

## Asphalt Binders Modified by SBS and SBS/Nanoclays: Effect on Rheological Properties

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Neste trabalho, investigou-se o efeito da vermiculita e montmorilonita organicamente modificadas (OVMT e OMMT, respectivamente) em ligante asfáltico (AB) modificado por SBS (butadieno-estireno-butadieno). As propriedades físicas e reológicas foram avaliadas para AB, 4,0% SBS MB e nanocompósitos AB modificados por 2,5% SBS com 2,5% de organoargilas. Os ligantes modificados (MB) resultaram no aumento do módulo complexo ( $G^*$ ) e na redução do ângulo de fase ( $\delta$ ), o que significa maior resistência destes à deformação permanente. A viscosidade, penetração e suscetibilidade térmica foram adequadas. Nos diagramas *black*, observou-se que o efeito da presença das nanoargilas OVMT e OMMT foi semelhante ao efeito da Cloisite®. As propriedades reológicas dos nanocompósitos foram comparáveis às do 4,0% SBS MB, identificando uma redução de custos, dado o potencial de substituição de polímero pela argila. A presença da OVMT melhorou a estabilidade à estocagem do SBS MB, um resultado importante, visto que a separação de fases é um dos maiores obstáculos ao uso do SBS na pavimentação.

In this work, it was investigated the effect of organically modified vermiculite and montmorillonite (OVMT and OMMT, respectively) in asphalt binders (AB) modified by SBS (styrene-butadiene-styrene). The physical and rheological properties were performed for AB, 4.0% SBS MB and nanocomposite AB modified by 2.5% SBS with 2.5% of organoclays. The modified binders (MB) result in the enhancement of complex modulus ( $G^*$ ) and reduction of phase angle ( $\delta$ ), which means greater resistance to permanent deformation. The viscosity, penetration and thermal susceptibility were appropriate. The black diagrams show that the effect of nanoclays OVMT and OMMT was similar to the effect of Cloisite®. The rheological properties of the nanocomposite were comparable to the 4.0% SBS MB, identifying a cost reduction due to the potential of replacing polymer with clay. The presence of OVMT improved the storage stability of SBS MB, an important result, as the phase separation is a major obstacle to the use of SBS in paving.

**Keywords:** asphalt binder, SBS, montmorillonite, vermiculite, rheology

## Introduction

Petroleum asphalt has been widely used as binder in road pavements to provide adhesive and protective coating to aggregates. The rheological behavior of a binder is complex, varying from viscous to elastic depending on loading rate and temperature. It has to be fluid enough at high temperature when pumped and mixed with aggregates and has to be stiff enough at service temperature so that, it can resist rutting. In addition, it can not be too stiff in order to avoid thermal cracking. Thus, rheological properties of asphalt binders are of major concern since they are directly related to the field performance.

For many years, conventional pure asphalt performed satisfactorily. Due to the increase of traffic loads and also to environmental factors, pure asphalt does not always perform as it is expected. Polymer modified asphalts were developed to overcome distress problems.<sup>1-3</sup> The use of polymers as additives has shown to greatly improve the performance of conventional asphalt binders,<sup>4</sup> *i.e.*, greater resistance to rutting and fatigue as well as decrease of the thermal susceptibility. In addition, it promotes increased resistance to cracking at low temperature.<sup>5</sup> The most important and restrictive requirement is the compatibility between the polymer and the asphalt, which needs to be guaranteed to minimize the risk of phase separation for storage stability.

Styrene-butadiene-styrene (SBS) copolymers have proven to improve the bitumen properties.<sup>6,7</sup> The

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thermoplastic nature of SBS has the ability to combine elastic, strength and adhesion properties that help to increase pavement durability. The rigid domains (polystyrene blocks) interconnected through the flexible chains (butadiene blocks) form a physical elastomeric network. Unfortunately, SBS tends to separate from the asphalt when stored at high temperatures. The polymeric phase segregates in the storage tank and pumping is no longer possible to move the material.<sup>8,9</sup> This is a major obstacle to the application of SBS in the paving industry. In spite of the small proportions of the polymer added to the binder, its high cost also somewhat restricts its broad use in road construction.

