“Isocyanate-functionalized castor oil as a novel bitumen modifier”

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ABSTRACT

The use of biomaterials from renewable sources in the synthesis of polyurethane-derived polymers is lately receiving great attention from social, environmental and economic standpoints. In this work, prepolymers having different -NCO/-OH ratio were synthesized, by reaction of 4,4´-diphenylmethane diisocyanate (MDI) with castor oil (CO), to be used as modifying agent of asphaltic bitumen. Reactions between MDI and CO, performed with -NCO/-OH molar ratios of 8:1 and 4:1, have led to suitable bitumen modifiers. Modification has been related to chemical reactions between -NCO groups, some bitumen compounds and air moisture (or added water), which gave rise to binders with enhanced resistance to permanent deformation. The results showed that a 2 wt.% of MDI-CO prepolymer leads to binders with higher viscosity than that corresponding to a 3 wt.% Styrene-Butadiene-Styrene (SBS) block copolymer, a polymer and concentration widely used in the paving industry. Furthermore, the resulting prepolymers are liquids that can be easily mixed with bitumen at 90 ºC, which significantly lowers the typical temperature used for commercial SBS-modified bitumen (about 180 ºC). This fact may represent energy savings, reduce bitumen oxidation and result in improvements of health and safety conditions during the product manufacture. However, if high processing temperatures are required, MDI-CO based modifiers have demonstrated much higher thermal stability than prepolymers derived from crude oil (e.g. based on polyethylene glycol). As a result, NCO-terminated prepolymers obtained from biomass-derived polyols (castor oil in this article) may become a promising alternative to the use of other petrochemicals in the paving industry.

Keywords: bitumen, polymer, rheology, viscoelasticity; product design, material processing.

1. INTRODUCTION

Bitumen, by-product from crude oil fractionation, is a complex material basically composed of hydrocarbons along with some other molecules, which contain small percentages of heteroatoms (sulphur, nitrogen and oxygen). Chromatographic techniques can be used to separate bitumen compounds into four different fractions (usually referred to as SARAs): saturates (S), aromatics (A) and resins (R), which make up the maltenes, and asphaltenes (As) (Claudy et al., 1991). According to the so-called Colloidal Model (Lesueur et al., 1996), bitumen physico-chemistry and its rheological properties strongly depend on both temperature and chemical composition.

On account of its properties, bitumen is the most suitable material to be used as a binder for pavements applications (Read and Whiteoak, 2003). Despite its small proportion in the pavement (around 5 wt. %), bitumen forms the continuous phase and represents its only deformable fraction. Consequently, it exerts major control on the performance of a road (Adedeji et al., 1996). Unfortunately, even the best designed and constructed road pavements deteriorate over time under the combined effects of traffic loading and weathering. Common road distresses are: a) rutting or permanent deformation of the pavement at the hottest climates (Kandhal and Cooley, 2003); and b) thermal cracking, also referred to as thermal fracture, due to pavement lack of flexibility at low temperatures (Lu et al., 2003).

Hence, the addition to bitumen of different types of “passive” virgin polymers (SBS, SBR, EVA, etc) or waste polymers (plastics from agriculture, crumb tyre rubber, etc) (Fawcett et al., 1999) has shown to improve its performance in a broad range of in-service temperatures. These polymers are just physically mixed with bitumen. On the contrary, “active” polymers are able to form chemical bonds with some bitumen fractions, which prevent the resulting blend from phase separation during its storage at high temperature (between 160-200 ºC) in absence of stirring (Pérez-Lepe et al., 2006). Some examples of reactive polymers/substances used can be found elsewhere: terpolymers containing glycidyl methacrylate (Polacco et al., 2004; Selvavathi et al., 2002), TDI production waste (Singh et al., 2003) and MDI-derived prepolymers (Martín-Alfonso et al., 2008; Navarro et al., 2006). The later type consists of a “soft or flexible segment” represented by polyols (PEG, PPG, etc), and a “hard or stiff segment” constituted by diisocyanates (MDI, HDI, etc). Additionally, there may be a chain extender (Eceiza et al., 2008). Recently, the utilization of renewable resources in the formulation of MDI-derived prepolymers becomes of increasing interest due to their great potential as substitute for petro-chemical derivates (Swamy et al., 2003). Among them, vegetable oils present advantages (Karak et al., 2009) such as: 1) renewability, 2) easy availability in a large quantity; 3) environmental friendliness; 4) biodegradability, and 5) overall low cost. In this sense, castor oil is the only commercially available natural oil polyol produced directly by nature. Due to its high content in ricinoleic acid (around 80 wt. %), it has widely been used in a range of industrial applications (coatings, sealants and adhesives to flexible foams, thermoplastics elastomers, etc). However, it is worth noting castor oil derivatives have not been proposed elsewhere as reactive bitumen modifiers.

On these grounds, this work deals with the synthesis of NCO-functionalised prepolymers derived from castor oil aiming to achieve asphaltic bitumen with optimal the thermal and rheological properties. Thus, the effect of their composition, by varying the -NCO/-OH molar ratio during their synthesis, was analysed. Different tests were conducted on these prepolymers (DTA/TG, GPC, dynamic shear and modulated DSC) and their resulting bituminous modified binders (viscous flow, dynamic shear, modulated DSC and AFM). Results evidence the adequacy of castor oil in the synthesis of MDI-derived prepolymers aimed at bitumen chemical modification, and constitute a step forward in the use of polyols derived from this and other renewable sources (Mutlu et al., 2010).

2. EXPERIMENTAL

2.1. MATERIALS

Bitumen with a penetration grade of 100/150 was used as base material for the polymer modification. The results of penetration and Ring and Ball softening temperature tests, according to ASTM D5 and ASTM D36 were, respectively, 114 dmm and 40 ºC.

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

a) On the one hand, castor oil (designated CO and with hydroxyl index of 125 mg KOH/g) was functionalised with isocyanate groups, by its reaction with polymeric 4,4’-diphenylmethane diisocyanate (with -NCO index of 31 wt.%). This reaction was carried out at 60 ºC, for 48 h, under agitation and with N_2 blanketing. Different -NCO/-OH molar ratios of 2:1, 4:1 and 8:1 were used. The average molecular weight (M_w) and free -NCO content of the three resulting reactive prepolymers (referred to as MDI-CO) are presented in Table 1. As previously reported, these MDI-CO prepolymers are expected to bring out “chemical” modification of bitumen, via free -NCO groups. In addition, and with the aim to establish a comparative analysis on the thermal stability of the castor oil-based prepolymer, another prepolymer was prepared with the same polymeric MDI and polyethylene glycol (designated PEG and with hydroxyl index of 180 mg KOH/g). This new prepolymer will be referred to as MDI-PEG.

b) On the other hand, the commercially available SBS triblock copolymer “Kraton D-1101” (31 wt.% styrene; M_w of $1.5 \cdot 10^5$ g/mol) was used for the preparation of a reference modified binder, by its mere dispersion into bitumen (“physical” modification).

2.2. SAMPLES PREPARATION

Blends of bitumen and 2 wt.% of MDI-CO prepolymers (with molar ratios of 4:1 and 8:1) were processed for 1 h and at 90 ºC in a cylindrical vessel (60 mm diameter and 140 mm height) with a four-bladed turbine rotating at 1200 rpm. Subsequently, the blend was set in an oven at 90 ºC for 24 h and the resulting binder was then divided into three parts: a) one was tested as such (“non-cured” binder); b) another one was further mixed with 2 wt.% water for 45 min at 90 ºC (“water-modified” binder); and c) the third part was poured onto aluminium foil, forming a thin layer which was exposed for up to 60 days to the ambient, under free access of air/moisture (“ambient cured” binder). In addition, a reference bitumen sample with 3 wt.% of SBS (formulation commonly used in road paving) was prepared for 1.5 h, at 180 ºC, under high shear conditions.

