

# Destabilization Mechanism of Polyethylene-Modified Bitumen

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**ABSTRACT:** Polymer-modified binders are widely used for pavement construction. Among different polymers used to modify bitumen, polyolefins have shown to impart beneficial effects on the bitumen, especially to prevent some of the pavement shortcomings at high temperatures, such as rutting. The phase separation problems of these polymers from the bitumen may affect the final properties of the pavement. The determination of the polymer phase destabilization mechanism and rate are crucial to defer or delay the polymer separation from the matrix. With this aim, several HDPE-modified binders were manufactured by using a high-shear mixing device. The binders were stored in tubes at temperatures as high as 180°C. During the storage, the unstable polymer phase creamed up to the surface. The

destabilization process was followed by means of optical microscopy observations through time, as the separation process proceeded. The segregation of the polymer phase is shown to be preceded by a coalescence mechanism. Enhanced mechanical properties have been obtained by HDPE modification. However, such binders may not be efficient for the pavement application, since phase separation may occur during the application of the binder on the road. Functionalized reactive polymers are envisaged to hinder the separation problems in bituminous binders. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 260–267, 2006

**Key words:** bitumen; polyethylene; rheology; destabilization

## INTRODUCTION

Bitumen, from crude oil distillation processes, is widely used as a binder for road paving applications.<sup>1</sup> Fillers and aggregates are mixed together with bitumen, which acts as a cohesive agent. The mixture is, then, extended and compacted on the road.

The addition of polyolefins to bitumen is known to enhance its service properties, and obtain improved thermomechanical resistance, elasticity, and adhesivity.<sup>2–5</sup> Blends of polyolefins and bitumen are better manufactured under high shear and high temperature,<sup>6,7</sup> to achieve a good mechanical dispersion of the polymer within the bituminous matrix. The microstructure of these blends is biphasic, at a microscopic level, with a polymer phase, swollen by the light aromatic components of the bitumen, within an asphaltene-enriched bitumen matrix, due to the so-called physical distillation process.<sup>8,9</sup> The microstructure of the bitumen phase is yet to be completely elucidated, although results obtained from atomic force microscopy (AFM)<sup>10</sup> support the existence of a structural

network made of small spherical aggregates of asphaltenes, with a diameter of 100 nm approximately, within a maltenic matrix.

The intermolecular interactions between polymer and bitumen are responsible for the enhancement of bitumen properties.<sup>11</sup> The degree of swelling of the polymer after the high-shear mixing with the bitumen, a measure of the degree of the interactions between both phases, can be assessed by differential scanning calorimetry.<sup>3,4,12</sup> Hildebrand solubility coefficients usually provide inaccurate predictions of interactions between polyolefins and bitumen,<sup>13</sup> but DSC transition temperature shifts do reveal the strength of these interactions. However, qualitatively, the solubility parameters can shed a light on the nonaffinity of the polymer used with the different components of the bitumen. HDPE and other polyolefins show a solubility parameter of  $16.2\text{--}16.4 \times 10^{-3}$  (J/m<sup>3</sup>)<sup>0.5</sup>, and the generic components of the bitumen:  $19.6\text{--}26 \times 10^{-3}$  for asphaltenes,  $14.3 \times 10^{-3}$  for saturates,  $17.8 \times 10^{-3}$  for aromatics, and  $19.4\text{--}20.1 \times 10^{-3}$  for resins. In addition, the intrinsic nonpolar and nonaromatic nature of the polyolefins, since polyolefins are produced from olefinic monomers, reflects their low solubility with a bitumen dispersion medium, which is polar and aromatic.<sup>14</sup>

Most of the polyolefins are not readily miscible with bituminous materials. After the manufacturing of the

