RHEOLOGICAL CHARACTERIZATION AND THERMAL STABILITY OF TRIBLOCK COPOLYMERS-MODIFIED ASPHALT REINFORCED WITH MONTMORILLONITE NANOPARTICLES IN PHYSICAL MIXING

CARACTERIZACIÓN REOLÓGICA Y ESTABILIDAD TÉRMICA DE ASFALTO MODIFICADO CON COPOLÍMEROS TRIBLOQUE Y MONTMORILLONITA EN UN MEZCLADO FÍSICO

M.A. Vargas-Hernández[1]* and H. Vázquez-Torres[2]

[1]*Tecnológico de Estudios Superiores de Ecatepec, Av. Tecnológico S/N, Valle de Anáhuac, 55210 Ecatepec de Morelos, Estado de México.*
[2]*Departamento de Física, Universidad Autónoma Metropolitana - Iztapalapa. Av. San Rafael Atlixco 186, col. Vicentina, México, D.F. C.P. 09340*

Abstract

Effects of montmorillonite (MMT) on the rheological, thermal stability and morphological properties of triblock copolymer modified asphalts are investigated. Modified asphalts were prepared by successively mixing the clay and SBS, SIS, or SEBS with the asphalt AC-20. Results show that the MMT modified asphalt may form an intercalated or exfoliated structure. MMT increased slightly both the softening point and the viscosity of the modified asphalts at high temperatures. Furthermore, the modified asphalts exhibited a relatively higher complex modulus and, in consequence, displayed enhanced viscoelastic properties, which improve its resistance to rutting at high temperatures. The high-temperature storage property can be increased by improving the compatibility between polymer and asphalt. The morphology observed by optical microscopy revealed the better compatibility between triblock asphalt/polymer/MMT, thus influencing the final rheological properties of the studied systems. Indeed, asphalt or asphalt/polymer blends gave a typical terminal relaxation behavior for polymer (G'~ ω^2, G''~ ω^1), which is modified by the addition of MMT particles. Furthermore, the activation energy of nanocomposites resulted slightly higher than that of asphalt/polymer blends without MMT.

Keywords: asphalt; montmorillonite; triblock polymers SBS, SIS, SEBS; modified asphalt; rheology; storage stability.

Resumen

Se estudió el efecto de la montmorillonita (MMT) sobre las propiedades reológicas, estabilidad térmica y morfología del asfalto AC-20 modificado con copolímeros tribloque. El asfalto modificado (AM) se preparó por mezclado sucesivo de nanopartículas y polímeros SBS, SIS y SEBS. Los resultados obtenidos muestran que la arcilla puede formar distribuciones intercaladas y/o exfoliadas. La presencia de la MMT en el AM aumenta ligeramente la temperatura de ablandamiento y la viscosidad del asfalto a temperaturas altas y disminuye el grado de penetración. Adicionalmente, estos materiales muestran un aumento en los módulos elástico y viscoso, lo que indica un considerable mejoramiento en la resistencia a la deformación permanente por acanalamiento a temperaturas elevadas. La estabilidad térmica del asfalto modificado aumenta con la presencia de MMT, debido a la mejora de la compatibilidad entre el asfalto y el polímero por sus interacciones con la arcilla. En efecto, la morfología del AM observada por microscopía óptica presenta una reducción en el tamaño de partícula del polímero en el sistema ternario asfalto/polímero/MMT, lo cual se ve reflejado en el mejoramiento de la compatibilidad y de sus propiedades viscoelásticas. El asfalto AC-20 y las mezclas binarias polímero/asfalto presentan una relajación terminal característica del polímero (G' ~ ω^2, G'' ~ ω^1),). Por su parte, las mezclas asfalto/polímero/MMT muestran un cambio en el espectro de relajación terminal (G' y G'' ~ ω^1), además de un ligero aumento en la energía de activación.

Palabras clave: asfalto modificado, arcilla MMT, polímeros tribloque, reología, estabilidad térmica.

Corresponding author. E-mail: : `angelesvh@yahoo.com`
Tel. 55-71-43-92

1 Introduction

Increasing traffic loads and traffic volume, combined with the rising cost of asphalt, have led to an urgent demand to improve the durability, safety and efficiency of asphalt pavements through asphalt modification. Asphalt usually is a byproduct of crude oil refining process in petroleum refineries, and it is a complex heterogeneous mixture of hydrocarbons, which are usually grouped into asphaltenes and maltenes. In turn, maltenes can be subdivided into saturated, aromatics, and resin compounds. No sudden transition in molecular structure has been found between resins and asphaltenes (Baochang *et al.*, 2009). Polymer-modified asphalts, PMA, have increasingly been used over the last decade to minimize low-temperature cracking and high-temperature rutting while improving the fatigue cracking resistance of asphalt concrete (Herrera *et al.*, 2012; Markanday *et al.*, 2010; You *et al.*, 2011; Yu *et al.*, 2009; Zare-Shahabadi *et al.*, 2010). When an asphalt binder and a polymer are mixed, a microheterogeneous material is made up of two distinct finely interlocked phases. The polymer phase is swollen by absorbing the asphalt aromatic oil fraction (maltenes). 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 PMA. In addition, the mixture compatibility depends on the polymer type and the content added to the asphalt, as well as on the asphalt binder chemical composition.

