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Study of rheological properties of pure and polymer-modified Brazilian asphalt binders

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In recent years, many authors have suggested techniques to study asphalt binders and establish structure-property correlations for these materials. Several works have shown that rheological analysis provides reliable information about the stability, elasticity, thermal susceptibility, and also that rheological behavior depends on chemical composition and structure of pure and modified binders. The objective of this work was to study the effect of the asphalt binder chemical composition and modifier polymer type on the linear viscoelastic properties and to correlate these properties to the PMB's thermal susceptibility. A set of polymer-modified asphalt binders (PMB) was prepared using two Brazilian asphalts. Both pure binders and PMB were analyzed by classical and dynamic rotational rheology tests. The rheological analysis results were also compared to storage stability data and PMB's morphology. The fitting capability of the Christensen-Anderson and Christensen-Anderson-Marasteanu rheological models was analyzed for the two pure asphalt binders. Both models presented lack of fitness in the regions of lowest and highest frequencies. When using elastomeric modifiers, it was possible to state the existence and interrelation between the width of the phase angle master curve plateau and the PMB's thermal susceptibility and stability. This interrelation was supported by PMB's storage stability data and microscopy analysis. © *2004 Kluwer Academic Publishers*

1. Introduction

Polymer modified asphalts have better mechanical properties and higher durability than the non-modified ones. Since 30 years ago in some European countries, polymers have been added into asphalt. In France, around 1993, more than 8% of the asphalt used in roads was modified with polymer [1]. In Brazil, polymer-modified asphalt was also used in some roads in the 90's [2] and nowadays it is increasingly used.

In a good modified asphalt binder, the polymer is blended with the asphalt binder, improving its resistance to rutting, abrasion, fatigue and aging at medium and high temperatures. The polymer in the modified binder should neither make it too viscous at mixing temperature nor too brittle at low temperatures. The asphalt and polymer microphase compatibility is highly desirable. Polymer-modified binders (PMB) must have good stability during storage and transportation in order to guarantee better mechanical properties than pure asphalt.

When an asphalt binder and a polymer are mixed, three types of mixture may result, according to the compatibility between polymer and asphalt binder [1, 3]. In the first one, a heterogeneous mixture, polymer and asphalt are incompatible and they are separated into two phases; the mixture is not a PMB. In the second one, a homogeneous mixture, polymer and asphalt are compatible. The asphalt oil fraction totally solvates the polymer and the PMB is very stable, but the enhancement of the binder properties with respect to the pure asphalt is poor and a non-desired increase is observed in its viscosity. The third mixture type, a microheterogeneous one, is made up of two distinct finely interlocked phases. The polymer phase is swollen by absorbing the asphalt aromatic oil fraction. The asphalt heavy oil fraction, i.e., resins and asphaltenes, constitutes the residual asphalt phase. This morphology implies better mechanical properties and characterizes a genuine PMB.

The mixture compatibility depends on the polymer type and content added to the asphalt and also on the asphalt binder chemical composition. Therefore, PMB's with the same polymer content, prepared with identical grade asphalt, but obtained from different sources, can present different microstructure and properties [4, 5].

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The asphalt binder chemical fractions are easily separated by liquid chromatography in saturates, aromatics, resins and asphaltenes [6]. These fractions are called SARA fractions and may be used to calculate the colloidal instability index, I_C of an asphalt binder. This index gives an idea about the PMB stability [7].

Analytical methods to better characterize a PMB are not well established yet and many of them have been employed by several authors [1–15]. The interaction between asphalt and polymer phases is also complex and the intrinsic characterization of the modified asphalt is difficult. Some studies on asphalt properties are based on its solubility in a solvent [6, 8]. However, dissolution affects intermolecular interactions and causes phase separation, so the results cannot be used to describe the asphalt binder properties under work conditions.

The classical tests applied for pure asphalt specification, like penetration, ring and ball point and viscosity, are not sufficient to well characterize a PMB. Many authors [1, 9–12] have suggested the use of thermal and rheological tests to predict the performance, stability and elasticity of PMB's. These tests are less destructive methods, where the sample dissolution is not necessary, giving more reliable information about the asphalt binders.

The thermal analysis allows one to determine the asphalt binder glass transition temperature (T_g). This temperature is a very important parameter because it defines the lowest temperature in which the asphalt can be properly used. Below the T_g the asphalt binder has high modulus, but it is as fragile as glass, becoming a breakable material [16].