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polymer/bitumen blends, phase separation may eventually occur,<sup>15</sup> as the blend is stored at moderate and high temperatures, due to the lack of compatibility of the polyolefins with bitumen. Compatibility is most often defined by the extent of segregation of the bitumen and polymer during hot storage (140–180°C).<sup>13,16</sup> Pavement construction techniques require the binder to remain stable previously and during the application on the road. Hence, a certain degree of storage stability is required for bituminous binders.<sup>17,18</sup>

The difference of density between polymer and bitumen may cause the creaming of the polymer particles.<sup>14</sup> As it is well-known, the viscosity of the continuous phase influences the ascending polymer particle motion (governed by the Stokes law). It is demonstrated that the stability of a polymer-modified bitumen depends not only on the difference in density and viscosity between bitumen and polymer but also on bitumen structure<sup>19</sup> and bitumen/polymer molecular interactions.<sup>13,20</sup>

The mechanism of phase separation can be pure creaming, although, in the case of polymer/bitumen blends, creaming is usually preceded by coalescence and flocculation phenomena.<sup>14</sup>

From a thermodynamic point-of-view, a polymer/bitumen binary blend segregates when the critical solution temperature is surpassed,<sup>13</sup> generally upon heating. Thus, blends can remain stable at low temperature and become segregated when the temperature is raised. The segregation or distribution of the phases in such blends generally proceeds by spinodal decomposition, preceded by nuclei growth, and followed by coarsening and coalescence.<sup>13</sup>

The overall objective of this research was to study the destabilization mechanism of HDPE-modified bitumens during their storage at high temperature.

## EXPERIMENTAL

A 60/70 penetration-grade bitumen provided by CEPISA (Spain), with an asphaltene content of 19.34% (ASTM D3279) and a specific gravity of 0.1 (25°C/25°C) (ASTM D70), was used as base binder. A pelleted high-density polyethylene (HDPE 6006-L), from Repsol (Spain), with a density of 0.956 g/cm<sup>3</sup> and an average molecular weight of 171,500 g/mol, was used as a binder modifying agent. A reactive terpolymer EGA (ethyl-glycidyl methacrylate (GMA)-butyl-acrylate), with a trade name of Elvaloy RE (density 0.940 g/cm<sup>3</sup> and GMA content 40 wt %) from DuPont (USA), was used as a reference reactive polymer.

Binders containing 1–5% polymer were prepared using a high-shear mixing device, at a pilot plant scale. The pilot plant device integrated a rotor-stator mixer SD41 SUPER-DISPAX from IKA (Germany) coupled with a storage/feed tank. The blends were manufactured at 180°C at a rotational speed of 8200 rpm.

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, and the samples were taken out, after different storage times, from the top part of the tube.

The rheological study was performed using a controlled-stress rheometer, RheoStress RS150 from Haake Gbr. (Germany), and a controlled-strain rheometer, ARES from Rheometric Scientific (Piscataway, NJ). Strain and 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, to avoid possible slip phenomena (10, 20, and 35 mm diameter; 1 and 2 mm gap). These frequency sweep tests were performed within the linear viscoelastic range of the materials.