2.3. SAMPLES TESTING

Different rheology tests were conducted in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria): a) viscous flow measurements, at 60 ºC; and b) temperature sweep tests in oscillatory shear, from -20 to 200 ºC (for MDI-CO prepolymers) and from 30 to 80 ºC (for their modified binders), at a heating rate of 1 ºC/min, a frequency of 10 rad/s and deformation of 1% strain (within LVE interval). Serrated plate-and-plate geometry (25 or 50 mm diameter, depending on the sample, and 1 mm gap) was always used. In order to ensure the repeatability of the results, all the tests were carried out at least twice.

Simultaneous thermo gravimetric/differential thermal analyses (TG/DTA) were conducted using a Seiko TG/DTA 6200 (Japan). Temperature ramps at 10 ºC/min, from 40 to 600 ºC, under N_2 atmosphere, and isothermal time sweeps at 180 ºC, for 120 min, with air, were carried out on 5-10 mg of sample (polymeric MDI, PEG, castor oil and the resulting prepolymers).

Modulated Differential Scanning Calorimetry (MDSC) was performed with a TA Q-100 (TA Instruments, USA). Samples of 5-10 mg were always subjected to the following testing procedure: temperature range from -60 to 190 ºC for MDI-CO prepolymers and from -40 to 85 ºC for modified binders; heating rate of 5 ºC/min; amplitude of modulation of ±0.5 ºC; a period of 60 s; and N_2 as purge gas, with a flow rate of 50 mL/min. In order to provide the same recent thermal history, all the samples were placed into hermetic aluminium pans for 24 h before measurement.

The average molecular weight (M_w) of the polymeric MDI, castor oil and the resulting prepolymers were determined by means of GPC, by using a Waters apparatus, equipped with a Styragel® HR 4E column and using THF as solvent. Polypropylene glycol (PPG) standards covering a wide range of molecular weights were used for the calibration.

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., USA). All the images were acquired in tapping mode at 30 ºC. The samples were prepared by heat-casting, a method that causes a negligible effect on the material morphology if compared to solvent-casting (Masson et al., 2006).

3. RESULTS AND DISCUSSION

3.1. PREPOLYMERS CHARACTERIZATION

MDI derived prepolymers are block copolymers with alternating soft and hard blocks that, due to their structural differences, separate into microphases or domains formed from the respective hard and soft segments. Figure 1 illustrates the reaction scheme for the synthesis of MDI-CO prepolymers. It can be observed urethane bonds between hydroxyl and isocyanate groups. The soft-segments, formed by the polyol (castor oil), provide extensibility, whilst the hard-segments, formed by the diisocyanate (MDI), play the role of a physical crosslinker and also act as high-modulus filler (Xu et al., 2008).

The morphology and thermorheological properties of these polymers depend on the structure and relative amount of soft and hard phases and their ordering. The thermal behaviour of polymeric MDI, castor oil (CO) and the resulting MDI-CO prepolymers was studied by means of MDSC and TG/DTA tests (Figures 2 and 3). This study may give an insight into the effect that different -NCO/-OH molar ratios exert on the prepolymers thermal properties and on their potential applicability as bitumen modifiers. In that sense, Figure 2, which presents reversing heat flow thermograms from -80 to 190 ºC, reveals glass transition temperatures at -49 and -63 ºC for the polymeric MDI and castor oil, respectively. On the other hand, MDI-CO(2:1) presents two well-defined glass transitions. The first one, located at -37 ºC, may be assigned to non-reacted polymeric MDI. The shortest chains in the polymeric MDI, with higher mobility, are assumed to react with the castor oil. Consequently, the longest chains, which would remain unbound, are the responsible for the higher value of T_g observed. The second peak, found at 135 ºC, is attributed to the products formed by the functionalization of the castor oil with isocyanate groups, following the reaction scheme illustrated above. Instead, MDI-CO(8:1) and MDI-CO(4:1) prepolymers only display one glass transition temperature each, located at -36 and -19 ºC, respectively. The reaction products would be homogeneously dispersed in a continuous phase of polymeric MDI in excess, giving rise to an overall single thermal event.

Therefore, the resulting MDI-CO prepolymers with molar ratios of 8:1 and 4:1 are light brownish liquids. On the contrary, a yellowish infusible solid (decomposes without melting), not suitable for bitumen reactive modification, is obtained by decreasing the excess of isocyanate down to a molar ratio of 2:1. In fact, this prepolymer cannot be dissolved in THF and was not characterized by GPC. However, the study of its properties may provide valuable information on the wide range of polyurethane products which can be obtained by a simple change in their formulation and may help to establish the adequate application limits. In that sense, this study has also been included in the present investigation.

As reported by Corcuera et al. (Corcuera et al., 2011), MDI-prepolymers thermal decomposition is known to occur as a result of multitude of physical and chemical phenomena and is not dominated by a single process. Thus, Figures 3A and 3B reveal the existence of three different degradation stages. The first one, from 160 to 340 ºC (with a DTG peak at 280 ºC) is related to the urethane bond decomposition into its parent isocyanate and alcohol, the formation of primary amines and a terminal olefinic group on the polyester chain and the formation of secondary amines and CO_2 (Hablot et al., 2008). The second stage, extending over a temperature range between 340 and 430 ºC, corresponds to the degradation of the soft segments (castor oil, in this case). Finally, it is possible to observe a third weight loss between 430 and 530 ºC (with a DTG peak at 470 ºC) which relates to the degradation of the polyurethanes networks formed or some other remaining structures (Corcuera et al., 2010). TG/DTG curves for castor oil and polymeric MDI are also included for the sake of comparison.

Interestingly, the thermal decomposition of these MDI-CO prepolymers was strongly influenced by the -NCO/-OH molar ratio. In this sense, a higher content in MDI (i.e., a larger -NCO/-OH ratio) had two clear effects. On the one hand, the DTG peak corresponding to the thermal decomposition of castor oil, at around 400 ºC, becomes significantly narrower. On the other hand, a notable decrease in the rate corresponding to the first degradation process is observed with decreasing the -NCO/-OH ratio. Furthermore, if compared to the polymeric MDI, which presents its first decomposition peak at 276 ºC, the MDI-CO(2:1) prepolymer peak is clearly seen to increase up to 324 ºC. These two later results may be attributed to the longest chains of polymeric MDI which remain unreacted after the polymerisation. In fact, they present lower mobility than the shortest chains and, as previously revealed by curves in Figure 2, their presence become more significant for the MDI-CO(2:1) prepolymer. For higher -NCO/-OH ratios, prepolymer molecules are diluted in a large excess of polymeric MDI.

On the other hand, isothermal TG experiments (at 180 ºC, for 2 h) were conducted on the different MDI-CO prepolymers and one selected MDI-PEG prepolymer, in order to establish a comparative analysis on their thermal stability. This study also allowed the influence of the selected -NCO/-OH molar ratio to be determined. Castor oil, polyethylene glycol and polymeric MDI curves are also included. As shown in Figure 4, PEG displays a very significant weight loss during a prolonged period of time, with mass going down to 10 wt.% of its initial value after 60 min of testing. In contrast, no weight loss was observed for the castor oil at 180 ºC. Moreover, the polymeric MDI also undergoes a very important weight loss of about 50 wt.% after 60 min. With regards to the resulting prepolymers, the combined effect of MDI/CO or MDI/PEG, influenced by their relative proportion, should be expected. Thus, the petroleum-based prepolymer (MDI-PEG), with a very high excess of polymeric MDI, presents a response very similar to this (Martín-Alfonso et al., 2009). However, results obtained for the vegetable oil-based prepolymer (MDI-CO) point out the strong influence that a small proportion of this type polyol can exert on their NCO-functionalised prepolymers. In fact, even for the MDI-CO prepolymer with the highest excess of -NCO (-NCO/-OH molar ratio of 8:1), a very high thermal stability, quite close to the pure castor oil's, can be observed (weight loss less than 15wt.% after 2 h). This mass loss goes down to 9 wt.% or even become negligible for MDI-CO(4:1) and MDI-CO(2:1), respectively.

