

Asphalt/polyethylene blends: Rheological properties, microstructure and viscosity modeling



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HIGHLIGHTS

- Different polyethylene and grafted polyethylene-based polymers were used to modify asphalt.
- Grafted polymers allow for an improvement in the miscibility between polymer and asphalt.
- Elastic properties of the binder at high temperatures were enhanced. These results allow knowing the reduction of rutting.
- Grafted polymers showed strong interactions, which are evidenced by the apparition of a plateau region at low frequencies.
- Frequency sweeps to estimate the ZSV in asphalts and blends were analyzed in this work.

ARTICLE INFO

Article history:

Received 22 November 2012

Received in revised form 13 March 2013

Accepted 15 March 2013

Available online 4 May 2013

Keywords:

Asphalt

LDPE

HDPE

Bimodal MWD

Grafted polyethylene

Blending

Morphology

Storage stability

Rutting

Zero shear viscosity

ABSTRACT

In this work, an analysis on chemically-grafted polyethylenes as asphalt modifiers was carried out. Results show that the softening point of asphalt increased, while the penetration degree decreased in blends prepared with grafted polyethylene. The phase distributions of micrographs from fluorescence microscopy show that non-grafted polyethylene polymers were not readily miscible with asphalt. Rheological tests indicate that most of asphalt blends exhibit improved performance at higher temperature with grafted polyethylene such as enhancing rutting resistance, flow activation energy and superior time–temperature-dependent response as compared to the reference polyethylene blends. Zero shear viscosity (ZSV) was calculated using the different models available in literature to determine its suitability in predicting the rutting behavior of asphalt binders.

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1. Introduction

The increase in road traffic during the last two decades, in addition to an insufficient degree of maintenance, has caused an accelerated deterioration of road structures in many countries [1–4]. For certain applications, such as bridges, runways and surfaces with high-traffic loading, special binders are urgently required. Polymer additives are well-known to improve the mechanical properties of asphalt. The purpose of asphalt modification (PMA) is to achieve the desired engineering properties to prevent asphalt from the main pavement defects, such as rutting at high temperatures, fati-

gue strength, and crack initiation and propagation in the low-temperature region [1,3,5–10]. Among the different polymers used in asphalt modification are polyolefins such as polyethylenes (PEs; low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high density polyethylene (HDPE)), polypropylenes (isotactic and atactic), and their copolymers [9–12]. The addition of polyolefins to asphalt is known to enhance its in-service properties, yielding improved thermo-mechanical resistance, elasticity and adhesion [13–18]. HDPE is known to exert an important change in the mechanical behavior of the asphalt. This influence was even more remarkable for HDPE-modified asphalt, because this polymer was more difficult to disperse within the asphalt than others, such as low-density polyethylene (LDPE) [17]. The intrinsic nonpolar and nonaromatic nature of the polyolefins, which are produced from olefinic monomers, reflects their low solubility with an asphalt

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dispersion medium, which is polar and aromatic [14]. Consequently, poor storage stability is found, thus making them unsuitable for use in roofing, paving, and other industrial specialty products [5]. The compatibility of constituents in the systems can be improved either by chemical anchorage/grafting of reactive monomers onto polymers or by modification of the asphalt by reactive species to form a polymer-linked asphalt system [19]. Maleic anhydride-grafted/polyethylene (MA-g-PE) has a remarkable importance for application as compatibilizer in polymer blends; it is an adhesion promoter for polymer and composites and bonding agent for polymer and metals [20–22]. It is expected that the grafted PE provides adequate storage stability to the system by forming chemical interactions between the anhydride (maleic) functionality of polymer and the functional groups of asphalt [23].

Other important topic is the adjustment of the molecular structure to improve the properties of polyethylene (PE) and its effect on asphalt. Recently, a novel PE with bimodal molecular weight distribution (BPE) composed of higher molecular weight and lower molecular weight fractions, exhibits good process-ability and excellent mechanical properties [24]. The high-molecular weight fractions endow the resin good mechanical properties, and the low-molecular weight fractions are beneficial to improve the process-ability. For the BPE products, the component homogeneity is a precondition for suitable properties, which are closely related to the miscibility of polyethylene. In turn, the rheological properties are sensitive to the miscibility of asphalt blends.

From a rheological point of view, conventional asphalt is a viscoelastic material having high temperature sensitivity, which usually behaves as a low molecular weight polymer. Moreover, it is generally believed that asphalt is also a rheologically simple material, but this is not always true for polymer-modified asphalts (PMAs) whose properties can be completely different from those of the base asphalt [25]. Due to the high temperature sensitivity, the master curves of the viscoelastic material-functions for PMA should cover a very large temperature (frequency) range in which the behavior of the sample changes from that of a Newtonian fluid to that of a glassy fragile solid.