Nanoscale mineral clays have been used for polymer modification, either as an agent to improve the physical and mechanical properties of the polymer or as a filler to reduce the amount of polymer used.<sup>10</sup> Thermal stability, high gas barrier and flame retardation properties were also observed.<sup>11-15</sup> Clays, which are cheap and abundant in nature, mostly consist of aluminosilicates. They also includes montmorillonite (MMT), vermiculite (VMT), rectorite (REC) and kaolinite clays (KC). The separation of the clay layers results in a nanoclay with a very special active specific surface area ( $700-800 \text{ m}^2 \text{ g}^{-1}$ ).<sup>11</sup>

In the clay mineral, the silicate layers are joined through weak dipolar forces, and the cations (for example,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ) are located in the interlayer. An important and necessary prerequisite for better interaction of the clay with the thermoplastic matrix is the modification of the clay polarity. This occurs through an ion exchange reaction by exchanging cations (present on the surface and in the basal spacing of the clay) with charged organic molecules, such as alkylammonium salts, resulting in a larger intercalary spacing.<sup>16-18</sup> This increased spacing between the layers allows the intercalation of polymers or other materials, which results in nanocomposites.<sup>10,19,20</sup>

The effect of the clay as a third component in polymer modified asphalt has been investigated. This is achieved by adding the clay either separately or premixed with the polymer.<sup>21,22</sup> In both cases, the results were intercalated nanocomposites. A physical mix of the asphalt binder and nanoclay leads to changes in rheological properties due to intercalation of the asphalt molecules in the nanoclay layers. From the rheological point of view, the premixed blend (SBS/clay as a nanocomposite) is not equivalent to the physical blend (adding polymer and clay separately to the asphalt). In all cases,<sup>23</sup> the term triple nanocomposite is used to characterize a blend of asphalt/polymer/nanoclay.

Some authors published that asphalts modified by different amounts of MMT and organomodified montmorillonite

(OMMT) improve the rheological properties of asphalt binders, such as increased elastic responses and stiffness, increasing the resistance to permanent deformation at high temperatures.<sup>24,25</sup> The effect of modifying the asphalt with SBS/MMT was also positive in terms of rheological and empirical properties.<sup>26</sup> The use of kaolinite clay (KC) in styrene-ethylene-butadiene-styrene block copolymer (SEBS) has also been proposed for application in asphalt binders. It was observed a positive effect on the storage stability, which was attributed to the presence of the clay.<sup>27</sup> It was also shown that the layered silicates can prevent oxygen diffusion to polymer modified asphalt, improving the aging resistance. However, the effect of OVMT as an additive for asphalt binder is still not known.

Vermiculite clay (VMT) belongs to the structural group of 2:1 aluminosilicate (the same as MMT). Paraíba State concentrates most of MMT in Brazil, whilst VMT occurs in reserves in the states of Piauí, Goiás, Paraíba and Bahia. As previously mentioned, MMT showed to improve the performance of asphalt binders. The effects of VMT, however, have not yet been assessed as an additive of polymer modified binders. In addition to its low cost, VMT has favorable properties towards intercalation.

In this work, organoclays OMMT and OVMT were prepared and characterized to be used as an additive in a SBS modified binder. The effect of the organoclays on conventional and rheological parameters correlated to permanent deformation (rutting), viscoelastic properties, thermal susceptibility and storage stability is investigated. A third nanoclay Cloisite® 20A was employed as a reference to test the effectiveness of OMMT and OVMT, and also to compare the changes in rheological properties. To the best of our knowledge, no work has reported results that were applied for OVMT as an additive in asphalt binder. It is a new application that can contribute to extend the knowledge in this field of research.

## Experimental

### Materials

Asphalt binder (AB) classified as a 50/70 penetration grade was provided by Lubnor/Petrobras (Lubrificantes e Derivados de Petróleo do Nordeste, Brazil), originated from the crude of Campo Fazenda Alegre located in the state of Espírito Santo, Brazil. The linear SBS copolymer with 30% of styrene was supplied by Petroflex. Vermiculite clay was supplied by the União Brasileira de Mineração (Brazil), while montmorillonite was provided by Mineração Vale do Juquiá Ltda. (Brazil). The comercial nanoclay Cloisite® 20A was supplied by Southern Clay Products,

Inc. (USA). Cloisite® 20A is a natural montmorillonite that is treated with an organic salt modifier (dimethyl, dehydrogenated tallow, quaternary ammonium-2M2HT, with X-ray result  $d_{001} = 24.2 \text{ \AA}$ ). Five types of binders were used in the investigation: (i) conventional asphalt binder (AB), (ii) modified by 4.0% of SBS, (iii) modified by 2.5% of SBS and 2.5% of OVMT, (iv) modified by 2.5% of SBS and 2.5% of OMMT and (v) modified by 2.5% of SBS and 2.5% of Cloisite® 20A. They were denoted by AB, SBS MB, SBS/OVMT MB, SBS/OMMT MB and SBS/C20 MB, respectively. The 4.0% SBS concentration was chosen based on researches of the same group,<sup>28</sup> which have shown significant improvement of the binder properties for this polymer content (4.0% SBS) when compared to a lower content (3.0% SBS). On the other hand, 4.0% SBS presented phase separation. Based on this result, it was decided to study the addition of organomodified clays aiming to improve asphalt/SBS polymer compatibility and to reduce the quantity of SBS that is required to prevent phase separation. In addition, it is also known that organomodified clay had a positive effect on the rheological behavior of the asphalt binder.<sup>24,25</sup> Thus, it was chosen a proportion of 2.5% SBS and 2.5% organoclays MB which can result in comparable effect with respect to 4.0% SBS MB.