A practical consequence, in relation with the bitumen-prepolymer mixing stage during the bitumen modification, derives from the result above. Hence, MDI-CO has shown its adequacy at the high processing temperatures required for those bitumens with low values of penetration. However, the weight loss observed for MDI-PEG may represent a handicap in that range of temperature.

Finally, the rheological behaviour of the three MDI-CO prepolymers was studied by means of temperature sweep tests in oscillatory shear mode (at a selected temperature interval for each of them). In this sense, Figure 5 shows the evolution with temperature of the dynamic viscous (G") and elastic (G') moduli. It can be seen that, for the MDI-CO(8:1) and MDI-CO(4:1) prepolymers, both moduli monotonously decrease with increasing temperature, from -20 to 20 ºC and from 30 to 100 ºC, respectively. Moreover, the viscous modulus clearly prevails over the elastic one in the entire temperature interval tested, which points out a predominantly viscous behaviour (liquid-like behaviour). In fact, the MDI-CO(8:1) prepolymer shows the typical behaviour corresponding to the so-called flow viscous region. However, MDI-CO(2:1) presents, in a temperature range between the second glass transition (135 ºC) and thermal degradation (about 200 ºC), constant values of the dynamic moduli, with a significantly higher contribution of G' (solid-like behaviour), which typically corresponds to cross-linked networks above T_g (Ross-Murphy, 1995).

3.2. BITUMEN MODIFICATION: RHEOLOGICAL BEHAVIOUR AND MICROSTRUCTURE

Figure 6 displays viscous flow curves, at 60 ºC, for 2 wt.% MDI-CO(8:1) modified binders as a function of curing time. Neat bitumen, the reference 3 wt.% SBS binder and the “water-modified” binder have been included for the sake of comparison. A nearly Newtonian behaviour in the whole range of shear rates tested is shown by neat bitumen. On the contrary, the chemical modification with 2 wt.% MDI-CO(8:1) leads to a different viscous flow behaviour, with a constant viscosity, η_0, at the lowest shear rates, followed by a shear-thinning region above a “critical” shear rate value, $\dot{\gamma}_c$.

As can be observed in Figure 6, the “non-cured” 2 wt.% MDI-CO(8:1) binder presents a clearly higher value of viscosity if compared to the neat bitumen (viscosity goes from 100 up to 200 Pa·s, approximately). Thus, during the bitumen-prepolymer blending and further storage at 90 ºC for 24 hours (“short-term” modification), a part of the free -NCO groups in the prepolymer are known to react with certain groups, mainly hydroxyl, present in the asphaltene molecules. This provokes a notable increase in the binder viscosity, due to the formation of urethane linkages according the following reaction (Singh et al., 2003):

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

However, a much higher degree of modification was observed when the binder was subjected to a further curing stage of up to 60 days at room temperature (“long-term” modification). With this regard, some water from the ambient is expected to slowly diffuse into the modified bitumen, promoting the two following series reactions (Carrera et al., 2010a):

$$R^1-NCO \;+\; H_2O \;\rightarrow\; R^1-NH_2 \;+\; CO_2\uparrow \qquad \text{(reaction 2)}$$

$$R^2-NCO \;+\; R^1-NH_2 \;\rightarrow\; R^2-NH-CO-NH-R^1 \qquad \text{(reaction 3)}$$

A significant increase in the binder viscosity derived from the development of a complex microstructure is achieved (Segura et al., 2005; Martín-Alfonso et al., 2008). This viscosity enhancement, which becomes larger with as curing time is longer, may be of up to one order of magnitude after 60 days of curing. On the other hand, water in a concentration of 2 wt.%, was added to the binder during its preparation, in an attempt to spare the time required for maturing. As a result, a binder with similar viscosity to that resulting from 15 days of curing, and higher than the reference rubber-modified binder is attained. In addition, viscous flow tests at 60 ºC were also conducted on samples modified by MDI-CO(4:1). The results, presented in Table 2, reveal the development of a more complex microstructure for the largest -NCO content (i.e., MDI-CO(8:1) prepolymer) and the longest curing time, as demonstrated by a higher value of viscosity along with a lower value of $\dot{\gamma}_c$ (Martín-Alfonso et al., 2008).

A modification index (M.I.^{60ºC}), written in terms of the zero-shear viscosity values at 60 ºC, results a very adequate parameter to quantify the bitumen modification at high in-service temperatures. This index is defined as follows:

$$\mathrm{M.I.}^{60ºC} = \frac{\eta_{0,\mathrm{mod}} - \eta_{0,\mathrm{neat}}}{\eta_{0,\mathrm{neat}}} \qquad (1)$$

where $\eta_{0,mod}$ and $\eta_{0,neat}$ are the zero-shear viscosity values, at 60 ºC, for MDI-CO modified binders and neat bitumen, respectively. So, $M.I.^{60ºC}$ is a measure of the viscosity increase produced by the modifier, relative to the original viscosity of the non-modified bitumen. Figure 7 presents the evolution of the modification index with curing time for the 2 wt.% MDI-CO bituminous binders. As references, modification indexes for 3 wt.% SBS and "water-modified" binders were also included. If no curing is conducted (only reaction (1) takes place) the degree of bitumen modification attained is just slightly affected by the type of MDI-CO used. In other words, "short-term" modification does not seem to greatly depend on the prepolymer -NCO/-OH molar ratio. However, when a thin sheet of the resulting modified bitumen is exposed to the environment for a prolonged period of time, the prepolymer with the highest -NCO/-OH ratio produces a much more significant increase in the modification index values. In this case, a larger content of free -NCO groups are yet available to react through the scheme detailed in reactions (2) and (3). For example, the binder with 2 wt.% MDI-CO(8:1) exhibits, just after 15 days of curing, a higher value of $M.I.^{60ºC}$ (about 3.45) than the 3 wt.% SBS binder (2.80). On the other hand, as previously commented, water addition on non-cured binders may lead to a material with improved resistance to permanent deformation (higher viscosity) without the need for curing. However, it was not possible to obtain a material equivalent to the 60 days-cured binder by mere addition of water. These observations confirm two ideas of paramount importance: a) on the one hand, water (either added or absorbed from air) promotes reactions with free -NCO groups which significantly improve the binders rheological response at 60 ºC; b) on the other hand, the slow diffusion for a prolonged period of time (of up to 60 days in this case) of water into previously MDI-CO modified binder results in a more efficient method of bitumen chemical modification, if compared to the direct water addition. Thus, reactions

(1), (2) and (3) would be occurring simultaneously during the curing stage. In terms of product application, it means that modification would be able to continue under environmental conditions even after asphalt laydown operations have concluded. On the contrary, direct addition of water would compete with bitumen for the free –NCO sites available and reaction (1) would be hampered, which limits the resulting degree of modification.

The viscoelastic performance of the MDI-CO modified binders has been evaluated by means of temperature sweep tests, in oscillatory shear mode from 30 to 80 ºC. Figure 8A displays the evolution of the "rutting parameter", $|G^*|/\sin\delta$, with temperature for neat bitumen, 3 wt.% SBS and two selected MDI-CO(8:1) ("non cured" and 60-days-cured) modified binders. This parameter has widely been used to evaluate the high temperature performance of bituminous binders. Some other parameters lately proposed, like zero-shear-viscosity (ZSV), have proved to better correlate permanent deformation in this range of temperatures. However, this procedure requires relatively high time-consuming measuring methods (Morea et al., 2009). Instead, the "rutting parameter" derived from simple dynamic temperature sweep tests may be considered an easier and more hands-on way to compare the degree of improvement attained after modification. On these grounds, the values of temperatures at which $|G^*|/\sin\delta$ (under certain testing conditions outlined by AASHTO MP1 (1993)) equals 1 kPa have been calculated and are shown in Figure 8B, for 2 wt.% MDI-CO modified binders, as a function of curing time. These temperatures represent the in-service limits at which the binder would offer a satisfactory response. As may be seen, the addition of 2 wt.% of MDI-CO(8:1) leads to a first increase in the $T_{|G^*|/\sin\delta}$ value just after processing, from 62 ºC for neat bitumen up to 65 ºC. Further, this value goes up to 73 ºC after 60 days of curing, which represents 11 ºC of increase if compared to the straight-run bitumen.