This work aims to evaluate the thermal stability, morphology, and viscoelastic properties of asphalts modified by various types of polyethylene (PE) and their grafted PE additives for potential use in asphalt pavement. The storage stability of these blends was studied by measuring the difference in softening point and rheological parameters of the top and bottom samples. Fluorescence microscopy was employed to obtain information of morphology of blends. Rheological tests were applied to assess the viscoelastic properties of asphalt blends. The additives considered are LDPE (low density polyethylene), HDPE (high density polyethylene), BHDPE (bimodal high density polyethylene), and maleic anhydride-grafted LDPE (LDPE-g-MA), maleic anhydride-grafted HDPE (HDPE-g-MA) and maleic anhydride-grafted BHDPE (BHDPE-g-MA). The basic properties of modified binders were studied and compared with neat asphalt.

2. Viscosity modeling

Recent observations reveal that the rutting parameter $G^*/\sin \delta$ is not very effective in predicting the rutting performance of binders, especially in case of modified binders [26,27]. The plot $G^*/\sin \delta$ cannot capture the recovery of the binder due to the fact that this parameter cannot distinguish between the total energy dissipated and energy dissipated under steady flow. The zero-shear viscosity (ZSV) is a good candidate to predict the rutting behavior of asphalt binders, as an indicator of two binder characteristics, namely, the stiffness of the binder and the resistance of the binder to permanent deformation under long term loading [28]. The ZSV is thus

becoming a specification parameter to characterize the asphalt contribution to pavement rutting behavior.

Here, the ZSV of PE-modified asphalt blends was calculated using different models to evaluate the rutting potential of the binders. Additionally, an attempt was made to compare different models available in the literature to calculate the ZSV of asphalt binders. The results are described in the following sections.

2.1. ZSV determination from frequency sweep

At high temperatures, asphalt behaves as a classical Newtonian fluid. The situation is more complicated in polymer-modified asphalts [26–28]. Most polymer-modified binders behave as non-Newtonian fluids at temperatures around 60 °C. An alternative to determine the ZSV is by oscillatory shear. When the oscillation frequency tends to zero, the ZSV can be determined in accordance with the following equation :

$$\eta_0 = \frac{1}{\omega J'} = \frac{G^*}{\omega \sin \delta} \quad (1)$$

where G^* is the complex modulus and δ is the phase angle. ZSV is obtained by using frequency sweeps with periodic sine changes and low frequency loading; when the angular frequency approaches zero, the viscosity can be approximately taken as the ZSV.

2.2. Prediction of ZSV based on Carreau's model

The dynamic viscosity of PMAs can be empirically described by the Carreau model:

$$\frac{G''}{\omega} = \eta' = \frac{\eta_0}{(1 + (\lambda_c \omega)^2)^s} \quad (2)$$

where s is a parameter related to the slope of the thinning region and λ_c is a characteristic time of the material [29].

2.3. ZSV determination based on the Cross model

Asphalt behavior is generally characterized by decreasing viscosity with increasing frequency between two well defined values: the zero-shear viscosity (η_0) and the limiting viscosity (η_∞) at high frequency. Here, the Cross model is used to fit the dynamic viscosity data (Eq. (3)) to obtain η_0 . However, in PMAs at low frequencies, the Cross model gives an unrealistically high value of ZSV. It is then convenient to calculate the viscosity at a very low frequency, for example 0.001 Hz for a reference temperature [30], which is known as “low shear viscosity” (LSV). The smaller the frequency at which LSV is taken, the closer the value to the real ZSV [27,28]. The model proposes is described by the following equation:

$$\eta' = \eta'_\infty + \frac{\eta'_0 - \eta'_\infty}{1 + (K\omega)^n} \quad (3)$$

where η_0 is the ZSV; η_∞ is the limiting viscosity; ω is the frequency (rad/s), K is a material parameter with dimensions of time, and n is a dimensionless material parameter.

2.4. Maxwell model

The linear viscoelastic behavior of the asphalt and blends may be described by a generalized Maxwell model:

$$G' = G_e + \sum_{i=1}^N G_i \frac{(\omega \lambda_i)^2}{1 + (\omega \lambda_i)^2} \quad (4)$$

$$G'' = \sum_{i=1}^N G_i \frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2} \quad (5)$$

where G_e is the storage modulus.

This model considers a superposition of a series of N independent relaxation processes, each process having a relaxation time λ_i and a relaxation strength G_i . The resulting distribution or spectrum of relaxation times may be used to obtain the zero-shear-limiting viscosity of the material, η_0 , as follows:

$$\eta_0 = \sum_{i=1}^N G_i \lambda_i \quad (6)$$

where $i = 1$ corresponds to 1 mode, $i = 2$ corresponds to 2 modes, etc.

3. Experimental section

3.1. Materials

Asphalt AC-20 from PEMEX, Mexico, has the following physical properties: penetration: 68 mm (25 °C, ASTM standard D5); softening point: 50 °C (ASTM standard D36) and solubility in n-heptane (ASTM standard D2042) gives 80 wt% maltenes and 20 wt% asphaltenes.

