Processing of bitumens modified by a bio-oil-derived polyurethane


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ABSTRACT

Castor oil (CO) functionalized by isocyanate groups (−NCO) is proposed as a novel bio-based reactive polyurethane (PU) for bitumen modification. This work presents a comparative analysis conducted on blends of bitumen and 2 wt.% of a PU prepolymer prepared by NCO-functionalization of castor oil. Four preparation procedures were evaluated, which resulted from the combination of two processing times (1h or 24h, at 90ºC) followed by two different post-treatments (water addition or ambient curing for up to 6 months). It was found that the degree of modification attained after post-treatment depends on the previous processing conditions. Thus, short processing times are required if the binder is further subjected to ambient curing. Instead, the success of the water-addition modification falls on a previous long processing step. As revealed by rheological tests, ambient curing was seen to be by far a more efficient way of modification if compared to direct addition of water, and makes clear that the resulting binder evolves towards a better performance when in service. In that sense, Thin Layer Chromatography tests, Modulated DSC and AFM images demonstrated a more complex microstructure characterized by the presence of a larger content of molecules with higher polarity, size and molecular weight.

Keywords: bitumen, rheology, isocyanate, castor oil, product design.
1. INTRODUCTION

Bitumen, residue from crude oil distillation, is a complex material basically composed of hydrocarbons along with some other molecules which contain small percentages of heteroatoms (sulphur, nitrogen and oxygen). Bitumen compounds can be classified by chromatographic techniques into four different fractions (usually referred to as SARAs): saturates (S), aromatics (A) and resins (R), which make up the maltenes, and asphaltenes (As). The complexity, aromaticity, heteroatom content, and molecular weight increase in the order S<A<R<As [1]. A colloidal model, consisting of asphaltenes being dispersed into an oily matrix of maltenes and peptized by resins, is traditionally used to describe bitumen behaviour [2,3].

On account of its properties, bitumen is the most suitable material to be used as a binder of mineral aggregates for paving applications [4]. In bituminous asphalt mixes, mineral fillers (with a particle size below 75 μm) typically represent from 2 to 12 wt.% on their total mineral matter [3]. Hence, a bitumen/filler blend (commonly referred to as mastic) naturally forms when bitumen and aggregates are mixed. In that sense, mastic is the actual product used to hold coarser aggregates particles together in the asphalt mixtures [5]. Consequently, bitumen is the only deformable component and forms the continuous matrix of the mastic (and, therefore, of the asphalt mixtures) contributing significantly to road performance [6].

Unfortunately, even the best designed and constructed road pavements deteriorate over time under the combined effects of traffic loading and weathering. The most common distresses are: a) rutting, or permanent deformation at high temperatures [7]; b) thermal cracking, or thermal fracture due to lack of flexibility at low temperatures [8]; and c) fatigue cracking, or series of longitudinal interconnected cracks caused by the repeated applications of wheel loads [4]. Hence, different blends of bitumen with a large variety
of modifiers have been studied [9,10]. The polymers used for the modification can be divided into three categories, namely thermoplastic elastomers, plastomers and reactive polymers [11,12]. However, the two first classes of polymers usually present a limited compatibility with bitumen. The addition of reactive polymers, which contain functional groups able to react with certain bitumen compounds, may yield some advantages in the resulting binder [11-14].

Interestingly, the use of polyurethane prepolymers presents, among others, two significant benefits. First, these prepolymers are liquids which facilitate their blends with bitumen at low temperature (i.e., 90 ºC). Second, the low concentration of additives required to achieve binders with enhanced rheological properties would result in a price reduction of the resulting product.

On the other hand, the utilization of renewable raw materials in polyurethane (PU) formulations has become of increasing interest recently. Moreover, apart from the environmental benefits, the prepolymers thermal stability has been found to improve when castor oil, instead of a polyethylene glycol (PEG), is used [15]. Bitumen modification with this type of prepolymer is expected to take place by reaction of the free –NCO groups in the prepolymer and bitumen pendant groups which contain active atoms (-OH mainly, typically present in the asphaltenes) [16,17]. However, previous studies on NCO-functionalized polyether prepolymers [18-20] point out that this type of bitumen modification is a complex process, greatly influenced by a post-process curing which involves ambient moisture. Thus, during the material’s service-life, water from the air is able to slowly diffuse into bitumen and react with -NCO groups in excess (“ambient” modification). Interestingly, this route has been simulated by direct addition of water to fresh material (“added-water” modification).