#### Preparation of SBS and SBS/organoclays modified binder

The SBS and SBS/organoclays MB samples were prepared by means of a high shear mixer (Silverson model L4R, at 2000 rpm). The AB was heated in a 1000 mL flask to reach a fluid condition (temperature of 160 °C). Then, the additives were slowly added to the AB. The rotation was maintained for 2 h after the physical mixtures of the additives, while keeping the temperature at 160 °C.

#### Procedures of organophilization

##### Vermiculite

The VMT 2:1 aluminosilicate was used to obtain organophilic clay. VMT was treated with 4 mol L<sup>-1</sup> NaCl solution (1:5) to obtain the homo-ionic Na<sup>+</sup> clay. Distilled water was added and the system was kept under stirring for 30 min at 80 °C and then, sonicated for 5 min in a sonicator, using a Sonifier® Model W-450 D-50% amplitude. OVMT was obtained from the reaction with a solution of cetyl trimethyl ammonium bromide (CTAB). The reaction was kept under agitation for 24 h to allow the cation exchange (ammonium ion surfactant and sodium ions) before filtering and washing with distilled water to remove excess of bromide anions. Then, the sample was dried in the oven at 60 °C.

##### Montmorillonite

The organophilic MMT was prepared from Na<sup>+</sup> MMT aluminosilicate clay by cation exchange between Na<sup>+</sup> and CTAB. The desired amount of MMT and distilled water were stirred until the mixture became homogeneous. A solution of CTAB was added and the system was kept under agitation for 24 h, and then stirred for 5 min in a sonicator, using a Sonifier® Model W-450 D-50% amplitude. The sample was washed and filtered to remove the excess of CTAB. Then, the sample was dried in the oven at 60 °C.

#### Methods

##### X-ray diffraction

The basal spacing of nanoclays was estimated from the position of the  $d_{001}$  peak in the X-ray diffraction (XRD). The XRD patterns were obtained using a PAN analytical X-ray diffractometer with geometry and mirror monochromator of cobalt radiation with a wavelength 1.78896 Å.

##### Conventional physical test

Pure asphalt binder, SBS MB and SBS/organoclays MB were subjected to the following tests: penetration, softening point, thermal susceptibility and rotational viscosity. The penetration (depth, in dmm that a 100 g standard needle penetrates into a sample after 5 s at a temperature of 25 °C) was performed in an automatic penetrometer P736 Normalab Analis, according to ASTM D5 norm.<sup>29</sup> The softening point test (ring and ball test) aims to determine the temperature at which a phase change occurs in the asphalt binder. The test was performed in automatic equipment ISL (RB36 model), according to ASTM D36 norm.<sup>30</sup> The Pfeiffer-Van Doormal thermal susceptibility index (IST) was obtained from the values of penetration (PEN, in dmm) and softening point (PA, in °C). The smaller the IST, the greater is the thermal susceptibility. It is obtained from equation 1:

$$IST = \frac{500 \log(\text{PEN}) + 10 \text{ PA} - 1951}{120 - 50 \log(\text{PEN}) + \text{PA}} \quad (1)$$

A Brookfield viscometer (Model DVII+, Brookfield Engineering Inc., USA) coupled to a temperature controller Thermosel was employed to measure the viscosity according to ASTM D4402.<sup>31</sup>

##### Rheological dynamic shear tests

The rheological tests for the pure asphalt binder, SBS MB and SBS/organoclays MB were performed in a dynamic shear rheometer (DSR), model TA AR 2000® Rheometer. Frequency sweep tests (from 0.01 to 10 Hz)

