [9, 14]. Mixtures above 4% (w/w) are SBS unstable, whereas they are stable at the same concentration if MAH is incorporated in the polymer. The new PMA formulas were analyzed by applying the rheological tools in oscillatory tests. Black diagrams showed the sensitivity of the mixture with respect to the system morphology [9, 14], which is an indicator of the stability of the sample. Among the options of asphalt modification, the SBS system has been widely studied. This understanding can be applied to develop better formulas for road pavements. Our objective was to investigate the SBS–asphalt system by isolating the maltene fraction of the asphalt and modifying it with a commercial SBS. We used rheological tools in oscillatory tests at several temperatures and tested for practical application by applying the performance grade (AASHTO TP5).

## Experimental

### Maltene–asphaltene separation

The separation of the maltene fraction from the asphalt was performed according to the procedure proposed in both ASTM D3279-90 and ASTM D4124-86 standards. Such procedure consists of using an Enlermeyer flask (1 L) with a known amount of asphalt (AC-20 from Salamanca, Mexico): a ratio of 10 mL *n*-heptane per gram of asphalt. The container should be placed in a heating plate with magnetic agitation and connected to a recirculation system. The mixture should be slowly heated up to 90 °C and maintained at such temperature during 2 h with constant agitation so that phase separation occurs: the maltenes dissolve in the *n*-heptane and the asphaltenes remain dispersed. The asphaltenes become the filter cake of a filtrate

operation, and the filtrate contains the maltene fraction in *n*-heptane; this maltene solution is reintroduced in the flask where the separation is carried out. The system is connected to a distillation system and distilled at 98 °C at atmospheric pressure to obtain the *n*-C<sub>7</sub> as the distillate and the maltene concentrated solution as the bottom. The maltene solution is further treated in the oven at 100 °C during 12 h to eliminate any traces of *n*-heptane.

Maltene–copolymers mixture preparation

The formulations were designed as if pure asphalt had been used. The weight of the polymer for the modification (SBS from Dynasol, used as received) was equivalent to 3, 4, 5, and 7% w/w in AC-20 asphalt (Table 1), and it was assumed that the asphalt contained 80% (w/w) of maltenes.

The samples were prepared as follows: In a flask of 150 mL, the maltenes fraction was weighed. This recipient was positioned in a hot oil bath (approximately at 170 °C) to soften the maltenes. When the maltenes became fluid, a magnetic agitator and a thermometer were set. Once the temperature was stabilized at 180 °C, the agitation was initiated at 275 rpm, and the SBS was added gradually. The temperature and agitation were maintained during 3 h. Additionally, in order to have a reference for the rheological characterization, a maltene fraction alone was treated as a blank sample with the same procedure. This was done to assure that all the samples underwent the same thermomechanical history and could be compared.

Microscopy

Morphology of the blends (i.e., distribution and shape of the polymer-rich phase) was observed on images from a fluorescence microscopy analysis of the blends using a Carl-Zeiss KS 300 microscope equipped with a lamp for 390–459 nm wavelength and 20× lens.

Rheological characterization

The rheological behavior of maltenes and maltenes–polymer samples was examined on a strain-controlled rheometer TA-Instruments AR-2000 using a parallel plate geometry (25 mm in diameter; 1 mm gap). The storage  $G'$  and loss  $G''$  moduli were determined through small

amplitude oscillatory shear flows at frequencies ranging from 0.1 to 300 rad/s at various temperatures under linear viscoelastic conditions. From strain sweep runs, the upper limit of the linear viscoelastic zone was located at a strain of about 0.02. In this domain, the experimental tests were essentially nondestructive and could be interpreted in terms of the molecular structure of the material. All samples were tested under various temperatures (25, 40, 50, and 60 °C) at least twice. This information was used to construct the master curves of  $G'$ ,  $G''$ ,  $G^*$ , and  $\delta$  from which the blends' rheological behavior was investigated.

