Effect of transesterification degree and post-treatment on the in-service performance of NCO-functionalized vegetable oil bituminous products

A.A. Cuadri, M. García-Morales, F.J. Navarro, P. Partal✉

Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro^{2}TecS), Campus de 'El Carmen', Universidad de Huelva, 21071, Huelva (Spain)

✉ Author to whom correspondence should be addressed:

Dr. Pedro Partal López

E-mail: partal@uhu.es

Phone: +34 959 21 9989

Fax: +34 959 21 93 85

ABSTRACT

The bitumen modification through polyurethane prepolymers presents significant benefits for the manufacture of bituminous products for the paving industry. In this sense, this work explores the use, as bitumen modifier, of a novel reactive prepolymer synthesized by reaction of 4,4´,diphenylmethane diisocyanate (MDI) and a vegetable oil-based polyol, castor oil (CO), previously transesterified with pentaerythritol. On the one hand, thermal analysis on transesterified CO revealed a highly stable prepolymer, making it suitable to be used for bitumen modification in a wide range of processing temperatures, 90-180 ºC. On the other hand, the bitumen modification achieved for the polyurethane-modified strongly depends on the transesterification degree and post-treatment procedures involved. In this sense, Atomic Force Microscopy (AFM) proved that MDI-prepolymers, based on castor oil transesterified with 4 wt.% pentaerythritol, lead to modified samples with a more complex microstructure which enhances rheological properties and reduces thermal susceptibility. In any case, viscoelastic and flow tests showed that the addition of small quantities of this reactive prepolymer to bitumen leads to products with enhanced performance at high in-service temperatures.

Keywords: bitumen, rheological properties, polymer, material processing, product design.

1. INTRODUCTION

Bitumen, a by-product coming 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). 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). 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. Thus, a variation in "SARAs" fraction alters bitumen colloidal structure and, therefore, affects its mechanical properties and chemical reactivity (Lesueur et al., 1996; Lesueur, 2009).

Impermeability, ductility, adhesivity or resistance to the effect of weathering and chemicals are some of the bitumen properties that make it a coating material suitable in many applications, among which road pavements construction (Read and Whiteoak, 2003) and roofing membranes manufacture (Fawcett and Lor, 1992) should be highlighted. Regarding the paving applications, the combined action of heavy truck traffic, dramatic changes of temperature and increase in axle loads provokes the well-known road distresses, which are: a) rutting, or permanent deformation at high temperatures (Kandhal and Cooley, 2003); b) thermal cracking, or thermal fracture due to lack of flexibility at low temperatures (Lu et al., 2003); and c) fatigue cracking, or series of longitudinal interconnected cracks caused by the repeated applications of wheel loads (Read and Whiteoak, 2003).

Hence, the addition to bitumen of "passive" polymers, which just physically mixed with bitumen, has shown to improve the performance of bituminous pavements under particularly severe conditions of service (Ait-Kadi et al., 1996; Blanco et al., 1996;

Newman, 1998; Yousefi, 2003). Nevertheless, “passive” polymers require both high shear and high processing temperatures in order to get to a suitable dispersion, what stands for a high risk of bitumen ageing and polymer degradation, leading to a decrease in its mechanical performance (Airey, 2004; Fawcett and McNally, 2001; Lu and Isacsson, 2002). On the contrary, “active” polymers containing functional groups supposedly able to bond with bitumen molecules (Iqbal et al., 2006; Polacco et al., 2004a, 2004b) may yield thermodynamically unstable modified bitumen with the consequent phase separation in absence of stirring (Pérez-Lepe et al., 2006).

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, bitumen/MDI-prepolymer processing should be carried out in safe conditions, since the polymeric MDI is a “Hazardous Chemicals” as defined by the OSHA Hazard Communication Standard (29 CFR 1910.1200). However, the degree of hazard depends of the volatility of the diisocyanate and its physical form.

Related to this, a novel prepolymer (synthesized by the reaction of 4,4´,diphenilmethane diisocyanate with a vegetable oil-based polyol, castor oil, transesterified with pentaerythritol) has been considered in the present work. Based on the isocyanate-bitumen chemistry, bitumen modification by MDI-prepolymers is expected to take place by reaction of the –NCO groups of the prepolymer with most of polar groups (–OH, –SH, >NH, –COOH, etc.) of asphaltenes and resins (Singh et al., 2004; Singh et al., 2006). The resultant material should display enhanced mechanical properties, giving rise to new products able to be used in advanced and complex construction applications.

This article studies the effect that the transesterification degree achieved and post-treatment procedures have on the rheological properties and microstructure of the modified bitumen, when this isocyanate-based prepolymer is used as modifying agent. With that purpose, the assessment of the material performance has been conducted through viscous flow tests, viscoelastic characterization, atomic force microscopy (AFM) and thermo-gravimetrical (TGA) analysis. The results obtained demonstrate that this novel modifying agent may become an alternative to those from petro-chemical, such as PPG or PEG, in agreement with the concept of sustainable and environmental development.