The polymer additives used for asphalt binders included high density polyethylene (HDPE), low density polyethylene (LDPE), bimodal polyethylene (BHDPE), poly (ethylene-graft-maleic anhydride): LDPE-g-MA, HDPE-g-MA and BHDPE-g-MA. The available information for polyethylenes is described in Table 1. LDPE, HDPE and BHDPE are commercial polymers, while that grafted PE's were obtained by reactive extrusion [20–22].

3.2. Sample preparation

Asphalt was heated to 160 °C for 10 min in a small container. Polymer additives (4 wt%) were mixed with the asphalt under conventional mechanical stirring speeds (POLYMIX PX-SR 90 D) at 500 rpm as an impeller type stirrer for 10 min. Then, the asphalt blend was stirred at 180 °C for 4 h to reach homogeneity; afterwards it was cooled at room temperature. At this point, samples were taken for further analysis. After preparation, the mixtures were characterized by the classical ring and ball softening point (ASTM D36-76) and penetration (25 °C, ASTM standard D5) tests.

3.3. High-temperature storage stability

Each PMA was stored in a test tube in vertical position at 160 °C for 72 h, then cooled down to room temperature and cut horizontally into three equal sections. Samples taken from the top and bottom sections were used to evaluate the storage

stability of the PE-modified asphalts by measuring their softening points. If the difference of the softening points between the top and the bottom sections was less than 4 °C, they were considered to have good high-temperature storage stability, which is related to the miscibility of asphalt–polymer blend. G^* values at 25 °C and 60 °C at 10 rad/s of the top and bottom sections were measured in a rheometer to calculate the separation index (I_s). This parameter assesses the miscibility 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 [31]:

$$I_s = \log \frac{G_{\text{BOTTOM-PHASE}}^*}{G_{\text{TOP-PHASE}}^*} \quad (7)$$

where G^* is the complex modulus.

3.4. Fluorescence microscopy

Fluorescence microscopy tests were performed with a Carl-Zeiss KS 300 microscope at ambient temperature with a wavelength of 390–450 nm at 20 \times . Micrographs were taken with a MC100 camera equipped with an automatic counter. The polymer rich phase appears white while the asphalt rich phase is dark. The micrographs were taken according to the variables involved: mixing system, time, temperature and the properties of the materials used.

3.5. Rheological characterization

Rheological tests were made in a controlled stress AR-1000-N rheometer using a parallel-plate with diameter of 2 cm and 1.0 mm gap. The temperature range covered from 25 to 75 °C 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. To evaluate the SHRP parameter, additional measurements were made from 0.1 to 100 rad/s at 100 °C maintaining a constant strain. Comparisons were made with pure asphalt submitted to the same thermo-mechanical history of the polyethylene/asphalt blends. All tests were conducted under nitrogen environment to avoid any possible degradation.

4. Results and discussion

4.1. Penetration and softening point

With PE addition to asphalt, penetration decreased and its softening point ($T_{R\&B}$) increased (Table 2). The increase in $T_{R\&B}$ depends on the polymer structure. The softening point change slightly in asphalt modified with LDPE. The addition of maleic anhydride

Table 1
Physicochemical properties of the different polyethylene used in this study.

Material	Source	Density (g/cm ³)	Tensile strength (MPa)	Flexural modulus (ASTM-D790-10)	MFI ^a (g/10 min)	MA (%) ^b	T_m (°C) ^c
LDPE (150 E)	DOW-plastics	0.921	13	93	0.25	–	120
HDPE (Padmex 56035)	PEMEX	0.956	21.7	481	0.35	–	132
BHDPE	Alathon L-5008HP	0.949	27.4	559	0.07	–	124/129
LDPE-g-MA			12.5			0.87	119
HDPE-g-MA			20.7			0.93	137
BHDPE-g-MA			24.9			1.16	125/130

^a Melt flow index.

^b Melting temperature.

^c Maleic anhydride (wt%).

Table 2
Properties of blends, $T_{R\&B}$ and separation index (I_s) of the storage stability test. Influence of PE's on the performance of modified asphalts and comparison among the Arrhenius parameters.

Material	Penetration (dmm)	$T_{R\&B}$ (°C)	Top section (°C)	Bottom section (°C)	Difference (°C)	I_s (25 °C)	I_s (60 °C)	Temperature $G^*/\sin \delta = 1$ kPa (°C) at 10 rad/s	E_a (kJ/mol)
Asphalt	68	50	–	–	–	–	–	72	165
LDPE	62	60	104	58	46	1.974	1.897	84	175
HDPE	52	84	110	68	42	1.216	1.284	90	191
BHDPE	46	96	82	58	24	1.543	1.586	92	194
LDPE-g-MA	58	68	96	67	29	1.326	1.423	90	200
HDPE-g-MA	43	94	70	64	6	0.687	0.706	98	180
BHDPE-g-MA	52	92	112	76	36	1.473	1.503	96	198

increases the softening point and reduces the penetration of the base asphalt. The difference in properties was more pronounced when the base asphalt is modified with HDPE-g-MA. A slight discrepancy was observed for the BHDPE-g-MA polymer that can be related to the low compatibility of the grafted polymer during mixing. The improvement observed with grafted polymers is attributed to the enhanced interactions within the system [19].