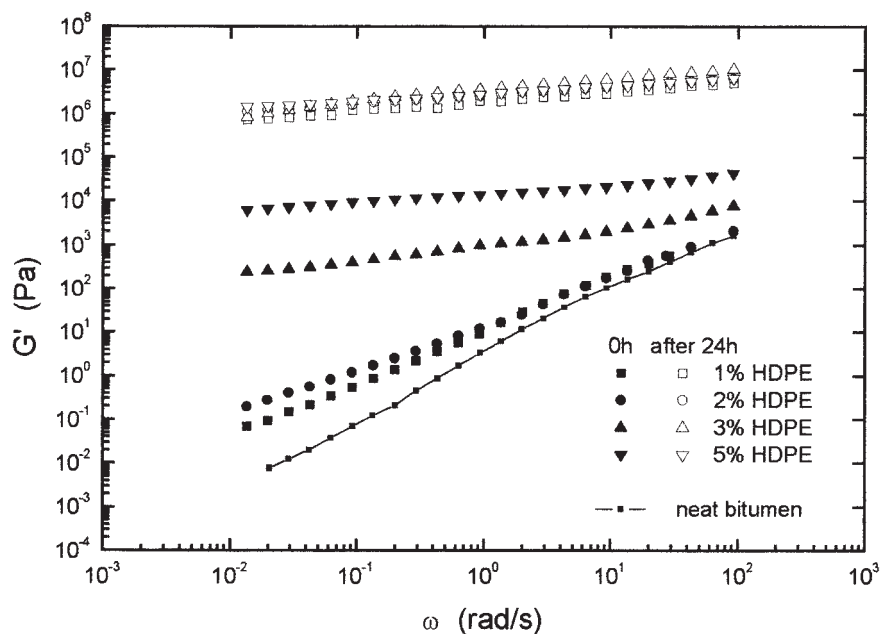
Viscous flow measurements were performed on both a controlled-strain Rheometrics ARES rheometer and a controlled-stress Haake Rheostress RS150 rheometer, using serrated plate-and-plate geometries. A good concordance between the experimental results obtained with both rheometers has been found.

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).

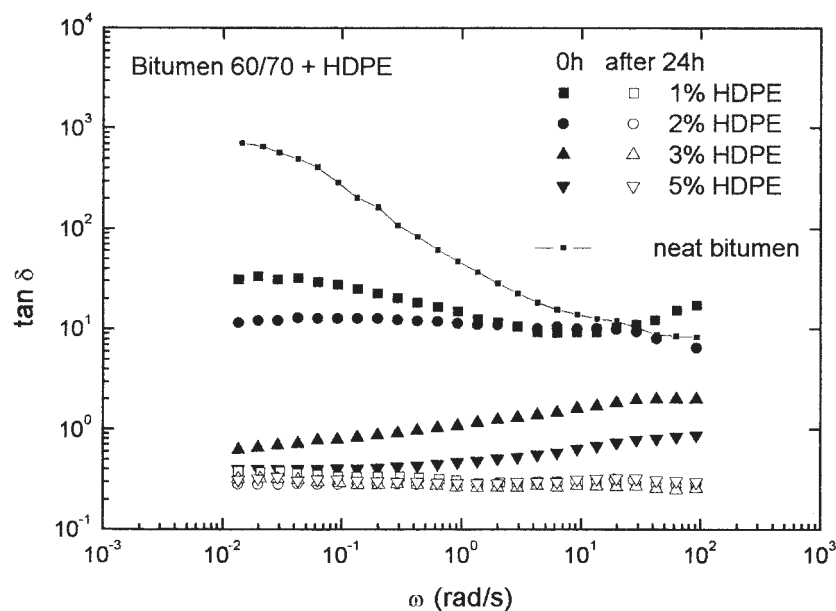
DSC tests were done with a DSC Q-100 from TA Instruments Waters (New Castle, DE), using 10–20 mg samples. The samples were pressed into aluminum pans and were submitted to the same measurement procedure. Thus, a cool-heat-cool-heat scan was programmed to provide the same thermal history for all the samples and avoid the influence of the polymerization process on the thermal transitions of the polymer and the possible effects of crystallization and/or rearrangements during sample storage. A heating rate of 10°C/min was selected. Temperature ranged from –80 to 200°C.

## RESULTS AND DISCUSSION

To quantify the extent of the modification exerted by the polymer on the bitumen and its influence on its stability at high temperature, several binders with different proportions of HDPE were manufactured. These binders were submitted to a stability test. With this aim, the binders were stored in a furnace at 180°C, following the method described in the experimental section and quite similar to that proposed by Bahia and Zhai.<sup>21</sup> The frequency dependence of the storage modulus and the loss tangent for the HDPE-modified binders, and their associated rich-polymer phases, are presented in Figure 1(A, B), respectively. As can be



(a)