were applied under a controlled-stress of 120 Pa according to ASTM D 7175-05.<sup>32</sup> Measurements of the complex shear modulus ( $G^*$ ), storage modulus ( $G'$ ), loss modulus ( $G''$ ) and the phase angle ( $\delta$ ) were obtained to evaluate the resistance to shear deformation in the linear viscoelastic range and were related to rutting and fatigue resistance of the materials.  $\delta$  is a measure of the viscoelastic balance of the material behavior (a combination of viscous and elastic responses). The tests were conducted in two different temperature ranges: 10 to 40 °C (first stage) and 45 to 80 °C (second stage). The samples were prepared in a silicon mold 2 mm thick and 8 mm diameter for the first stage and 1 mm thick and 25 mm diameter for the second stage. The samples were tested with parallel plates and diameters of 8 and 25 mm, respectively, during the two referred stages. The linear viscoelastic parameters  $G^*$ ,  $G'$ ,  $G''$  and  $\delta$  were measured for different temperatures and loading frequencies. These data were used to create a master curve based on the time-temperature superposition principle (TTSP).<sup>33</sup> There is a general equivalence between frequency and temperature for thermorheological simple materials such as asphalt binder. This allows the construction of a master curve relating the rheological parameters to load frequency for a selected temperature. This is mainly done in order to determine the viscoelastic functions of the binder over the entire temperature and loading time domain. The TTSP principle allows for the data (curves from DSR tests performed at different temperature and frequency) to be superposed by keeping one of them fixed (a reference temperature, 25 °C) and shifting all the others by different amounts horizontally, parallel to the logarithmic frequency axis, thereby aligning the various curves to form a single master curve. The master curve of the modulus/phase angle describes the frequency (time) dependence of the materials. In this work, the well-known Williams-Landel-Ferry (WLF)<sup>34</sup> equation was used to obtain the shift factors that are required to superpose the curves by using the proper computer software in the computer. The WLF equation that was originally developed in an empirical way holds extremely well for a wide range of polymers and asphalt binders.

#### Storage stability test

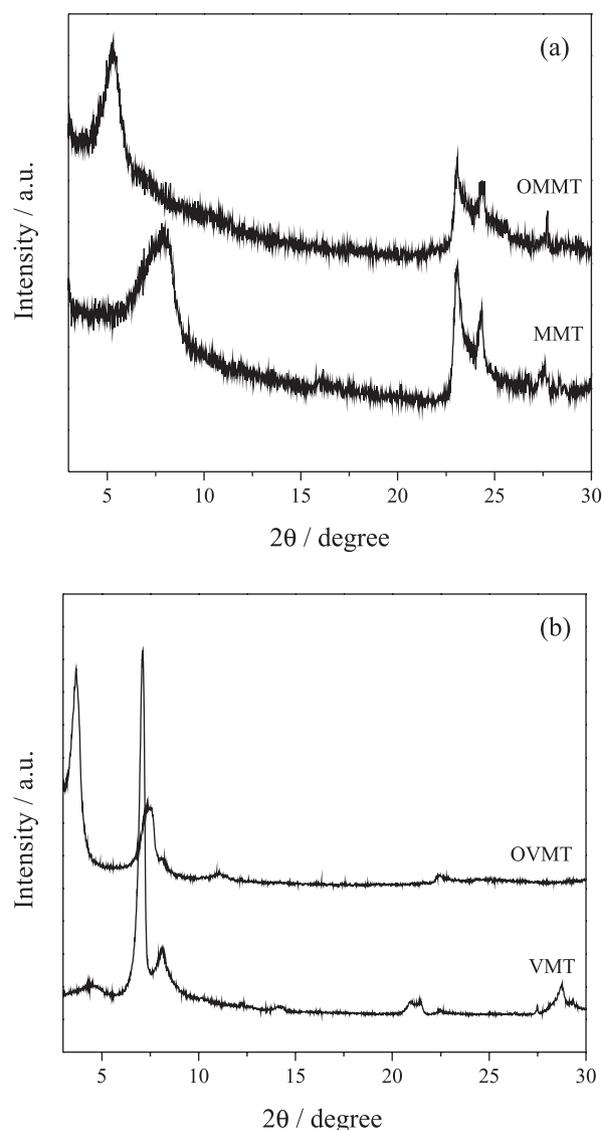
Storage stability tests of modified binders were performed according to ABNT 15166.<sup>35</sup> The samples SBS MB and SBS/OVTM MB were transferred into an aluminum toothpaste tube (25 mm in diameter and 147 mm in height) and stored at 163 °C for 48 h in an oven, and then at -6.7 °C for 4 h in a freezer. A piece of the sample was subsequently taken from the top and bottom of the tube, to be subjected to a frequency sweep test: 0.01 to 100 Hz under a controlled stress of 120 Pa at 60 °C. The logarithm

of the ratio between  $G^*$  of the bottom part and  $G^*$  of the top part is defined as the separation index (Is). The closer to zero is parameter Is, the better is the storage stability of the asphalt binder. This test helps to assess the miscibility of the polymer and the asphalt binder, which is critical for storage at high temperature.