In the rheological tests performed in the dynamic mode, data are taken in the range of deformation corresponding to linear viscoelastic behavior and are generally expressed by master curves using the time-temperature superposition principle (TTSP). Thus, the shearing frequencies used in the sample characterization can be correlated to traffic conditions. Frequencies between 10^{-2} and 10^2 Hz are used to simulate the normal vehicle traffic on the pavement [3]. Higher and lower frequencies respectively simulate heavier and lighter traffic. Therefore, an analysis within a 10^{-4}–10^7 Hz frequency range is generally necessary to cover the entire domain of traffic conditions. Although many distress mechanisms for asphalt binders involve failure components which in essence are non-linear events (fatigue, tertiary creep, low-temperature cracking, raveling, moisture damage), linear viscoelastic properties provide relevant information about the structure an asphalt binder and its mechanical response. 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 modifiers on asphalt binder properties, however they do not allow to obtain quantitative information about the performance of the modified binder under final use conditions.

Two important parameters obtained from rheological tests in dynamic mode are the complex modulus (G^*) and the phase angle (δ). The former can be related to the material strength and the latter provides information about the ratio between elastic and viscous response during the shearing process. Although some authors suggest that TTSP does not accurately apply to asphalt binders with high asphaltene content, mainly at high temperatures (or low frequencies) [11, 12], master curves provide a powerful tool for understanding rheological properties of viscoelastic materials. For this reason, many researchers have been studying the modeling of master curves for asphalt binders and many models related to this issue have been proposed [11, 13–15, 17, 18]. Among these models, that proposed by Christensen and Anderson is one of the most widely used in the literature [11, 13], as well as its modified version presented by Marasteanu *et al.* [18].

In this work, a set of PMB was prepared using two Brazilian asphalts from different sources but with the same viscosity grade. The pure asphalt binders and their PMB's were analyzed by dynamic rotational rheology. The aim of this work was to study the effect of the asphalt binder chemical composition and modifier polymer type on the linear viscoelastic properties and to correlate these properties to the PMB's thermal susceptibility. The rheological analysis results were also compared to storage stability data and PMB's morphology. The fitting capability of the Christensen-Anderson and Christensen-Anderson-Marasteanu rheological models was analyzed for the two pure asphalt binders. The model parameters for both pure asphalt binders were estimated by non-linear regression.

2. Experimental procedure

2.1. Materials

In this work, two asphalt binders with 20 viscosity-grade (AC-20) from different Brazilian refineries were used. Four commercial polymers were used as asphalt modifiers, a triblock copolymer styrene-ethylene/butene-styrene (SEBS), a maleic anhydride functionalyzed polyethylene (PE), a linear and a star-shaped triblock copolymer styrene-butadiene-styrene (SBS).

2.2. Modification of the asphalt binder

The asphalt binder modification was carried out at 190 ± 10°C in a 5-liter steel reactor coupled to a shear mill. The reactor was equipped with pneumatic agitation and connected to a thermal oil heater to control the mixture process temperature. The asphalt binder was preheated in a furnace until 190 ± 10°C, then loaded to the reactor and agitated during 30 min. After that, the polymer modifier was gradually added until a weight percent content of 4.5%. The mixture was processed in a shear mill during 2 h at the same temperature. Finally, the mixture was cooled and stored at room temperature.

2.3. Classical asphalt testing

The asphalt binders were analyzed by classical methods. The classical properties evaluated were penetration at 25°C, Ring and Ball softening point ($T_{\mathrm{R\&B}}$) and viscosity. Penetration is expressed in units of 1/10 mm, into which a needle under a 100 g load penetrates the asphalt after 5 s loading time. The measurement at 25°C defines the penetration grade of the tested asphalt, as the ASTM D5-86. The $T_{\mathrm{R\&B}}$ is defined as the temperature in which a steel ball embeds an asphalt film, as the ASTM D36-76. Viscosity was determined in a Brookfield viscometer as the ASTM D4402-91.

2.4. Chemical characterization

The pure asphalt binders were characterized by their SARA chemical composition (saturates, aromatics, resins and asphaltenes). A thin layer liquid chromatograph on silica with a flame detector was employed to determine each fraction's percentage. The eluents were *n*-heptane, toluene and a toluene/methanol 50/50 mixture.

2.5. Differential scanning calorimetry (DSC)

The pure asphalt binders were analyzed by DSC on a Waters TA 2010 equipment to determine its glass transition temperature (T_g). The procedure used was the same as that used by Claudy *et al.* [16], in which the samples were rapidly cooled down to −100°C and then evaluated upon heating at 5°C/min.

2.6. Storage stability test

This is a typical test used in Brazilian asphalt industries to determine the PMB's storage stability. The test consists of keeping the PMB specimen in a test tube at 160°C for 4 days and then taking away samples from the top and from the bottom of that test tube. The $T_{\mathrm{R\&B}}$ difference between these two fractions, expressed in °C, is used as a measurement of the storage stability of the material [2]. If this difference is lower than 4, the material is classified as a stable PMB.