Although improvements in asphalt performance have been achieved by addition of polymers, it is interesting to explore nanoscience and nanotechnology for improving asphalts pavement performance (Markanday *et al.*, 2010; Zhang *et al.*, 2009). Nanotechnology is the creation of new materials, devices, and systems at the molecular level as phenomena associated with atomic and molecular interactions, which strongly influence macroscopic material properties. While engineers are interested in material properties at the macro and meso scales, the nano and micro scales provide fundamental insight for the development of science and technology.

In addition, researchers suggest that nanoclays improve some characteristics of asphalt binders and asphalt mixtures, but more work is required before it can be applied on a large scale (Markanday *et al.*, 2010). Efforts should be made for exploring the use of new-layered silicates with low cost and abundance, which consist of tetrahedral silicate and octahedral

hydroxide sheets, for modifying asphalts (Fang *et al.*, 2012; Ouyang *et al.*, 2006). Layered clays include montmorillonite (MMT), rectorite (REC), vermiculite (VMT), and kaolinite (KC). MMT improved the physical properties, rheological behaviors and the storage stability of the asphalt blends, while organo-modified OMMT exhibited even better improving on the properties of asphalt (Polacco *et al.*, 2008; Baochang *et al.*, 2009). MMT-modified asphalt may form an intercalated structure, whereas the OMMT-modified asphalt may form an exfoliated structure, as revealed by X-ray diffraction (XRD) (Ouyang *et al.*, 2006; You *et al.*, 2011). The intercalated structures correspond to well-ordered multilayered structures where the asphalt chains are inserted into the gallery space between the silicate layers. The exfoliated structures correspond to delaminating structures where the individual silicate layers are no longer close enough to interact with the gallery cations (Polacco *et al.*, 2008). Generally, the exfoliated nanocomposites are materials with better physical properties when compared to intercalated nanocomposites (Ouyang *et al.*, 2006; Yu *et al.*, 2007). Although, it is difficult to achieve complete exfoliation of clays, most of the polymer nanocomposites exhibit intercalated or mixed (intercalated-exfoliated) nanostructures (Yu *et al.*, 2007). In general, there are two mixing procedure: The first one is the physical mixing (PM) by adding the polymer and nanoparticles separately to the asphalt, while the second one consists of adding the melted blend polymer/nanoparticles (MB) in the form of a master batch (Polacco *et al.*, 2008). The obtained polymer modified asphalt nanoparticles (PMANs) were reported to have intercalated features in both cases. Typical clays capable of forming intercalated or exfoliated structures include montmorillonite, flurohectorite, and bentonite (Zare-Shahabadi *et al.*, 2010). Nanocomposites are usually added in percentages between 2 and 5 wt% for achieving an important enhancement on mechanical properties of materials. Therefore, one of their advantages is the low weight, which is economically interesting, besides the enhancement of mechanical behavior (Ouyang *et al.*, 2005).

Commonly, X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and rheometric flows have been used in the study of nanocomposites (Ouyang *et al.*, 2006). Rheological studies showed a transition from liquid-like to solid-like behavior with little difference between intercalated and exfoliated nanocomposites. The time-temperature superposition principle is

quite frequently used when studying the dynamic properties of nanocomposites, and some examples of rheologically simple nanocomposite systems are given (Markanday *et al*., 2010).

The degree of exfoliation can be determined from the low frequency viscoelastic behavior, whereas the high frequency behavior of dynamic moduli allowed estimation of the quality of dispersion. It was also concluded that the elastic modulus (storage modulus G') of the modified asphalt was higher than that of the virgin asphalt, while the loss modulus (G") was much lower in the modified binder than in the virgin binder (Yu *et al*., 2007).

In the present work, triblock polymers/MMT modified asphalts were prepared by adding montmorillonite and triblock polymers to the asphalt, each one separately. The characteristics and properties include conventional test methods, morphology by optical microscopy, high-temperature storage stability and rheological behaviors. The effects of MMT on characteristics and rheological properties of modified asphalts were also discussed.

