High Temperature Stability of Different Polymer-Modified Bitumens: A Rheological Evaluation

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ABSTRACT: Polymer-modified binders are increasingly used by the pavement industry. In practice, the bituminous binders are stored at high temperatures previous to its application on the road. The instability problems of the bitumen due to the polymer-rich phase separation may affect the final properties of the pavement. Most polymers tend to be insoluble, to some degree, in the bitumen matrix, and phase separation may result. Chemical compatibility between the polymer additive and the bitumen, and processing conditions, are crucial to obtain suitable properties of the polymer-modified bitumens. In this work, different polymer-modified binders were manufactured by using a high-shear mixing device. Once a good mechanical dispersion of the poly-

mer in the bitumen matrix was achieved, the binders were stored in tubes at high temperatures. During the storage, the unstable polymer-rich phase segregates and starts to ascend up to the surface. The progression of the polymer phase separation was followed through the evolution of the linear viscoelastic and the viscous properties of the samples collected, after different storage periods, from the top part of the storage tube. From the experimental results obtained, we may conclude that the use of a reactive polymer as additive is a promising alternative to obtain more stable binders. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1166–1174, 2007

Key words: bitumen; polymer; rheology; storage stability

INTRODUCTION

Bitumen is widely used as a binder for road-paving applications.[1] Pavement distresses, such as rutting at high temperatures and cracking in the low temperature region, can be reduced by using modified binders. The addition of polymers to bitumen is known to impart enhanced service properties, such as improved thermomechanical resistance, elasticity, and adhesivity.[2] Styrene–butadiene–styrene copolymer (SBS), ethylene–vinyl acetate (EVA), and high-density polyethylene (HDPE), among others, are currently being used as polymer modifiers.[3–9]

One of the main problems for the industrial application of polymer-modified binders is the potential phase separation that may occur after the preparation of the polymer/bitumen blend.[10,11] Because of the lack of compatibility of some polymers with bitumen, once the polymer is dispersed into the bitumen phase, the binder obtained can undergo phase separation, at a macroscopic scale, when the binder is stored at high temperatures. In practice, once the binder is prepared, it is

stored, in a liquid state, at the paving application temperature. Hence, a certain degree of storage stability is required for bituminous binders.[12]

The difference of density between both, polymer and bitumen, plays an important role in the stability of binders. This density difference may cause the creaming of the polymer particles, and the associated ulterior phase separation.[10] Thus, it is important to achieve, by means of an effective mixing process, a small particle size, so that the Brownian motion of the polymer particles is able to compensate the gravitational separation motion, rendering polymer particles stabilized within the bituminous matrix.[10]

Another important factor against polymer creaming is the continuous phase viscosity. A high viscosity would reduce the ascending particle motion (governed by the Stokes law). The viscosity of a 60/70 penetration grade bitumen, at 180°C, is ~ 0.1 Pa s.[13] It is demonstrated that the stability of polymer-modified bitumen depends not only on the difference in density and viscosity between bitumen and polymer but also on bitumen structure[14] and bitumen/polymer molecular interactions.[15] Compatibility is most often defined by the extent of segregation of the bitumen and polymer during hot storage (140–180°C).[15,16]

The mechanism of phase separation is related to pure creaming, but, in the case of polymer/bitumen blends, creaming is usually preceded by coalescence and flocculation phenomena.[10] Consequently, poly-

mer stabilization may not always be achieved by mechanical dispersion of the modifier,[12] swollen by compatible components from the maltene fraction of the bitumen.[17] In this sense, different authors claim to have found ways of stabilizing unstable polymers within the matrix by using polymer vulcanization with sulfur[18–20] or adding phosphoric acid.[14]

On the other hand, the use of copolymers, in addition to the traditional ones (i.e., HDPE, LDPE, etc) to obtain steric or, even, chemical stabilization of a more insoluble base polymer into bitumen is considered to be effective in such operations.[10,21,22]

More recently, the use of reactive polymers as bitumen additives has been proposed.[23] Chemical stabilization of reactive polymers within the bitumen, such as epoxy-functionalized polymers or EGA (ethylene-glycidil methacrylate-acrylate), occurs when polymer chains interact, yielding the formation of chemical crosslinks.

In a previous study,[24] the authors studied the optimization of the manufacturing process of different polymer-modified bitumens (HDPE, LDPE, SBS, and EPDM). It was concluded that a high energy mixing process is always necessary to stabilize and disperse a polymer in polymer-modified binders. This influence was even more remarkable for HDPE-modified bitumen.