2.7. Fluorescence microscopic analysis

PMB's morphology was observed under a Standard 25 ZEISS photomicroscope with reflection light. PMB's drops were taken from the mixture and placed between two glass slides. They were cooled at room temperature and analyzed using a fluorescent filter of 470 nm (blue), called exciter filter. The pure asphalt reflects black and the polymer reflects green when pure and yellow when swollen. The micrographs were taken at 200 times magnification.

2.8. Rheological measurements

All samples of pure and modified asphalt binders were analyzed on a controlled strain rheometer ARES, from Rheometrics Scientific. To cover all the desired range of frequency, between 10^{-4} and 10^{7} Hz, it was necessary to carry out frequency sweeps at different temperatures. Frequency sweeps from 0.01 to 10 Hz were performed using a tool for solid torsion for temperatures ranging from −10 to 15°C and 25 mm diameter parallel plates for temperatures ranging from 30 to 70°C. Strain sweeps at 0.1 and 500 rad/s were also performed for each sample, in order to determine the strain level to be used in the frequency sweeps, so that non-linearity never exceeds 5%. Master curves were obtained at 40°C, using the time-temperature superposition principle (TTSP).

2.9. Rheological models

In the Christensen-Anderson model (CA model) (17), the complex shear modulus (G^*) and the phase angle (δ) are described by Equations 1 and 2, respectively:

$$\log Gr = -\frac{R}{\log 2}\log\left[1+\left(\frac{\omega}{\omega_0}\right)^{-\frac{\log 2}{R}}\right] \qquad (1)$$

$$\delta(\omega) = \frac{\pi}{2}\left[1+\left(\frac{\omega}{\omega_0}\right)^{\frac{\log 2}{R}}\right]^{-1} \qquad (2)$$

where Gr = reduced modulus; $Gr = G^*(\omega)/G_g$, $G^*(\omega)$ = complex modulus, G_g = glassy modulus, $\delta(\omega)$ = phase angle, ω = reduced frequency, $\omega_0 = 1/\tau_m$, τ_m = mean relaxation time, and R = rheological index (associated with the width of the relaxation spectrum).

In the Christensen-Anderson-Marasteanu model (CAM model) (18), these properties are described by Equations 3 and 4, respectively:

$$\log Gr = -\frac{w}{v}\log\left[1+\left(\frac{\omega}{\omega_0}\right)^{-v}\right] \qquad (3)$$

$$\delta(\omega) = \frac{\pi}{2}w\left[1+\left(\frac{\omega}{\omega_0}\right)^{v}\right]^{-1} \qquad (4)$$

Comparing these two models, it can be noted that the $\log(2)/R$ ratio of the CA model is equivalent to the v parameter of the CAM model. The most important difference between these models is that the CAM model presents the additional parameter w, which is associated to the convergence velocity of the phase angle data to asymptotic values from zero to 90 degrees [18].

3. Results and discussion

The three styrene thermoplastic elastomers (linear SBS, star-shaped SBS and SEBS) used in this work as asphalt modifiers were taken from those commercial ones used by PMB's producers. A maleic anhydride funcionalyzed PE was used as a new polymer option for asphalt modification, in order to compare it with those already used in commercial scale. The thermoplastic elastomers have styrene content around 30%. The average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, and the polidispersity ($\bar{M}_w/\bar{M}_n$) of all polymer samples are shown in Table I.

TABLE I Asphalt modifiers polymers molecular weights

	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
Linear SBS	129000	149000	1.15
Star-shaped SBS	331000	413000	1.25
Linear SEBS	90500	94000	1.04
PE	1880	6300	3.35

$\bar{M}_n$ = number-average molecular weight.
$\bar{M}_w$ = weight-average molecular weight.

The two asphalt binders employed in this work, named here as AC-1 and AC-2 binders, are from different Brazilian refineries that process crude oil from distinct sources. These binders are used in the PMB's industrial production and nowadays in some Brazilian roads.

Both pure and modified asphalts were evaluated by classical and rheological tests and the results were correlated.

3.1. Classical, chemical and thermal tests for pure asphalts

SARA chemical composition, colloidal instability index (I_C), penetration, Ring & Ball softening point, viscosity and glass transition temperature (T_g) values of asphalt binders AC-1 and AC-2 are shown in Table II.

Asphalt's properties are strongly related to its chemical composition. As can be seen in Table II, the AC-2 binder has lower penetration and higher R & B point, viscosity and T_g than the AC-1 binder. These properties are a consequence of the asphalt's chemical composition, since AC-2 binder has higher solid fractions content, resins and asphaltenes, and lower aromatic oil content than AC-1 binder.