2. EXPERIMENTAL

2.1. Materials

Bitumen with a penetration grade of 100/150 was used as base material for the bitumen modification. Details of technological properties (penetration grade and ring and ball softening temperature, according to EN 1426:2007 and EN 1427:2007, respectively) and chemical composition, in terms of “SARAs” fractions, are shown in Table 1. The neat bitumen “SARAs” fraction was determined by thin layer chromatography coupled with a flame ionization detector (TLC/FID), using an Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan). The elutions were performed in hexane, toluene and dichloromethane/methanol (95/5), following the procedure outlined elsewhere (Ecker, 2001).

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

A) “Active” polymers (i.e. NCO-based prepolymers):

The vegetable isocyanate-prepolymers were synthetized from polymeric MDI and castor oil through two steps:

Step 1: Modification of castor oil by transesterification with pentaerythritol

Castor oil (designated as CO) supplied by Guinama (Spain), with hydroxyl index of 125 mg KOH/g (measured according to standard ASTM D1957), was transesterified using different concentrations of pentaerythritol, between 4 and 12 wt.% (Valero et al., 2008). The transesterification reaction was carried out at 210 ºC, for 2 h, in a 500 mL four-necked flask equipped with a magnetic stirred, thermometer, inert atmosphere and a reflux condenser. Lead oxide (PbO) was used as catalyser (at 0.0005 PbO/CO weight ratio). According to their actual degree of transesterification achieved, the modified castor oils were denoted as $CO^{n\%}$ (where "n" is the reacted pentaerythritol concentration that will be discussed later).

Step 2: Synthesis of prepolymers from modified castor oil and polymeric MDI

Modified castor oils, $CO^{n\%}$, were functionalized with isocyanate groups, -NCO, 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 N_2 blanketing. Adequate amounts of polymeric MDI and modified castor oil (according to their free isocyanate content and hydroxyl index, respectively) were mixed to achieve a -NCO/-OH molar ratio of 8:1 in all the systems. As a result, vegetable isocyanate-prepolymers with different transesterification degree were synthesized and referred to as MDI-$CO^{n\%}$, hereinafter.

On the other hand, and with the aim to establish a comparative analysis on the thermal stability of the castor oil-based prepolymers, another one was prepared from the same polymeric MDI and polyethylene glycol (designated PEG, donated by Repsol YPF (Spain) with a molecular weight of 350 $g \cdot mol^{-1}$ and a hydroxyl index of 180 mg

KOH/g). This "active" prepolymer, with a -NCO/-OH molar ratio of 5:1, will be referred to as MDI-PEG.

B) "Passive" polymer:

A commercial Styrene-Butadiene-Styrene (SBS) triblock copolymer (trade name "Kraton D-1101"), provided by Shell Chemical Company U.K., was used for the sake of comparison, as it leads to physical (instead of chemical) bitumen modification. This copolymer contains 31 wt.% styrene and has a molecular weight of $1.5 \cdot 10^5$ $g \cdot mol^{-1}$.

2.2. Sample preparation

The processing protocol followed to manufacture the binders depended on the selected modifying agent:

1) For the MDI-CO$^{n\%}$ prepolymers, modification was carried out by mixing neat bitumen and 2 wt.% MDI-CO$^{n\%}$, at 90 ºC for 1 h, with a four-bladed turbine rotating at 1200 r.p.m. Subsequently, the sample was set inside an oven for 24 h at 90 ºC. Then, different post-treatments were carried out on the resulting binder:
    a) A fraction was used as such (MDI-CO$^{n\%}$ binder, hereinafter).
    b) Another one was mixed with 2 wt. % water for 45 min at 90 ºC (MDI-CO$^{n\%}$/water binder).
    c) The next sample was obtained after addition of 2 wt.% castor oil transesterified with 4 wt.% of pentaerythritol, CO$^{4\%}$, for 45 min at 90 ºC (labeled as MDI-CO$^{n\%}$/CO$^{4\%}$ binder).
    d) The sample "c" was subsequently cured in closed vessels for 7 days in an oven at 90 ºC (giving the MDI-CO$^{n\%}$/CO$^{4\%}$-90ºC binder). The ageing during the processing was assessed by subjecting neat bitumen, without

prepolymer addition, to the same high temperature curing process described before ("cured-neat" sample, hereinafter).

In addition, bitumen was also mixed for 2 h at 180 ºC with 2 wt.% MDI-CO$^{n\%}$ and 2 wt.% CO$^{4\%}$, being the latter added after 1 h of processing, leading to the MDI-CO$^{n\%}$/CO$^{4\%}$-180ºC modified bitumens.

2) Regarding the "passive" polymer, a sample of bitumen with 3 wt. % of SBS (binder formulation commonly used by the paving industry) was prepared for 1.5 h, at 180 ºC, with a Silverson homogenizer.

