

Hybrid modification of bitumen with Crumb Tyre Rubber and thermoplastic copolymers

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Abstract

Hybrid modification of bitumen with Crumb Tyre Rubber (CTR) and a thermoplastic polymer tries to take advantage of the complementary properties of the modifiers and to improve the storage stability at high temperatures as well. Aiming to this, in this paper Hybrid Systems (HSs) were formulated by the addition of a thermoplastic polymer (reactive or non-reactive) to a Crumb Tyre Rubber Modified Bitumen previously obtained. The resulting samples were submitted to a thermorheological analysis, technological characterisation, fluorescence microscopy and modulated differential scanning calorimetry. The obtained results point out a positive synergistic effect of the swollen thermoplastic polymer with non-dissolved Crumb Tyre Rubber (CTR) particles. In general, both in-service performance and storage stability result markedly improved because of the development of a multiphasic structure composed of non-dissolved CTR particles, a polymer-rich phase and an asphaltene rich-phase. The best results are obtained when the thermoplastic polymer contains reactive groups able to react with bitumen molecules. Keywords: Crumb Tyre Rubber, viscoelasticity, Reactive polymers.

1. INTRODUCTION

Use of Crumb Tyre Rubber (CTR) in road paving applications is not new but still remains a topic of great interest as confirmed by the increasing number of publications on this matter [1-12].

Incorporation of CTR by wet processes involves a notable size reduction and partial rubber digestion during processing, as a consequence of depolymerisation/devulcanization reactions of the three dimensional network of the vulcanised tyre rubber [1-2]. The resultant higher homogeneity of the rubberised bitumen makes wet methods more popular and appealing but, conversely, more complex and expensive. However, complete rubber degradation is not achieved and the final product typically presents a certain amount of non-digested CTR particles, which become further swollen by the absorption of light bitumen compounds [2-7]. The presence of these rubber particles leads to two opposite effects, an enhancement of the binder elastic characteristics along with a poor storage stability and workability [2, 3].

Consequently, the development of rubberised binders with improved homogeneity and hot storage stability, produced in standard plants, would have valuable practical implications, resulting in an environmental-friendly and cost-effective alternative to traditional modified bitumens. To that end, a previous work has raised the possibility of enhancing hot storage stability by promoting interactions of a new polymer-rich phase with non-digested rubber particles, producing the so-called Hybrid Systems (HSs) [10]. Depending on the type of polymer used, HSs can be classified in two categories: non-reactive or passive HSs (where final composition is formed by physical means) and active or reactive HSs (where chemical reactions happen involving the polymer phase and some bitumen molecules).

With this aim, this work assesses two ethylene copolymers of different nature, reactive and non-reactive, in the formulation of new compatible Hybrid Systems (HSs), which results may be of special interest for the asphalt industry.

2. EXPERIMENTAL

2.1. Materials, mixing and curing stage

A modified bitumen containing 10 wt.% Crumb Tyre Rubber (referred to as RB70) was firstly obtained to serve as a base binder for the formulation of Hybrid Systems (HSs). After processing, this base binder presents a penetration grade of 70 dmm. Two ethylene based copolymers, provided by Repsol S. A., were used to formulate HSs. Melt flow rates MFR, at 230°C, and polymer composition are gathered in Table 1.

Table 1. Polymer composition of the ethylene-based polymers used.

Name	Description	MFR	Composition
PBE	ethylene-propylene elastomer	8	Ethylene 11 wt.%
EMA	maleic anhydride-functionalized ethylene-co-1-octene copolymer	8	Maleic Anhydride 0.35 wt.%

PBE is a non-reactive propylene-based elastomer formed by isotactic propylene repeated units with random ethylene blocks, produced using metallocene catalyst technology, and with 11% of ethylene content. EMA is a fully saturated ethylene-co-1-octene copolymer functionalized by reactive extrusion with maleic anhydride, containing 0.35 wt.% pendant succinic anhydride groups.