## Results and Discussion

### X-ray diffraction

The X-ray diffractogram of the montmorillonite (MMT) and organophilic montmorillonite (OMMT) are shown in Figure 1(a). The X-ray diffractogram of vermiculite (VMT) and organophilic vermiculite (OVMT) are shown in Figure 1(b). The basal interlayer spacing can



**Figure 1.** X-ray diffractograms for (a) OMMT and MMT and (b) OVMT and VMT.

be calculated from the peak according to the Bragg equation (equation 2), where  $n$  is an integer,  $d$  is the interlayer distance,  $\theta$  is the diffraction angle and  $\lambda$  is the wavelength of incident X-rays of the diffractometer. The nanoclay has a main peak correspondent to an interlayer spacing ( $d_{001}$ ).

$$n\lambda = 2d\sin\theta \quad (2)$$

The X-ray powder diffraction (XRD) pattern of OMMT and MMT shows that the MMT characteristic peak ( $d_{001}$ ) is  $2\theta = 8.0^\circ$ . This peak refers to the basal spacing of 12.9 Å. As shown in Figure 1(a), the peak shifts to a lower angle ( $2\theta = 5.1^\circ$ ), indicating an increase in basal spacing for 20.0 Å. The XRD pattern of OVMT and VMT are shown in Figure 1(b). The characteristic peak for VMT ( $d_{001}$ ) is  $2\theta = 7.1^\circ$ . This peak refers to the basal spacing of 14.5 Å. It was observed that after dispersion of the clay in the CTAB solution, the peak shifted to  $2\theta = 3.7^\circ$ , showing an increase in the basal spacing to 27.6 Å. These results indicate that the organo salt CTAB is able to intercalate into clays increasing interlayer spacing.

#### Conventional test result

The physical properties (penetration, softening point, thermal susceptibility and rotational viscosity) of AB, SBS MB and SBS/organoclays MB are shown in Table 1.

As expected, modification causes an increase in the asphalt binder consistence. A decrease in the penetration values and an increase in the softening point temperature were observed. An increase in the softening point is favorable since asphalt binders with higher values may be less susceptible to permanent deformation. SBS MB presented the largest increase in the softening point. SBS tends to flow at higher temperatures due to the styrene domains that remain solid up to about 80 °C.<sup>21</sup> However, the stiffening effect caused by the presence of SBS/organoclays was very significant. There is also a slightly decrease in the penetration values for SBS/organoclays MB when compared to SBS MB. As expected, it was observed that the viscosity decreases with increasing temperature for all

binders. The modified binders presented higher viscosities, especially at low temperatures when compared to the pure asphalt binder.

The thermal susceptibility index for SBS/organoclays MB indicated that the samples are appropriate for road use. Binders that are more sensitive to the effect of temperature are more prone to permanent deformation at high temperatures and become very rigid and brittle at low temperatures.

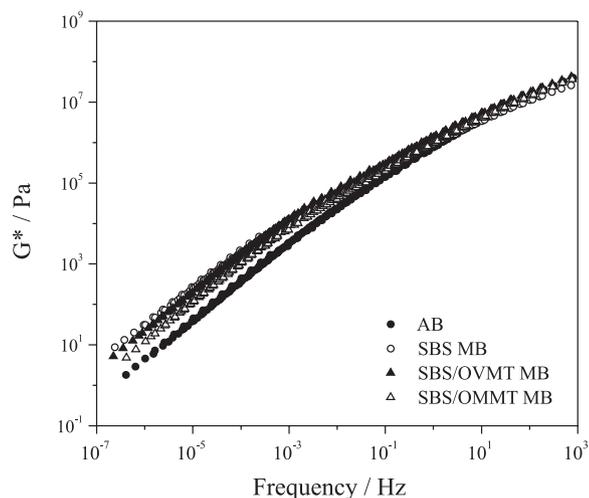
#### Rheological properties

The frequency dependence of  $G^*$  for the asphalt binders is shown in Figure 2, which presents the  $G^*$  master curves. For all the modified AB, it was observed higher values of  $G^*$  when compared to pure AB.  $G^*$  provides a measure of the total resistance to deformation when the asphalt binder is subjected to shear loading and reflects the total stiffness. Consequently, the modified binders seem to be more resistant to rutting. This effect is more pronounced at low frequencies (equivalent to high temperatures) in which the SBS polymer network is dominant. SBS/OVMT MB (with lower content of SBS, 2.5%) and 4.0% SBS MB behaved quite similarly, suggesting that the former composition can result in comparable effects to the latter one regarding the stiffness, especially at high temperatures. The values of  $G^*$  for SBS/OMMT MB were slightly lower than for SBS/OVMT MB, especially when considering lower frequencies (higher temperatures). At higher frequency (equivalent to low temperatures), there is only a slightly reduction in  $G^*$  for SBS MB in comparison to SBS/OVMT MB and SBS/OMMT MB. Thus, at low temperature, the behavior of the modified binders remains closer to the pure asphalt binder.