4.2. Fluorescence microscopy

Fluorescence microscopy was used to evaluate the compatibility between PE's and asphalt. After mixing with the base asphalt, markedly biphasic materials were obtained in all blends. Morphology of asphalt/LDPE is shown in Fig. 1a. A fluorescent, polymer-based phase is dispersed in a dark asphalt phase in the form of almost spherical particles. Both the facts that the dispersed phase is in spherical shape and that no linkages are visible between particles indicate that the asphalt and polymer are strongly immiscible and very low interfacial adhesion exists between the two phases. Asphalt/LDPE-g-MA shows smaller sphere sizes as expected, resulting from enhanced polarity of the grafted polymer and improved compatibility (Fig. 1b). MA-grafted polyethylene may strongly interact with carboxylic groups present in asphalt molecules. They may

even react and prevent phase separation with resulting improved storage stability. The high polarity of the polymer enhances its solubility with asphalt. In the asphalt/HDPE blend the polymer-rich phase is limited in extent, the droplets being barely discernible (Fig. 1c). In the asphalt/HDPE-g-MA blend, the polymer-rich phase covers all the area (Fig. 1d). The dimensions of the particles are smaller than those reported in asphalt/LDPE. This is an indication that some enhancement in compatibility was obtained, even with a significant effect on $T_{R\&B}$ and penetration.

Asphalt/BHDPE shows that the dispersed phase is composed of spherical particles repelling the asphalt matrix (Fig. 1e). The state of dispersion of asphalt/BHDPE-g-MA is shown in Fig. 1f. Despite some irregularities in the shapes of the particles, small and lamellar structures coexist. The relative high number of functional groups present in BHDPE-g-MA (1.16 wt%) could favor gel formation. Contrary to enhanced interaction within the system by the grafted polymer, the system shows bad dispersion of polymer particles.

The micrographs clearly show that the viscosity of the polymer is important for dispersion in asphalt. Due to the molecular weight dependence, dispersing a polymer with a melt flow index less than 1 in asphalt is very difficult, and resulting blends will not have very good engineering properties [12].