3.2. Rheological tests for pure asphalts

Pure asphalts' complex shear modulus (G^*) and phase angle (δ) were plotted against reduced frequency (ω), in a master curve at the reference temperature of 40°C, in the frequency range of 10^{-5} to 10^9 Hz. Fig. 1 shows AC-1 and AC-2 asphalt binders' G^* and δ master curves. In the low frequency zone, 10^{-4} up to 10^1 Hz, AC-2 binder presents slightly higher modulus values and slightly lower slope than AC-1 binder. The higher modulus values of AC-2 binder indicate that it has higher molecular mass components and this is in agreement with the chemical composition data of Table II. The difference between the G^* curve slopes of the two binders in the low frequency zone suggests that AC-2 binder has possibly a wider molecular weight distribution. The δ curve also provides valuable information. The inflexion point position in both curves is related to the asphalt binder's T_g. The inflection point of AC-1 binder δ master curve is located at higher frequency than that for AC-2 binder, indicating that AC-1 binder has lower T_g value. This is in agreement with T_g data determined by thermal analysis (Table II). AC-1 binder also showed a more abrupt decrease in the δ curve. This can be taken as another indicative that AC-1 binder presents a narrower molecular weight distribution than AC-2 binder.

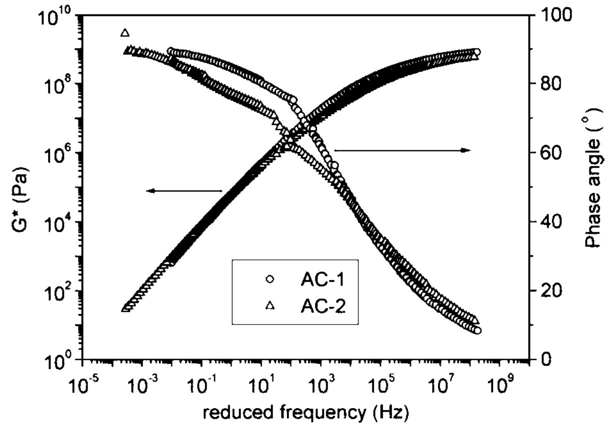


Figure 1 Viscoelastic behavior of pure asphalt binders.

From Fig. 1, it can be also noted that AC-2 binder δ master curve shows large extent dispersion data at low frequencies, suggesting that the time-temperature superposition principle (TTSP) applies better to AC-1 than to AC-2 binder. This is in accordance with the results of other studies [10]. Lesueur *et al.* [11] state that binders with high asphaltene content are less likely to follow the TTSP at low frequencies or high temperatures. This behavior can be attributed to an additional relaxation mechanism involving morphological changes that can occur at low frequencies or high temperatures. It must be noted that the points' dispersion in the master curve at low frequencies zone is wider to phase angle than to modulus. This behavior has also been pointed out by Lesueur *et al.* when studying asphalt binder rheological behavior of a non-paraffin crude oil, with asphaltene content of 12%.

Fig. 1 data were used to estimate the parameters G_g, τ_m and R of the Christensen and Anderson model for the AC-1 and AC-2 pure asphalt binders. The values of the estimated parameters, which were used to obtain the predict curve, are presented in Table III. The comparison between experimental data and CA and CAM predict curves are shown in Fig. 2.

TABLE II Characteristics of the pure asphalt binders

	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)	I_C	Penetration (1/10 mm)	R&B (°C)	Viscosity (cP) 60°C	Viscosity (cP) 135°C	T_g (°C)
AC-1	3	69	16	12	0.18	52	48.7	279300	362.5	−19.9
AC-2	11	47	24	18	0.41	47	51.2	450800	472.0	−16.7

R&B = Ring & Ball softening point.
I_C = Colloidal Instability Index.

TABLE III CA and CAM estimated parameters for AC-1 and AC-2 binders

Model	Parameter	AC-1	AC-2
CA	G_g (GPa)	0.103	0.125
	τ_m ($\times 10^5$ s)	6.88	10.0
	R	2.53	3.47
CAM	G_g (GPa)	0.110	0.110
	w	1.034	0.994
	ω_0 (rad/s)	1.002×10^4	9.970×10^3
	v	2.568×10^{-1}	2.066×10^{-1}

It can be noted in Fig. 2, by comparing the experimental and predict curves, that fit is better to G^* vs. ω than to δ vs. ω curves, for both AC-1 and AC-2 binders. Such behavior can be attributed to a difference in the functional form of dependence between these properties and the viscous and elastic components of the shearing process. The complex modulus is a function of the sum of the squares of these components, while the phase angle is a function of the ratio between them, being more affected by small differences in their values [19].