The viscous modulus ( $G''$ ) in Figure 3(a) presented the same behavior as observed for  $G^*$  over the frequency-temperature domain. This indicates that the viscous modulus increased as the  $G^*$  (stiffness). With respect to the elastic modulus ( $G'$ ) presented in Figure 3(b), it can be noted that at low frequency-high temperatures SBS MB showed an increase in comparison to

**Table 1.** Physicochemical characteristics of the pure and modified asphalt binder used

	AB	SBS MB	SBS/OVMT MB	SBS/OMMT MB
Penetration / dmm	53	46	43	44
Softening point / °C	52	61	57	58
Viscosity / (mPa s)	135 °C	475	1517	1445
	150 °C	228	908	687
	175 °C	90	363	225
Thermal susceptibility index	-0.6	1.0	0.1	0.2



**Figure 2.** Master curves of complex modulus ( $G^*$ ) for pure asphalt binder and modified binders as a function of frequency at a reference temperature of 25 °C.

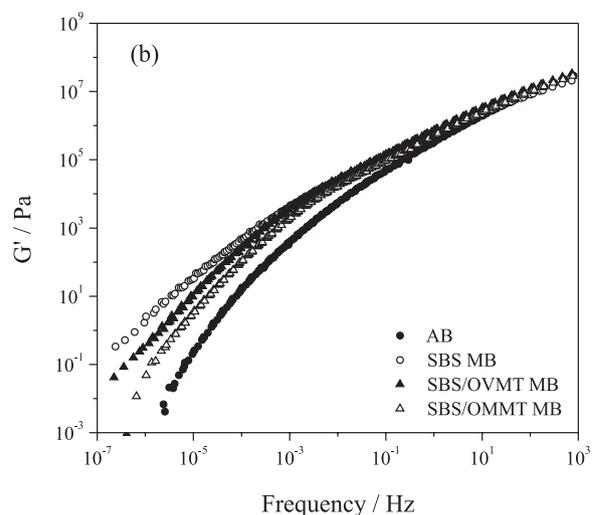
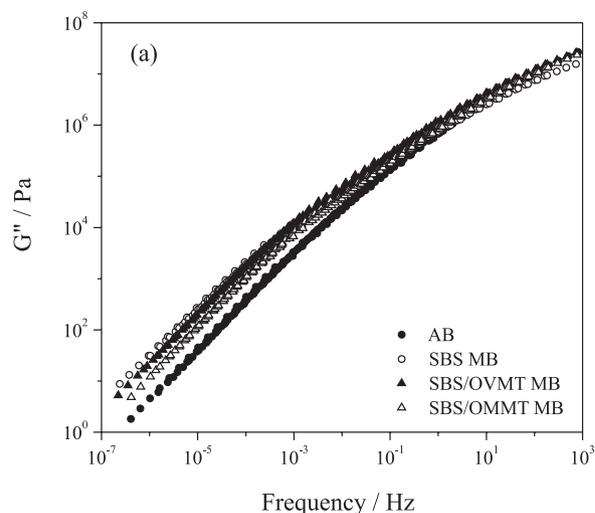
SBS/organoclays MB and pure asphalt binder. The  $G'$  for SBS/OVMT MB is higher than that for SBS/OMMT MB. However, at high frequency-low temperature, the rheological parameter  $G'$  qualitatively resembled that of pure AB and SBS/organoclays MB.

The phase angle ( $\delta$ ) as a function of frequency for the four asphalt binders is presented in the  $\delta$  master curves in Figure 4. It is observed that the incorporation of SBS and SBS/organoclays in the pure asphalt binder causes a decrease in the phase angle. Such decrease represents an improvement in the elastic response when compared to their respective pure AB. It can also be observed the presence of a  $\delta$  plateau at intermediate loading frequency-temperature for modified binders as an indication of a polymer elastic network.<sup>23</sup> The similarity of the plots of  $\delta$  as a function of frequency along the entire range (for all the binders) suggests that the molecular interaction between additives and the asphalt binder is quite similar. The master curves of  $G^*$ ,  $G'$ ,  $G''$  and  $\delta$  indicate that the degree of SBS and SBS/organoclays modification is more significant at low frequency (high temperatures).