Hybrid Systems, or ternary blends, were prepared by hot mixing of rubberised binder (RB70) and 3 wt.% of these polymers. Initially, polymeric modifier was mixed with RB70 at 180°C for 2 hours in a high shear mixer Silverson L4RT. Then, chemical reaction was completed by curing in an oven at 160°C for 24 h.

2.2. Tests and measurements

All modified bitumens were characterized by selected technological tests (penetration and softening point) according to EN 14023 standard. Hot storage stability, at 180°C, was determined by the difference of softening point temperatures of the top and bottom sections of aluminium toothpaste tubes, in accordance to UNE-EN 13399. Binder microstructure was obtained by means of fluorescence microscopy following UNE-EN 13632, using a Leica DM 2500 microscope (Germany) with a 400X magnification, at room temperature.

Small amplitude oscillatory shear (SAOS) tests were conducted to characterize the linear viscoelastic response of the HSs. Binder temperature dependence was studied by temperature sweep tests from 40 to 100 °C, at a heating rate of

1 °C min⁻¹, applying an strain value within the linear viscoelastic region, and a selected frequency of 10 rad/s. All rheological measurements were performed in a Dynamic Shear Rheometer (DSR-Physica MCR302, Anton Paar, Austria).

Calorimetric tests were performed in a DSC-Q100 calorimeter (TA Instruments, USA) under N₂ atmosphere. Samples were hermetically sealed in aluminium pans and heated at 150°C for 5 min and, then, placed at room temperature for 24 h before measurement, to ensure the same thermal history. During the test, they were quenched-cooled to -80 °C, kept for 5 min at this temperature, and, then, heated up to 120-200 °C. A heating ramp of 3°C/min was selected.

3. RESULTS AND DISCUSSION

Table 2 gathers the results of technological tests, according to EN 14023, and discloses the poor high temperature storage stability of RB70. As may be seen, this binder presents a difference of 10°C between the softening point at the top and bottom sections of the settling tube, which noticeably exceeds the limit of 5°C established by EN 13399. This well-known phenomenon results from the settling of non-dissolved rubber particles during hot storage [1, 7].

Table 2. Technological properties for the bituminous binders studied.

Property	unit	RB-PBE	RB-EMA	RB 70
Penetration	0.1 mm	60	63	70
Softening Point, TR&B	°C	56	63	51
Dif. of R&B Softening Point (Stability)	°C	2.1	7.5	10

It is clear that all polymers used in this study lead to an improvement in hot storage stability, particularly RB-PEB because fulfils the stability requirement established by the European standard EN 13399. Furthermore, Table 2 also points out that technological properties such as penetration and softening point are enhanced, particularly, after the addition of the reactive ethylene copolymer, EMA.

The effects of rubber and polymeric modifiers on the performance of binders over a wide range of temperatures can be easily analysed by means of the dynamic shear temperature sweeps (Figure 1).