The goal of the present work is explore the effect of processing on the rheological
behaviour of bituminous products modified with isocyanate-functionalized castor oil. Furthermore, we aim to understand the microstructural changes behind “ambient” and “added-water” modifications with this type of prepolymer. Accordingly, different rheological tests and some other supporting techniques (TLC/FID, MDSC and AFM) have been conducted.

2. EXPERIMENTAL

2.1. Materials

Bitumen with a penetration grade of 100/150 was used as base material for the modification. Details of technological properties (penetration grade and R&B softening temperature, according to ASTM D5 and D36, respectively) and chemical composition, in terms of SARAs fractions, are shown in Table 1.

Two different types of polymers, which correspond to “active” (chemical modification) and “passive” (physical modification) categories, respectively, have been considered:

a) Castor oil (designated as CO) supplied by Guinama (Spain), with hydroxyl index of 125 mg KOH/g (measured according to standard ASTM D1957), was functionalized with isocyanate groups, by its reaction with a polymeric 4,4’-diphenylmethane diisocyanate (-NCO content of 31 wt.%) provided by T.H. TECNIC, S.L (Spain). This reaction was carried out at 60 ºC, for 48 h, under agitation and with N₂ blanketing. In order to ensure an excess of non-reacted –NCO groups in the reaction product, an equivalent ratio -NCO/-OH of 8:1 was selected. This ratio was found optimal in a previous work [15]. The resulting reactive prepolymer (referred to as MDI-CO) has an average molecular weight of 2640 g/mol, and is expected to bring about “chemical” modification of bitumen, via -NCO groups.
b) For the sake of comparison, the commercially available SBS triblock copolymer “Kraton D-1101” (31 wt.% styrene; $M_w$ of $1.5 \times 10^5$ g/mol) was used to carry out “physical modification”, through mere physical dispersion in bitumen.

2.2. Sample preparation

MDI-CO/bitumen blends were prepared in a batch mixer composed of a glass vessel (60 mm diameter and 140 mm height), an IKA RW-20 (Germany) stirring device and a four-blade turbine. Bitumen modification, always with 2 wt.% PU prepolymer, was performed by the following two different procedures:

i) In the first procedure, bitumen and MDI-CO were mixed for 1 h, at 90 ºC and 1200 rpm, and the resulting modified bitumen was then divided into three parts: a) one was used as such (“non-treated” or fresh binder); b) the second one was mixed with 2 wt.% water for 45 min at 90 ºC (“added-water” binder); and c) the third part was poured onto aluminium foil, forming a thin layer which was exposed for up to 6 months to ambient conditions (“ambient” binders). All these samples will be referred to as “1h-processing” samples.

ii) In the second procedure, prepolymer and bitumen were mixed for 1 h and then the blend was set inside an oven for 24 h at 90 ºC; afterwards, the resulting binder was divided into the same three parts as above. All these samples will be referred to as “24h-processing” samples.

In addition, a bituminous reference sample with 3 wt.% of SBS (formulation typically used in paving) was prepared for 1.5 h, at 180 ºC, with a Silverson homogeneizer.
Finally, two samples of neat bitumen subjected to the above processing protocols i) and ii) did not show any relevant change in their rheological response if compared to the original neat bitumen.

2.3. Testing procedures

Different rheological tests were conducted in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria): a) viscous flow measurements, at 60 °C; and b) temperature sweep tests in oscillatory shear, between 30 and 100 °C, at a heating rate of 1 °C/min, a frequency of 10 rad/s and deformation of 1% strain (within LVE interval). A plate-and-plate geometry (25 mm diameter; 1 mm gap) was always used. In order to ensure the repeatability of the results, all the tests were carried out at least twice.

Modulated Differential Scanning Calorimetry (MDSC) was performed with a TA Q-100 (TA Instruments, U.S.). Samples (5-10 mg) were subjected to the following testing procedure: temperature interval between -50 and 90 °C; heating rate of 5 °C/min; amplitude of modulation of ±0.5 °C; period of modulation of 60 s; and nitrogen as purge gas, with a flow rate of 50 mL/min. In order to provide the same recent thermal history, all the modified binders were placed into hermetic aluminium pans for 24 h before measurement.