Once more, the effect of the -NCO/-OH molar ratio is almost negligible for the “non-cured” binders, but results very noticeable as the curing time increases (same as shown for viscosity). In conclusion, bitumen modification by MDI-CO prepolymers would reduce the progressive accumulation of permanent deformations produced by the traffic at high temperatures, with rutting resistance being favoured by a larger -NCO/-OH ratio and longer curing times.

The above-mentioned enhancements in the binders rheological behaviour suggest significant changes in their microstructure, which can be detected by means of the non-reversing component of the heat flow curve obtained by modulated DSC. 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 (Masson and Polomark, 2001; Masson et al., 2002), they order in four stages upon cooling from melt, yielding four specific thermal events in the non-reversing heat flow curve. Figure 9 shows the non-reversing thermograms for neat bitumen and the 2 wt.% MDI-CO(8:1) modified binders, as a function of curing time. If attention is paid to the modified binder after 60 days of curing, those four thermal events can be appreciated: a) a broad endothermic background from -40 ºC to 80 ºC (first event); b) two exotherms, located at about -20 ºC and 35 ºC (second and third events, respectively); c) an endothermic at around 50 ºC (fourth event). Interestingly, 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 curing, and corroborates the rearrangement of domains composed by large molecular weight structures, with melting temperatures between 40 and 80 ºC, which form by the addition of the modifier. 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 60 days-cured modified bitumen.

Finally, additional support to previous results is provided by the AFM pictures, taken at 30 ºC, shown in Figure 10 for neat bitumen, “water-modified” binder and 2 wt.% MDI-CO(8:1) modified binder after 60 days of curing. Bitumen microstructure, pictured as solid particles of asphaltenes (black and white streaks) covered by a shell of resins (light areas) and surrounded by the molten maltenic matrix (darkest areas) (Masson et al., 2006), matches pretty well the traditional bitumen colloidal model (Lesueur et al., 1996; Lesueur, 2009). If compared to neat bitumen, the MDI-CO modified binders present much larger asphaltenic regions, particularly for the modified binder exposed at room curing for 60 days (see previous explanations on that issue). Consequently, AFM observations seem to be in accordance with previous viscous flow, viscoelasticity and calorimetry tests results. Also it constitutes a valuable tool for providing evidence on the existence of a more compact microstructure originated by the formation of covalent bonds between the MDI-CO prepolymers and certain bitumen groups (Carrera et al., 2010b). This microstructure leads to observed enhancement in bitumen performance.

4. CONCLUDING REMARKS

With the aim to obtain efficient bitumen modifiers for the development of a more sustainable paving practice, castor oil was used as an alternative source of hydroxyl groups in the synthesis of polyurethane prepolymers. The evaluation was conducted by preparing two different formulations, resulting from the blend of bitumen and two different prepolymers (with -NCO/-OH molar ratios of 8:1 and 4:1) which had previously been obtained. After preparation, both formulations were exposed to ambient for up to 60 days. The results obtained showed a very significant degree of modification after addition of 2 wt.% of prepolymer, which was further enhanced by the curing stage, mainly for the polyurethane prepolymer with the highest -NCO/-OH molar ratio. Thus, the blend containing the prepolymer with ratio of 8:1 presented, just after 15 days of ambient curing, a value of viscosity higher than that corresponding to 3 wt.% SBS modified bitumen. Furthermore, a viscosity increase of one decade was observed after 60 days of curing. In that sense, two different modification routes were identified: a) "short-term" modification, taking place during mixing and storage for 24 h, and b) "long-term" modification, which develops during the binder curing. Alternatively, long-term modification may be replaced by the addition of 2wt.% water, to reduce the time required for binder modification. Further to the use these MDI-bio-oil based modifiers, the selected processing conditions significantly lower the typical temperature used for commercial SBS-modified bitumen (about 180 ºC). This fact represents a significant energy savings, prevents bitumen from oxidation during its mixing with the polymer (i.e the so-called "primary aging") and results in improvements of health and safety conditions of the product manufacture. Moreover, if high processing temperatures are required, MDI-CO based modifiers have demonstrated much higher thermal stability than prepolymers derived from crude oil such as those based on polyethylene glycol, as shown by isothermal thermogravimetry measurements.

To conclude, castor oil appears to be a promising alternative to the use of petroleum-based polyols in the manufacture of polyurethane prepolymers for bitumen modification. With regard to current environmental concerns, this work may constitute a step forward in the development of novel bitumen modifiers for the paving technology, based on polyols derived from renewable sources.

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Table 1. Average molecular weight (M_w), -NCO content (wt.%) and glass transition temperature ($T_{g,DSC}$) of the polymeric MDI, castor oil and the resulting MDI-CO prepolymers.

<table>
<tr><th></th><th>M_w (g/mol)</th><th>-NCO content (% wt.)[a]</th><th colspan="2">$T_{g,DSC}$ (ºC)</th></tr>
<tr><td>MDI-CO(8:1)</td><td>2640</td><td>19</td><td colspan="2">-36</td></tr>
<tr><td>MDI-CO(4:1)</td><td>3375</td><td>13</td><td colspan="2">-19</td></tr>
<tr><td>MDI-CO(2:1)</td><td>−</td><td>6</td><td>-37</td><td>135</td></tr>
<tr><td>Polymeric MDI</td><td>363</td><td>31</td><td colspan="2">-49</td></tr>
<tr><td>Castor oil</td><td>1087</td><td>−</td><td colspan="2">-63</td></tr>
</table>

[a] *According to ASTM D2572*

Table 2. Evolution with curing time of the zero-shear limiting viscosity (η_0) and "critical" shear rate ($\dot{\gamma}_c$) for 2 wt.% MDI-CO modified binders. Neat bitumen and 3 wt.% SBS are included as references.

			η_0 (Pa·s)	$\dot{\gamma}_c$ (s^{-1})
		Neat bitumen	110	–
		3 wt. % SBS	438	0.1
MDI-CO (4:1)	**MODIFED BITUMENS**	Non-cured	199	5.8
		15 days	305	4.1
		30 days	321	4.0
		60 days	375	3.6
		2 wt. % H_2O	266	4.1
MDI-CO (8:1)		Non-cured	202	10.2
		15 days	489	2.2
		30 days	598	1.9
		60 days	824	1.2
		2 wt. % H_2O	539	1.4

Table 3. Enthalpy values associated to the fourth thermal event, for neat bitumen and the 2 wt.% MDI-CO(8:1) modified binders, as a function of curing time.

	ΔH_{4th} (J/g)
Neat bitumen	--
Non-cured	0.50
15 days	1.72
30 days	2.07
60 days	4.40

Figure captions

Figure 1. Reaction scheme for the synthesis of MDI-CO prepolymers.

Figure 2. Reversing heat flow thermograms for the polymeric MDI, castor oil, and the resulting MDI-CO prepolymers.

Figure 3. TG/DTG curves under N_2 atmosphere for the polymeric MDI, castor oil, and the resulting MDI-CO prepolymers.

Figure 4. Isothermal weight loss curves at 180 ºC under air atmosphere for the polymeric MDI, castor oil, polyethylene glycol (PEG), and the resulting MDI-PEG and MDI-CO prepolymers.

Figure 5. Dynamic shear temperature sweep tests for the MDI-CO prepolymers.

Figure 6. Viscous flow curves, at 60 ºC, for the selected 2 wt.% MDI:CO(8:1) modified binder, as a function of curing time. Neat bitumen, 3 wt.% SBS and "water-modified" binders are also included as references.