2 Experimental section

2.1 Materials

Paving Asphalt AC-20 was provided by PEMEX (Salamanca, México) and showed the following physical properties: penetration, 67 dmm at 25 ºC (ASTM D5); softening point, 49.0 ºC (ASTM D36).

The modifying polymers were: linear-like styrene-butadiene-styrene triblock copolymer, SBS, Kraton D1102, containing 30 wt% of styrene, with M_w=71330 g/mol; branch-like styrene-isoprene-styrene triblock copolymer, SIS, containing 30 wt% styrene, with M_w=81680 g/ mol; and a linear-like styrene-ethylene-butadiene-styrene tetrablock terpolymer SEBS, containing 30 wt% of styrene, with M_w=71660 g/mol. These triblock copolymers were supplied by Chemcentral, México.

Sodium MMT clay (MMT) from Nanocor Inc. (Arlington Heights, IL, USA) with ionic interchange capacity of 135 meq/100 g, specific gravity of 2.6 and mean particle size of 22 μm, was employed as the dispersed phase.

2.2 Preparation of MMT/triblock modified asphalt

The triblock polymers/MMT modified asphalt was prepared in a steel container at 180 ºC, a shearing speed of 500 rpm and inert atmosphere (N_2). First, asphalt (200 g) was heated up to 180 ºC, and 4 wt% of triblock copolymer was added to the asphalt and sheared for 20 min; then, 2.5 wt% of MMT was added into this mixture, and the mixture was maintained at these conditions of temperature and shearing for 4 h to ensure a well dispersion of MMT nanoclay. Asphalt and triblock/asphalt in the absence of MMT were prepared and characterized under the same conditions in order to compare its properties with those of asphalt and triblock polymer/MMT-modified asphalt. To exclude the effect of asphalt aging during the mixing process to evaluate accurately the presence of polymer and its effects, the base asphalt (blank sample) was obtained under the same conditions as the modified blends. Slight differences among the values of both viscoelastic functions for pure asphalt and blank sample of asphalt were observed.

2.3 Physical properties test

The physical properties of asphalt, including softening point and penetration at 25 ºC, were tested according to ASTM D36 and ASTM D5, respectively.

2.4 High-temperature storage stability test

The high-temperature storage stability of modified asphalts was tested as follows: a certain amount of the modified asphalt was poured into an aluminum foil tube (32 mm in diameter and 160 mm in height), the tube was sealed and placed vertically in an oven at 160 ºC for 72 h; then it was taken out, cooled down to room temperature, and cut in equal three section. The specimens obtained from the bottom and top sections were used to evaluate the storage stability of the triblock polymer/MMT modified asphalts by measuring their softening points and rheological properties. If the difference of the softening points between the bottom and the top sections was less than 2.5 ºC, the modified asphalt was considered to be stable under high-temperature storage condition. Otherwise, it was labeled as unstable.

2.5 Fluorescence microscopy

Fluorescence microscopy tests were performed with a Carl-Zeiss KS 300 microscope at ambient temperature at wavelength of 390-450 nm with a 20X objective. Microphotographs were taken with a MC100 camera equipped with an automatic counter. The polymer rich phase appeared white, while the asphalt rich phase was dark.

2.6 Rheological characterization

Rheological tests were made in a controlled stress AR-1000-N rheometer using a parallel-plate with diameter of 2 cm and a gap of 1.0 mm. The temperature ranged from 25 to 75 ºC with 2 °C increments keeping the strain for each temperature within the linear viscoelastic range. The frequency was varied from 0.1 to 100 rad/s at a constant temperature and strain. A stabilization time of 15 min was allowed for each sample. In each test, about 1.0 g of sample was placed on the bottom plate, covering the entire surface, and the plate was then mounted in the rheometer. After the sample was heated to become a melt, the top plate was brought into contact with the sample, and the sample was trimmed.

3 Results and discussion

3.1 Physical properties

The effect of the MMT on physical properties of the asphalt and modified asphalts is shown in Table 1. Slight differences among the average values of both penetration and softening point for each sample tested by triplicate were observed.

Triblock/MMT modified asphalts exhibited a slight improvement on penetration and softening point of asphalt. The penetration of the triblock/MMT modified asphalts decreased, while the softening point of the modified asphalts increased as compared to those without MMT. In this study, the softening point of the asphalt/SEBS/MMT was slightly higher and the penetration lower than those of the other samples. Yu *et al.* (2007) showed that the increase in the softening point may be due to the formation of an intercalated structure in MMT modified asphalt and, concomitantly, to an obstruction of the movement of asphalt molecule chains by the intercalated structure at high temperature.