Table 2 gathers the nomenclature, processing temperatures and post-treatment procedures used for the bituminous modified binders. In addition, the different reactions involving prepolymer/bitumen/water are also indicated. These reactions will be explained in the "Results and discussion" section.

2.3. Testing procedures

Different rheology tests were conducted in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria): (a) viscous flow measurements, at 30 ºC (for CO$^{n\%}$ and MDI-CO$^{n\%}$ samples) and at 60 ºC (for the modified binders); (b) temperature sweep tests in oscillatory shear, from 30 to 100 ºC, using a continuous heating ramp of 1 ºC/min, a frequency of 10 rad/s and deformation of 1% strain (within linear viscoelastic interval). In both cases, a plate-and-plate geometry (25 and 50 mm diameters; 1-2.5 mm gap) was used. In order to ensure the repeatability of the results, all the tests were carried out at least twice.

Thermo-gravimetric analysis (TGA) tests were conducted using a Seiko TG/DTA 6200 (Seiko Instruments Inc., Japan). Isothermal tests were carried out, under air atmosphere, on 5-10 mg samples of sample (polymeric MDI, polyethylene glycol (PEG), castor oils ($CO^{n\%}$) and the resulting prepolymers).

The microstructural characterization of the samples was carried out by means of atomic force microscopy (AFM), with an atomic force microscope connected to a Nanoscope IV scanning probe microscope controller (Digital Instruments, Veeco Metrology Group Inc., Santa Barbara, CA). 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 compared to solvent-casting (Masson et al., 2006).

3. RESULTS AND DISCUSSION

3.1. Prepolymer synthesis and characteristics

Figure 1 shows the reaction scheme for castor oil transesterification with pentaerythritol. Valero et al. (2008) quantified the products obtained from this transesterification reaction by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy. They found that, among pentaerythritol ricinoleates and glycerides of ricinoleic acid, the most abundant are the mono-ricinoleate (21.1 wt.%) and the mono-glyceride (40.5 wt.%), respectively. After the reaction with native castor oil, a white precipitate due to unreacted pentaerythritol was observed for the highest concentrations (8 and 12 wt. % pentaerythritol) (Valero et al., 2008) and separated by centrifugation. Then, the resulting modified castor oils, $CO^{n\%}$, were titrated according to ASTM D1957. As a result, the reacted concentration of pentaerythritol (n%) may be calculated by comparing the hydroxyl indexes for the different modified castor oils with the theoretical value for pure pentaerythritol (calculated as 1646 mg KOH/g). The hydroxyl indexes and the reacted concentrations for these systems are gathered in Table 3, showing that 8 wt. % is the highest transesterification achieved.

According to such hydroxyl indexes, MDI-CO$^{n\%}$ prepolymers were synthesized by selecting the same -NCO/-OH molar ratio of 8:1 (see previous “Experimental section”), which was found optimal in a previous work (Cuadri et al., 2013). Figure 2 illustrates the reaction scheme for the synthesis of MDI-CO$^{n\%}$ prepolymers, where urethane bonds between hydroxyl and isocyanate groups can be observed. In this figure, the most abundant products derived from castor oil transesterification have been selected to react with polymeric MDI. In addition, Table 4 shows the free -NCO contents, according to ASTM D2572, for the MDI-CO$^{n\%}$ prepolymers. Therefore, MDI-CO bitumen modification will take place through prepolymers having similar concentrations of free -NCO groups available for reaction with bitumen’s compound.

Concerning the rheological behaviour, unmodified/modified castor oils (CO$^{n\%}$) and vegetable isocyanate-prepolymers (MDI-CO$^{n\%}$) present a Newtonian behaviour, at 30 ºC (viscous flow curves not shown). In that sense, Table 5 shows the Newtonian viscosity for these systems as a function of reacted pentaerythritol concentration (n%). As can be observed, castor oil transesterification leads to more viscous polyols as pentaerythritol concentration rises. This increase can be attributed to the presence of new polar groups (i.e. a higher number hydroxyl groups, as seen in Table 3) that increase the interactions between molecules (Mutlu and Meier, 2010; Valero et al., 2008). In addition, functionalization of CO$^{n\%}$ gives rise to larger and more complex structures (see Figure 2) and, consequently, the resulting prepolymers (MDI-CO$^{n\%}$) are more viscous than their corresponding transesterified polyols (CO$^{n\%}$). Likewise, higher transesterification degree leads to an increase in Newtonian viscosity of MDI-CO$^{n\%}$. However, the prepolymer synthetized from unmodified castor oil (MDI-CO$^{0\%}$) shows a Newtonian viscosity, at 30 ºC, between those obtained for MDI-CO$^{4\%}$ and MDI-CO$^{7\%}$ prepolymers, probably due to its lower content on free -NCO (see Table 4).