Results and discussion

Figure 1 shows the  $G'$  and  $G''$  moduli evolution at 25 °C. Similar trends with respect to frequency were observed for all samples, which also maintained some viscous behavior ( $G'' > G'$ ) within the frequency range examined. Both viscoelastic moduli declined as frequency decreased. The results of the mechanical spectra showed a power law-type dependency on the frequency [3] characteristic of materials with viscoelastic behavior. As the polymer concentration rose, the corresponding viscoelastic behavior also increased (>4% w/w), as well as the trend towards a less viscous material, undoubtedly indicating the existence of a network whose strength increased with polymer concentration. The structural rearrangements induced by the test conditions finally translate into different mechanical

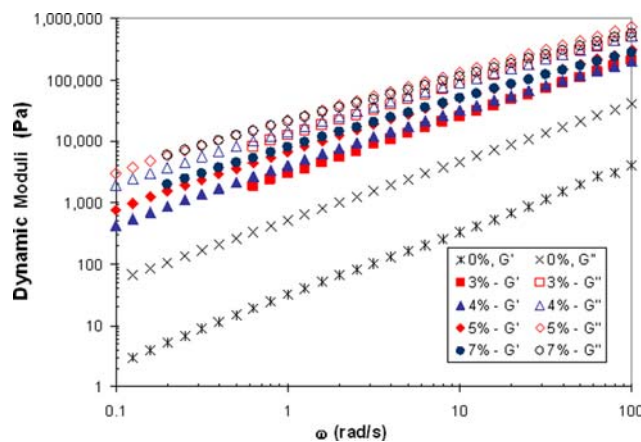
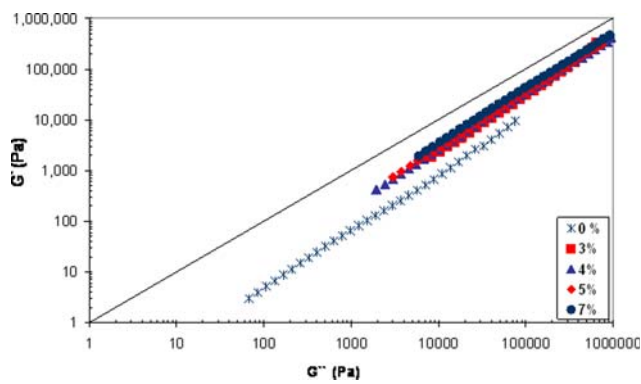


Fig. 1 Evolution of the viscoelastic moduli at 25 °C

**Table 1** Polymer concentrations based on 100 g of AC-20 asphalt–polymer blend

Maltenes (g)	SBS (g)	Polymer concentration in maltenes (%)	Equivalence: wt% of polymer in asphalt
77.6	3	3.72	3
76.8	4	4.95	4
76	5	6.17	5
74.4	7	8.59	7

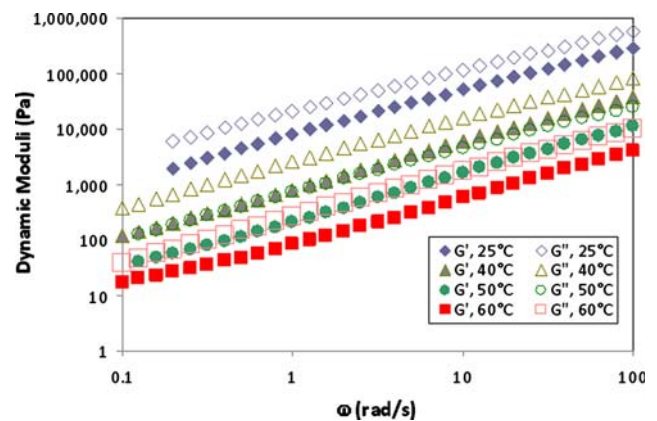


**Fig. 2** Evolution of the viscoelastic moduli in a Han plot at 25 °C

properties. These results suggest that, within the range of  $\omega$  investigated, the polymer-modified maltenes (PMM) behave as a viscoelastic material able to dissipate stress without presenting structural changes. This behavior could be attributed to an additional relaxation mechanism involving morphological changes that possibly occur at low frequencies or high temperatures. Similar behaviors of asphalt-modified mixtures have already been found in the literature [7, 10, 11], including modified maltenes [2], and rheologically complex fluids [19].