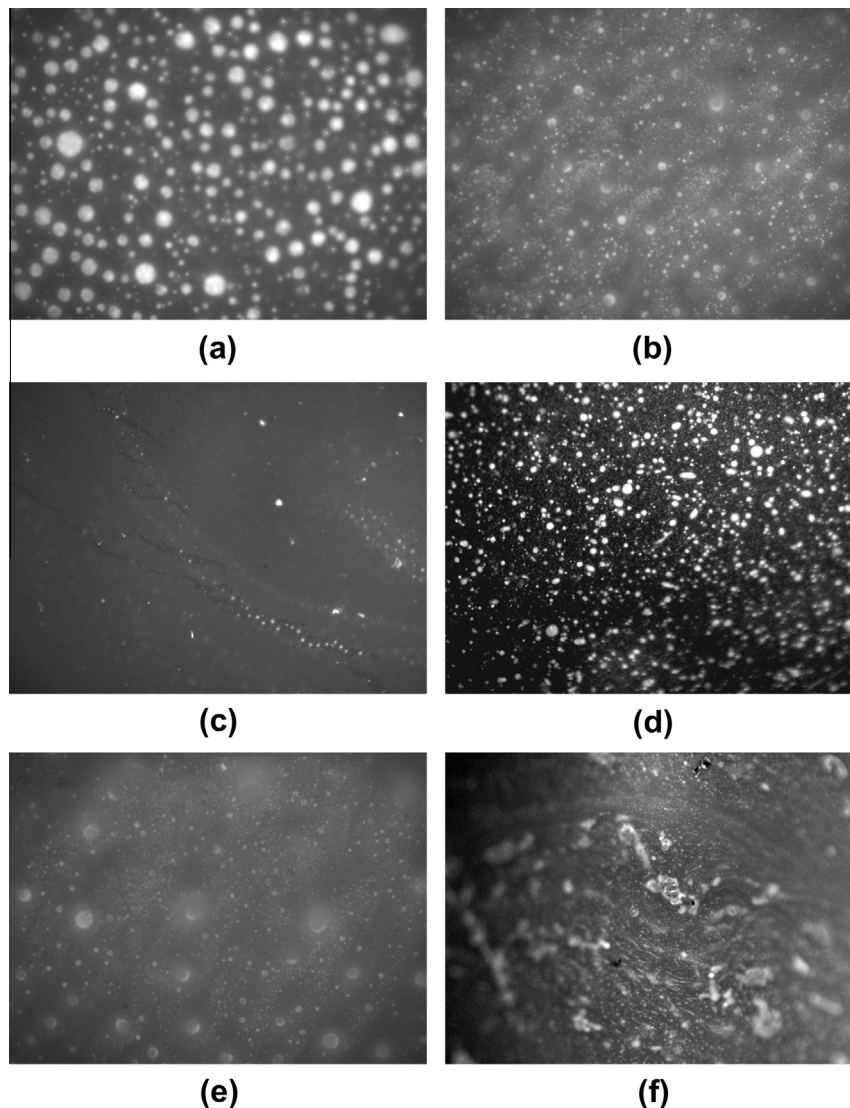


Fig. 1. Fluorescence photomicrographs of (a) asphalt/LDPE, (b) asphalt/LDPE-g-MA, (c) asphalt/HDPE, (d) asphalt/HDPE-g-MA, (e) asphalt/BHDPE and (f) asphalt/BHDPE-g-MA.

4.3. Storage stability test

Phase separation is related to the storage stability of the asphalt blends; the difference between softening point of the top portion and softening point of bottom portion shall not differ by more than 4 °C. As summarized in Table 2, significant differences in $T_{R&B}$ occur in asphalt blends, except HDPE-g-MA. Grafted-polymer blends exhibit differences in softening point of the top and bottom portions between 6 and 36 °C compared with 24–46 °C for the base asphalt blend. This would suggest a substantial phase separation between the polymer and the asphalt. The presence of maleic anhydride contributes substantially in the improvement of storage stability of the resulting system, but not for Asphalt/BHPE-g-MA, which could present gel formation. For the HDPE-g-MA-based asphalt blend, the difference in the softening point of its top and bottom portions was further reduced to 6 °C and 29 °C for LDPE-g-MA.

The storage period coincides with a curing time during which functional groups of the polymer and asphalt are supposed to react. Significant storage problems can be related to gel formation if the polymer is not added properly. From an experimental point of view, it is quite simple to identify the gel point because it can be associated with the solubility limit. This could occur in Asphalt/BHPE-g-MA blend (Fig. 1f).

Values of separation index I_s are shown in Table 2, revealing that the blends prepared with the grafted PEs are more stable (lower I_s values) than those prepared with the partner PEs. LDPE shows the highest degree of phase separation, opposite to HDPE-g-MA. Also, BHDPE shows better storage stability than LDPE. BHDPE-g-MA is more rigid as it contains larger MA amounts than LDPE-g-MA and HDPE-g-MA (see Table 1), being less compatible with asphalt. Here is supposed that functional MA groups can react with carboxylic groups present in the asphaltenes. Then, the material is able to enhance their rheo-mechanical properties after the mixing stage, and no phase separation is expected to occur [23]. This effect can be observed in the contrast between the asphalt/HDPE and asphalt/HDPE-g-MA systems.

4.4. Rheological analysis

Dynamic viscosity (η') at 75 °C as a function of frequency (ω) is shown in Fig. 2. The base asphalt shows typical Newtonian behavior over almost the whole frequency range. Addition of 4% of a polymer leads to increases in η' of blends at low frequency, depending on the type of the polymer. HDPE-g-MA shows the highest rise in viscosity at low frequency. HDPE-modified asphalt displayed the same viscosity as BHDPE-g-MA at high frequency.

According to the SHRP criterion, the point when $|G^*|/\sin \delta$ attains 1 kPa at 10 rad/s defines the maximum temperature for a good viscoelastic performance of the original binder once in the pavement. To define the maximum pavement temperature, the analysis related to aging of the RTFOT asphalt binder is needed. Values of these points are shown in Table 2 for asphalt and PE's blends, revealing that polymer modification improves the service temperature according to the SHRP specification. BHDPE-g-MA and HDPE-g-MA attain the highest service temperature (98 and 100 °C, respectively) at $|G^*|/\sin \delta = 1$ kPa. Higher values of $|G^*|/\sin \delta$ are expected to reveal high resistance to permanent deformation.

The temperature dependence of the viscoelastic behavior for asphalt, as indicated by the shift factors determined from construction of the master curves, can be represented by the Arrhenius equation [25]:

$$a(T) = \exp \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (8)$$

where $a(T)$ is the shift factor at a temperature T relative to the reference temperature T_0 ; E_a is the activation energy and $R = 8.314$ J/

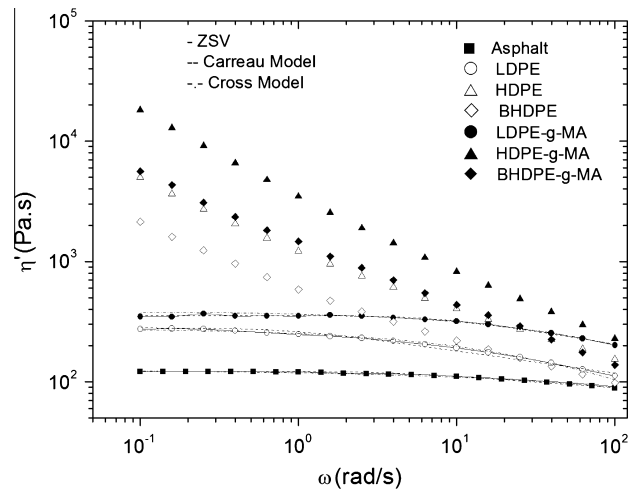


Fig. 2. Dynamic viscosity $\eta'(\omega)$ of asphalt and polymer-modified asphalts at 75 °C, including predictions of viscosity models.