Figure 7. Evolution of the modification index with curing time for 2 wt.% MDI-CO modified binders. "Water-modified" and 3 wt. % SBS binders are also included as references.

Figure 8. a) Evolution with temperature of the "rutting parameter", $|G^*|/\sin\delta$, for neat bitumen, 3 wt.% SBS and two selected 2 wt.% MDI-CO(8:1) binders (non-cured and 60-days-cured); b) Evolution of $T_{|G^*|/\sin\delta=1kPa}$ with curing time for 2 wt.% MDI-CO binders as a function of the -NCO/-OH molar ratio. References are also included.

Figure 9. Non-reversing heat flow thermograms for neat bitumen and 2 wt.% MDI-CO(8:1) modified binders after different curing times.

Figure 10. AFM micrographs (50 x 50 µm), at 30 ºC, for neat bitumen, "water-modified" binder and 2 wt.% MDI-CO(8:1) modified binder after 60 days of curing.

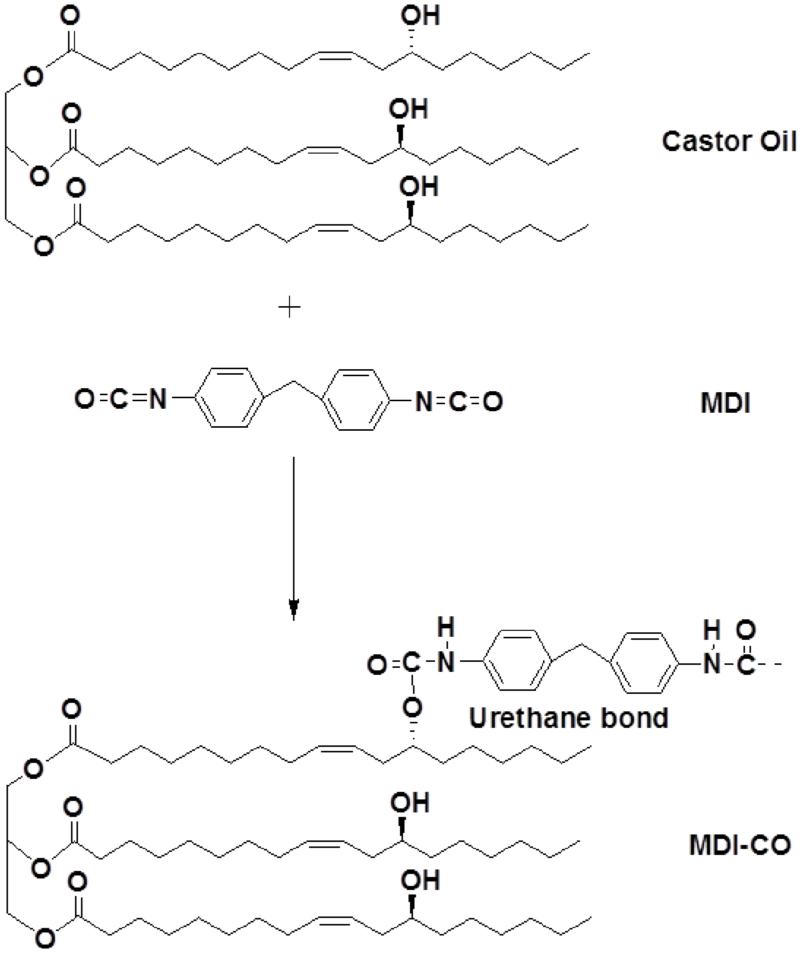


Figure 1

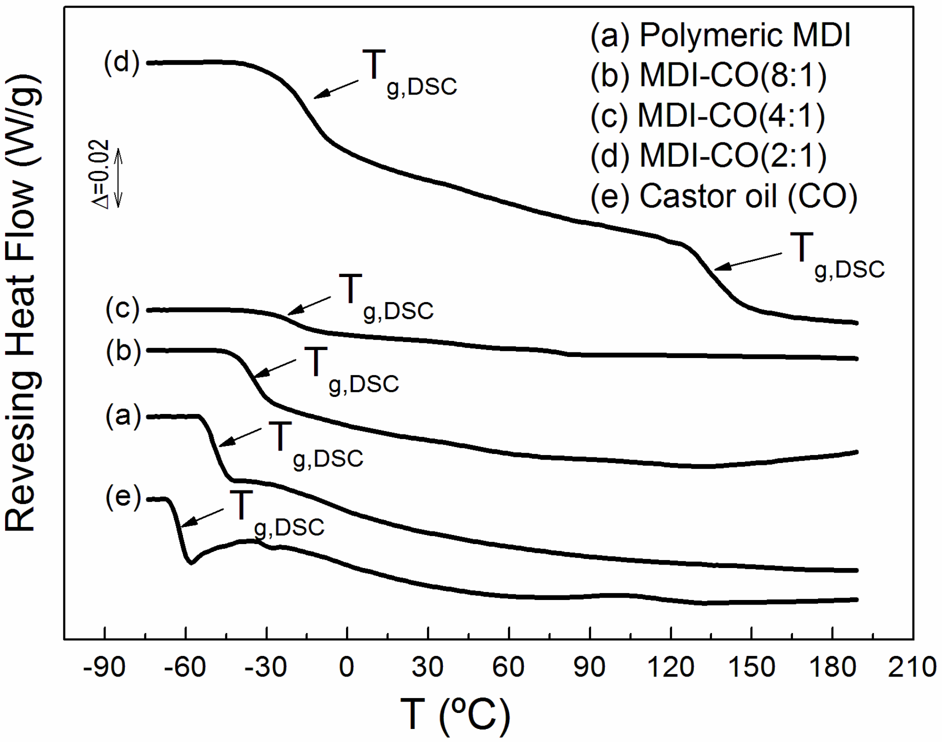

(a) Polymeric MDI
(b) MDI-CO(8:1)
(c) MDI-CO(4:1)
(d) MDI-CO(2:1)
(e) Castor oil (CO)
(d)
(c)
(b)
(a)
(e)
T g,DSC
Δ=0.02
Revesing Heat Flow (W/g)
T (ºC)
-90
-60
-30
0
30
60
90
120
150
180
210