3.2 Fluorescence microscopy

The morphology of the modified asphalts was observed under fluorescence microscope by characterizing the distribution and the fineness of modifier in the asphalt matrix, and unmodified asphalt as a control (Fig. 1a). Asphalt/MMT blend showed fine, white, little discernible, and non-uniformly distributed MMT particles dispersed in the asphalt matrix (Fig. 1b). In contrast, asphalt/polymer blends presented a two-phase morphology, with well-defined dark and grey areas (Figs. 1c, 1e, and 1g). As can be seen in these figures, the efficiency of the added triblock polymers to phase-separate in asphalts follows the order: SIS>SBS>SEBS. The dark zones correspond to the asphaltene-rich phase, while the grey part is the polymer-rich phase, swollen by the saturated and aromatics compounds, which have a lower polarity than those of resins and asphaltenes. The addition of MMT to triblock polymer/asphalt blends resulted in a significant decrease in size and better dispersion of the particles of separated phase (Figs. 1d, 1f, and 1h), being the best effect on the SIS containing asphalt (Fig. 1f).

Table 1. Effects of MMT on the properties of triblock modified asphalt and high temperature storage stability.

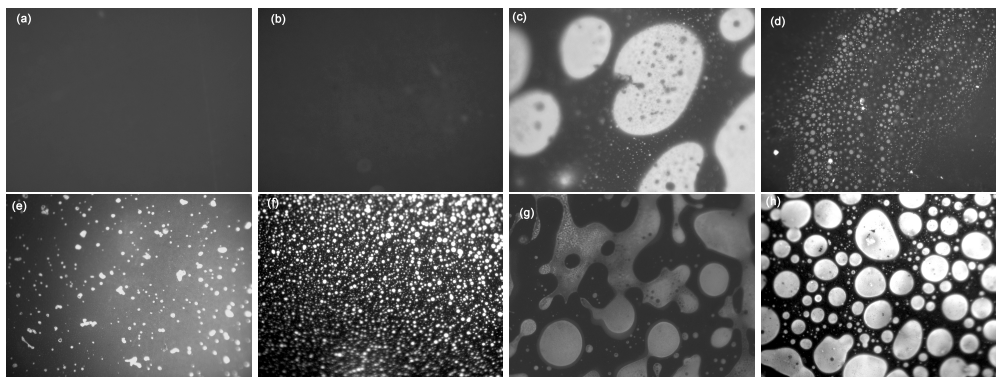| Material	Softening point (ºC)	Penetration at 25 ºC (dmm)	Softening point (ºC)		Difference (ºC)
			Bottom	Top	
Asphalt	46	64	-	-	-
Asphalt/Na$^+$MMT	50	60	-	-	-
SBS	55	54	57	69	12
SIS	58	51	60	71	9
SEBS	60	48	64	72	8
SBS/Na$^+$MMT	61	50	62	70	8
SIS/Na$^+$MMT	65	43	68	74	6
SEBS/Na$^+$MMT	68	41	72	76	4

Fig. 1 Morphology of triblock modified asphalt before and after adding MMT at 25 ºC and magnification 20X; (a) asphalt; (b) asphalt/MMT; (c) asphalt/SBS; (d) asphalt/SBS/MMT; (e) asphalt/SIS; (f) asphalt/SIS/MMT; (g) asphalt/SEBS and (h) asphalt/SEBS/MMT.

Polacco *et al*. (2008) assumed that in the MB case (master batch) the nanoparticles remained confined in the polymeric phase, whilst in PM (polymer mixing) could show stronger interaction with the asphalt phase (resins and asphaltenes). On this basis, a more homogeneous dispersion of the nanoparticles could be obtained by the master batch procedure than by adding the polymer and nanoparticles because they compete with asphalt components, and part of the polymer probably did not interact with the clay, due to a reduction of surfactant action of the clay. Therefore, it can be assumed that the asphalt/triblock/MMT did not show a substantial improvement on the compatibility when prepared by the mixing process (PM). Hence, XRD analysis was not applied for addressing a possible intercalation or complete exfoliation of MMT particles by the polymer-modified asphalt. However, the morphology revealed by fluorescence microscopy of asphalt/polymer/nanoparticles showed a size refinement and homogeneous distribution of polymer in asphalt, especially in asphalt/SIS/MMT blend, due to the polar interaction of MMT with asphaltenes that swell the polymer-rich phase.

3.3 High-temperature storage stability

Phase separation between modifier and asphalt in modified asphalts occurred often during storage, pumping and usage in the pavement (Yu *et al*., 2009). So, the storage stability of modified asphalt is an important subject of investigation. Two approaches have been accepted to ascertain if phase separation occurred during the high-temperature storage stability test: softening point variation and rheology characterization. The softening points between the top and bottom of the samples after the high-temperature storage stability test should not be higher than 2.5 °C in order to address that there is no substantial phase separation (storage stability). The average high-temperature storage stability of triblock polymer/asphalt and polymer/MMT/asphalt is presented in Table 1. For asphalts modified by triblock polymer in the absence of MMT, the differences in the softening points is relatively large, which implies that a serious phase separation took place in the polymer/asphalt mixture. In contrast the asphalt/polymer/MMT system showed improved storage stability. Indeed, the difference in softening point between top and bottom of these blends were 8, 6, and 4 ºC for the asphalt containing SBS/MMT, SIS/MMT, and SEBS/MMT, respectively. These results are in accord with the size reduction of particles observed in these three modified asphalts.