SARAs fractions of neat bitumen and modified binders were determined by means of Thin Layer Chromatography coupled with a Flame Ionization Detector (TLC/FID), using an Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan). Elutions were performed with hexane, toluene and dichloromethane/methanol (95/5), following the procedure outlined elsewhere [21].
The microstructural characterization of the bituminous binders was carried out by means of Atomic Force Microscopy (AFM), with a MultiMode AFM connected to a Nanoscope IV scanning probe microscope controller (Digital Instruments, Veeco Metrology Group Inc., U.S.). All the images were acquired in tapping mode at 30 °C. The samples were prepared by heat-casting, a method that causes a negligible effect on the material morphology if compared to solvent-casting [22].

3. RESULTS AND DISCUSSION

3.1. Study on the modification degree through viscous flow tests

Figure 1 shows the flow viscous behaviour of “1h-processing” samples, at 60 °C, as a function of curing time. Neat bitumen, 3 wt.% SBS formulation and “added-water” binder have been included for the sake of comparison. A nearly Newtonian behaviour over the whole range of shear rates tested is shown by the neat bitumen. On the contrary, modification with the MDI-CO prepolymer leads to a different viscous flow behaviour, characterized by a constant viscosity, $\eta_0$, at the lowest shear rates, followed by a shear-thinning region above a “critical” shear rate value, $\dot{\gamma}_c$. This behaviour can be described by the Carreau’s model:

$$\frac{\eta}{\eta_0} = \frac{1}{1 + (\lambda \dot{\gamma})^2}$$

(1)

where $\eta_0$ (Pa·s) is the zero-shear-limiting viscosity, $\lambda$ (s) is a characteristic time whose inverse approximately matches the threshold shear rate mentioned above ($\dot{\gamma}_c$) and ‘s’ is a parameter related to the slope of the shear-thinning region. Table 2 presents the Carreau’s model parameters for the different samples studied. It reveals that ambient
curing on MDI-CO binders leads to materials with higher viscosity and more sensitivity to the application of shear stresses (denoted by larger values of $\lambda$). These two features, which increase as curing time does, point out the development of a more “solid-like” microstructure, if compared to the corresponding neat bitumen or “non-treated” sample [19].

Figure 1 demonstrates that, even with no curing, the neat bitumen experiences a clear increase in viscosity after the addition of 2 wt.% MDI-CO. As reported by Carrera et al.[20], a fraction of the -NCO groups in the prepolymer chains (functionality between 2 and 3) is known to react, during its blending with bitumen, with –OH pendant groups present in the most polar molecules of bitumen (asphaltenic regions). Hence, the resulting urethane linkages,

$$R^1 \text{-NCO} + R^2 \text{-OH} \rightarrow R^1 \text{-NH-} \text{COO-} R^2$$  \hspace{1cm} \text{(reaction 1)}

lead to larger and more complex domains, which still have free –NCO sites available for further reaction. However, the most extraordinary increase in viscosity was found when the fresh 2 wt.% MDI-CO sample was subjected to ambient curing for 1, 2 and, mainly, 6 months. In fact, the binder exhibits, just after 1 month of curing, much higher viscosity than the reference 3 wt.% SBS formulation. On the other hand, a significant degree of modification was also observed after addition of 2 wt.% water to the “non-treated” sample. In any case, water (absorbed from air or added) is present in the formulation, and promotes two series reactions involving the mentioned excess of –NCO groups:

$$R^1 \text{-NCO} + H_2O \rightarrow R^1 \text{-NH}_2 + CO_2$$  \hspace{1cm} \text{(reaction 2)}

$$R^2 \text{-NCO} + R^1 \text{-NH}_2 \rightarrow R^2 \text{-NH} \text{-CO-} \text{NH-} R^1$$  \hspace{1cm} \text{(reaction 3)}
Consequently, reactions 2 and 3 are expected to build up a more compact microstructure, through the formation of urea linkages between smaller units which, as commented, still had reactive –NCO sites available [17,20].

In order to more conveniently visualize the degree of modification achieved at high in-service temperatures with every procedure studied, a modification index (M.I.\textsuperscript{60ºC}), in terms of the Newtonian viscosities at 60 °C (Table 2), has been defined as follows:

\[
\text{M.I.}^{60\textdegree\text{C}} = \frac{\eta_{0,\text{treated}} - \eta_{0,\text{non-treated}}}{\eta_{0,\text{non-treated}}} \tag{2}
\]

This index expresses the viscosity increase due to a certain treatment (curing or water addition) relative to the “non-treated” binder. Hence, it provides information about the effect on the modification degree of every type of procedure. Along with the “1h-processing” samples in Figure 1, “24h-processing” samples (blends which were set inside an oven at 90 ºC for 24h after their preparation) have been included in this study.