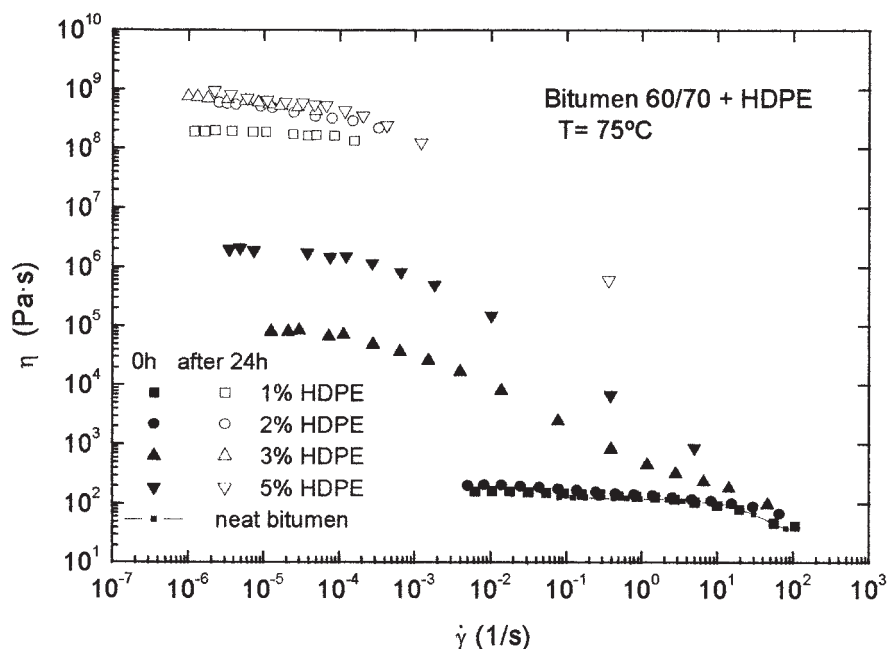


(b)

**Figure 1** (a) Frequency dependence of the storage modulus, at 75°C, for different HDPE-modified binders and their associated rich-polymer phases after 24 h of storage. (b) Frequency dependence of the loss tangent, at 75°C, for different HDPE-modified binders and their associated rich-polymer phases after 24 h of storage.

observed, all the polymer-rich phases, obtained after 24 h of high-temperature storage, show a very similar mechanical behavior, without any influence of polymer concentration. The behavior of neat bitumen, submitted to the mixing process, is also depicted. On the other hand, Figure 2 shows the viscous flow behavior of these samples. Once again, the polymer-rich phases, after 24 h of storage, display quite similar values of the apparent viscosity in

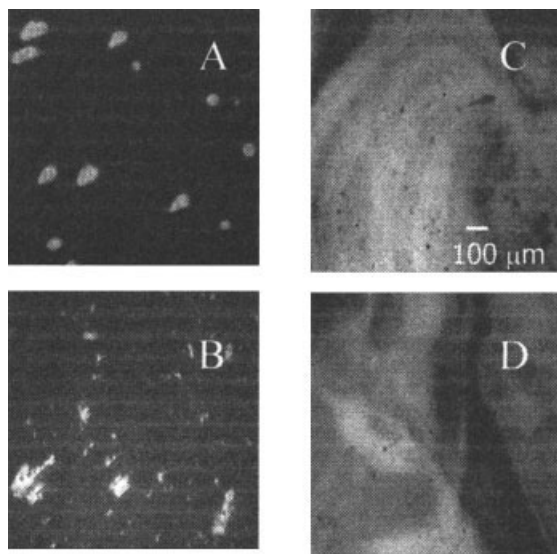
the shear rate range studied, with the peculiarity of the binder containing 1% HDPE, which shows lower values of viscosity, above all at low-shear rates. Consequently, the high degree of separation of the polyethylene from the bituminous matrix is apparent, even at very low concentration levels. As a reference value, the viscosity of the neat bitumen at 75°C is, in this case, 89 Pa s, as obtained from steady-state flow measurements.