The main objective of this research was to study the stability against phase separation of different polymer-modified binders at high temperature. With this aim, polymer-modified binders were stored at 180°C. The progression of the polymer phase separation was followed through the evolution of the linear viscoelastic and the viscous properties of the samples, at 75°C, collected after different storage periods. At 75°C, binders soften sufficiently, and hence, polymer relaxation processes are the main contribution to the bulk rheological behavior of the complex mixture.[25]

EXPERIMENTAL

Two 60/70 penetration grade bitumens provided by REPSOL-YPF (Spain) and CEPSA (Spain), with an asphaltene content of 24.62 and 19.34 wt % respectively, were used as base binders. The softening R and B point is 54 and 50°C, respectively. The specific gravity of both bitumens is 1.00 (25°C/25°C) (ASTM D70). A styrene–butadiene–styrene three-block copolymer Kraton D-1101 (31 wt % styrene content; density 0.880 g/cm^3) from Shell (U.K.), a high density polyethylene HDPE 6006-L (density 0.956 g/cm^3) from REPSOL-YPF (Spain), a low density polyethylene LDPE 302R (density 0.924 g/cm^3) from Dow Chemicals (Belgium), and an ethylene–propylene–diene terpolymer EPDM EGP 8454 (ethylene/propylene/ethyldiene norbornene ratio 54/42/4; density 0.860 g/cm^3) from BAYER

AG (Germany) were employed as binder modifying agents. A reactive terpolymer EGA (ethyl-glycidil metha-acrylate (GMA) - butyl-acrylate), with a trade name of Elvaloy RE (density 0.940 g/cm^3 and GMA content 40 wt %) from DuPont (USA) was used as a reference reactive polymer.

Binders containing 5% polymer (EPDM, PE, EPDM/PE, SBS), or 2% in the case of EGA, were prepared using a high shear mixing device, at a pilot plant scale.

In addition, blends of any of polyethylene (high and low density) with EPDM were prepared, in the molten state, using a twin-screw extruder Collin ZK25 at 160°C. Blend compositions 25/75, 50/50, and 75/25 (EPDM/PE) were chosen to illustrate the effectiveness of such modification. Afterwards, binders containing 5% of these EPDM/PE blends were prepared.

The pilot plant device integrated a rotor-stator mixer SD41 SUPER-DISPAX from IKA (Germany) coupled with a storage/feed tank. Bitumen/polymer blends were manufactured at 8200 rpm and 180°C.

The storage stability tests were carried out by pouring the hot bituminous blend from the mixing device into 43-mm diameter and 300-mm length tubes, to avoid potential wall effects. Then, the tubes were stored at 180°C, temperature at which bitumen was mixed with the polymer. Samples were taken out at different storage times from the top part of the tube.

The rheological study was performed using a CS-rheometer, RheoStress RS150 from Haake Gbr. (Germany), and a CR-rheometer, ARES from Rheometric Scientific (USA). Frequency sweep tests in oscillatory shear and viscous flow measurements were performed. Frequency sweep runs were applied over a range from 0.01 to 100 rad/s under isothermal conditions, using a serrated plate-and-plate geometry. Frequency sweep tests were performed within the linear viscoelastic range of the materials. Viscous flow measurements were performed on both a controlled-strain Rheometrics ARES rheometer and a controlled-stress Haake Rheostress RS150 rheometer, using serrated plate-and-plate geometries. A good concordance between the experimental results obtained with both rheometers was found.

Optical microscopy was used to study the morphology of polymer-modified bitumens. A drop of a heated sample was placed between microscope slides. Samples were observed, at room temperature, in an optical microscope IX70 from Olympus (Japan).

RESULTS AND DISCUSSION

SBS-modified bitumen

Styrene–butadiene–styrene copolymers are widely used as bitumen modifiers for paving applications. For this reason, SBS copolymer was used, in this
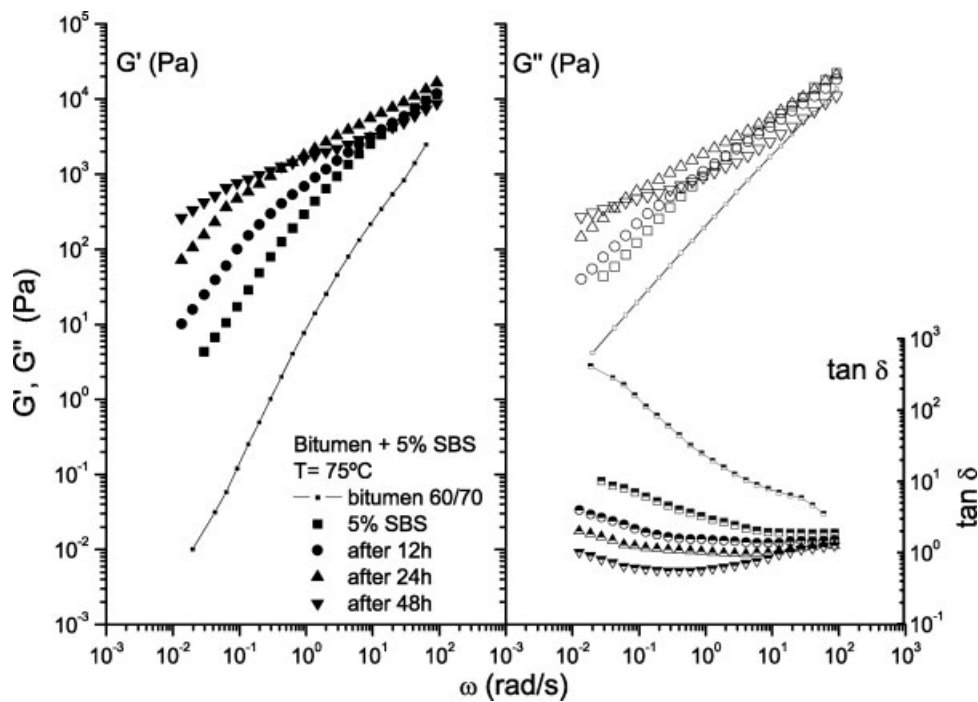
Figure 1 Frequency dependence of the storage and loss moduli, at 75°C, for unmodified bitumen, a SBS-modified binder, and its associated polymer-rich phases after 12, 24, and 48 h of storage. Inset: Frequency dependence of the loss tangent, at 75°C, for the same systems.