Asphalt is commonly considered as a dynamic colloid system consisting of a suspension of high molecular weight asphaltenes micelles dispersed in a lower molecular weight oily medium (maltenes). As mentioned above, the polymer modified asphalts may have a tendency to separate into two phases, one being polymer-rich phase and the other asphalt-rich phase, because the introduction of any polymer will disturb the dynamic equilibrium and reduce the homogeneity of the asphalt system. The case is utmost serious under quiescent conditions at high temperature. Polymer modified asphalt can be considered as a suspension system, in which the particles in the liquid experience a buoyancy force combined with a gravitational force, and the falling velocity of the particles in the system follows Stoke's law (Zhang *et al*., 2008):

$$V = \frac{2(\rho_0 - \rho_1)gr^2}{9\eta} \qquad (1)$$

where ρ_0 is the density of asphalt, ρ_1 is the density of polymer, g is the gravitational force constant, r is the average radius of the polymer particles, and η is the viscosity of the modified asphalt. To prevent the phase separation of polymer from asphalt, a critical way is to reduce the falling velocity of the particles. As shown in Eq. (1), there are two ways to reduce the falling velocity, one is to reduce the particle size, and the other is to decrease the density difference. It is known that the density of the asphalt is 1.02 g/cm^3, whereas for SBS is 0.95 g/cm^3, for SEBS is 0.93 g/cm^3, and that for MMT is around 2.15 g/cm^3 at room temperature. The density difference of the polymer and asphalt becomes larger at high temperatures because the oily fraction of the asphalt swells the polymer. However, when the MMT is attached to polymer, the density difference decreased (density of SBS/MMT is approx. 0.963 g/cm^3, while SEBS/MMT is 0.944 g/cm3) and the force for driving separation approaches zero at a certain content of MMT; so, the high-temperature storage stability is improved (see Table 1), because the density difference of the compounds decreases slowly as the swelling proceeds, (Zhang *et al.*, 2011).

After 24 h of storage at 160 ºC, G* was measured at 25 ºC at 10 rad/s with a rheometer for the top and bottom sections of the samples to calculate the separation index (I_s). This parameter assesses the compatibility degree of the polymer-asphalt blend, which is critical for storage and final use of PMA. The storage stability was evaluated with the magnitude of the separation index I_S, defined according to the following expression (Perez-Lepe *et al.*, 2006):

$$I_S = \log \frac{G*_{BOTTOM-PHASE}}{G*_{TOP-PHASE}} \qquad (2)$$

where G* is the complex modulus.

The separation index values for the binders studied in the present work are shown in Table 2. Modified asphalt without phase separation during hot storage show I_s values close to zero (Chung *et al.*, 2008). A higher value of I_s was attained for SBS/asphalt, while the lower one (1.10) corresponds to the asphalt/SIS/MMT.

In Strategic Highway Research Program (SHRP) specifications, the rheological parameter, $G^*/\sin \delta$, was selected to express the contribution of the asphalt binder to permanent deformation (AASHTO T 315). This value reflects the total resistance of a binder to deform under repeated loading ($G*$) and the relative

amount of energy dissipated into non-recoverable deformation ($\sin\delta$) during a loading cycle (Kuo *et al.*, 2011). The $G^*/\sin \delta$ value should be larger than 1 kPa at 10 rad/s for the binder at a maximum pavement design temperature. With a higher value of the parameter rate, there is a higher resistance to permanent deformation. Additional measurements were carried out at 100 ºC and 10 rad/s in order to evaluate $G^*/\sin \delta$ for all systems. The effect of MMT contents on the performance grade of the modified asphalt is listed in Table 2. As can be seen, the performance grade of polymer/MMT modified asphalt was improved and they had a higher performance grade than asphalt/polymer blends, which indicated that nanoparticles could be helpful for the improvement of rutting resistance. These results agree with the morphological features observed in the modified asphalts (Figs. 1a-f) and, in consequence, there is a great increase in rutting factors of the nanocomposites as compared with the asphalt matrix and polymer-asphalt blends, which can be attributed to the increase in G^* and decrease in phase angle due to the presence of MMT in blends. The best result was obtained in asphalt/SIS/MMT at the temperature of 86 ºC.