Figure 2

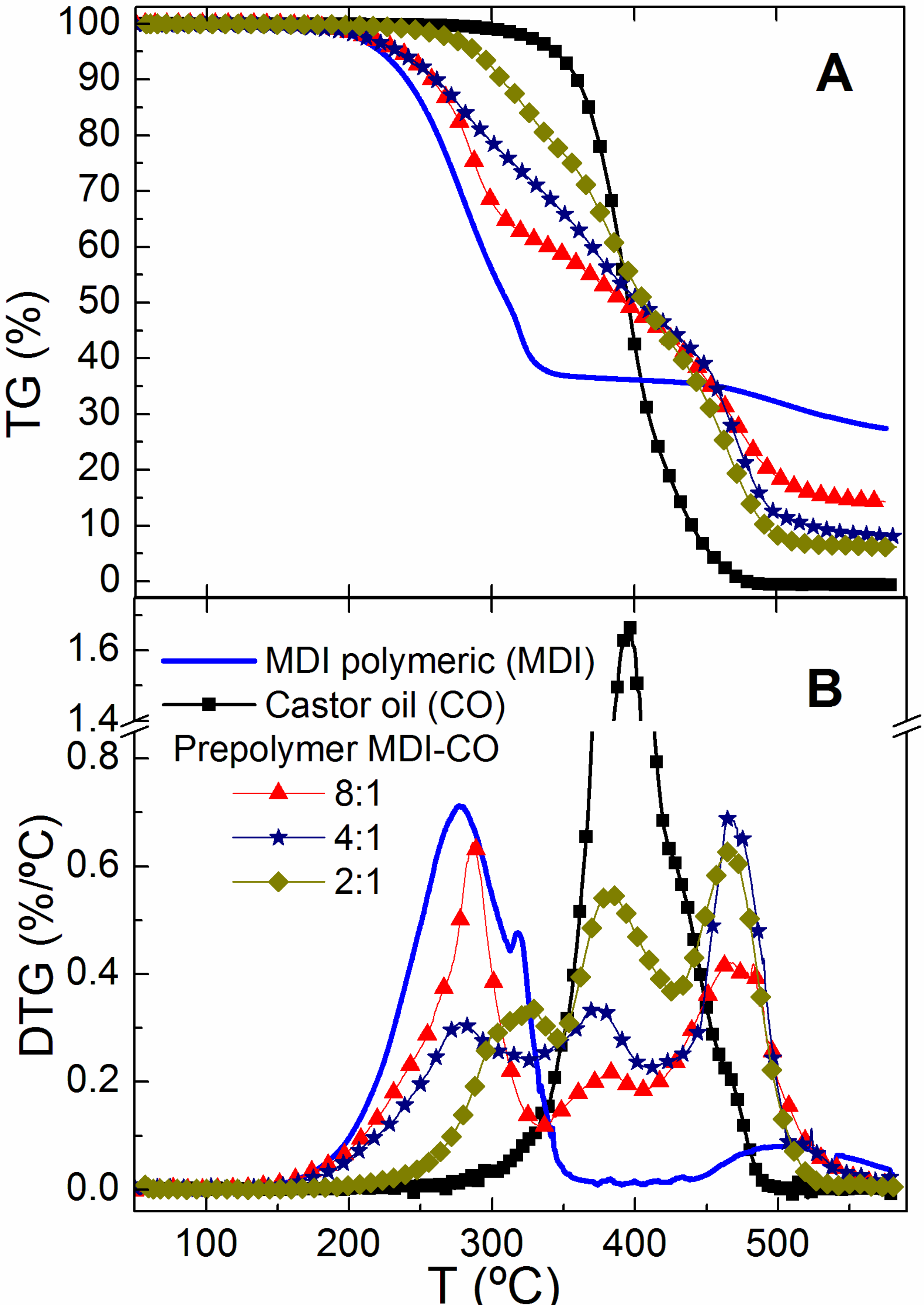
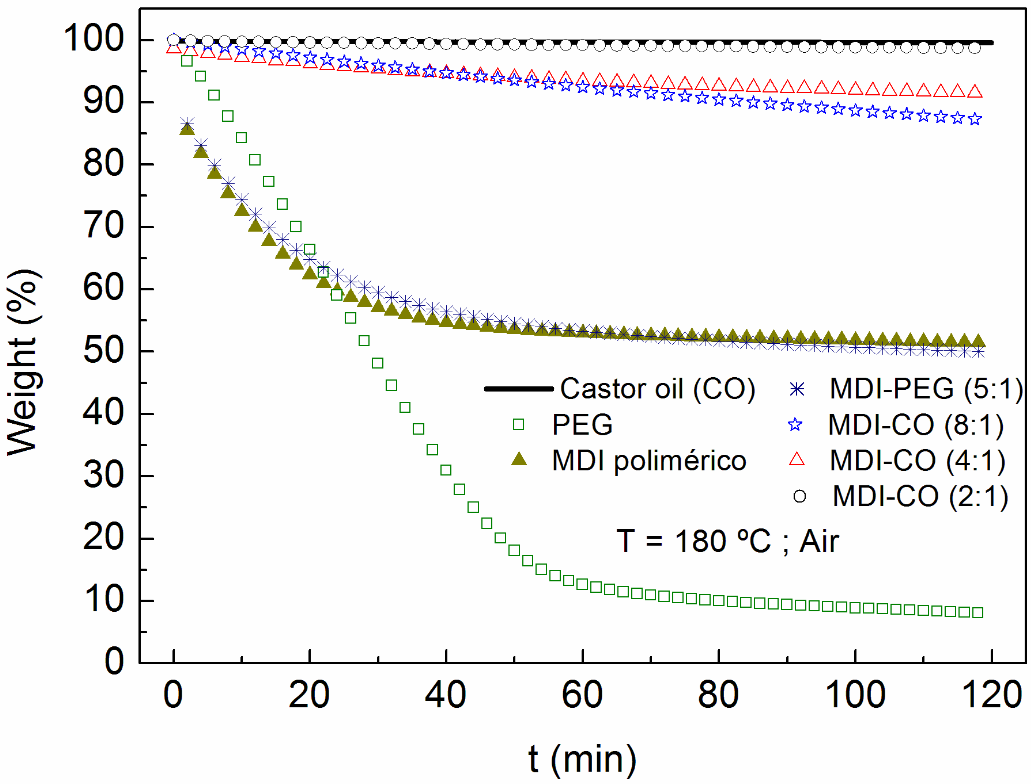
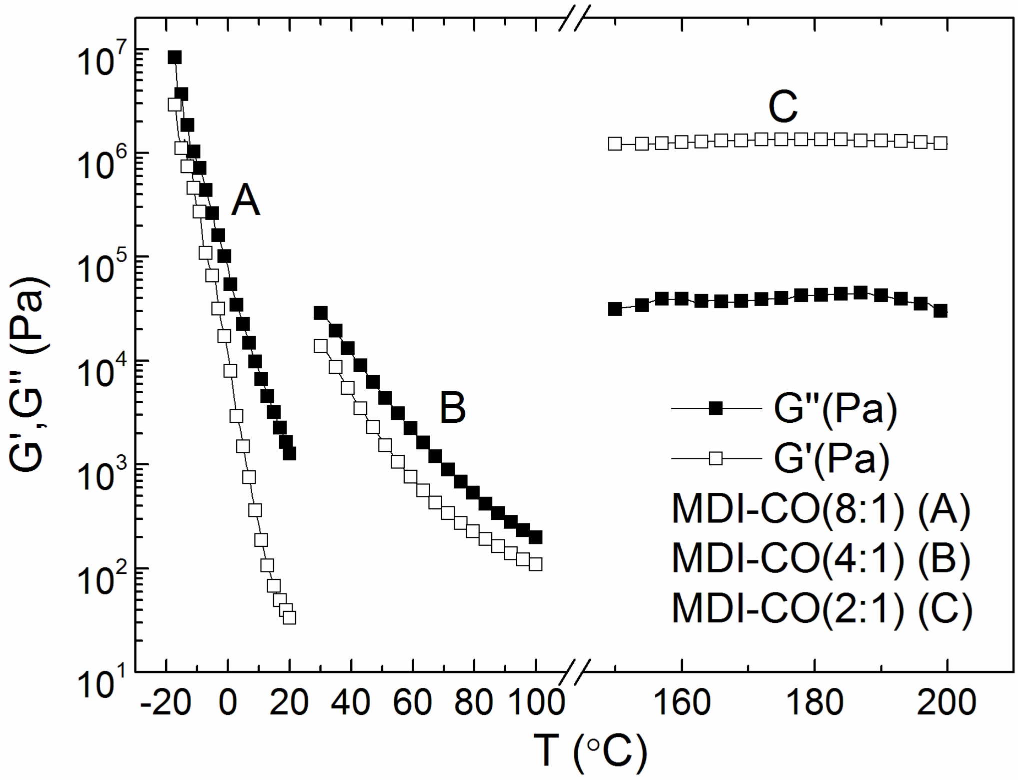

A
TG (%)
100
90
80
70
60
50
40
30
20
10
0
B
DTG (%/ºC)
1.6
1.4
0.8
0.6
0.4
0.2
0.0
100
200
300
400
500
T (ºC)
MDI polymeric (MDI)
Castor oil (CO)
Prepolymer MDI-CO
8:1
4:1
2:1

Figure 3



Weight (%)
t (min)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
Castor oil (CO)
PEG
MDI polimérico
MDI-PEG (5:1)
MDI-CO (8:1)
MDI-CO (4:1)
MDI-CO (2:1)
T = 180 ºC ; Air