Figure 2 shows the values of the modification index for the different MDI-CO modified binders studied. Regarding the “added-water” binders, a higher degree of modification is observed when the prepolymer and bitumen are allowed to react for 24h at 90 °C, before 2 wt.% water is added. A much longer reaction time, at the same temperature, before water addition favours a higher content of large asphaltic domains, formed by urethane bonds (reaction 1), with –NCO sites available for further reactions. This makes the subsequent water-involved reactions (reactions 2 and 3) more effective. Otherwise, most of the –NCO in excess would correspond to non-linked prepolymer chains, resulting in a notable reduction in the degree of modification, as revealed by the “1h-processing” sample in Figure 2.
On the contrary, important differences are observed when a thin sheet of the “1h-processing” or “24h-processing” modified binders are exposed to ambient curing for a long period of time (of up to several months). On the one hand, the degree of modification with respect to their corresponding “non-treated” binders is noticeably higher than in the “added-water” binders. On the other hand, much higher values of M.I.° are obtained if the binder is not stored at 90°C for 24h before being exposed to ambient curing. In that sense, reactions 2 and 3 do not compete with reaction 1 when an excess of 2 wt.% water is added to the binder (“added-water” modification). So, a previous step of storage at 90°C for 24h is necessary in order to promote the formation of large asphaltenic domains, with reactive -NCO sites, which constitute the basis of a further successful modification. However, during the ambient curing, reactions 2 and 3 are controlled by the presence of a limited quantity of absorbed water, as well as a lower temperature (room temperature). Thus, reactions 1, 2 and 3 occur simultaneously. So, the success of this treatment is based on a higher content of non-reacted –NCO groups, which limits the previous blending step to no more than 1h.

As a conclusion, “added-water” modification requires the promotion of bitumen-prepolymer reactions in a large extent before the water addition [23]. Thus, water-involved reactions do not contribute significantly if the prepolymer is not previously linked to asphaltenic domains. By contrast, a higher concentration of free –NCO groups is the key factor of “ambient” modification, as the linkage between PU prepolymer chains and the asphaltenic domains (reaction 1) and growth of those (reactions 2 and 3) occur simultaneously as curing time goes by. Interestingly, “ambient” modification results in a much more effective way, if compared to accelerated curing through the added water.

3.2. In-service performance of the modified bitumens
Temperature sweep tests in oscillatory shear, from 30 to 100 °C, were carried out on the neat bitumen, and different “1h-processing” and “24h-processing” binders, before (“non-treated”) and after (“added-water” or “ambient”) treatments. Figure 3 displays the evolution with temperature of the storage modulus, G', and loss tangent, tanδ. It is observed a prevailing viscous behaviour, with tan δ>1, over the entire temperature interval tested. However, large differences are noticed between “non-treated” and “treated” binders. Thus, “treated” samples (and also neat bitumen) display a direct transition to the viscous flow (or terminal) region as temperature is increased. On the contrary, the “non-treated” MDI-CO modified binder presents a very different linear viscoelastic response, with G' showing a shoulder (or pseudo-plateau) at high temperature, which gives rise to a maximum in the loss tangent curve. Interestingly, this shoulder in G' (whose peak in tanδ moves from about 65 up to 75°C when the binder is stored at 90°C for 24h) resembles that described for synthetic binders containing SBS in their formulations below a critical phase-inversion concentration [24]. Under these conditions, the shoulder in G' arises as a consequence of the deformation-relaxation of the dispersed polymer-rich phase [25]. In the same way, we assume that the “non-treated” MDI-CO binder may have a dispersed polymer-rich phase as a result of local reactions between –NCO groups and asphaltene domains (reaction 1). Thus, this phase exerts a prevailing contribution to the overall rheological response as temperature increases and the viscosity of the continuous bituminous phase is low enough. However, if temperature is further increased, tanδ is also seen to experience an exponential increase (not shown in the temperature interval studied in Figure 3) as expected from the terminal region. Interestingly, the transition above disappears after water addition or long curing [26,27].