study, as a reference additive for polymer-modified bitumen.

However, as can be observed in Figure 1, this binder shows significant polymer-rich-phase separation under severe temperature storage conditions. To perform this study, samples from the top part of the tube (polymer-rich phase) were taken after 12, 24, and 48 h of storage. Thus, Figure 1 shows the evolution of the storage and loss moduli with frequency, at 75°C, for the 5% SBS-modified binder as a function of storage time, as well as for the unmodified bitumen. As can be observed, the behavior of the bitumen itself is viscoelastic.[26] The values of both moduli generally increase with the storage time, except for the sample taken after 48 h of storage. This sample shows a quite different behavior, with values of the storage modulus higher than the loss modulus, at intermediate frequencies, as a result of the development of an apparent plateau region in the mechanical spectrum of this sample. This effect can also be observed in the evolution of the loss tangent with frequency, in the inset of Figure 1. A decrease in the loss tangent values with the storage time is observed. The sample collected after 48 h shows values of the loss tangent lower than one, within almost the entire range of frequencies studied, and a clear minimum at intermediate shear rates related to the development of the above-mentioned plateau region. This behavior is due to the increasing polymer content in the top portion of the tube, as the stability test proceeds.

The viscous flow properties, at 75°C, of the SBS-modified bitumen samples after different storage time are represented in Figure 2. As can be observed, the apparent viscosity significantly increases with the storage time, above all at low and intermediate shear rates. The behavior found is typical of a structural fluid. That is, all the samples show a limiting viscosity at low shear rate, and a monotonic decrease in viscos-
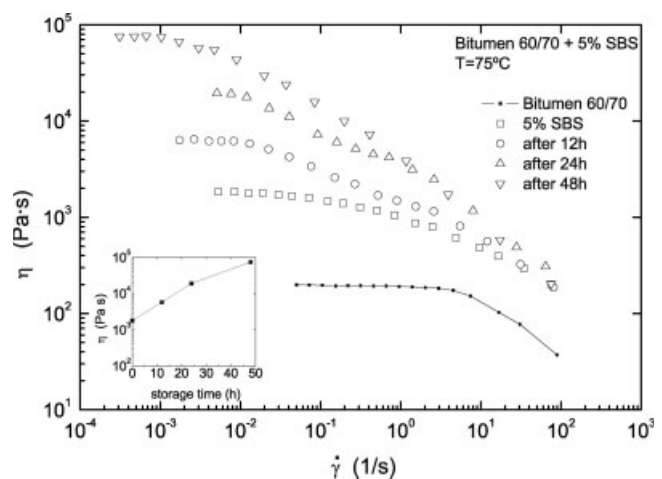

Figure 2 Viscous flow behavior, at 75°C, for modified bitumen, SBS-modified binder, and its associated polymer-rich phases after 12, 24, and 48 h of storage. Inset: Evolution of the zero-shear-rate-limiting viscosity with the storage time for the same systems.
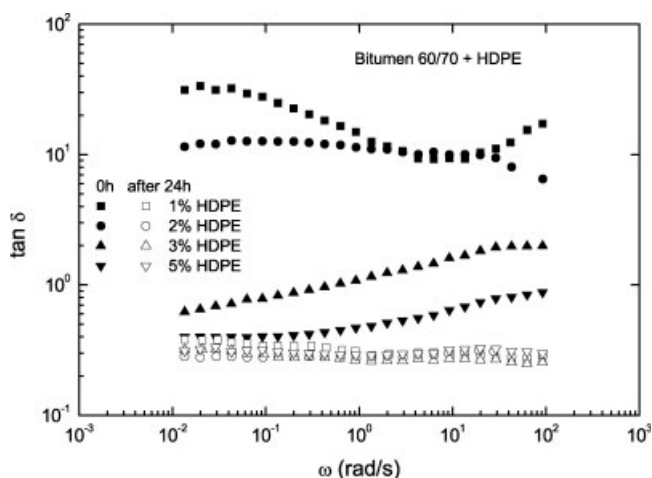
Figure 3 Frequency dependence of the loss tangent, at 75°C, for different HDPE-modified binders and their associated polymer-rich phases after 24 h of storage.

ity after a critical shear rate value. This critical shear rate for the onset of a shear-thinning behavior appears at lower shear rate values as the storage time of the sample increases, pointing out that the polymer-rich phase is increasingly more sensitive to shear.