On the other hand, thermal stability is a key factor to establish the feasible use of these prepolymers as bitumen modifiers. To that end, isothermal TG experiments (at 180 ºC, for 2 h, under air atmosphere) were conducted on the vegetable prepolymers (MDI-$CO^{n\%}$) and compared to other previously studied polyurethane bitumen modifier (e.g. MDI-PEG, a petroleum-based prepolymer used by Martín-Alfonso et al. (2009). Native castor oil ($CO^{0\%}$), polyethylene glycol (PEG) and polymeric MDI curves are also included. As shown in Figure 3, MDI-PEG prepolymer and polymeric MDI present similar weight loss curves, with mass going down to 50 wt. % of their initial values after 60 min of testing. Such a fast degradation rate arises from the poor thermal stability of PEG and from the MDI degradation into aromatic nitriles and hydrogen cyanide (Han et al., 1995; Martín-Alfonso et al., 2009). In contrast, no weight loss was observed for unmodified castor oil ($CO^{0\%}$) and the same response was obtained for the modified castor oils, $CO^{n\%}$ (results not shown in this figure for sake of clarity).

Finally, MDI-$CO^{n\%}$ prepolymers obtained from transesterified castor oils ($CO^{n\%}$) present lower thermal stability than that prepared with native castor oil ($CO^{0\%}$), most probably due to the lower weight content of MDI in MDI-$CO^{n\%}$ prepolymers (see Table 4). Thus, MDI-$CO^{0\%}$ prepolymer undergoes a weight loss of 10 wt.% after 2 h of testing. However, for prepolymers MDI-$CO^{4,7,8\%}$ this mass loss go up to 20 wt.%, most probably due to the added excess of polymeric MDI (see Table 4). In any case, the use of a natural polyol (castor oil, in this case) leads to MDI-derived prepolymers with much higher thermal stability compared to that prepared from a polyethylene glycol (PEG) polyol (Cuadri et al., 2013). Therefore, if compared to PEG derived prepolymers, the volatility (and so the toxicity) of the resulting prepolymers is strongly reduced when using castor oil as polyols.

3.2 Bitumen reactive modification through urethane/urea chemical bonds

Figure 4 shows the viscous flow behaviour, at 60 ºC, of selected binders obtained from 2 wt. % MDI-CO$^{8\%}$ subjected to different post-treatments. As reference systems, the viscosities at 60 ºC of the neat bitumen and the 3 wt. % SBS modified bitumen have also been included. It can be observed that neat bitumen shows an almost constant value of viscosity in the whole range of the shear rates tested. Instead, the addition of 2 wt.% MDI-CO$^{8\%}$ leads to a different viscous flow behaviour, characterized by a constant viscosity, η_0, at low shear rates, followed by a shear-thinning region once a “critical” value of shear rate, $\dot{\gamma}_c$, is reached. Interestingly, the addition of 2 wt. % water to the MDI-CO$^{8\%}$ modified binder (i.e, MDI-CO$^{8\%}$/water modified bitumen) produces a much more viscous product than that obtained by adding 3 wt.% SBS.

The results obtained can be explained on the basis of the isocyanate-bitumen chemistry described by Carrera et al. (2010). As reported by these researchers, during the blending of bitumen and prepolymer, -NCO groups are known to partially react with hydroxyl pendant groups present in the most polar molecules of bitumen (asphaltenic regions). Hence, the resulting urethane linkages,

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

lead to larger and more complex domains, which still have free –NCO sites available for further reaction. However, the most significant increase in viscosity was found after addition of 2 wt. % water to MDI-CO$^{8\%}$ binder. Thus, water addition promotes two series reactions involving the mentioned excess of -NCO groups:

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

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

Thus, water reacts with the remaining isocyanate groups, leading the formation of an amine and carbon dioxide. Further reactions occur between the highly reactive amine and the isocyanate groups left in the cluster previously formed, with the development of a more compact microstructure, through the formation of urea linkages between smaller units which, as commented, still had reactive –NCO sites available (Carrera et al., 2009; Martín-Alfonso et al., 2008a, 2008b; Segura et al., 2005).

On the other hand, Carreau model was applied to the experimental viscous behaviour at 60 ºC obtained from the different MDI-CO$^{n\%}$ binders. In this model,

$$\frac{\eta}{\eta_0} = \frac{1}{\left[1+\left(\lambda\cdot\dot{\gamma}\right)^2\right]^s} \qquad (1)$$

η_0 is the zero-shear-limiting viscosity at 60 ºC; λ is a time constant whose inverse matches the threshold shear rate, $\dot{\gamma}_c$; and “s” is a parameter related to the slope of the shear-thinning region. From the Carreau’s model parameters, gathered in Table 6, valuable information about changes in binder microstructure and bitumen modification degree can be deduced. Thus, these results confirm that water addition, after reactive modification of bitumen through MDI-CO prepolymers, promotes more apparent shear-thinning behaviours (with longer times, λ and lower “s” values), which suggests the development of binders with higher level of microstructural complexity and more sensitivity to the application of shear stresses than the unmodified neat bitumen (Martín-Alfonso et al., 2008a).