Figure 4



G',G'' (Pa)
10^7
10^6
10^5
10^4
10^3
10^2
10^1
-20
0
20
40
60
80
100
160
180
200
T (°C)
A
B
C
G''(Pa)
G'(Pa)
MDI-CO(8:1) (A)
MDI-CO(4:1) (B)
MDI-CO(2:1) (C)

Figure 5

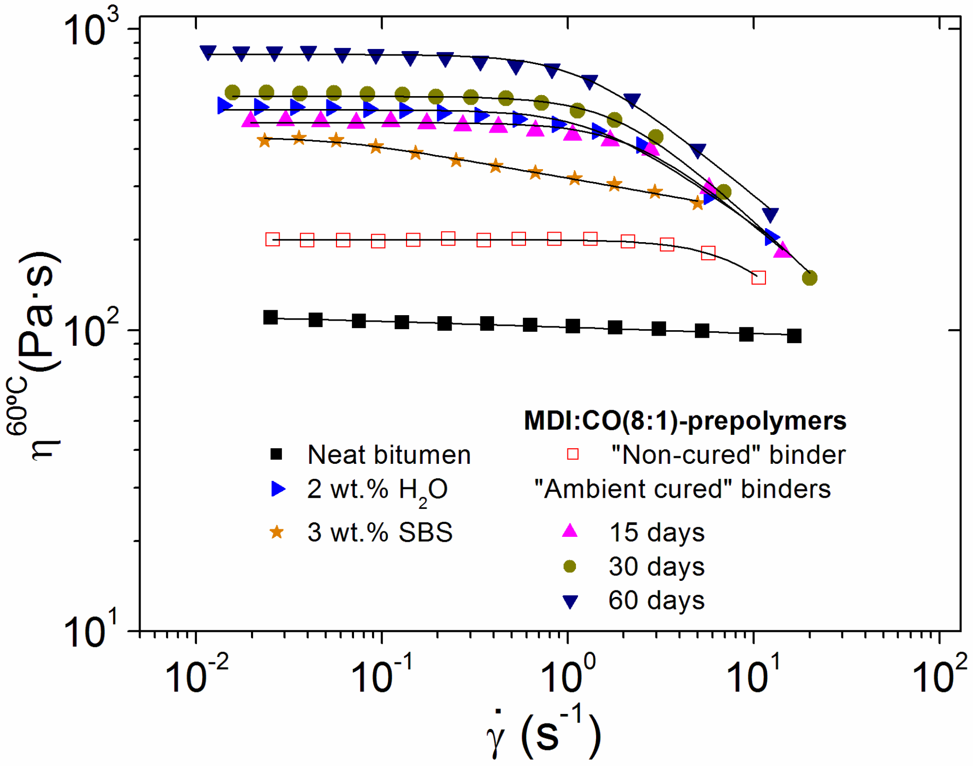

10^3
10^2
10^1
$\eta^{60^\circ C}$(Pa·s)
10^{-2}
10^{-1}
10^0
10^1
10^2
$\dot{\gamma}$ (s^{-1})
MDI:CO(8:1)-prepolymers
Neat bitumen
2 wt.% H_2O
3 wt.% SBS
"Non-cured" binder
"Ambient cured" binders
15 days
30 days
60 days

Figure 6

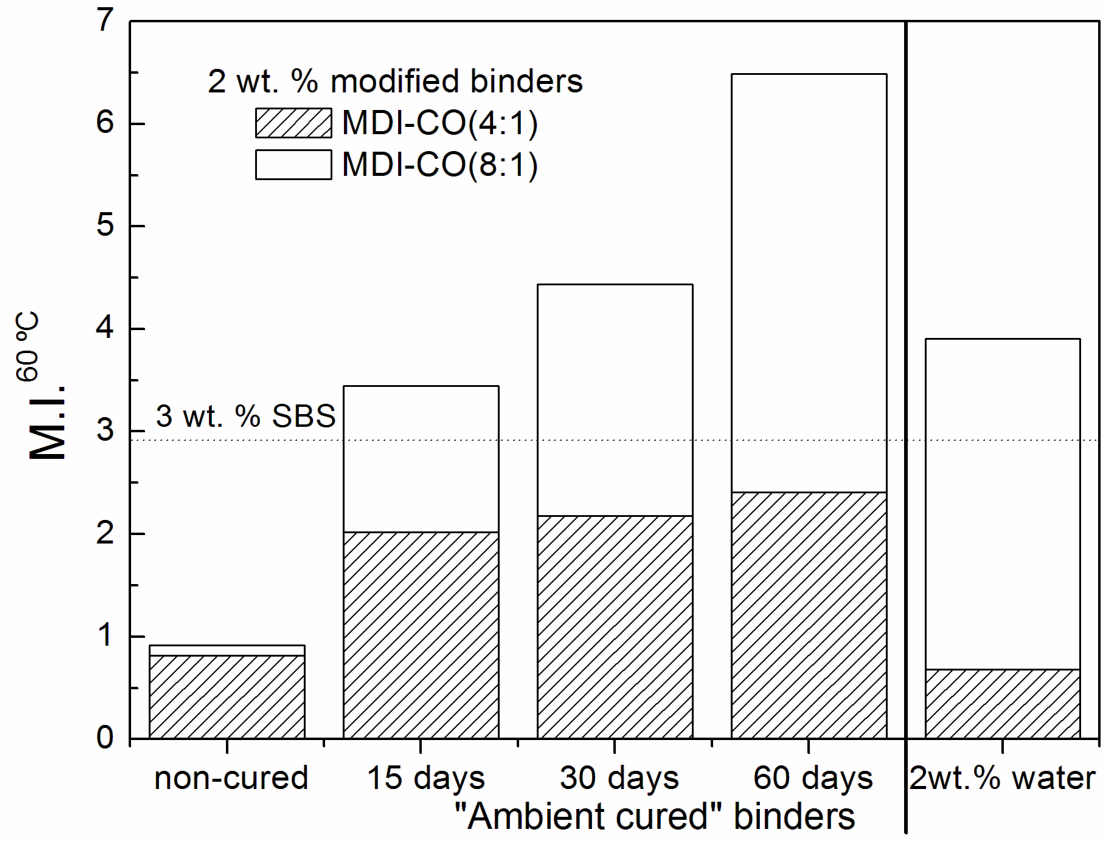

2 wt. % modified binders
MDI-CO(4:1)
MDI-CO(8:1)
3 wt. % SBS
M.I.$^{60\ °C}$
0
1
2
3
4
5
6
7
non-cured
15 days
30 days
60 days
2wt.% water
"Ambient cured" binders