In the inset of Figure 2, the evolution of the zero-shear-rate-limiting viscosity with the elapsed storage time is represented. As may be seen, the progressive increase in the viscosity values decreases after 24 h. A significant amount of the polymer is, thus, separated by this storage time. Hence, under high temperature conditions, the binder modified with SBS shows an evident phase separation during the storage at 180°C.

HDPE-modified bitumen

To study the influence of polymer concentration on the stability of HDPE-modified bitumen, different binders containing up to 5% HDPE were manufactured. Figure 3 shows the frequency dependence of the loss tangent for different HDPE-modified binders and their associated polymer-rich phases obtained after 24 h of storage at 180°C. As can be observed, an increase in polymer concentration produces a significant decrease in the values of the loss tangent for the reference systems. Thus, the minimum values correspond to the sample containing 5% HDPE, which are of the same order, in the low frequency region, of those found with polymer-rich phase samples of the different HDPE-modified binders studied. These polymer-rich phases always show a similar mechanical behavior, with values of the loss tangent lower than one in the whole frequency range studied. From the experimental results obtained, it can be deduced that most of the polymer creams during the stability experiment. The extent of this segregation is independent of the quantity of polymer (up to a 5% w/w).

The segregated upper phase consists of polymer swollen by some light components of the bitumen maltenic fraction,[27] by means of a physical distillation process.[28,29] The degree of swelling of the polymer by the light components of the bitumen can be assessed by means of DSC measurements. The degree of swelling is proportional to the extent of the thermal transition shift, down to lower temperatures, in relation to the melting point of the polyethylene, due to the plasticizing effect of the bitumen on the polymer.[30] In the case of HDPE-modified bitumen, a shift of about −10°C, independent of polymer concentration in the bitumen, has been found.[30]

On the other hand, the viscous flow behavior of the above-mentioned samples is displayed in Figure 4. As can be observed, there is a dramatic increase in viscosity after 24 h storage for all the HDPE concentrations studied. Furthermore, these polymer-rich phases reach similar values of low-shear-rate viscosity, except for the case of the modified binder containing 1% HDPE, which shows lower values of viscosity, probably due to the lesser quantity of polymer at the top of the tube, after the separation.

Consequently, the instability of the HDPE-modified binders is apparent. This instability may also be deduced from optical observations of the binders prior and after storage. Thus, Figure 5 displays the morphologies of two binders modified with 1% (A) and 2% (B) of HDPE, and their associated separated polymer phases, after 24 h of storage (C and D, respectively). As can be observed, after the stability test, the polymer appears as the continuous phase at the top part of the tube, swollen by the miscible components of bitumen.

Likewise, the morphology of this HDPE-modified binders can shed a light on why the modification exerted by HDPE is better than that by other polymers
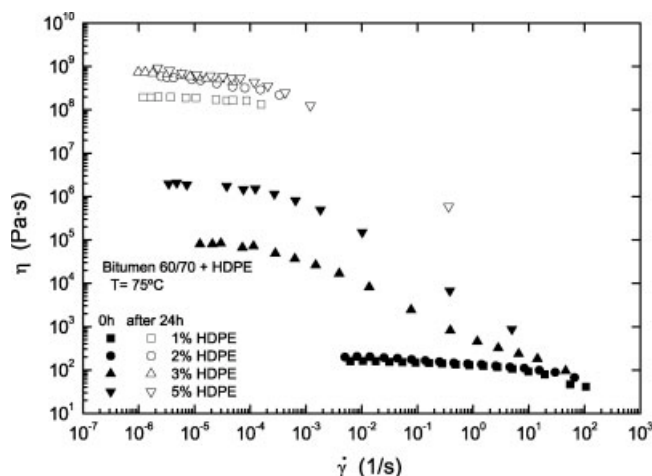