On the other hand, zero-shear-limiting viscosity (η_0) is a useful parameter to quantify the bitumen modification achieved at high in-service temperature (60 ºC). Thus, a modification index (M.I.^{60ºC}),

$$\mathrm{M.I.}^{60^{\circ}\mathrm{C}} = \frac{\eta_{0,\mathrm{mod}} - \eta_{0,\mathrm{neat}}}{\eta_{0,\mathrm{neat}}} \qquad (2)$$

has been defined with respect to the viscosity of neat sample. So, $\mathrm{M.I.}^{60^{\circ}\mathrm{C}}$, is a measure of the viscosity increase produced by the modifier ($\eta_{0,\mathrm{mod}}$) relative to the original viscosity of the unmodified bitumen ($\eta_{0,\mathrm{neat}}$).

On these grounds, Figure 5 shows the $\mathrm{M.I.}^{60^{\circ}\mathrm{C}}$ values for selected MDI-$\mathrm{CO}^{n\%}$ binders. Even though viscosity increases after the addition of MDI-$\mathrm{CO}^{n\%}$ (due to reaction 1), the subsequent addition of 2 wt. % water leads to the highest degree of modification (see MDI-$\mathrm{CO}^{n\%}$/water binders in Figure 5). Thus, MDI-$\mathrm{CO}^{4\%}$/water binder exhibits a higher value of $\mathrm{M.I.}^{60^{\circ}\mathrm{C}}$ (about 5.4) than its corresponding modified binder before water addition (2.10). Therefore, this observation confirms the relevant role that reactions 2 and 3, which involving water and free -NCO groups still available in the bituminous matrix, exert on the bitumen modification route experienced by these polyurethane-modified binders.

3.3. Urethane-based bitumen modification

With the aim of processing at higher temperatures, avoiding possible bitumen foaming derived from the CO_2 produced in reaction 2 and obtaining a polymer network composed of flexible molecular chains, instead of water, 2 wt.% $\mathrm{CO}^{4\%}$ was added to consume the remaining -NCO groups still present after the initial addition of 2 wt.% MDI-$\mathrm{CO}^{n\%}$. Accordingly, this modification procedure is expected to take place exclusively through the reaction 1 (i.e. through urethane linkages), giving the MDI-$\mathrm{CO}^{n\%}$/$\mathrm{CO}^{4\%}$ modified bitumens. However, as can be observed in Figure 5, the addition of 2 wt.% $\mathrm{CO}^{4\%}$ to modified binders just after processing (MDI-$\mathrm{CO}^{n\%}$ binders) has a plasticizing effect. Thus, the MDI-$\mathrm{CO}^{n\%}$/$\mathrm{CO}^{4\%}$ binder presents lower values of

M.I.^{60ºC} than their corresponding modified binder tested after processing and before CO$^{4\%}$ addition (see Figure 5). Such an effect is more pronounced as the reacted concentration of pentaerythritol, n%, rises.

This result seems to be related to the slow reaction rate at this temperature (90 ºC). In this regard, Figure 6a shows the viscous flow curves, at 60 ºC, for neat bitumen and MDI-CO$^{n\%}$/CO$^{4\%}$ binders after being stored at 90 ºC for 7 days (the so-called high temperature curing, which leads to the MDI-CO$^{n\%}$/CO$^{4\%}$-90ºC binders). As expected, this curing process causes an increase in neat bitumen viscosity (giving rise to the "cured-neat" sample), as a result of the oxidation of the maltene fraction (Navarro et al., 2006). Both samples, neat and cured-neat bitumens, present a Newtonian behaviour. Nevertheless, MDI-CO$^{n\%}$/CO$^{4\%}$-90ºC binders show a constant viscosity at low shear rates followed by a shear-thinning region. Once again, this non-Newtonian behaviour can be described by the Carreau's model fairly well (Equation 1) and their fitting parameters are gathered in Table 6. As may be seen in Figure 6a, the MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC modified sample yields the most extraordinary increase in viscosity, almost two orders of magnitude higher than that measured for the cured-neat sample. Likewise, the viscosity change undergone by the MDI-CO$^{n\%}$/CO$^{4\%}$-90ºC binders can be quantified by means of an "adapted" modification index, M.I.^{60ºC}(cured), written as:

$$\text{M.I.}^{60ºC}(\text{cured}) = \frac{\eta_{0,\text{mod}} - \eta_{0,\text{cured neat}}}{\eta_{0,\text{cured neat}}} \qquad (3)$$

where $\eta_{0,\text{mod}}$ and $\eta_{0,\text{cured neat}}$ refer to the zero-shear-limiting viscosity for modified and cured-neat bitumen viscosities, respectively. Therefore, this adapted modification index, M.I.^{60ºC}(cured), only quantifies viscosity changes due to the high temperature curing stage experienced by the MDI-CO$^{n\%}$/CO$^{4\%}$-90ºC binders, regardless of the expected bitumen oxidation. In this sense, Figure 6b shows M.I.^{60ºC}(cured) values for the different samples studied as well as for SBS-reference binder. The MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC binder presents, by far, the highest degree of modification (about 27.0), much higher than that obtained from MDI-CO$^{7\%}$/CO$^{4\%}$-90ºC binder (5.0). In any case, both modified binders, which were obtained after CO$^{4\%}$ addition to modified binder, and further high temperature curing, display a longer viscosity enhancement compared to SBS-reference sample.