Figure 2 shows both moduli in the form of a Han diagram, which shows more clearly the changes that occurred between the elastic and viscous components with the addition of the polymer. Data under the 45° straight crossing line indicate a behavior dominated by the viscous or loss component of the modulus, that is, stress dissipated by flow. Data above the straight line means that the elastic mechanisms dominate the behavior under the conditions of the test. A crossing on the straight line means the crossover between both moduli. Although frequency is not shown, the higher modulus values correspond to higher frequency conditions. As expected, the polymer blends were predominantly viscous where increases in the polymer concentration changed the polymer blends towards a more elastic mixture where no crossover was observed (i.e., no transition occurred). In this situation, the polymer blends behaved congruent with that of thermo-rheologically stable materials where the molecular interactions take place and the concentration of the polymer minimally influences the results of the Han diagram [11, 14].

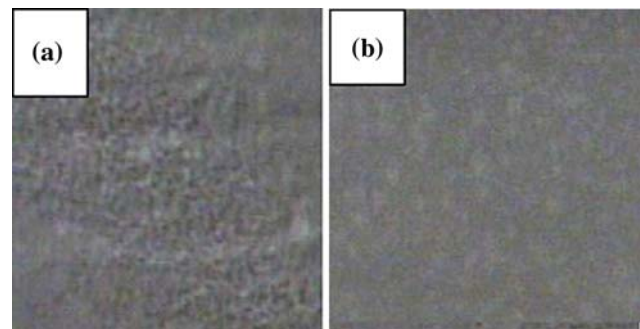
Figure 3 shows the evolution of the modulus  $G'$  and  $G''$  as a function of temperature for the 7% (w/w) PMM. The highest concentration was selected since it was the one that presented the largest elastic behavior at low temperatures; hence, the sample with the highest level of interactions usually occurred either at low frequencies or at high temperatures. As expected, as the temperature increased the moduli decreased where both depended on deformation and where the viscous modulus was larger than the elastic



**Fig. 3** Evolution of the viscoelastic modulus at 7% SBS

modulus [10, 11, 17, 19]. These results suggested the SBS copolymers had been well incorporated within the maltenes and, consequently, the polymer phase was determining the rheological behavior of the blend [9]. The results could be explained by considering the development of a microstructure whose strength depends on the polymer concentration. The polymer absorbed part of the maltene fraction [19] forming a biphasic system since the asphaltene fraction had been removed. Because of the results reported in the literature, a phase inversion was expected [7, 8, 17, 19] and was indeed noticed in the fluorescence images (Fig. 4).

Results of the analysis of the PMAs by fluorescence microscopy indicate that both low- and high-polymer blends exhibited considerable swelling of the polymer caused by the maltenes. We interpret the images as a heterogeneous system where the two phases can be identified, as shown in the literature [7–9, 11]. The left side with 3% (w/w) SBS appears darker than the image with 7% (w/w) with small black spots in the center of the image. When we examined the fact that the asphalt corresponds to the black parts of the image and the polymer corresponds to the white regions, we may conclude that even at 3% (w/w) the system contained the polymer as the continuous phase.



**Fig. 4** Fluorescence images at 3% (a) and 7% (b) SBS



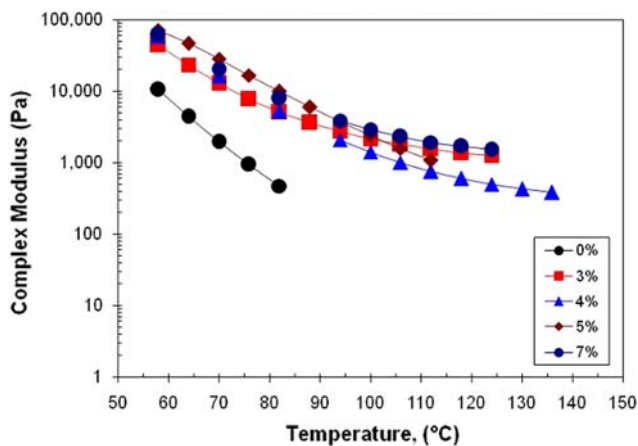


Fig. 5 Evolution of the storage modulus at 12 Hz

This could be corroborated in Fig. 5, where the storage modulus,  $G'$ , is shown. Three concentrations show a plateau, 3, 4, and 7% (w/w). As pointed out by Lu and Isacson [17], SBS-modified asphalts display rubber-like elasticity when a continuous polymer-rich phase controls the system, and this is shown as a plateau region of the storage modulus versus temperature, at high temperature. The plateau region corresponds with the minimum expected value in the phase angle ( $<60^\circ$ ). This behavior was not displayed by modified asphalts with small discrete particles of polymer dispersed therein, like the virgin asphalt, maltenes sample of 5% (w/w), and some asphalt-modified samples that we have used in other experiments but have not been reported here. Those results went to a minimum (Fig. 5) which could not even be seen, for some samples, on the diagram. The temperature at which  $G'$  decays and  $\delta$  increases depends on the nature of the polymer modifier, particularly the melting temperature [7].