Figure 4 Viscous flow behavior, at 75°C, for different HDPE-modified binders and their associated polymer-rich phases after 24 h of storage.
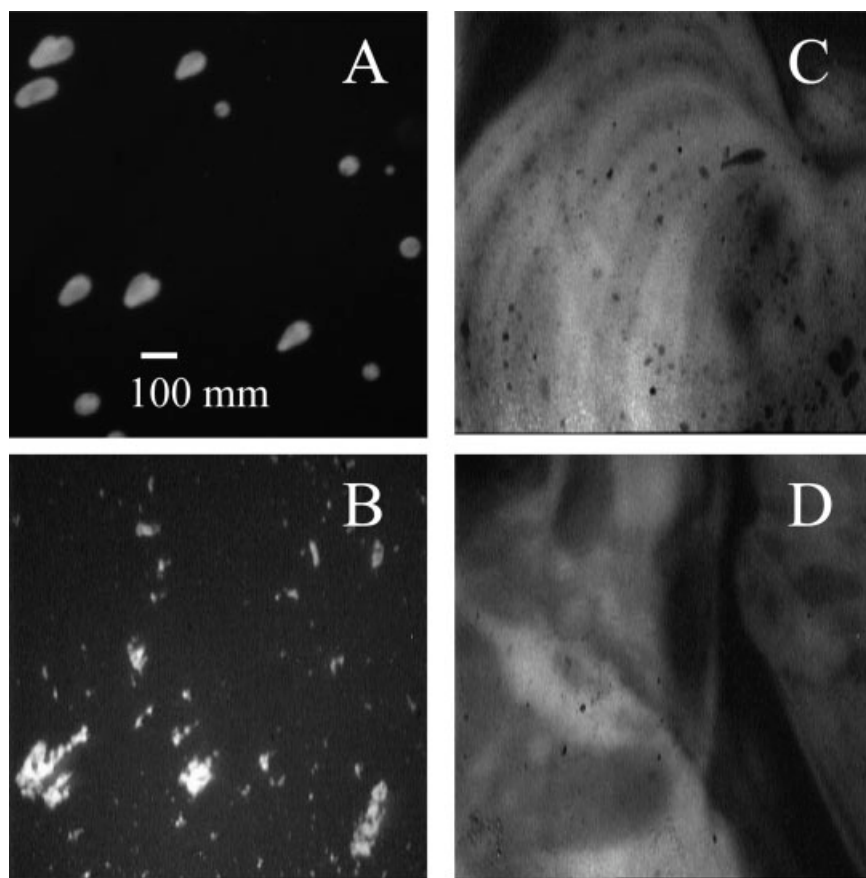
Figure 5 Microscopic observations of HDPE-modified binders (A: 1% HDPE; B: 2% HDPE), and their associated polymer-rich phases after 24 h of storage: (C: 1% HDPE; D: 2% HDPE).

tested, from the mechanical point of view. In the case of 3 and 5% HDPE-modified binders an interconnected polymer phase, including bitumen phase within, forming a three dimensional sponge-like structure is attained.[30,31] This morphology would give, as a result, a structured material, due to the interconnection of the dispersed phase. As can be seen in Figure 3, the modification exerted by 3 and 5% of HDPE enhances the elastic properties of the binder at high temperatures, in the region where permanent deformation can affect the pavement service. However, although suitable bitumen mechanical properties have been obtained by HDPE modification, such binders may not be relevant for the pavement application, since phase separation may occur during the application of the binder on the road. An effective way of stabilizing HDPE within the bitumen is still to be developed.[27]

HDPE/EPDM-modified bitumen

Taking into account the previous results, blends of EPDM copolymer and HDPE were studied to improve the stability against phase separation of HDPE-bitumen. These blends were prepared by using a screw extruder and added to bitumen (60/70 pen grade) by

using a high shear device. Polymer-rich phase separation is usually preceded by droplet coalescence.[10,27] The stabilization of HDPE into the bituminous matrix by means of a copolymer, which acts as a steric stabilizer, may defer the phase separation, since the copolymer would hinder the coalescence of the polyethylene drops, as an emulsion stabilizer.[10,21] This third component (block copolymer) can promote the interactions between the dispersed phase (polyethylene) and the matrix (bitumen) by positioning itself across the interface. The precise mechanism of coalescence suppression has not yet been fully elucidated.[32] One hypothesis to explain this phenomenon is the steric hindrance, produced by the barrier provided by the compatibilizer.[33]