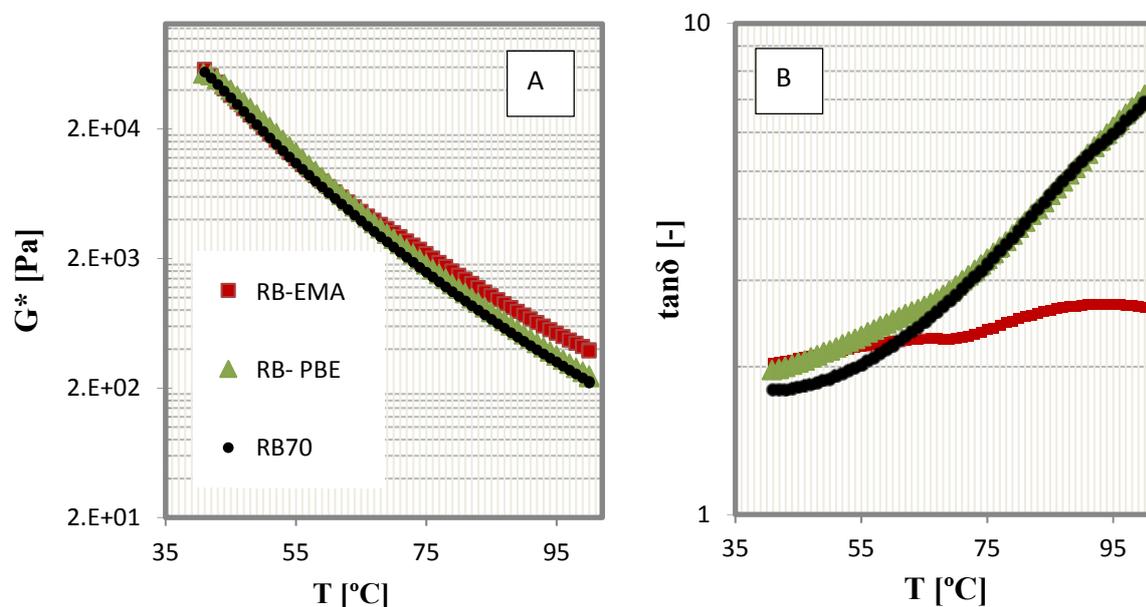


Figure 1. Evolution of complex shear modulus (A) and loss tangent (B) with temperature, at 10 rad/s.

As expected, complex shear modulus undergoes a continuous decrease with testing temperature, from 30 to 100 °C, for all samples (Figure 1A). Hybrid reactive modification causes a remarkable increase in G^* , more evident as temperature is raised, when compared to the reference binder RB70. This result points out a better performance in the intermediate and high in-service temperature range and presumably enhanced resistance to permanent

deformation as well [11, 12]. Similarly, loss tangent presents a greater sensitivity to modification changes (Figure 1B) so that, the lower the values of $\tan\delta$, the better the modification achieved. Thus, samples can be classified according to modification achieved, resulting: $RB70 \ll RB-PBE \ll RB-EMA$. Furthermore, Figure 1B points out two different types of rheological responses after the addition of the polymer. On one side, non-reactive systems RB70 and RB-PBEs, show qualitatively similar behavior, with a continuous increase of the loss tangent, a predominant viscous behaviour ($\tan\delta > 1$) and, therefore, a direct transition from the glassy to the Newtonian region. Instead, the reactive Hybrid system RB-EMA presents a much lower dependence on temperature, with values close to 1, which is considered the rheological response of a critical gel [7].

The thermomechanical behaviour of HSs could be explained by the formation of a complex multiphasic system composed of different polymeric phases [11], as may be supported by fluorescence microscopy (Figure 2).

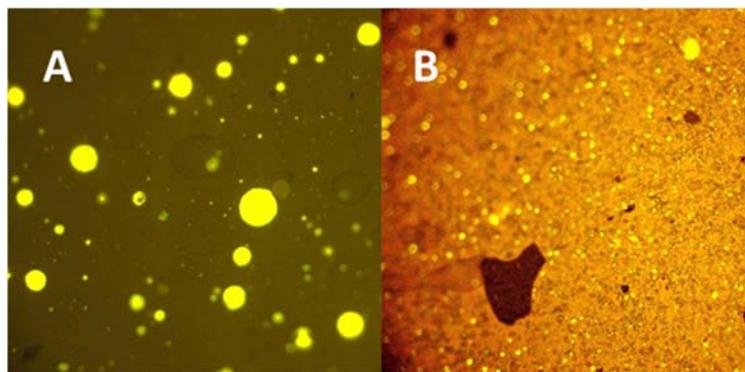


Figure 2. Fluorescence optical microscopy images for selected samples: (A) RB-PBE and (B) RB-EMA

Figure 2 shows, as darker colour regions, the presence of non-dissolved CTR resulting from the digestion of the original rubber [2, 11]. These fine elastic particles, together with the dissolved rubber chains, give rise to the observed improvement for RB70 and are responsible for its poor storage stability.