Figure 7

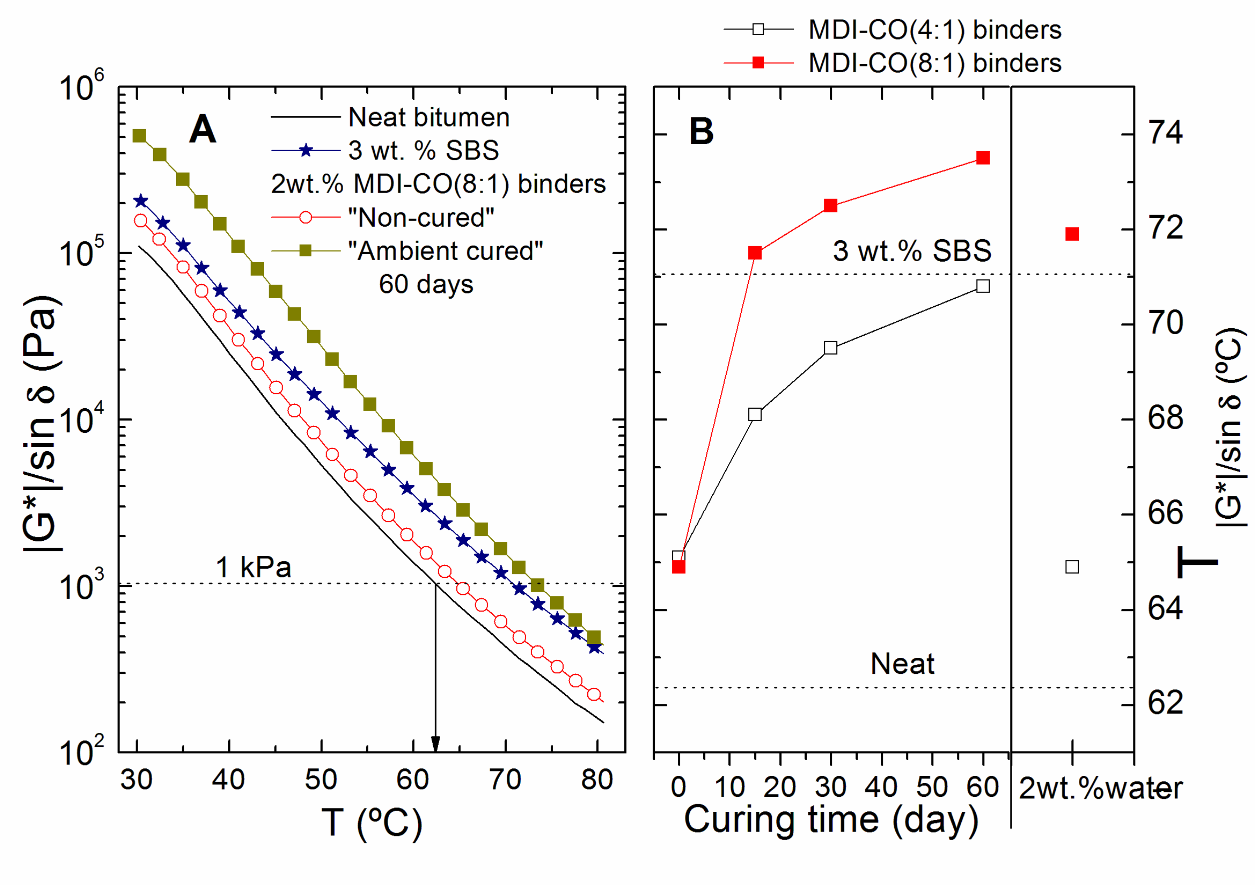
A
B
10^6
10^5
10^4
10^3
10^2
|G*|/sin δ (Pa)
T (ºC)
30
40
50
60
70
80
Neat bitumen
3 wt. % SBS
2wt.% MDI-CO(8:1) binders
"Non-cured"
"Ambient cured"
60 days
1 kPa
MDI-CO(4:1) binders
MDI-CO(8:1) binders
3 wt.% SBS
Neat
0
10
20
30
40
50
60
2wt.%water
Curing time (day)
62
64
66
68
70
72
74
$T_{|G^*|/\sin\delta}$ (ºC)

Figure 8

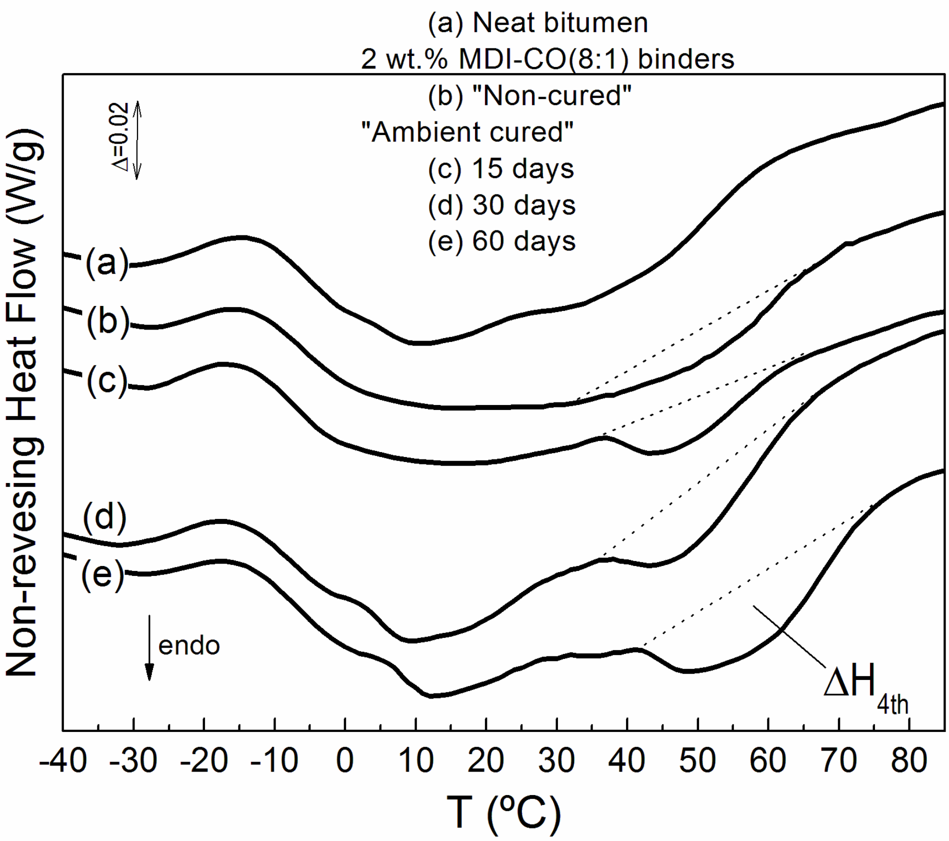

(a) Neat bitumen
2 wt.% MDI-CO(8:1) binders
(b) "Non-cured"
"Ambient cured"
(c) 15 days
(d) 30 days
(e) 60 days
Δ=0.02
(a)
(b)
(c)
(d)
(e)
endo
ΔH4th
Non-revesing Heat Flow (W/g)
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
T (ºC)

Figure 9

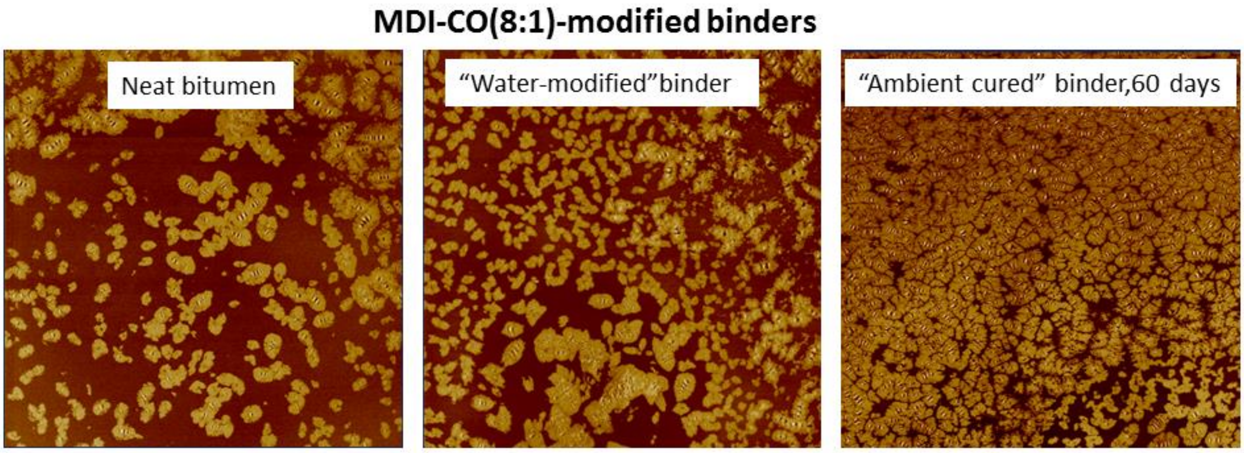

MDI-CO(8:1)-modified binders
Neat bitumen
“Water-modified”binder
“Ambient cured” binder,60 days

Figure 10