With this aim, the frequency dependence of the loss tangent, at 75°C, for different HDPE/EPDM-modified binders was studied. These binders were also submitted to the storage stability test and the values of the loss tangent versus frequency of the samples collected from the top portion of the tube, after 24 h storage at 180°C, are also represented in Figure 6. As can be observed, the binder modified with EPDM does not show an important change, after 24 h, in the shape of the loss tangent versus frequency curve, although
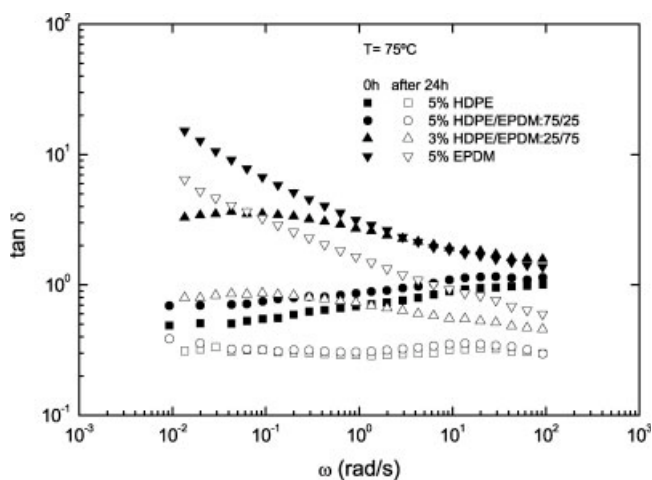
Figure 6 Frequency dependence of the loss tangent, at 75°C, for binders modified with HDPE, EPDM and mixtures of these, and their associated polymer-rich phases after 24 h of storage.

lower values are obtained. Thus, the EPDM-modified binder shows a low degree of instability. It is worth pointing out that EPDM is commonly used commercially for modification of bitumen for roofing applications, showing a good stability.[34] As expected, the HDPE-modified binder shows an important change in the evolution of the loss tangent with frequency, after 24 h storage. For the binder modified with a blend of HDPE/EPDM: 75/25, the polymer-rich phase sample, taken from the upper portion of the stability tube after 24 h, shows a behavior similar to that displayed by the HDPE-modified binder. Thus, EPDM was not able to readily prevent the HDPE from separating during the storage at high temperature. This is probably due to the lack of compatibility between HDPE and EPDM.[35] For the binder modified with a blend of HDPE/EPDM: 25/75, the polymer-rich phase, obtained after the stability

test, shows values of the loss tangent lower than those obtained for the EPDM-modified binder and higher than those for the HDPE-modified binder separated phase. The HDPE content in this binder makes it more unstable than in the case of EPDM modification.

The viscous flow behavior of these binders, at 75°C, is presented in Figure 7. As can been seen, the binder modified with 5% of EPDM undergoes a small change in viscosity after storage, at high temperatures. On the contrary, all the binders with HDPE-containing blends show much higher degrees of instability.

LDPE-modified bitumen

A similar study to that carried out with HDPE was performed with a low density polyethylene. LDPE is known to interact better with EPDM than the HDPE does.[35] However, no promising results have been obtained, since the LDPE-containing blends showed high levels of instability, as can be inferred from the frequency dependence of the loss tangent, at 75°C, represented in Figure 8, for binders modified with LDPE and/or EPDM and their associated polymer-rich phases after 24 h of storage, and the corresponding viscous flow measurements (Fig. 9).

In conclusion, EPDM can not entangle sufficiently either with HDPE or LDPE, in the absence of cross-linking promoters, such as sulfuric, phenolic, or per-oxide curing agents,[36] thus the stabilizing effect is not fulfilled.

EGA-modified bitumen

The modification of bitumen with a reactive polymer was also studied. Specifically, an ethyl-glycidil methacrylate-butilacrylate terpolymer (EGA) was used.
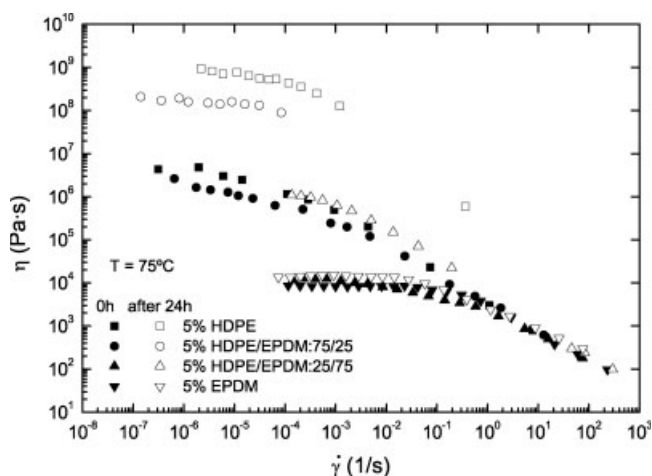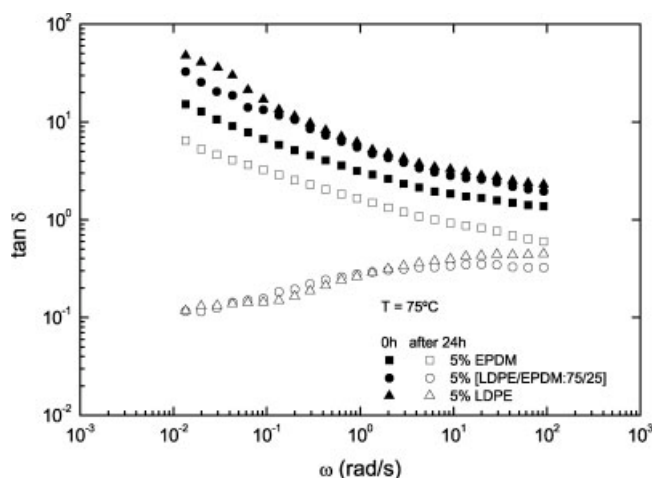

Figure 7 Viscous flow behavior, at 75°C, for binders modified with HDPE, EPDM and mixtures of these, and their associated polymer-rich phases after 24 h of storage.