Fig. 2 also shows that both CA and CAM model were not able to generate accurate predictions in the whole range of frequencies studied. To better evaluate this fact, a set of calculations was carried out with the CA model to analyze the sensitivity of the model prediction to the parameter values. In each calculation, two parameters were kept at the estimated values and the third one was modified by the multiplication of the estimated value by a factor of (1.0 ± 0.2), i.e., an error of 20% was introduced into the third parameter. The curves resulting from these calculations are shown in Fig. 3. It can be noted that the effect of the variation in the mean relaxation time (τ_m) and in the glassy modulus (G_g) on the prediction of the model is quite small compared to the effect of the variation in the rheological index (R). This behavior gives support to some authors who stated that the glassy shear modulus G_g could be taken as approximately 1 GPa for any asphalt binder [15, 20, 21]. The parameter τ_m in the model determines where changes in the properties as a function of the frequency are more intense, but has little influence on the curve's shape. On the other hand, the rheological index R is associated to the width of the relaxation spectrum and, consequently, directly affects the curve shape. Some authors [11, 17] related R to the binder asphaltene content, finding that it grows as the asphaltene content increases. This is in accordance with results shown in Table III, where AC-2 presents the highest value of R, due to its highest asphaltene content (Table II). However, the lack of fitness of the model in the region of lowest and highest frequencies suggests that it is not possible to describe the viscoelastic behavior of asphalt binder by using just one parameter related to the shape of the relaxation spectrum. This difficulty could be related to the complex structure of the binder and to the existence of relaxation mechanisms associated to morphological changes in the bulk material.

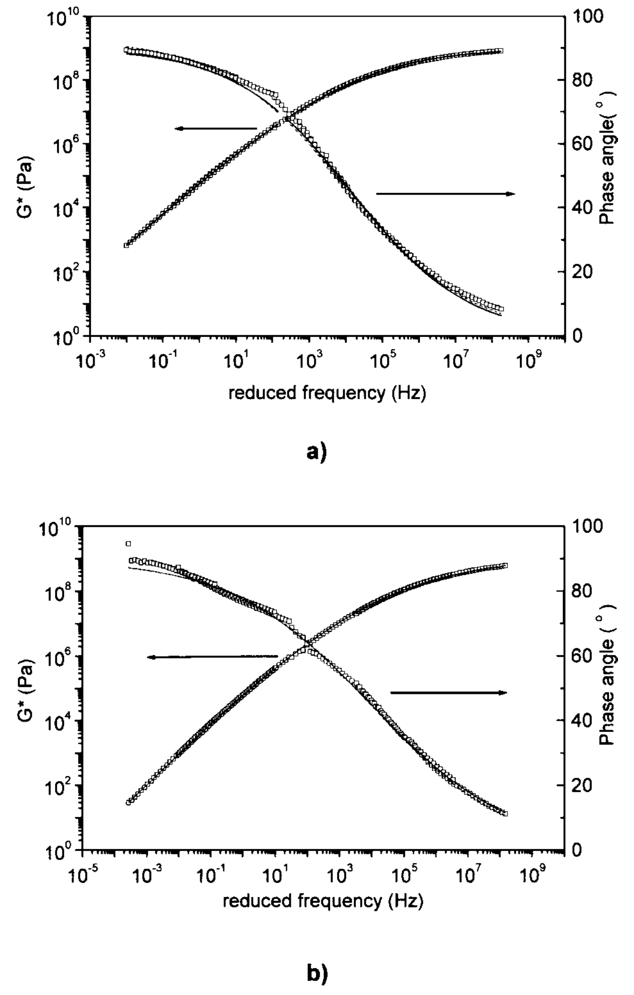


Figure 2 Viscoelastic behavior of pure asphalt binders using the CA (———) and CAM (- - - - -) models. AC-1 (a) and AC-2 (b) binders predict and experimental (□ □ □ □) G^* and δ curves.