mol K. From experimentally determined values of the shift factor, we find that the Arrhenius equation described the temperature dependence of shift factor very well. Here the reference temperature was 25 °C. E_a values for each material are shown in Table 2. The activation energy ranges from around 165 to 200 kJ/mol, in agreement with other works [25], where the activation energy was found around 170–200 kJ/mol. E_a increases with LDPE-g-MA as compared to LDPE, while both BHDPE and BHDPE-g-MA show similar behavior. The activation energy decreases in HDPE-g-MA-modified asphalt as compared with that of HDPE. Low-activation energies are preferred since the change of viscosity is small with changing temperature. This behavior is presumably due to the rigid nature of the HDPE (high crystalline polymer) and to the MA content in polymer, which increases cross-linking of the polymer/asphalt molecules and hence the elasticity of PMA. This polymer modification should be dominated by chemical interactions.

Elastic modulus (G') as a function of reduced frequency (ω^*a_T) obtained from temperature-frequency sweeps is shown in Fig. 3a at the reference temperature of 25 °C. Time-temperature superposition holds for asphalt, asphalt/LDPE and asphalt/LDPE-g-MA blends. The other blends show a non-uniform dependence on temperature that may be considered as a thermodynamically complex materials.

At low frequency, the HDPE-g-MA blend shows the highest G' . In general, polymer-grafted systems display higher elasticity in comparison to the non-grafted moieties. In the high frequency range, the effect of polymer type is not substantial, whereas the low frequency range (long time behavior) reflects the high temperature behavior of PMA. This suggests that HDPE-g-MA would show large modulus at high temperature, which is preferred for hot climates. Hence, HDPE-g-MA is expected to have the best high-temperature resistance to permanent deformations (rutting). These results are in agreement with previous findings observed in Fig. 2 (dynamic viscosity at 75 °C), in which the dynamic viscosity of the asphalt/HDPE-g-MA blend is the largest. LDPE displayed the lowest modulus among the PMA's.

At low frequency, the slopes of base asphalt, LDPE and LDPE-g-MA blends are 1.8, 0.7 and 0.6, respectively. The elastic properties of HDPE, HDPE-g-MA, BHDPE and BHDPE-g-MA are expected to be less temperature-sensitive compared to that of LDPE. These binders show a slight plateau region, with values of the storage modulus higher than the loss modulus. The plateau in the curve could be attributed to the possible formation of molecular entanglements among the macromolecular components.

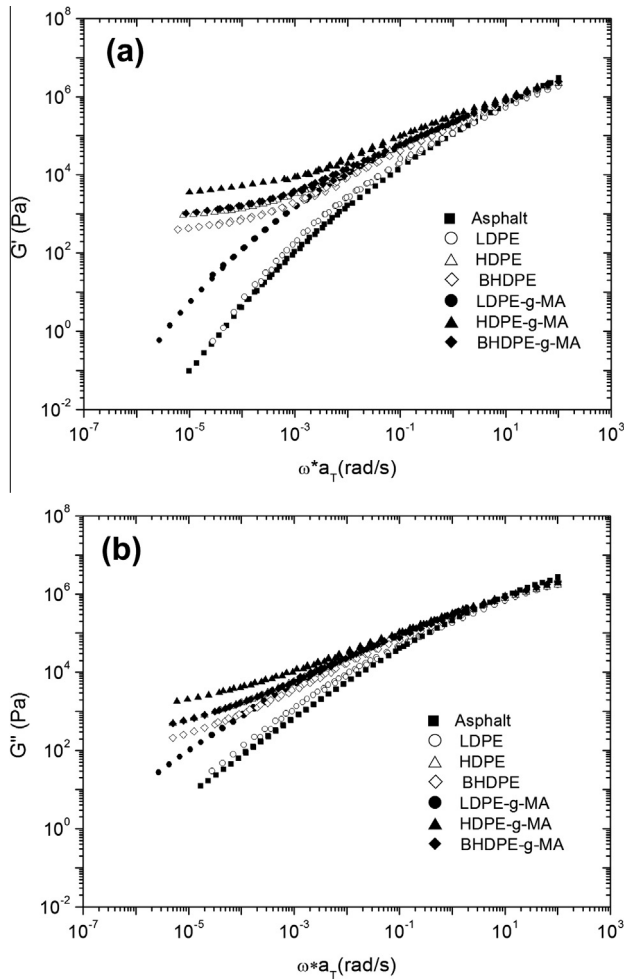


Fig. 3. Master curves for the storage modulus G' (a), and loss modulus G'' (b), obtained by using frequency-temperature superposition at a reference temperature of $T_{ref} = 25^\circ\text{C}$. $a(T)$ is the shift factor.