Figure 8 Frequency dependence of the loss tangent, at 75°C, for binders modified with LDPE, EPDM and mixtures of these, and their associated polymer-rich phases after 24 h of storage.
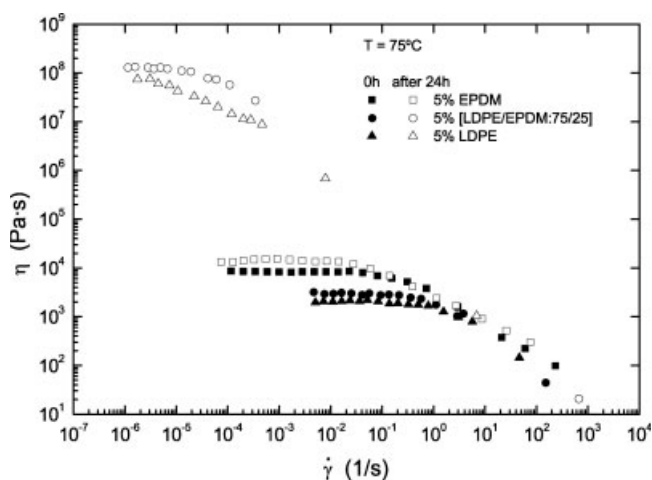
Figure 9 Viscous flow behavior, at 75°C, for binders modified with LDPE, EPDM and mixtures of these, and their associated polymer-rich phases after 24 h of storage.

The epoxide ring of the glycidic structure seems to undergo an addition reaction with the carboxylic functional group of an asphaltene molecule,[23,31] yielding an aromatic ester. This bond will prevent phase separation and improve storage stability. A certain amount of this polymer (2 wt %) was mixed with bitumen 60/70, at 180°C, and the blend was cured for 24 h at the same temperature. Once the blend was completed, it was submitted to the tube stability test. After mixing with bitumen, a curing is recommended at the storage temperature to let the epoxy rings react. When a bitumen is modified with such a reactive polymer, the polymer amount has to be chosen carefully, since an excessive quantity can cause the formation of an insoluble bitumen gel.[31]

Figure 10 shows the evolution of the loss tangent with frequency, at 75°C, for these systems. As can be observed, the sample taken from the top portion of the
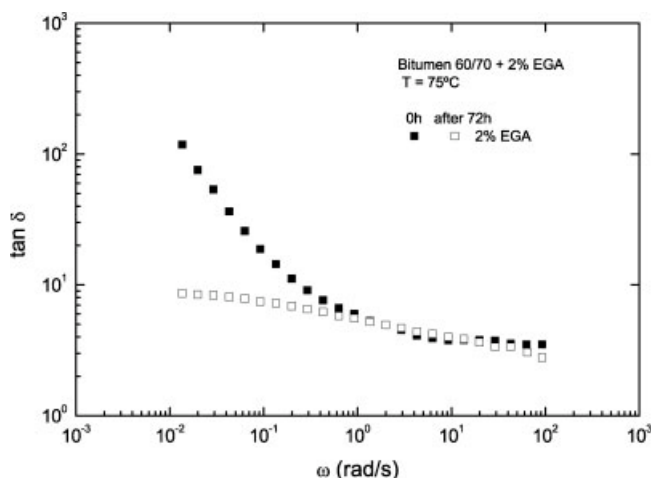

Figure 10 Frequency dependence of the loss tangent, at 75°C, for an EGA-modified binder and its associated polymer-rich phase after 72 h of storage.
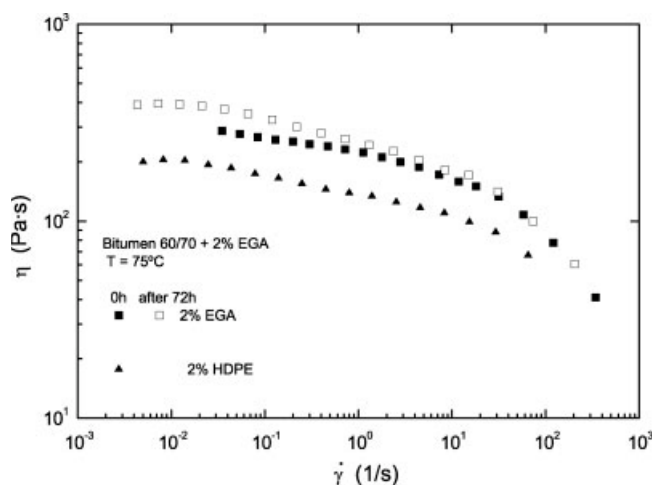
Figure 11 Viscous flow behavior, at 75°C, for an EGA-modified binder and its associated polymer-rich phase after 72 h of storage.