3.4 Rheological properties

Master curves of the dynamic material functions (storage G', loss G" moduli and complex viscosity η^*) were built by applying the time-temperature superposition principle at reference temperature of 25 ºC. No anomalous behavior of these material functions was observed; indicating that the time-temperature superposed master curves for each one of the nanocomposites can be constructed by using the horizontal (a_T) shift factor, which was easily calculated with its Arrhenius form (Yu *et al.*, 2007):

$$a(T) = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \qquad (3)$$

where a_T is the shift factor at a temperature T relative to the reference temperature T_0; E_a is the activation energy, which is a quantitative measure of the molecular mobility, and R = 8.314 J/mol K. E_a for asphalt and blends is shown in Table 2, in which it can be observed that asphalt/MMT and blends with nanoparticles showed activation energy slightly higher than that of blends without nanoparticles. This is an indication that the relaxation of the polymer chains in the exfoliated or intercalated nanocomposites

Table 2. Effects of MMT on the performance of modified asphalt: Separation index IS, apparent activation energies, relaxation time and slopes of G', G", and complex viscosity (η^*).

Sample	I_S	SHRP T (ºC), 10 rad (G*/sin δ = 1 kPa)	Ea (kJ/mol)	$\left(\dfrac{dG'}{d\omega}\right)_{\omega\to 0}$	$\left(\dfrac{dG''}{d\omega}\right)_{\omega\to 0}$	Crossover frequency rad/s	Relaxation time $\lambda\sim(1/\omega_x)$ s^{-1}	$\left(\dfrac{d\eta^*}{d\omega}\right)_{\omega\to 0}$
Asphalt	-	65	162	1.50	0.95	19.26-101	0.01-0.052	-0.0437
Asphalt/Na$^+$MMT	-	69	167	1.30	0.87	3.98-62.5	0.016-0.25	-0.1074
SBS	1.62	74	175	1.23	0.83	6.31–101	0.010-0.16	-0.1197
SIS	1.40	80	180	1.14	0.90	3.98-62.46	0.016-0.25	-0.1723
SEBS	1.43	82	183	1.10	0.81	3.98-39.72	0.025-0.25	-0.1265
SBS/Na$^+$MMT	1.34	80	181	1.10	0.78	3.98–39.72	0.025-0.25	-0.1943
SIS/Na$^+$MMT	1.10	86	184	0.98	0.73	1.58-15.80	0.063-0.63	-0.1768
SEBS/Na$^+$MMT	1.14	84	187	1.09	0.81	2.51-25.13	0.040-0.40	-0.1313