Moreover, an average slope value of the tanδ(T) curve within the interval 30-55 °C may
help evaluate the binder’s thermal susceptibility at medium/high in-service temperatures. In that sense, the average slope is seen to decrease from about $2 \times 10^{-2}$ down to $8 \times 10^{-3}$ °C when the neat bitumen is blended with 2 wt.% MDI-CO for 1h and then subjected to 6 months of ambient curing. In addition, this treatment (MDI-CO modification and curing) produces a significant increase in the elastic modulus (and also in the viscous modulus, not shown in Figure 3) if compared to the base bitumen. Consequently, all these results suggest an improved thermal resistance [28,29], as clearly revealed by the rutting parameter presented in Figure 4.

According to the criterion outlined in AASHTO MP1 (1993), the “rutting parameter” is the temperature at which $|G'|/\sin \delta$ equals 1 kPa. Since then, this has been a controversial matter of debate, as some authors [30,31] have claimed others parameters (like zero-shear-viscosity, ZSV) to be more adequate in predicting the resistance of bitumen to permanent deformation at high in-service temperatures. Nevertheless, if compared to the time-consuming method of the ZSV determination at several temperatures, the testing procedure presented in Figure 4 for MDI-CO modified binders stands for an easier way to establish a comparative analysis on the degree of improvement attained. As shown in Table 2, such as temperature (and, therefore, rutting resistance) is notably increased after modification and curing, mainly for “1h-processing” samples. An increase of about 15°C, with respect to the neat bitumen, is observed for the 6 months-cured “1h-processing” binder, clearly higher than the reference SBS formulation. Anyway, curing-induced enhancement must not be understood as a handicap in the use of this type of PU prepolymer. In fact, even though the resulting binder evolves towards a better performance when in service, they can satisfactorily perform as such from the very first moment.

Moreover, it is worth mentioning that the low processing temperature used (90 °C)
prevents the well-known “primary” oxidation occurred during the processing and reduce energy consumption and greenhouse gas emissions, improving worker health and safety. In addition, this reduced temperature may be of great interest in future deployments of semi-warm and warm paving technologies that permit the production of asphalt mixes at lower temperatures compared to that used for traditional hot-mix asphalts.

3.3. Chemical modification and microstructure

The previous rheological tests demonstrated that the modification degree achieved depends on both processing method and post-treatment carried out. With the aim to gain further insight into this issue, additional techniques were used. Firstly, the thermal behaviour of neat bitumen and the different MDI-CO modified binders has been evaluated by means of modulated differential scanning calorimetry (MDSC), a technique which allows for the characterization of reversing and non-reversing thermal events. With this regard, bitumen is well known to be a multiphase system mainly composed of two fractions: maltenes (which include three different families of compounds: saturates, aromatics and resins) and asphaltenes. According to Masson and co-workers [32,33], they order in four stages upon cooling from melt, yielding four specific thermal events in the non-reversing heat flow curve.

Figure 5 displays non-reversing heat flow thermograms for neat bitumen, “added-water” binders and “ambient” binders (6 months of curing). If attention is paid to the MDI-CO modified binders, those four thermal events can be clearly appreciated: a) a broad endothermic background from -50 °C to 90 °C (first event); b) two exotherms, located at about -15 °C and 40 °C (second and third events, respectively); c) an endotherm at around 50 °C (fourth event). Interestingly, under the testing conditions set in the MDSC
apparatus, the third and fourth events are not clearly defined in the neat bitumen curve. The analysis of the fourth thermal event may provide an approximate idea on changes occurred at a microstructural level. In fact, that endotherm at 50 ºC relates to the diffusion of relatively large structures with high molecular weight, as those found in resins and asphaltenes, to form independent domains. Thus, the extent of that endotherm is clearly seen to increase after modification and further treatment (addition of water or, mainly, 6 months of curing). This result supports the existence of regions composed by large molecular weight structures, with melting temperatures between 40 and 80 ºC, which form by the addition of the NCO-functionalized prepolymer and influenced by water-involved reactions. In order to provide a comparative analysis, enthalpy values associated to this event are listed in Table 3, with the largest value corresponding to the “1h-processing” sample which was subjected to 6 months of curing. Interestingly, in case of “added-water” binders, the energy value is higher after 24h of storage at 90ºC.