**Figure 2** Viscous flow behavior, at 75°C, for different HDPE-modified binders and their associated rich-polymer phases after 24 h of storage.

In Figure 3, the morphologies of two binders modified with 1% (A) and 2% (C) of HDPE, and their associated separated polymer phases, after 24 h of storage (B and D, respectively), are shown. As can be observed, after storage, the polymer appears as the continuous phase [see Figs. 3(C) and 3(D)] swollen by the miscible components of the bitumen.

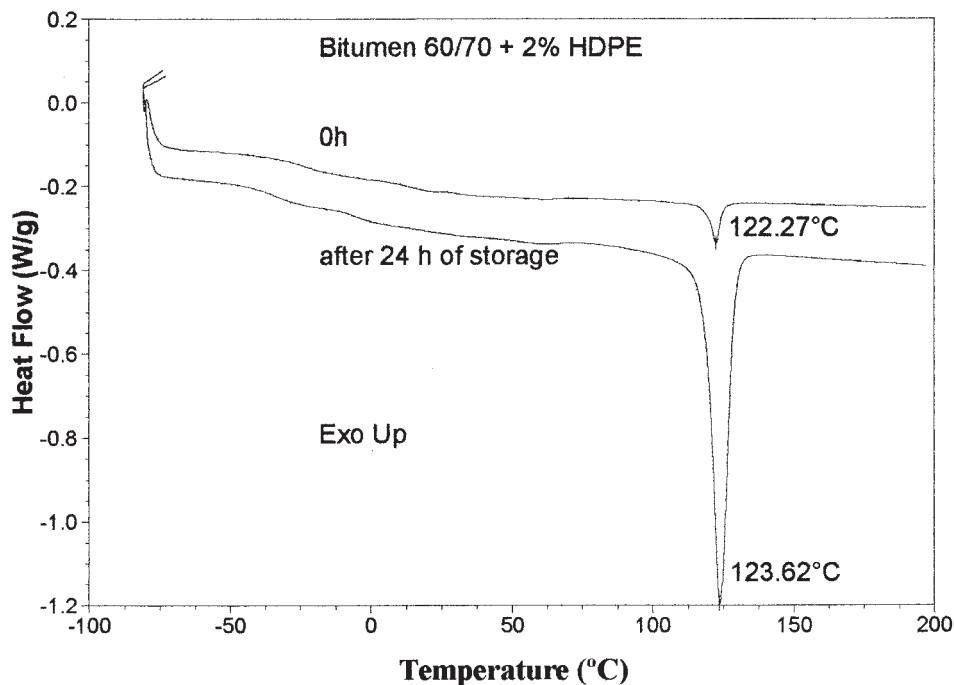
The degree of swelling of the polymer by the light components of the bitumen can be assessed by the



**Figure 3** Microscopic observations of HDPE-modified binders: 1% HDPE (A) and 2% HDPE (B) and their associated rich-polymer phases after 24 h of storage: 1% HDPE (C) and 2% HDPE (D).

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.<sup>22,23</sup> The melting transition temperature of the HDPE used in this study is close to 132°C.<sup>22</sup> For a binder modified with 2% of HDPE, the melting temperature appears at 122.27°C, as can be seen in Figure 4, about 10°C lower than the melting point of polyethylene, as a consequence of the swelling of the polymer with some of the components of the maltene fraction. At these polymer concentration levels, up to 5% of HDPE, the extent of polymer swelling is independent of polymer concentration in the bitumen.<sup>22</sup> During the storage of the binder at 180°C, the degree of swelling of the polymer may change, due to the separation process. However, as can be observed in Figure 4 for a 2% HDPE-blend, after 24 h of storage, the transition temperature of the binder is not significantly changed. This result indicates that once the polymer is dispersed within the bitumen, with the high-shear device, the state of the polymer does not further evolve, apart from the creaming process previously described.