In addition to viscous flow curves, temperature sweep tests in oscillatory shear (at a continuous heating rate of 1 ºC/min and frequency of 10 rad/s) have been carried out on high temperature cured samples (MDI-CO$^{n\%}$/CO$^{4\%}$-90ºC binders). Figure 7a shows the evolution with temperature of the loss tangent (tan δ=G''/G'), making clear the prevailing viscous behaviour of the samples, tan δ>1, over the entire temperature interval tested. The high temperature curing process produces a decrease in tan δ values (enhancing binder elastic properties), which is more significant for the binder obtained from MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC. In addition, these bituminous binders show a notable decrease in the average slope of tan δ curves between 50 and 70 ºC, which would result in lower thermal susceptibility in this temperature range. Further, such an enhanced elasticity (and the lower thermal susceptibility) is expected to reduce the progressive accumulation of permanent deformation (the so-called "rutting") produced by traffic at high in-service temperatures (Carrera et al., 2010).

In that sense, data obtained from dynamic shear temperature sweeps were plotted in the form of |G*|/sin δ in Figure 7b. This parameter was established by the Strategic Highway Research Program (SHRP) in order to determine the binder's average seven-day maximum pavement design temperature (according to AASHTO M320, and by application of AASHTO T315). In our case, the actual aim was to present the results in such a way that the rutting resistance of the different samples at high in-service temperatures can be quantitatively compared. In that sense, Table 7 displays the values of temperatures at which |G*|/sin δ equals 1 kPa, established by SHRP as those below which the binder will show a satisfactory performance. Hence, this method stands for an easy and time-saving way to establish a comparative analysis on the degree of improvement attained. If compared with the "cured-neat" sample, the value of temperature in Table 7 indicates an increase of nearly 18 ºC for the MDI-$CO^{4\%}$/$CO^{4\%}$-90ºC binder, which is clearly higher than the value reached after SBS rubber modification. In general, the obtained rheological results (Figures 6 and 7) reveal that, after the high temperature curing stage, binders coming from transesterified prepolymers present an enhancement in rheological behaviour. However, higher degrees of transesterification than 4 wt.% worsen the rheological properties. In this sense, MDI-$CO^{4\%}$ is considered the optimum modifier.

The previous enhancements in viscous behaviour, at 60 ºC, found after subjecting the MDI-$CO^{n\%}$ binders to different post-treatments (final water addition or high temperature curing process), hint significant changes in binder microstructure. To that end, AFM 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 (Masson et al., 2006). 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 (Nahar et al., 2013). 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 (Loeber et al., 1998; Masson et al., 2006) 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 (Nahar et al., 2013; Pauli et al., 2011).

In any case, Figure 8 compares neat bitumen with two selected samples obtained by its modification with the MDI-CO$^{4\%}$ prepolymer: MDI-CO$^{4\%}$/water and MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC binders. These samples 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 both prepolymer modification and post-treatments. In this sense, by comparing AFM phase images at 30 ºC, it can be easily deduced that the different procedures carried out on MDI-CO$^{n\%}$ binders greatly influence bitumen's microstructure. Hence, the MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC binder, which was obtained after CO$^{4\%}$ addition to modified binder and further high temperature curing stage (for 7 days at 90 ºC), presents much larger ellipsoids. 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 observed for the MDI-CO$^{4\%}$/water binder.

As mentioned earlier, the bitumen modification by MDI-CO$^{4\%}$ seems to yield the most remarkable improvement in bitumen behaviour at high in-service temperatures. This result is particularly evident for the MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC binder. Even though, MDI-CO$^{4\%}$ prepolymer has similar concentration of free -NCO groups to the other transesterified prepolymers (see Table 4), the MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC exhibits enhanced reactivity with bitumen compounds (and modification degree). The improved modification ability shown by MDI-CO$^{4\%}$ seems to be related to its lower viscosity (as commented in Table 5), which would favour the transport of the polymer chains all over the bulk reaction during the high temperature curing process.