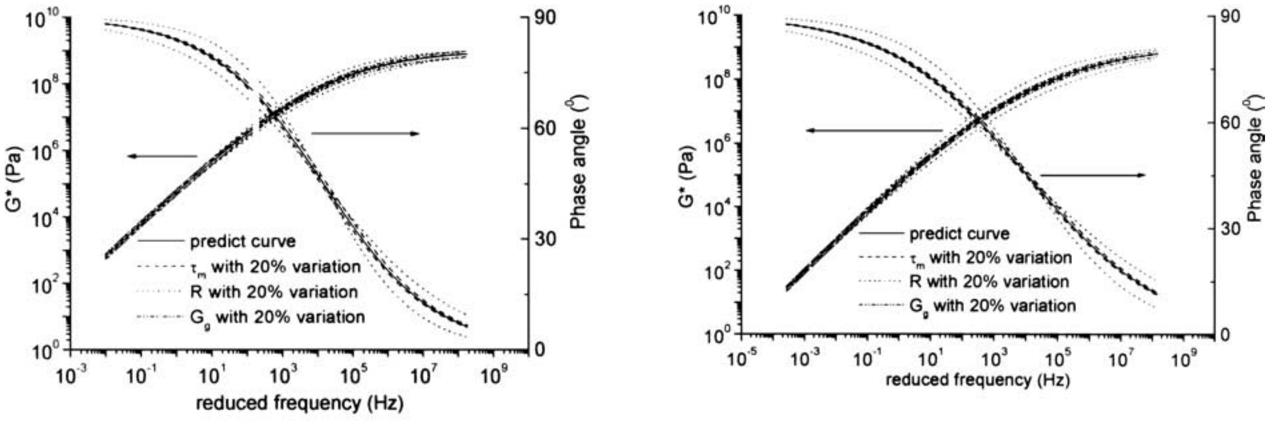
3.3. Classical tests for modified binders

The Penetration, Ring & Ball softening point and viscosity values of the PMB's modified with 4.5% of polymer are presented in the Table IV. It can be seen that all the PMB's showed lower penetration, higher R&B softening point and higher viscosity than the pure asphalts (Table II). The thermoplastic elastomer modifiers (linear SBS, star-shaped SBS and SEBS) increased the viscosity of the asphalt binder more than the thermoplastic modifier PE.

TABLE IV Classical properties of the polymer-modified asphalt binders

	Penetration (1/10 mm)	R&B (°C)	Viscosity (cP) 60°C	Viscosity (cP) 135°C
AC-1 + linear SBS	34	57.0	2250000	1042
AC-1 + star-shaped SBS	31	61.5	nd	1310
AC-1 + linear SEBS	22	71.9	nd	1915
AC-1 + PE	30	59.1	1062000	446
AC-2 + linear SBS	28	65.2	nd	2385
AC-2 + star-shaped SBS	25	71.6	nd	4166
AC-2 + PE	20	74.6	nd	973.3

R&B = Ring & Ball softening point.
nd = not determined.



a)

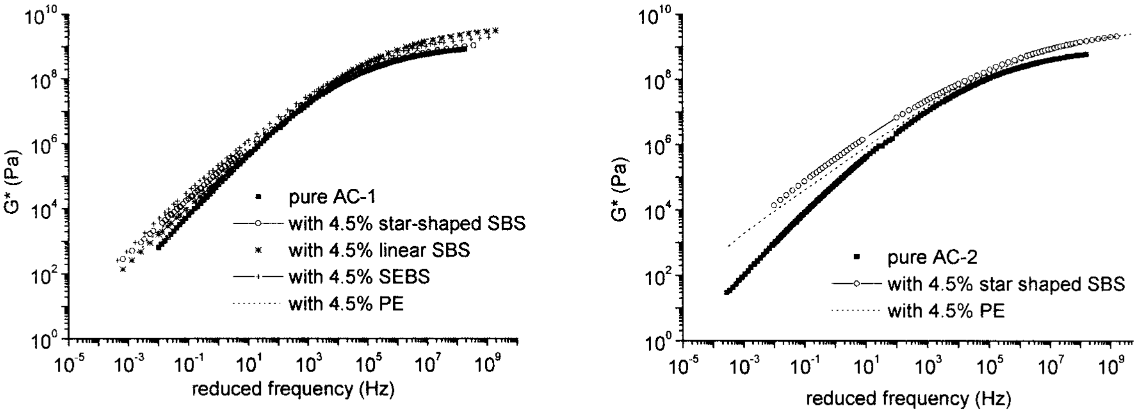
b)

Figure 3 Effect of changes in parameters of the CA model in the AC-1 (a) and AC-2 (b) binders master curves.

3.4. Rheological tests for modified binders

The effect of the polymer addition on the G^* and δ master curves of the asphalt binders can be observed in Figs 4 and 5. Fig 4a and b show the G^* vs. ω master curves of pure and modified AC-1 and AC-2 binders, respectively. The PMB's presented higher complex modulus than pure binders in the whole range of frequencies studied. This increase in binder's modulus due to modifier addition occurs because all the polymeric modifiers used have higher modulus than the pure binders.