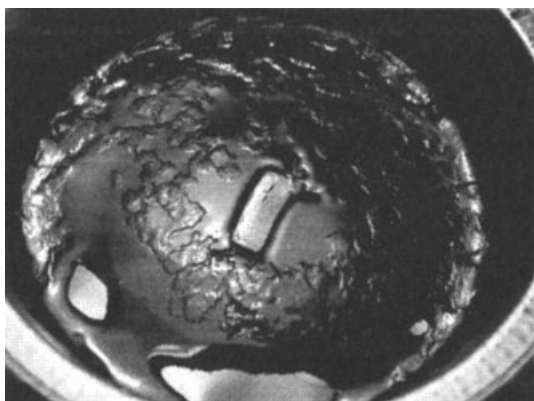
By observing the surface of a 5% HDPE-modified binder sample, which was heated, within an aluminum cup, in a furnace at 150°C for 15 min (same conditions as those used to prepare the microscopy samples), it was noticed that the sample was overlaid with a thin bright disrupted layer (Fig. 5). The HDPE, first dispersed within the bitumen matrix, forms an interconnected three-dimensional sponge-like structure yielding a gel-type morphology.<sup>22,24</sup> However,



**Figure 4** DSC thermograms of a 2% HDPE-modified binder and its associated rich polymer phase, after 24 h of storage at 180°C.

after a short period of storage at high temperature (above the fusion temperature of the swollen polymer, i.e., around 120°C, see Fig. 4), the polymer network (as predicted by the rheological and optical characterization, see Figs. 1(A), 1(B), (2) and Ref. 22) would collapse, followed by a coalescence and creaming process of the polymer up to the surface.

From a practical point-of-view, such a binder is not appropriate for paving applications, since the binder is stored at high temperature prior to its mixture with the mineral aggregates and further laid down. Both processes are carried out at high temperature. Consequently, it is necessary to stabilize the HDPE within

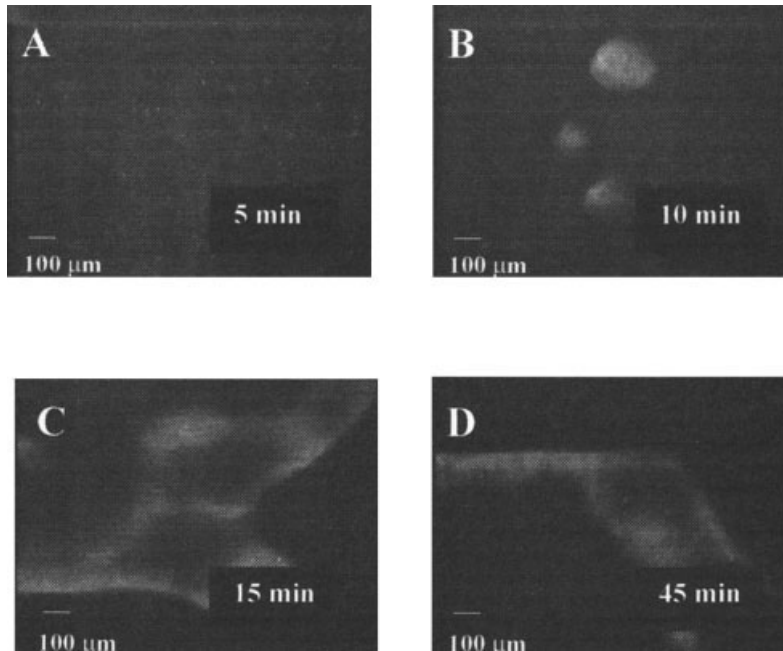


**Figure 5** Upper view of a 5% HDPE-modified bitumen sample stored at 150°C for 15 min.

the matrix of bitumen, to achieve an acceptable performance of the bitumen.