Aiming to confirm such assumption, bitumen modification was carried out by MDI-CO$^{4\%}$ and MDI-CO$^{7\%}$ at a higher mixing temperature of 180 ºC for 2 h, adding 2 wt.% CO$^{4\%}$ at 60 min processing, which gave rise MDI-CO$^{n\%}$/CO$^{4\%}$-180ºC binders. It is worth noting this is the typical processing temperature used in the asphalt industry for the SBS/bitumen at which these MDI-CO based prepolymers were found stable enough under such conditions (Figure 3). Figure 9 shows, as expected, both prepolymers lead to modified samples with similar viscosity values, at 60 ºC, when processed at 180 ºC. What is more, these processing conditions lead to similar viscosities compared to MDI-CO$^{n\%}$/water binder at 90 ºC, but significantly lower than those obtained after curing for 7 days at 90 ºC (MDI-CO$^{n\%}$/CO$^{4\%}$-90ºC binders). This result would suggest that, in addition to reactions 1-3, other chemical process may arise at 180 ºC. In fact, at high enough temperature the addition reactions of isocyanate with compounds that have active hydrogens are reversible and, thus, in the presence of high shear stresses and high processing temperature, the urethane linkages may be broken. In this sense, it is been reported in the literature that, in the case of MDI/polyols based prepolymers, the urethane bond is unstable above 170 °C (Yang et al., 1986). This fact would explain the lower viscosity values when binders are processed at 180ºC.

4. CONCLUDING REMARKS

In this research, bitumen modification through MDI-derived prepolymers, based on a vegetable oil-based polyol (castor oil) transesterified with pentaerythritol, has been evaluated. The new prepolymers synthesized are characterized by molecules containing more sites available to react with bitumen compounds. In addition, thermal analysis on modified castor oils, $CO^{n\%}$, revealed a highly stable polymer, making it suitable to be used as bitumen modifiers in a wide processing temperature range, 90-180 ºC.

The rheological results (viscosity curves, at 60 ºC, and temperature sweep tests) demonstrated that the bitumen modification achieved strongly depends on both transesterification degree and post-treatment involved. The optimum transesterification degree is found to be 4 wt.%. In this sense, different procedures have been assessed to manufacture the bituminous products, involving the final addition of water or castor oil. Among them, the high temperature curing process (at 90 ºC for 7 days) on MDI-$CO^{n\%}$/$CO^{4\%}$ binders seems to yield a significant improvement in viscous behaviour at 60 ºC. In addition, the improved modification ability shown by MDI-$CO^{4\%}$ prepolymer seems to be related to its lower viscosity, which would favour the transport of the polymer chains all over the bulk reaction during the high temperature curing stage. Alternatively, MDI-$CO^{n\%}$ bitumen modification may be conducted at 90 ºC by adding 2 wt.% water or at 180ºC by adding of 2 wt.% $CO^{4\%}$.

5. ACKNOWLEDGEMENTS

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Table 1. Penetration value, ring&ball softening temperature, "SARAs" fraction and colloidal index value for the neat bitumen studied.

	Bitumen 100/150
Penetration (dmm)[a]	114
R&B softening point (°C)[b]	40
Saturates (wt. %)	7
Aromatics (wt. %)	61
Resins (wt. %)	20
Asphaltenes (wt. %)	12
Colloidal Index (C.I.)[c]	0.23

[a] *According to ASTM D5*

[b] *According to ASTM D36*

[c] *Colloidal Index = (asphaltenes + saturates) / (resins + aromatics)*

Table 2. Nomenclature, processing temperatures and post-treatment procedures used for the bituminous modified binders.

Modified binder[d]	$T_{proc.}$ = 90 ºC[a]	$T_{proc.}$ = 180 ºC[a]	Water addition	$CO^{4\%}$ addition	High temperature curing[c]	Reaction[b]
[d]MDI-$CO^{n\%}$	X					1
[d]MDI-$CO^{n\%}$/water	X		X			1, 2 and 3
[d]MDI-$CO^{n\%}$/$CO^{4\%}$	X			X		1
[d]MDI-$CO^{n\%}$/$CO^{4\%}$-90ºC	X			X	X	1
[d]MDI-$CO^{n\%}$/$CO^{4\%}$-180ºC		X		X		1

[a] Processing temperature between MDI-$CO^{n\%}$ prepolymer and bitumen.

[b] Reactions involving prepolymer/bitumen/water.

[c] High temperature curing stage at 90 ºC for 7 days.

[d] "n" is the wt.% reacted pentaerythritol concentration (see Table 3)

Table 3. Hydroxyl indexes and nomenclature for the unmodified/modified castor oils.

	Added wt. % pentaerythritol	Reacted wt. % pentaerythritol	Hydroxyl value, mg KOH/g[a]	$CO^{n\%}$
Unmodified castor oil	0	0	125	$CO^{0\%}$
Modified castor oil 1	4	4	190	$CO^{4\%}$
Modified castor oil 2	8	7	230	$CO^{7\%}$
Modified castor oil 3	12	8	246	$CO^{8\%}$

[a] *According to ASTM D1957*

Table 4. Free -NCO content and MDI/MDI-CO$^{n\%}$ weight ratio for MDI-CO$^{n\%}$ prepolymers.