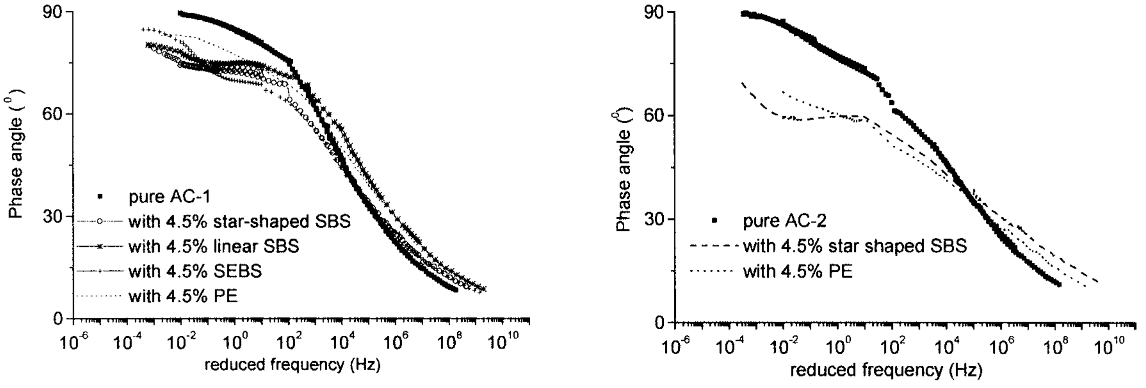
Fig. 5a and b show δ vs. ω master curves for pure and modified AC-1 and AC-2 binders, respectively. It can be observed that there was a drastic change in the phase angle curves shape with the polymer addition in the



a)

b)

Figure 4 Complex modulus G^* master curves for pure and modified AC-1 (a) and AC-2 (b) binders.



a)

b)

Figure 5 Phase angle master curves for pure and modified AC-1 (a) and AC-2 (b) binders.

pure binder. The thermoplastics elastomers (SBS and SEBS) have caused the appearance of a plateau in the phase angle curves. This plateau means that in this region the elastic (G') and viscous (G'') complex modulus components vary in the same proportion, in such a way that the phase angle does not change ($\tan\delta = G''/G'$). Then, this plateau indicates that the polymer addition decreases the asphalt thermal susceptibility. This does not mean that the PMB complex modulus does not decrease when temperature is increased, but that the elastic component is constant in a broader range of temperature than that of the pure binder. Besides, plateaus rheological curves are a characteristic of the viscoelastic response of rubbers. Thus this plateau indicates that in this range of frequency the modified binder presents a rubber-like behavior, which indicates a more effective contribution of the elastomeric modifier to the binder mechanical response. So, the appearance of this plateau in phase angle curves can be taken as an indicative of a better interaction between the polymeric modifiers and the asphalt binders, leading to an effective modification of the asphalt relaxation mechanisms. Similarly, the width of this plateau could be related to the compatibility between polymer and asphalt phases. This statement is in agreement with the phase angle curves shape for the three elastomeric modifiers (Fig. 5a). AC-1 binder modified with linear and star-shaped SBS, which have the same chemical composition, presented similar width plateaus, while for AC-1 binder modified with SEBS, which has its middle block hydrogenated, this plateau was narrower. It must be noted that the SEBS hydrogenated middle block has less affinity to the asphalt fractions than to the SBS butadiene middle block.

It must also be mentioned that the non-appearance of a plateau, in the phase angle curve for AC-1 binder modified with functionalyzed PE, does not indicate a lack of compatibility between this polymer and the asphalt binder, but this can be related to the fact that this polymer is not an elastomeric one.

The viscoelastic behavior of the samples of modified AC-2 binder with functionalyzed PE and star-shaped SBS (Fig. 5b) was similar to those of modified AC-1 binder with the same polymers. However, it can be seen that the size of the plateau for the AC-2 binder modified with star-shaped SBS was smaller than for AC-1 binder modified with the same polymer. This plateau difference shows the effect of the asphalt binder composition on the viscoelastic behavior of the modified binder. The AC-2 binder has lower aromatic oil content than the AC-1 binder, what may hinder solvation, stabilization and dispersion of the polymer into the asphalt. The AC-2 binder aromatical fraction (oils) might not be sufficient for both solid fractions (asphaltenes) and added polymer solvation. So, for the star-shaped SBS ($M_\mathrm{n} = 330.917$ g/mol) this effect must be more intense, considering its higher molecular weight.