Figure 6 shows the implication of the polymer controlling the rheological behavior of the samples [8]. Similar to

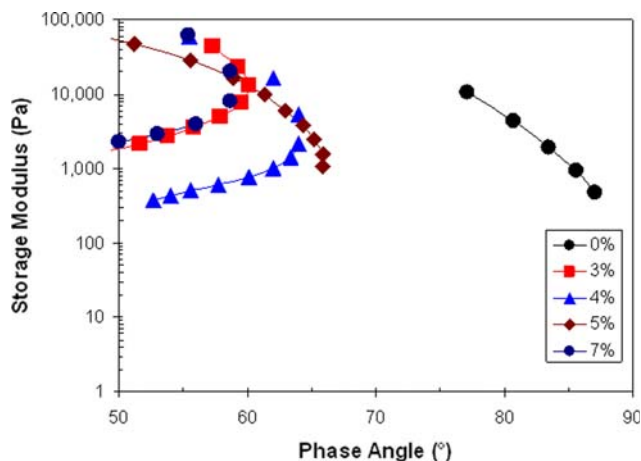


Fig. 6 Storage modulus versus phase angle at 12 Hz

the complex modulus' behavior, the plateau at the end of the storage modulus, specially at high temperatures, was evidence of extreme polymer modification with a dominant polymer network [6], as shown for all the samples except the virgin asphalt and the sample with 5% (w/w) content of polymer. The fact that the phase angle did not decrease for that sample (at low complex modulus,  $G^*$ ) is indicative of the rheological control of the asphalt [6]. We have not been able to explain the behavior of sample 5% (w/w) since it was processed the same as the other samples; in fact it showed the differences between rheological behaviors.

In summary, both low- and high-polymer blends displayed a higher viscoelastic and elastic character than the asphalts, and such differences were more evident when the samples were subjected to low shear frequency. Rheological characterization, on the other hand, provided more information on how both low- (3% w/w) and high-polymer (7% w/w) blends could be explained by recognizing that the rheological response of the blend was mainly determined by the behavior of the polymer phase.

Finally, the performance grade of the samples was determined (Table 2). The results are plotted in Figs. 7 and 8. The AASHTO TP5 test is very illustrative in terms of applicability. Some of the samples did not even reach the expected PG temperature (temperature at which  $G^*/\text{sen } \delta = 1 \text{ kPa}$ ). Furthermore, no proportionality between concentration and temperature was found in terms of the

Table 2 Fail temperature and phase angle at fail temperature

Sample (%)	$T_F$ (°C)	At $T_F$ (°)
0	75.6	85.5
3	>124	<45
4	108	62.2
5	116.5	66
7	136	<40

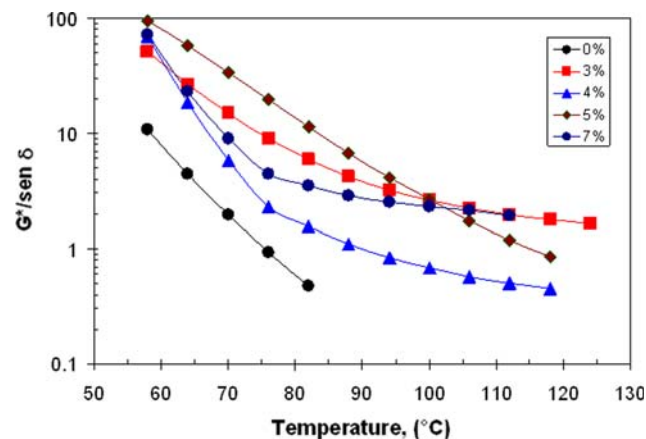
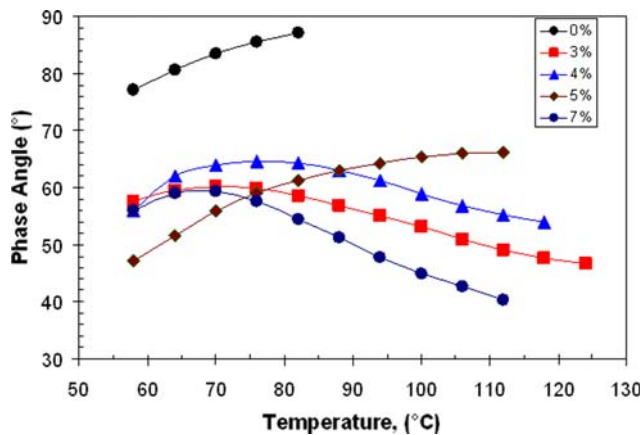