In order to better understand changes in the chemical composition after the modification, Figure 6 presents the evolution of the SARAs fractions, as a function of curing time, for the different bituminous binders studied. Regardless of the type of modification, an increase in the asphaltene fraction is always seen (which, again, is more important for the 6 months-cured samples). As the pure prepolymer would give a peak which does not correspond to the asphaltene peak, we assume the formation of new compounds, through reactions 1, 2 and 3, involving prepolymer, asphaltenes and even resins, during processing and post-treatment. Hence, these new compounds (referred to as NCO/polars) present so high polarity that cannot be eluted by any of the three different solvents used in the chromatographic method to separate saturates, aromatics and resins. Consequently, they appear together with the asphaltenic fraction in the TLC/FID tests.
Moreover, a “modified” Gaestel colloidal index, C.I.\textsubscript{mod}, which accounts for the changes in the binder’s chemical composition due to –NCO reactive modification, has been defined, in terms of the SARAs fractions, as follows:

\[
\text{C.I.}_{\text{mod}} = \frac{\text{saturates} + \text{asphaltenes} + \text{NCO/polars}}{\text{aromatics} + \text{resins}}
\]  

(3)

where NCO/polars refers to the resulting species originated by reactions 1, 2 and 3, detailed above (asphaltenes + NCO/polars characterized by a same single peak). Figure 7 shows the evolution of the “modified” colloidal index values for the modified binders studied. According to the C.I.\textsubscript{mod} defined above and to the bitumen colloidal model, a higher index value would be related to a material which exhibits a more significant solid-like behaviour [20,23,26,27]. Longer curing times, above all after only 1h of processing, enhance the material’s microstructure (larger quality of its colloidal microstructure or a more solid-like behaviour). By contrast, only a slight increase is noticed for the “added-water” sample. So, the evolution of C.I.\textsubscript{mod} is in good agreement with the results of the rheological tests and calorimetry scans (Figures 1-5).

Finally, additional support to the thermo-rheological results, and their interpretation, is provided by Atomic Force Microscopy (AFM) observations in tapping mode. Phase imaging provides enhanced image contrast by monitoring the difference between the oscillation signal sent to the instrumental cantilever and its actual oscillation as affected by tip-sample interactions. Thus, it provides a map of domains with different rheological or mechanical properties [22]. As observed in Figure 8, bitumen microstructure is characterised by a two phase system where randomly distributed ellipsoids, often referred to as “bee-shaped” structures, are dispersed in a continuous phase [34]. However, the chemical composition and origin of the observed phases is a
controversial topic and a matter of debate. In this sense, some authors postulate that the bee-structures consist of the most polar fraction of bitumen [22,35] and so they resemble the colloidal model. On the other hand, others authors have attributed the “bee” structures as the result of co-precipitation of non-wax asphalt compounds with crystallizing non-polar waxes [34,36].

In any case, Figure 8 compares neat bitumen and its different blends with MDI-CO, which are expected to maintain the initial wax content. Even though waxes might be the main constituent of the structures observed by AFM, there must be something else which is exerting a great influence on the level of complexity found. We assume this latter to be the quality of the colloidal structure, which is enhanced after polymer modification. In this sense, by comparing AFM phase images at 30 ºC, it can be easily deduced that processing and post-treatment greatly influence bitumen’s microstructure. Hence, the MDI-CO bituminous binders cured for 6 months at room temperature present much larger ellipsoids, particularly for those samples processed for 1h. The higher level of interactions expected among the large density of bee-sharped structures observed at 30 ºC provides an explanation to the remarkable modification degree previously shown by rheology measurements. Much less important is the change in the microstructure of “added-water” binders.

4. CONCLUDING REMARKS

With the aim to evaluate the influence of the manufacture and post-treatment on the end-performance of bituminous binders modified by a castor oil-derived PU prepolymer, four different procedures were studied. These procedures resulted from the combination of two processing times (1h or 24h, at 90°C) followed by two different post-treatments (water addition or ambient curing for up to 6 months).
The degree of modification attained after post-treatment was found to depend on the previous processing conditions. On the one hand, “added-water” modification requires the promotion of bitumen-prepolymer reactions in a large extent before the water addition. Otherwise, water-involved reactions do not contribute significantly. For this reason, the success of the “added-water” modification falls on a previous long processing step. On the other hand, short processing times are needed if the binder is further subjected to ambient curing. Hence, a higher concentration of free –NCO groups is the key factor of “ambient” modification, as the linkage of the PU prepolymer chains and the asphaltenic domains (reaction 1) and growth of those (reactions 2 and 3) occur simultaneously as curing time goes by. Interestingly, “ambient” modification results in a much more effective way, if compared to accelerated curing through the added water. With this regard, different techniques unambiguously demonstrated a more complex microstructure characterized by the presence of a larger content of molecules with higher polarity, size and molecular weight. Anyway, curing-induced enhancement must not be understood as a handicap in the use of this type of PU prepolymers. In fact, even though the resulting binder evolves towards a better performance when in service, they can satisfactorily perform as such from the very first moment.