At high frequency, the behavior of the loss modulus (G'') of all referred polymers approaches similar values (Fig. 3b). Therefore, the high-temperature performance is the important attribute to select the polymer type. This suggests possible applications under hot climates where temperature sensitivity is important. In general, the storage and loss modulus of the grafted PE's blends were significantly higher than the base PE's at temperatures from 75°C to 40°C .

As previously reported, asphalt thermo-rheological simplicity is a standing controversial issue, particularly in polymer-modified asphalts [31]. A very simple method has been proposed to evaluate material thermo-rheological simplicity through the Black diagrams. If the time-temperature superposition principle holds for a given material, the phase angle δ plotted versus the corresponding values of the complex modulus $|G^*|$ obtained at different temperatures should superpose on a single curve. In contrast, if the curves obtained at different temperatures do not superpose and, furthermore, they are not parallel, the material shows a non-uniform dependence on temperature and can be considered as a thermo-rheological complex material. Black diagrams of the binders studied are observed in Fig. 4. For the binder containing LDPE and LDPE-g-MA, a tendency toward viscous behavior appears at high temperatures, with δ values close to 90° . At low temperatures, a tendency toward the glassy region, with values of the complex modulus close to $\sim 1 \times 10^7$ Pa, can be observed for all the binders.

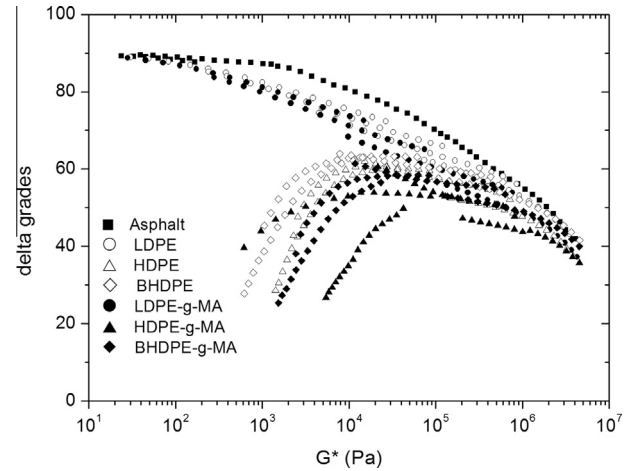


Fig. 4. Black diagrams of asphalt and blends.

Curves of binders containing LDPE and LDPE-g-MA can be superposed to obtain a master frequency curve, which is typical of thermo-rheological simple materials. In contrast, binders containing HDPE, HDPE-g-MA, BHDPE and BHDPE-g-MA do not show a tendency toward viscous behavior at high temperatures in their Black diagrams, displaying an apparent thermo-rheological complex behavior. Furthermore, an important change in the mechanical behavior of the binders is observed at high temperatures. At 75°C , δ values as low as 20° are found for these binders. Thus, the addition of grafted HDPE or BHDPE to asphalt enhances the elastic properties of the binders, yielding polymer-modified asphalts with improved resistance to permanent deformation at high temperatures.

4.5. Viscosity modeling

4.5.1. ZSV determination from frequency sweeps

Frequency sweeps were done in the range from 0.1 to 100 rad/s at 75°C for the unmodified asphalts and blends (Fig. 2). Base asphalt, asphalt/LDPE and asphalt/LDPE-g-MA show typical Newtonian behavior over almost the entire frequency range, but the other binders display non-Newtonian behavior, which is more pronounced in HDPE, BHDPE, HDPE-g-MA and BHDPE-g-MA. At 0.1 rad/s, the dynamic viscosity (η') of the HDPE-g-MA modified asphalt is twofold higher than that of the base asphalt. The ZSVs of the asphalt, LDPE and LDPE-g-MA binders are calculated from this frequency sweep by means of the models mentioned above (Section 2).

4.5.2. Prediction of ZSV based on Carreau's model

Excellent fit of the Carreau model was observed for asphalt, LDPE and LDPE-g-MA blends (Fig. 2). The calculated parameters, at 75°C , are presented in Table 3. At the in-service temperatures of the asphalt (always below 70°C) the viscosity of the binder is high enough to avoid permanent deformation (rutting). Strong changes in rutting resistance appear when the asphalt binder presents LSV values lower than 500 Pa s [30]. Morea et al. found that the asphalt blend shows drastic changes in the rutting resistance when the original asphalt binder achieved LSV values lower than 500 Pa s throughout the temperature range and in all asphalt systems studied. For these asphalt mixtures the viscosity signals a limit to the partial contribution of the asphalt binder to the rutting resistance. Based on this viscosity level, maximum temperatures for each asphalt binder (below which the asphalt mixture rutting resistance is acceptable) may be defined.

Table 3
Parameters of Carreau model Eq. (2), Cross model Eq. (3) and Maxwell model Eq. (6) at $T = 75^\circ\text{C}$.