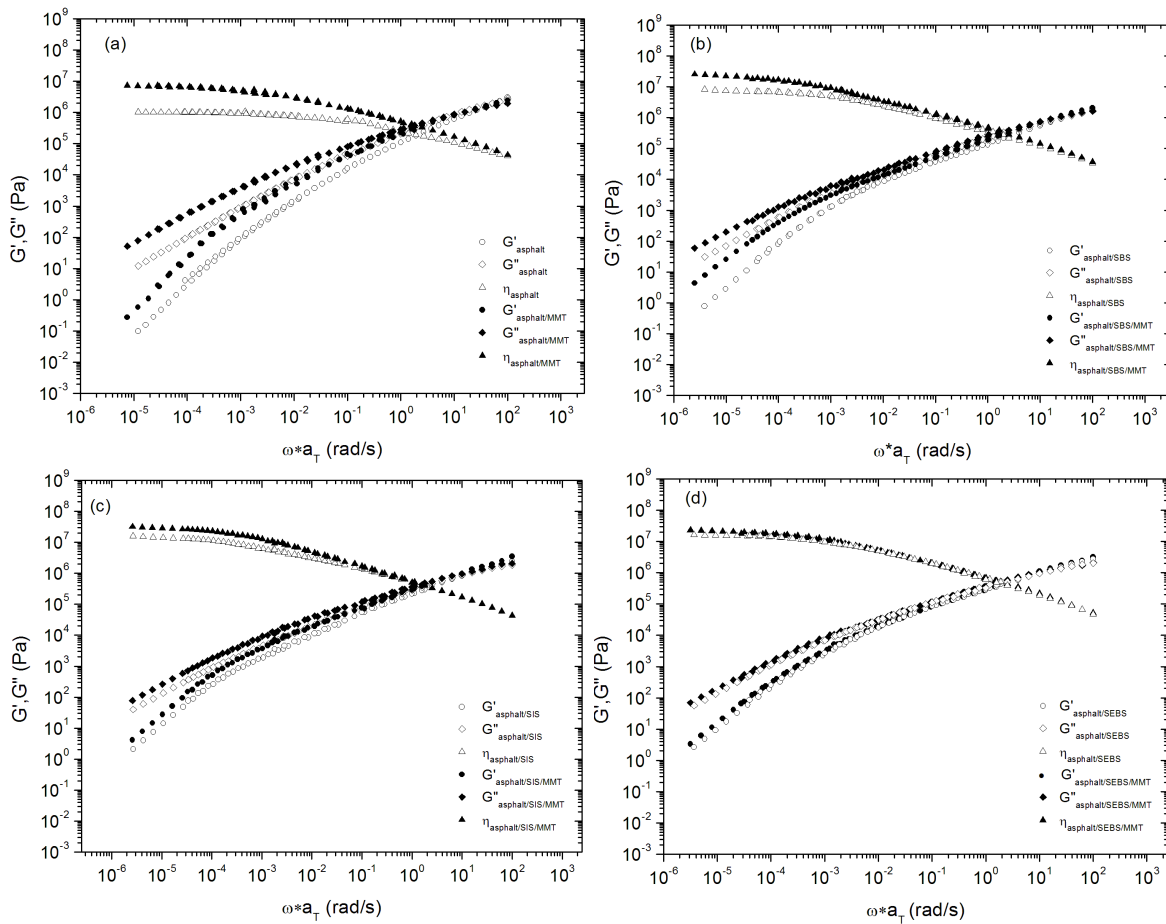

Fig. 2 Master curves of G', G", and complex viscosity (η^*) obtained using frequency-temperature superposition method at reference temperature of 25 ºC. a_T is the shift factor: (a) pure asphalt and asphalt/MMT; (b) asphalt/SBS and asphalt/SBS/MMT; (c) asphalt/SIS and asphalt/SIS/MMT; (d) asphalt/SEBS and asphalt/SEBS/MMT.

was no affected by the presence of the MMT, at least within the sensitivity of the dynamic mechanical measurements (Kuo *et al.*, 2011).

The time-temperature superposition principle was found to hold for all the investigated materials and the horizontal shift factor was satisfactorily described

by the Arrhenius relation (Eq. 3). It can provide more information than with a single temperature test and allows the asphalts characteristics to be predicted for some specific frequency zones which are technically interesting, but experimentally out of reach. The master curves of G', G" and η^* for all

samples are plotted in Fig. 2. Asphalt and blends exhibit higher values of the G" than the G' in the experimental frequency. These results demonstrate the predominantly viscous characteristics of these materials at higher temperatures. The addition of MMT to asphalt increases the storage and viscous moduli particularly at low frequencies (Fig. 2a). The behavior of asphalt/SBS and asphalt/SBS/MMT are qualitatively different. According to Fig. 2b, the terminal modulus of G' of asphalt/SBS/MMT was about one decade higher than that of the G' of asphalt/SBS blend at lower frequencies, and the nanocomposite exhibits a more viscoelastic behavior than that of asphalt/SBS. In contrast, modulus G' for both blends showed similar values at high frequency. The mixture of asphalt/SIS/MMT exhibits higher elastic and viscous moduli than those of the other mixtures, which should be due to an increase of interactions between asphalt/polymer/nanoparticles and fine network structure formation, in accordance to the fluorescence results described above. On the other hand, the curves differentiate, but those relative to asphalt/SEBS and asphalt/SEBS/MMT remain very close to each other at lower frequencies (Fig. 2d); i.e., the addition of clay did not lead to dramatic changes in the behavior of the master curves of storage and loss moduli of this blend. Compared to asphalt/polymer, asphalt/polymer/MMT exhibits higher values of G' and G", especially at relatively low temperatures, which may be due to a possible exfoliation or intercalation of MMT layers in asphalt leading to a fine network structure in polymer/MMT modified asphalts. These results suggest that MMT can improve the viscoelastic behavior of asphalt and that the nanocomposites enhance the viscoelastic behaviors and rutting resistance at high temperature. It has been pointed out that as the frequency increases, the nanoclay molecules play a minor role in bearing the shearing load compared to low frequency or increased traffic loading where the action of the nanoclay molecules starts to become evident. Therefore, it could be stated that at low frequency, both the action of the asphalt binder and nanoclay are significant, whereas at high frequency the asphalt binder tends to become more significant than the nanoclay. Also, the slopes of G' and G" are smaller than 2 and 1, respectively, for all the blends, especially for nanocomposites (Table 2). A deviation from the Maxwell-behavior is characteristic for these materials, where the asphalt/SIS/MMT system presents the smallest slope among the systems studied.

In addition, as can be seen in Table 2 and Figs. 2, a crossover for G' and G" curves takes place in the frequency region from 10^0 to 10^1 for all the materials, the lower value being for the asphalt/SIS/MMT nanocomposite, and corresponds to a higher relaxation time (Table 2), which indicates an improving of rutting resistance.