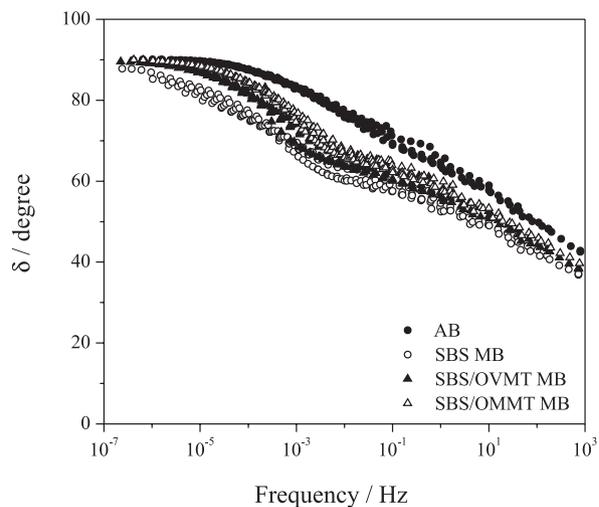
#### Black diagrams

The effect of SBS, SBS/organoclays and SBS/Cloisite® 20A modification on the complex modulus  $G^*$  and phase angle ( $\delta$ ) are shown in the black diagrams, a plot of phase angle ( $\delta$ ) vs. complex modulus ( $G^*$ ) containing no reference to temperature or frequency (Figure 5).

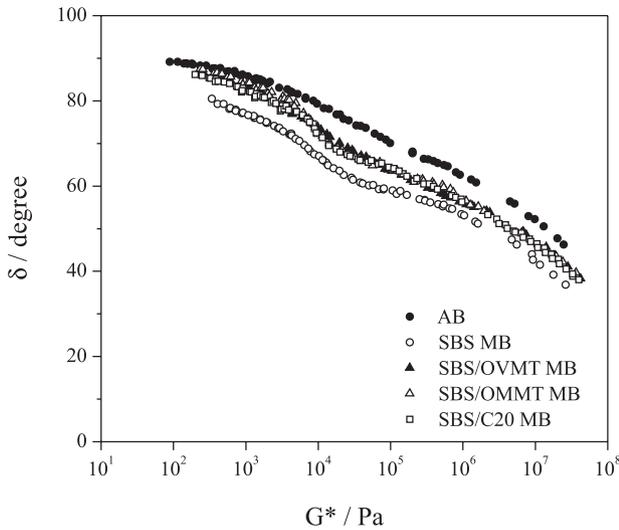
The black diagrams were produced to compare the rheological performance of the organoclays OMVT and OMMT in relation to the commercial Cloisite® 20A as an additive for SBS MB. Effects that were caused by



**Figure 3.** Master curves for (a) viscous modulus ( $G''$ ) and (b) elastic modulus ( $G'$ ) for pure asphalt binder and modified binders as a function of frequency at a reference temperature of 25 °C.



**Figure 4.** Master curves of phase angle ( $\delta$ ) for pure asphalt binder and modified binders as a function of frequency at a reference temperature of 25 °C.

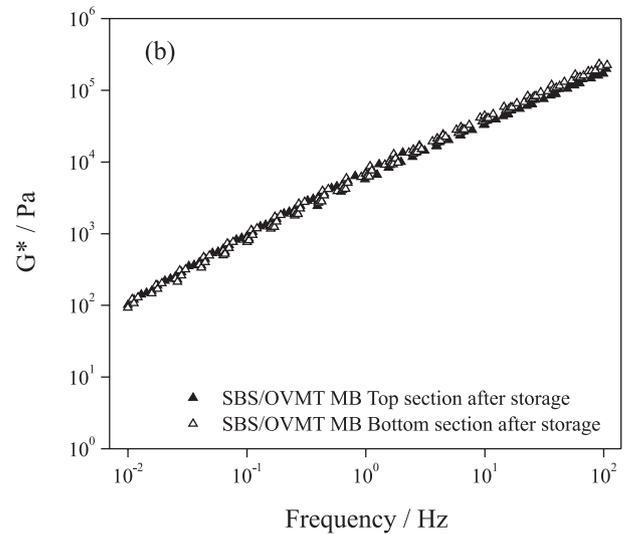
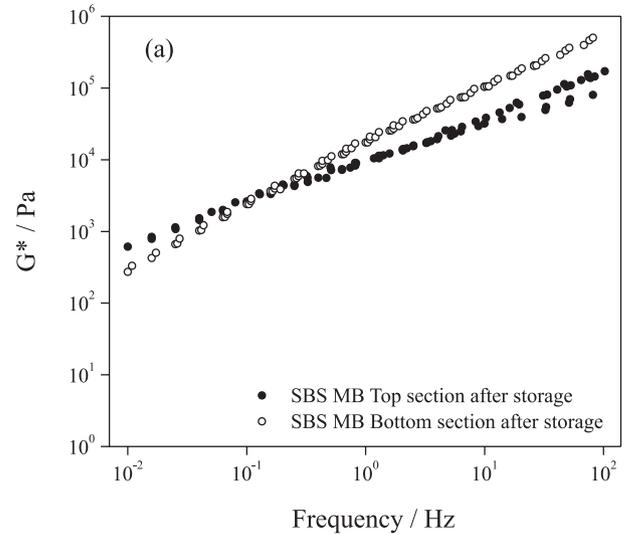