In addition, Figure 2 also displays the existence of dispersed light-toned regions, pointing out the presence of a polymer-rich phase for both HSs. However, different proportions and size distributions of the polymer rich phases are clearly distinguished. On the one hand, physical modifier for HS (RB-PBE) appears as spherical droplets randomly distributed, covering a surface fraction of roughly 8%, greater than that of the polymer concentration in the blend (3 wt.%). This fact suggests the polymer swelling by maltenic oils and reveals their partial compatibility, which is required to improve the performance [11]. On the other hand, reactive modifier for HS presents a dispersed polymer-rich phase still recognisable, but with a much lower particle size. Thus, the surface fractions of the light-toned regions are clearly below the proportion of added polymer (3 wt.%).

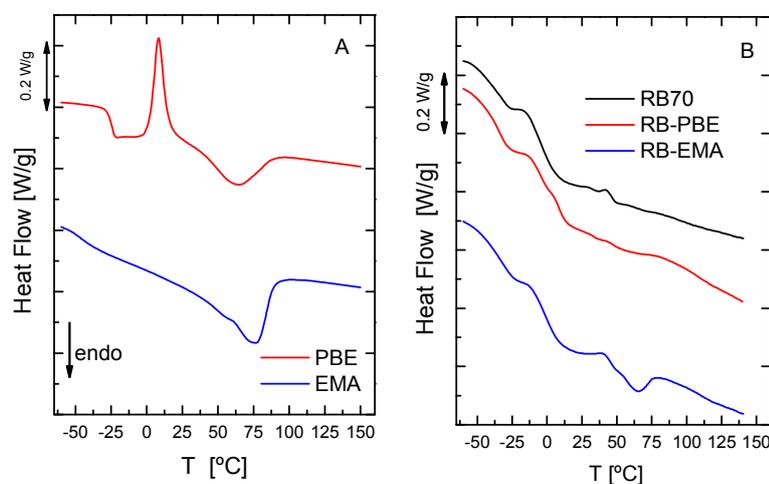


Figure 3. Total heat flow curves for neat polymers (A) and binders (B), obtained from DSC experiments

Total heat flow curves of polymers and HSs presented in Figure 3 display multiple thermal events resulting from both bituminous and polymer-rich phases, and confirm above-commented swelling processes. For sake of clarity curves have been vertically shifted and therefore, no absolute values are presented

By comparing DSC curves of neat polymers (Figure 3A) and their corresponding HSs (Figure 3B), a compatibility (and swelling) analysis of the crystalline fraction with bitumen can be performed. As neat bitumen and RB70 do not show any relevant peaks in total heat flow curves, these samples are not presented. The change in crystallinity of the polymer phase can be estimated from the melting enthalpies of HSs, compared to pure polymer, which is considered a quantitative indication of the compatibility with bitumen. In the case of non-reactive polymer (PBE), Figure 3 points out a lowering of the melting point of about 8 °C (if endothermic events found for neat polymer and RB-PBE are compared). Moreover, a significant reduction of polymer crystallinity is noticed when mixed with RB-70. Both effects are due to the migration of maltenic molecules to the polymer crystalline regions. Conversely, the reactive polymer and its corresponding modified bitumen display a much higher crystalline fraction than PBE and its HS. Likewise, these systems are characterised by a smaller melting point depression, as well as a lower reduction of its crystalline fraction.

4. CONCLUSION

This study proposes the combined use of CTR with a second polymeric phase to formulate the so-called Hybrid Systems (HSs), which seems to be a promising alternative to improve hot storage stability and binder quality.

HSs formulated with the non-reactive polymer (RB-PBE), a semi-crystalline ethylene/propylene based elastomer, are stable binders with slightly improved in-service properties. Alternatively, HSs with added reactive polymers (HS-EMA), evidence a much higher degree of improvement, related to its functional groups (pendant succinic anhydride) that react with bitumen polar molecules.

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