The viscosity of asphalts strongly depends on its constitutive components and the interactions. The presence of foreign solid particles such as MMT in the asphalts matrix should contribute to the enhancement of the asphalts viscosity. The adsorption capacity of these particles and polymer are determining factors. The effect of MMT on the viscosity of the modified asphalt is shown in Fig. 2. The curves describing the evolution of the η^* with the frequency is superposed. At low frequency region, complex viscosity of the samples showed a Newtonian behavior (Table 2). It can be seen that the difference between the complex viscosity of asphalt/MMT and asphalt/polymer/MMT increases at low frequency, as result of a possible formation of intercalated or/and exfoliated structure of MMT (Table 2).

The applicability of the time-temperature superposition principle was verified for all the studied materials by constructing the van Gurp-Palmen (Yu *et al.*, 2007) plots of the phase angle versus the magnitude of the complex modulus, also called Black diagram (Fig. 3). As can be seen, at a fixed value of the complex modulus of 1×10^7 Pa (within the low temperature region), the modified asphalt presents a lower phase angle value than the neat asphalt. The addition of nanoparticles leads to a slight improvement of elasticity at high in-service temperatures of the blends. It is clear that the absence of the pronounced plateau modulus yields a smooth plot for neat asphalt and asphalt/MMT. Similar plots can be constructed for the rest of the systems (base asphalt modified by polymer and nanocomposites) studied. The main difference apparent from such plots is the clear split between blends and asphalt neat, as well as asphalt/MMT. The shapes of all the blends are remarkably similar. Since the most important effect of modifiers is the enhancement of elasticity, dynamic shear test can be used to determine the complex modulus (G*). So, its increasing reflects the rutting resistance of modified asphalt at high temperature, due to the fine network structure in triblock/MMT modified asphalts.
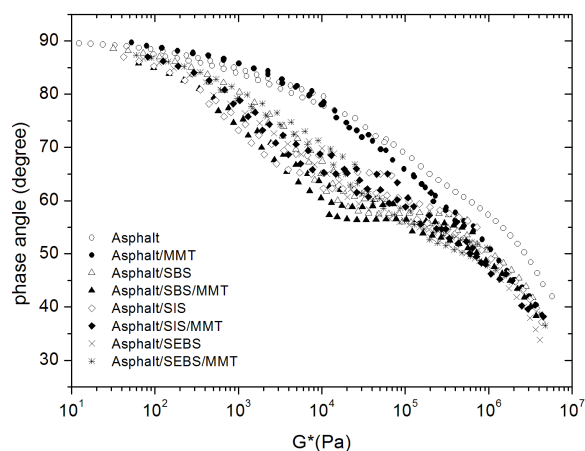
Fig. 3 The Van Gurp-Palmen plots: (o) Asphalt; (●) asphalt/MMT; (△) asphalt/SBS; (▲) asphalt/SBS/MMT; (◇) asphalt/SIS; (♦) asphalt/SIS/MMT; (□) asphalt/SEBS; (■) asphalt/SEBS/MMT.

Conclusions

The effects of MMT on the physical properties and dynamic rheological behaviors of the modified asphalt were investigated. Ternary blends were prepared by adding the clay and polymer to the asphalt, each one separately. MMT lead to higher values of both the softening point and viscosity, decreasing the penetration and increasing the rutting resistance of asphalt/polymer blends studied here. High-temperature storage stability tests indicated that the polymer-modified asphalts were more stable with nanoparticles by decreasing the density difference between polymer and asphalt. Morphological analysis showed that the clay favored the dispersion of polymer in the asphalt matrix by contributing to the formation of a fine network structure in asphalt/SIS/MMT system. Considering the chemical structure of the blends, MMT clay may have a higher affinity for asphalt than for the polymer, leading to a possible intercalation of asphalt molecules, and making the asphalt/polymer blends slightly compatible. The addition of MMT did not produce dramatic changes on the behavior of the master curves of storage and loss moduli of the studied modified asphalt. The results indicate that PMAs show a viscoelastic behavior, where the asphalt blends exhibit higher values of G" than that of G' in the experimental frequency. Besides, the slope of G' curves of asphalt blends decreases with the presence of MMT. Also, the terminal relaxation behavior of asphalt or asphalt/polymer blends, typical of polymers (G' $\sim \omega^2$, G" $\sim \omega^1$) slightly changed by incorporation of nanoparticles, and a major amount of this would result in the spectrum in the terminal relaxation regime (both G', G" $\sim \omega^1$). Finally, MMT enhanced the asphalts viscosity, and produced a slight increasing on activation energy of polymer asphalt blends.

Acknowledgments

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