Fig. 7 Performance grade ( $G^*/\text{sen } \delta = 1 \text{ kPa}$ ) according to the TP5



**Fig. 8** Phase angle corresponding to the results of Fig. 7

continuous phase [10]. Figure 8 shows the corresponding phase angles whose behavior is very similar to that observed previously [4] who, from observations, found that the polymer content triggers important changes in the storage modulus. Furthermore, the symmetry in the parabolas (Fig. 6) is a proof of polyblend compatibility [14, 20, 21].

In our investigation, a peak in the phase angle with symmetrical parabolas, showing equivalent relaxation times, can be observed in Fig. 6. The sample at 5% w/w has a larger phase angle at high temperatures and follows the trend of the maltenes sample without the added polymer. This is indicative of an improbable phase inversion that can also be observed as an increasing phase angle when compared with the other samples whose phase angle reaches a maximum value (Fig. 8). This is because the SBS possesses a similar capacity to combine itself with the maltenes and to form a polymer phase, which is mainly responsible for the rheological behavior of the material. All the samples, except that of 5% (w/w), have a characteristic phase angle profile for asphalt viscoelastic materials with low phase angles at high temperatures and were markedly more elastic than maltenes. Evidently there is an interaction between the components whose level is not directly related to the concentration since the 5% w/w sample should behave similarly. According to results reported previously [22], plots of the phase angle versus temperature for very high elastic systems attain a maximum value in the phase angle, i.e., both high elasticity and flow resistance (Elvaloy from Dupont, for example). The Elvaloy is a well-known commercially available modifier that provides the lowest phase angle among the modifiers in the market [22]. Although the company who owns the brand does not allow a full investigation of its product, we well know that it is an excellent modifier, but with the inconvenience of the initial cost. And from our experience, the best modifiers are those that provide the largest elastic behavior at the application temperatures (i.e., low frequency) where the values found

in this investigation correspond with the ones shown in Fig. 8.

## Conclusions

Maltenes obtained from AC-20 asphalt (Salamanca, Mexico) were modified with a SBS linear polymer at different concentrations, and the viscous character predominated in the elastic samples under frequency scans ( $G'' > G'$ ). This result contrasts with the elastic character presented in the SBS polymers. This behavior could be attributed to an additional relaxation mechanism involving morphological changes that can occur at low frequencies or high temperatures. Thus, we conclude that the mechanical properties of the maltenes when they are modified with SBS copolymers cause rheological behaviors as a function of the concentration, temperature, and the interactions between the components (including the asphaltenes that were removed).

The fluorescence microscopy results indicate that all blends are bi-phase heterogeneous systems. The polymer phase (7% w/w) can be a three-dimensional network, with threads of maltenes-swollen elastomeric mid-blocks tied through polystyrene end blocks. For low-polymer concentration blends, the polymer-rich phase was the disperse phase, and for high-polymer concentration blends, it was the continuous phase.

Finally, from the performance grade analysis, we expected a proportionality between temperature and polymer concentration that was not seen. The lack of correspondence could have suggested a phase inversion in some of the mixtures. All the samples had a predominantly viscous behavior (at the temperature interval investigated) under the conditions of the test according to the TP5, although the phase angle values were within the range of the desirable values in practice. From our experience, the occurrence of the maximum delta value at relatively low temperatures indicates that the polymer is dominating the rheological behavior of the sample; thus, the polymer may be playing the continuous phase. The behavior of sample 5% w/w differs from the others, and the discussion above led us to conclude that in that sample the maltenes fraction is playing the continuous phase. We must remind the reader that these tests were performed without the asphaltenes phase, a suspended phase that undoubtedly plays a very important role in the global behavior of the modified asphalt due to the diverse interactions between components and already reported in the literature.

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