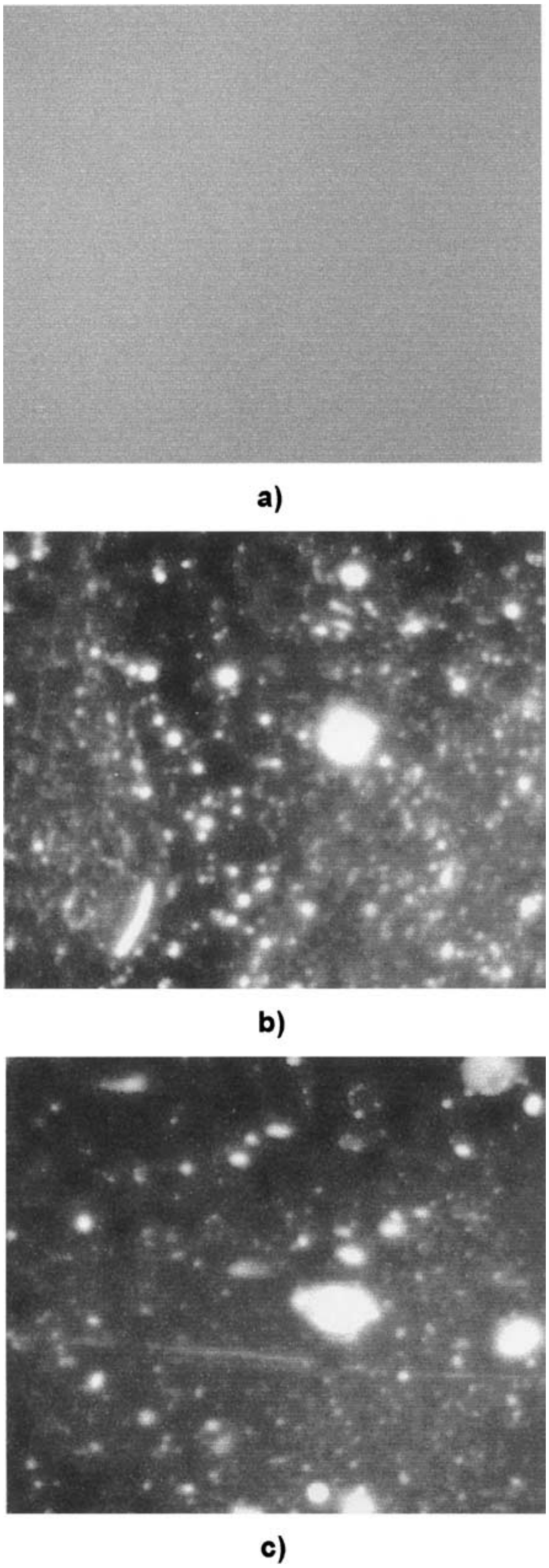


Figure 6 Photomicrographs of star-shaped SBS (a) and SEBS (b) modified AC-1 binders and star-shaped SBS (c) modified AC-2 binder (200×).

It must be remarked that the relation between the shape of phase angle curves and the stability of the PMB's, which was discussed above, is in agreement with the storage stability test and fluorescence microscopy results, presented in Table V and Fig. 6, respectively. For example, by comparing star shaped SBS and SEBS modified AC-1 binders, it can be noted that the former presents broader plateau in the phase angle curve (Fig. 5a) and also higher storage stability (Table V). The fluorescence photomicrographs of the

TABLE V PMB's storage stability data for 4 days at 160°C

Sample	Stability (°)
AC-1 with star-shaped SBS	0.9
AC-1 with SEBS	5.6
AC-2 with star-shaped SBS	7.0

star-shaped SBS modified AC-1 binder appears as a truly microheterogeneous material (Fig. 6a) while the SEBS modified AC-1 binder shows a poor phase dispersion (Fig. 6b), with coarse elastomer particles. Similar conclusions can be obtained when comparing star-shaped SBS modified AC-1 and AC-2 binders.

The fitting capability of the CA and CAM models to the modified asphalt binders was not evaluated since it is known that these models are not able to fit satisfactorily the plateau in phase angle curves [17, 18].

4. Conclusions

It was possible to determine the influence of different modifiers on the properties of two pure Brazilian asphalt binders (AC-1 and AC-2) and to correlate their performance with their structure and rheological properties. It was found that phase angle master curve shape may be related to the thermal susceptibility and stability of the PMB's. The occurrence of a plateau in the angle phase curves indicates a higher interaction level between the polymeric modifier and asphalt binder. The width of this plateau can be taken as a qualitative measurement of the PMB's stability. Support for these statements can be found in the fact that they are in accordance with the results of the storage stability tests and fluorescent microscopy analysis.

The Christensen-Anderson and Christensen-Anderson-Marasteanu models describe the viscoelastic behavior of pure asphalt with precision in the intermediate frequency range, but both present lack of fitness in the higher and lower frequency ranges. Sensibility analysis has shown that the use of only one parameter related to the shape of the relaxation spectrum (rheological index R in the CA model or v in the CAM model) is not enough to describe the asphalt binder viscoelastic behavior. This difficulty in modeling the rheological behavior of asphalt is mainly due to its complex structure and to the phenomenological changes that can occur during heating and deformation.

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