With the aim of understanding the separation process of the polymer phase when the binder is stored at high temperature, different samples of a 5% HDPE-modified binder, which was frozen immediately after the manufacture of the binder, were placed on crystal slides. These samples were heated in a furnace at different temperatures (above and under the fusion temperature of the swollen polymer within the blend) and, subsequently, microscopic observations were carried out at different elapsed times.

In Figure 6, the evolution of the morphology during ageing, at 150°C, can be observed. Thus, large polymer inclusions (light green) start to be formed, due to the coalescence of the droplets, after 10 min of storage [Fig. 6(B)]. After 15 min [Fig. 6(C)], several continuous polymer areas appear. After 45 min [Fig. 6(D)], the morphology is very similar to that found after 15 min. Consequently, most of the polymer is supposed to be segregated after 15 min heating. Besides, the mechanism of separation of the polyethylene from the bitumen is preceded by the coalescence of the disperse phase. Coalescence, driven by interfacial tension, usually appears, for incompatible systems, even in quiescent conditions. Thus, the polymer droplets can coalesce simply by interacting with each other. Usually, with polymers, van der Waals interactions are sufficient for droplets to merge into a larger resulting droplet.<sup>25</sup> Three coalescence theories are usually used

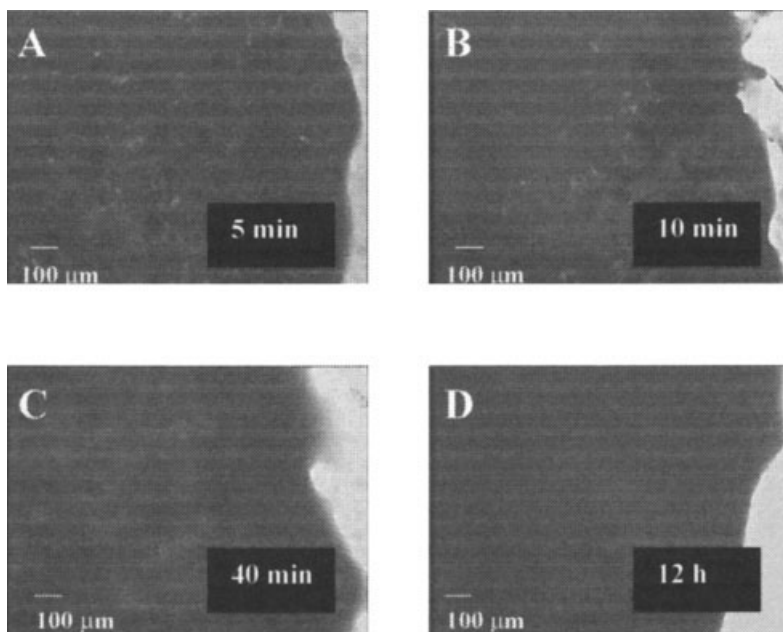


**Figure 6** Evolution of the morphology with the elapsed time, after storage at 150°C, for a 5% HDPE-modified bitumen. (A) after 5 min, (B) after 10 min, (C) after 15 min, and (D) after 45 min.

to explain the mechanism: Smoluchowski (no hydrodynamic interactions), trajectory (hydrodynamic interactions), and film drainage theory (particle deformation influence).<sup>26</sup>

A similar study was carried out on samples stored at 100°C. As can be observed in Figure 7, the morphology of the sample does not evolve significantly after 12 h of storage at the above-mentioned temperature.

As was previously mentioned, the melting temperature of these modified bitumens occurs at ~123°C. Well above this temperature, 150°C, the HDPE-modified binders suffer from coalescence-creaming and gross phase separation, within short periods of time (15 min). Under the melting temperature of the binders (100°C), the binders remain stable, even after long periods of time.



**Figure 7** Evolution of the morphology with the elapsed time, after storage at 100°C, for a 5% HDPE-modified bitumen. (A) after 5 min, (B) after 10 min, (C) after 40 min, and (D) after 12 h.