**Figure 5.** Black diagrams for pure asphalt binder and modified binders.

the modifications are highlighted by this diagram.<sup>36</sup> The behavior of the curves (modified and unmodified binders) presented the same pattern, black curves differing only in the magnitude of the parameters. The modification is more pronounced at intermediate temperatures (equivalent to frequencies from  $10^4$  to  $10^6$  Pa). However, some differences are observed over the entire frequency-temperature domain: the stiffness values of the SBS/OVMT, SBS/Cloisite<sup>®</sup> and SBS/OMMT presented almost the same behavior from intermediate to low temperature-high frequency, and SBS MB showed a slight shift towards the lower phase. However, SBS/OVMT MB and SBS/Cloisite<sup>®</sup> MB presented the same behavior along the entire range and remained closer to SBS MB. So, it seems that OVMT caused the same effects that commercial Cloisite<sup>®</sup> 20A used for asphalt modification.

**Storage stability**

Phase separation was measured at 60 °C on samples taken from top and bottom of the test tube. The rheological parameter  $G^*$  used was obtained from the DSR. Figure 6 shows the results of  $G^*$  as a function of frequency before and after the storage of the modified samples.  $G^*$  of the bottom sample became greater than that of the top sample. This is a consequence of the instability caused by the density difference between the SBS copolymer and the asphalt binder.<sup>23</sup>



**Figure 6.**  $G^*$  as a function of frequency for (a) SBS MB and (b) SBS/OVMT MB after storage at a temperature of 60 °C.

Table 2 presents the separation index ( $I_s$ ). The results showed that the separation was attenuated in the presence of the organoclay. In other words, the high temperature storage stability is improved in the presence of the organoclay vermiculite.

The results indicate that OVMT can improve the homogeneity and the stabilization of SBS in asphalt binders. Therefore, the use of OMVT as an additive for SBS modified asphalt represents an alternative to cost reduction for the asphalt industry.

**Table 2.** Separation index of SBS MB and SBS/OVMT MB as evaluated by DSR at 60 °C, 1 and 10 rad s<sup>-1</sup>

Sample	$G^* / (1 \text{ rad s}^{-1})$		$G^* / (10 \text{ rad s}^{-1})$		$I_s$	
	Top	Bottom	Top	Bottom	1 rad s <sup>-1</sup>	10 rad s <sup>-1</sup>
SBS MB	3311	105	12130	25610	-1.50	0.32
SBS/OVMT MB	1306	1171	10130	9015	-0.04	-0.05

## Conclusions

Vermiculite and montmorillonite organoclays (OVMT and OMMT) were obtained using quaternary ammonium salt CTAB<sup>®</sup>. This was confirmed by X-ray diffraction. The effect of the intercalated OMMT and OVMT as a third component in SBS modified asphalt leads to the improvement on the physical and rheological properties probably due to the intercalation of the asphalt molecules in the nanoclay layers. It was observed an improvement in the stiffening effect, thermal susceptibility, and also in the penetration values caused by the presence of SBS/organoclays when compared to SBS MB. Master curves of rheological parameters showed a positive effect in the elastic response and in the resistance to deformation. Generally, the effect of SBS and SBS/organoclays modification is more significant at low frequencies (corresponding to high temperatures). The binder modified by 2.5% of SBS and 2.5% of clays OMMT and OVMT showed a similar behavior to the binder modified by 4.0% of SBS, which confirms that the addition of organically modified clay in the binder leads to a considerable saving of the required polymer. Although there are only minor differences, there is evidence that SBS/OVMT MB presented better performance along the entire frequency-temperature ranges. Black curves of SBS/OVMT MB and SBS/Cloisite<sup>®</sup> MB are quite similar. Therefore, it seems that OVMT caused the same effects that commercial Cloisite<sup>®</sup> 20A used for asphalt modification. The preliminary results indicate that OVMT can improve the homogeneity and stabilization of SBS in asphalt binders and contributes to better storage stability. Therefore, the use of OVMT as additive for SBS modified asphalt represents an economically viable alternative for the asphalt industry.

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