Finally, the control of the processing/post-treatment appears to be a key factor in the final properties of these products. Moreover, bitumen modification by PU prepolymers derived from this natural polyol (castor oil) may constitute a sustainable alternative to the use of petro-chemical stuff (such as PPG, PEG, etc.).

5. ACKNOWLEDGEMENTS

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6. REFERENCES


Table 1. Penetration values, R&B softening temperatures and SARAs fractions for the neat bitumen studied.

<table>
<thead>
<tr>
<th></th>
<th>Bitumen 100/150</th>
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<tbody>
<tr>
<td>Penetration (1/10 mm)</td>
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<tr>
<td>R&amp;B softening point (°C)</td>
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</tr>
<tr>
<td>Saturates (wt.%)</td>
<td>7</td>
</tr>
<tr>
<td>Aromatics (wt.%)</td>
<td>61</td>
</tr>
<tr>
<td>Resins (wt.%)</td>
<td>20</td>
</tr>
<tr>
<td>Asphaltenes (wt.%)</td>
<td>12</td>
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</tbody>
</table>
Table 2. Evolution with curing time of the Carreau’s model parameters and SHRP maximum temperatures for neat bitumen, reference SBS binder, and the different “1h-processing” and “24h-processing” samples studied.

<table>
<thead>
<tr>
<th>MDI-CO MODIFIED BITUMENS</th>
<th>Neat bitumen</th>
<th>3 wt.% SBS</th>
<th>Non-treated</th>
<th>1 month</th>
<th>2 months</th>
<th>6 months</th>
<th>Added-water</th>
<th>1 month</th>
<th>2 months</th>
<th>6 months</th>
<th>Added-water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η₀ (Pa·s)</td>
<td>λ (s)</td>
<td>s</td>
<td>T[</td>
<td>G*/sinδ=1kPa (°C)]</td>
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<td></td>
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<tr>
<td>Neat bitumen</td>
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<td>-</td>
<td>-</td>
<td>62.4</td>
<td></td>
<td></td>
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<tr>
<td>3 wt.% SBS</td>
<td>438</td>
<td>16.67</td>
<td>0.05</td>
<td>71.1</td>
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Table 3. Enthalpy values for the endothermic fourth event ($\Delta H_{4th}$) from non-reversing heat flow curve for neat bitumen, and selected “1h-processing” and “24h-processing” samples.

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Figure captions

Figure 1. Viscous flow curves, at 60 °C, for neat bitumen, reference 3 wt.% SBS binder, and the different (non-treated, added-water and 1-2-6 months-cured) “1h-processing” samples studied.

Figure 2. Modification index values, at 60 °C, for the reference 3 wt.% SBS binder and selected (added-water and 1-2-6 months-cured) “1h-processing” and “24h-processing” samples studied.

Figure 3. Evolution with temperature of: a) storage modulus (G'); and b) loss tangent (tanδ), for neat bitumen, and selected (non-treated, added-water and 6 months-cured) “1h-processing” and “24h-processing” samples.

Figure 4. Evolution with temperature of the “rutting parameter” (|G*|/sinδ) for neat bitumen and selected (non-treated, added-water and 6 months-cured) “1h-processing” and “24h-processing” samples.

Figure 5. Non-reversing heat flow curves for neat bitumen and selected (added-water and 6 months-cured) “1h-processing” and “24h-processing” samples.

Figure 6. Bitumen SARAs fractions for neat bitumen and the different (non-treated, added-water and 1-2-6 months-cured) “1h-processing” and “24h-processing” samples studied.

Figure 7. “Modified” colloidal index values for neat bitumen and the different (non-treated, added-water and 1-2-6 months-cured) “1h-processing” and “24h-processing” samples.

Figure 8. AFM micrographs (20 x 20 µm²), at 30 °C, for neat bitumen and selected (added-water and 6 months-cured) “1h-processing” and “24h-processing” samples.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8