TABLE I  
Values of the Instability Index for Different Polymer-Modified Bitumens

Polymer additive	Storage at 180°C (h)	$I_I(\eta) = \left( \frac{\eta_{0\text{prp}} - \eta_0}{\eta_0} \right)$
5% HDPE	24	201.96
5% HDPE/EPDM:75/25	24	83.31
2% EGA	72	0.29

When the creaming of the polymer is preceded by droplet coalescence, as it was proven to be (see Fig. 6), the stabilization of the polymer into the bituminous matrix may be achieved by means of a copolymer, which would act as a steric stabilizer.<sup>14,27,28</sup> The copolymer may defer the phase separation, since the copolymer would hinder the coalescence of the polyethylene drops.<sup>14</sup> The use of an ethylene copolymer (EPDM), in conjunction with the HDPE, has been, however, reported not to yield a significant improvement of the stability of this type of binders.<sup>29</sup> To prove that, 5% w/w of a blend HDPE/EPDM: 75/25 was added to the bitumen and, after high-shear mixing, the binder was stored at 180°C. After 24 h of storage, a rich-polymer phase had segregated from the matrix and moved up to the surface of the container.

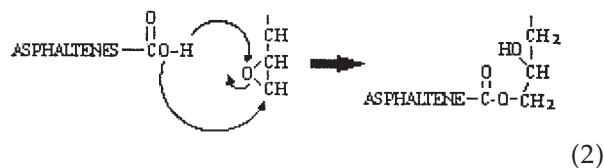
An instability index has been calculated by comparing the viscosity, at 75°C, of the polymer-rich phase separated from the blend after 24 h of storage at 180°C and the viscosity of the binder.<sup>30</sup>

$$I_I(\eta) = \left( \frac{\eta_{0\text{prp}} - \eta_0}{\eta_0} \right) \quad (1)$$

where  $I_I(\eta)$  is the storage instability index;  $\eta_0$  is the zero-shear-rate-limiting viscosity of the binder, at 75°C, and  $\eta_{0\text{prp}}$  represents the zero-shear-rate-limiting viscosity, at 75°C, of the polymer-rich phase (the top portion of the binder in the stability tube), after storage at 180°C.

The instability index values for some of the binders studied are shown in Table I. A value lower than 100 was obtained for the binder modified by a HDPE/EPDM blend, while a value of about 200 was attained for the 5% HDPE-modified bitumen.<sup>29</sup>

More promising results, concerning high temperature storage stability, have been obtained by using of reactive polymers. The use of EGA copolymers (ethylene-glycidylmethacrylate-acrylate) for bitumen modification has been recently reported.<sup>29,31</sup> This polymer undergoes a chemical reaction with some components of the bitumen, precisely between the epoxide ring of the polymer and the carboxylic groups of the asphaltene, as follows:



In this study, 2% of this polymer was added to a 60/70 penetration-grade bitumen, and the binder obtained was cured for 24 h and stored at 180°C. After 72 h of storage, an instability index quite close to zero was obtained. This observation points out that the use of reactive polymers is one of the envisaged alternatives for the production of storage-stable polymer-modified binders.

## CONCLUSIONS

A HDPE has been used for bitumen modification. As it has been described, the polyethylene has been dispersed, at high temperature, within the bitumen matrix, by means of a high-energy mixing process. The experimental results demonstrate that this polymer is partially swollen by some light aromatic components of the bitumen. However, after a short period of storage at high temperature (above the melting point of the polyethylene), a gross separation of the polymer phase occurs.

The mechanism of the polymer-rich phase separation has been proved to be creaming, preceded by coalescence. Owing to the incompatibility of the polymer with the bitumen, and the difference in densities, the polyethylene-rich phase destabilizes and coarsens. An insight into the interfacial properties of the systems, to a better understanding of the coalescence mechanism, will be addressed by the authors in a forthcoming article.

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. However, functionalized reactive polymers are envisaged to make up the separation problems in bituminous binders.

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