Material	Carreau model			Cross model			Maxwell model	
	η_0 (Pa s)	λ_c (s)	s	η_0 (Pa s)	K (s)	n	η_0 (Pa s)	N
Asphalt	122	0.248	0.05	125	0.0012	0.44	120	5
LDPE	355	0.128	0.11	386	0.0083	0.6	300	3
LDPE-g-MA	280	1.1	0.09	277	0.023	0.61	280	4

In addition, the slope (s) does not show clear tendency between asphalt, LDPE and LDPE-g-MA binders, wherein the relaxation time λ_c is relatively large for the LDPE-g-MA blend.

4.5.3. ZSV determination based on the Cross model

Complex viscosity data can be fitted with Eq. (5) with $\eta_\infty = 0$ to determine the ZSV over the entire frequency range. At low frequencies, the viscosity tends to a plateau; a trend that is clearly visible for conventional asphalts, LDPE and LDPE-g-MA blends but not for the other blends. At low frequencies, the viscosity of the blends (HDPE, BHDPE, HDPE-g-MA and BHDPE-g-MA) does not present asymptotic behavior and the fit with the Cross model cannot be applied (see Fig. 2).

The parameter n is a measure of the width of the relaxation spectrum and, in the case of polymers, is related to the span of their molecular weight distribution. For a single relaxation time, the theoretical value of n is unity [32]. For the materials tested, the values found for n ranged from 0.44 to 0.61. Parameter K and n may characterize the pseudo-plasticity of these non-Newtonian liquids. In particular, parameter K is proportional to the ZSV zero-shear viscosity since is related to the consistency of the system, while parameter n is related to the shear susceptibility. In this regard, the Carreau's model forces the formation of a plateau at low frequencies, predicting smaller ZSVs compared to the predicted by the Cross' model (Table 3).

4.5.4. Maxwell model

The Maxwell model is used to fit the dynamic viscosity data (Eqs. (4)–(6)) at 75°C . The ZSV is estimated through (Eq. (6)) with five modes ($N = 5$) for asphalt (see Table 3). η_0 undergoes an exponential increase in HDPE, HDPE-g-MA, BHDPE and BHDPE-g-MA. Values of the dynamic viscosity (η') obtained from Eq. (5) for asphalt, LDPE and LDPE blends, which present Newtonian behavior, agree with those of the Carreau or Cross models.

These results confirm that the rutting behavior varies with the type of asphalt binder at a given temperature. The relationship between rutting performance, rheological properties (ZSV) and temperature is of interest in practice. According to the binder properties, some asphalt mixtures may not present an acceptable rutting behavior at high temperatures (e.g. LDPE and LDPE-g-MA); but they can behave efficiently at lower temperatures.

5. Conclusions

Different polyethylene and grafted polyethylene-based polymers were used to modify asphalt. Penetration at 25°C decreases in the blends, which allows improved shear resistance from medium to high temperatures. Softening points tend to increase with the addition of polymers, which indicates improvements in resistance to deformation.

As expected, the polymer-modified asphalts have biphasic structure. Florescence micrographs confirm that the grafted PE in asphalt blends results in better dispersion of the discrete polymer phase in the asphalt phase than the non-grafted PE.

Stability tests reveal that blends containing PE are susceptible of phase separation after 72 h of storage at 160°C . Phase separa-

tion is more severe in the case of blends of non-grafted PE. Very good stability results are obtained for blends containing grafted PE, especially HDPE-g-MA blend, since no phase separation is detected after 3 days. Grafted polymers allow for an improvement in the miscibility between polymer and asphalt.

The effect of the polymer is more apparent at high temperatures (75°C), since the modification exerted by the HDPE, BHDPE, HDPE-g-MA and BHDPE-g-MA enhances the elastic properties of the binder at high temperatures, in the region where permanent deformation can affect the pavement service. Thus, strong interactions are evidenced by the apparition of a plateau region at low frequencies in the storage modulus.

The addition of LDPE and LDPE-g-MA to asphalt is sufficient to modify the mechanical behavior of the asphalt, as revealed by the SHRP parameter. These results allow knowing the reduction of rutting at high temperatures.

The grafted high density polyethylene (HDPE-g-MA) blend shows a larger compatibility with asphalt and leads to enhanced and better mechanical properties when compared with properties obtained in the other blends.

Frequency sweeps to estimate the ZSV in asphalts and blends were analyzed in this work. ZSV values calculated from different models are similar, especially in systems with Newtonian behavior at high temperature (asphalt, LDPE and LDPE-g-MA blends). The analysis undertaken here concludes that the suitability of the Carreau, Cross and multi-mode Maxwell models to estimate the ZSV of modified binders is questionable, since the curves do not reach a plateau at low frequencies. This may reflect the presence of yield stresses, which can be identified in simple shear tests.

Acknowledgments

The authors wish to thank the collaboration of Mr. S. López-Morales and Alexa Carranza in the sample-characterization and experimental work respectively.

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