tube, after 72 h of storage, shows lower values of loss tangent at low frequencies, as well as a slight increase in viscosity at low shear rates (see Fig. 11). For the sake of comparison, the viscous flow curve for the 2% HDPE-modified bitumen has also been included in this figure. The results obtained point out that even a bitumen modified with a reactive polymer shows a certain degree of instability, under severe temperature and time conditions. The modification with this polymer, however, can be considered very favorable from a practical point of view.

Instability index

To evaluate the magnitude of the separation, for the sake of comparison, an instability index was calculated for all the binders, by comparing the viscosity, at 75°C, of the polymer-rich phase after 24 h storage and the viscosity of the binder. Other parameters and indices to quantify the extent of the segregation in polymer-modified bitumens have been recently proposed. That is the case for the separation ratio, R_s, proposed by Youtcheff et al., and Bahia and Zhai,[37,12] in which the segregation is evaluated by dividing the response of the material (G^* or δ) at the top of a stability tube (LAST device) by the response of the material at the bottom of the tube, upon heating (165°C) during time. In the present case, the viscosity was chosen as a reliable parameter to detect the phase segregation and accumulation of the polymer at the top of the tube. Thus, the instability index for the binders was calculated as:

$$I_I = \left(\frac{\eta_{0\mathrm{rpf}} - \eta_0}{\eta_0} \right) \qquad (1)$$

where I_I is the storage instability index; η_0 is the zero-shear-rate-limiting viscosity, at 75°C, of the binder;
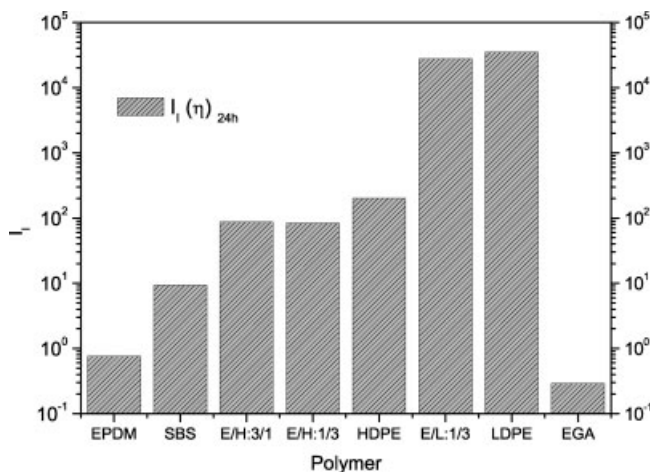
Figure 12 Instability index values, at 75°C, for different polymer-modified binders.

and η_{0rpf} represents the zero-shear-rate-limiting viscosity, at 75°C, of the polymer-rich phase (the top portion of the stability tube), after 24 h storage at 180°C.

The values of this instability index for different binders are presented in Figure 12. EGA and EPDM copolymers are the most suitable bitumen additives, because they show the minimum values of I_I, even lower than those obtained with SBS-modified bitumen. The LDPE-modified bitumen undergoes a higher degree of separation than the HDPE-modified bitumen. The binder prepared with a blend of EPDM and HDPE shows lower values of the instability index than the binder modified with HDPE. This fact points out a slight stabilization effect exerted by the copolymer, although not readily effective.

CONCLUSIONS

As a general rule, polymer addition to bitumen enhances the mechanical properties of the modified binder, although this enhancement depends on polymer nature and concentration, and, of course, the mixing process. As can be deduced from the results obtained in this research, HDPE-containing binders show a remarkable enhancement of the mechanical properties, as compared to those modified with LDPE, EPDM, and SBS. HDPE is the only polymer, among the polymers here evaluated, that is able to form a polymer network, with 3 and 5% content, this network being responsible for the enhanced properties.

All the polymer-modified binders studied show a certain degree of instability when they are stored under severe temperature conditions. Binder with SBS copolymer, although widely used by the pavement industry, presents higher instability levels than binders with EPDM copolymer and reactive polymer (EGA). HDPE-modified bitumen, although it is the preferred binder from the mechanical point of view, suffers from phase separation problems. A way to stabilize HDPE within the bitumen matrix is, thus, necessary to achieve a powerful binder, able to sustain the pavement demands, in the high temperature region. The use of EPDM/HDPE blends does not effectively hinder the separation of the polyethylene from the bitumen matrix, although a slight stabilization effect is apparent.

From the experimental results shown, we may conclude that the use of reactive polymers is a promising alternative to yield stable binders.

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