	-NCO content (wt. %)[a]	MDI/MDI-CO$^{n\%}$ weight ratio
MDI-CO$^{0\%}$	19.4	2.5
MDI-CO$^{4\%}$	21.6	3.7
MDI-CO$^{7\%}$	22.4	4.5
MDI-CO$^{8\%}$	22.5	4.8

[a] *According to ASTM D2572*

Table 5. Newtonian viscosity, at 30 ºC, for native/transesterified castor oils ($CO^{n\%}$) and MDI-$CO^{n\%}$ prepolymers.

	Newtonian viscosity, at 30 ºC (Pa·s)	
Reacted pentaerytritol wt.% (n%)	$CO^{n\%}$	MDI-$CO^{n\%}$
0	$3.6 \cdot 10^{-1}$	$3.3 \cdot 10^{1}$
4	$5.2 \cdot 10^{-1}$	$1.1 \cdot 10^{1}$
7	$6.7 \cdot 10^{-1}$	$3.9 \cdot 10^{1}$
8	$7.6 \cdot 10^{-1}$	$6.4 \cdot 10^{1}$

Table 6. Carreau's model parameters for all the systems studied.

		η_0 (Pa·s)	λ (s)	s
	Neat bitumen	110	--	--
	3 wt. % SBS binder	438	16.67	0.05
	"Cured-neat" sample	223	--	--
MDI-CO$^{n\%}$ MODIFIED BINDERS	MDI-CO$^{0\%}$	200	0.08	0.39
	MDI-CO$^{0\%}$/CO$^{4\%}$	157	1.30	0.06
	MDI-CO$^{0\%}$/CO$^{4\%}$-90ºC	407	1.73	0.11
	MDI-CO$^{0\%}$/water	541	0.75	0.22
	MDI-CO$^{4\%}$	343	0.16	0.44
	MDI-CO$^{4\%}$/CO$^{4\%}$	313	1.23	0.14
	MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC	6288	26.7	0.16
	MDI-CO$^{4\%}$/water	697	1.78	0.16
	MDI-CO$^{7\%}$	305	0.19	0.26
	MDI-CO$^{7\%}$/CO$^{4\%}$	261	2.04	0.09
	MDI-CO$^{7\%}$/CO$^{4\%}$-90ºC	1295	13.79	0.10
	MDI-CO$^{7\%}$/water	561	1.01	0.17
	MDI-CO$^{8\%}$	300	0.19	0.23
	MDI-CO$^{8\%}$/CO$^{4\%}$	187	0.50	0.17
	MDI-CO$^{8\%}$/CO$^{4\%}$-90ºC	465	0.56	0.19
	MDI-CO$^{8\%}$/water	578	0.71	0.33

Table 7. SHRP maximum temperatures for MDI-CO$^{n\%-}$CO$^{4\%}$-90ºC modified binders.

	$T_{\|G^*\|/\sin\delta=1\text{kPa}}$
Neat bitumen	59.4
3 wt. % SBS	67.8
Neat cured	64.9
MDI-CO$^{0\%}$/CO$^{4\%}$-90ºC	70.0
MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC	82.3
MDI-CO$^{7\%}$/CO$^{4\%}$-90ºC	76.5
MDI-CO$^{8\%}$/CO$^{4\%}$-90ºC	68.7

Figure captions

Figure 1. Reaction scheme for the transesterification reaction of castor oil with pentaerythritol.

Figure 2. Reaction scheme for the synthesis of MDI-CO$^{n\%}$ prepolymers.

Figure 3. Isothermal weight loss at 180 ºC for polymeric MDI, polyethylene glycol (PEG), castor oils (CO$^{n\%}$), MDI-CO$^{n\%}$ and MDI-PEG prepolymers.

Figure 4. Viscous flow curves, at 60 ºC, for selected binders modified by 2 wt. % MDI-CO$^{8\%}$. Neat and 3 wt.% SBS-modified bitumens are also included.

Figure 5. Modified index, I.M.^{60ºC}, for MDI-CO$^{n\%}$ modified bitumens.

Figure 6. (A) Viscous flow curves, at 60 ºC, and (B) "adapted" modification indexes, M.I.^{60ºC}(cured), for MDI-CO$^{n\%}$/CO$^{4\%}$-90 modified bitumens. Neat bitumen, "cured-neat" sample and 3 wt.% SBS-reference sample are also included.

Figure 7. (A) Evolution with the temperature loss tangent, tan δ, and (B) temperature dependence of the "rutting parameter", $|G^*|/\sin\delta$, for MDI-CO$^{n\%}$/CO$^{4\%}$-90 modified bitumens. Neat, "cured neat" and 3 wt.% SBS- reference sample are also included.

Figure 8. AFM micrographs (30 x 30 μm^2), at 30 ºC, for neat bitumen, MDI-CO$^{4\%}$/water and MDI-CO$^{4\%}$/CO$^{4\%}$-90 modified bitumens.

Figure 9. Viscous flow curves, at 60 ºC, for selected MDI-CO$^{n\%}$ modified bitumens. Neat and 3 wt.% SBS- reference sample are also included.

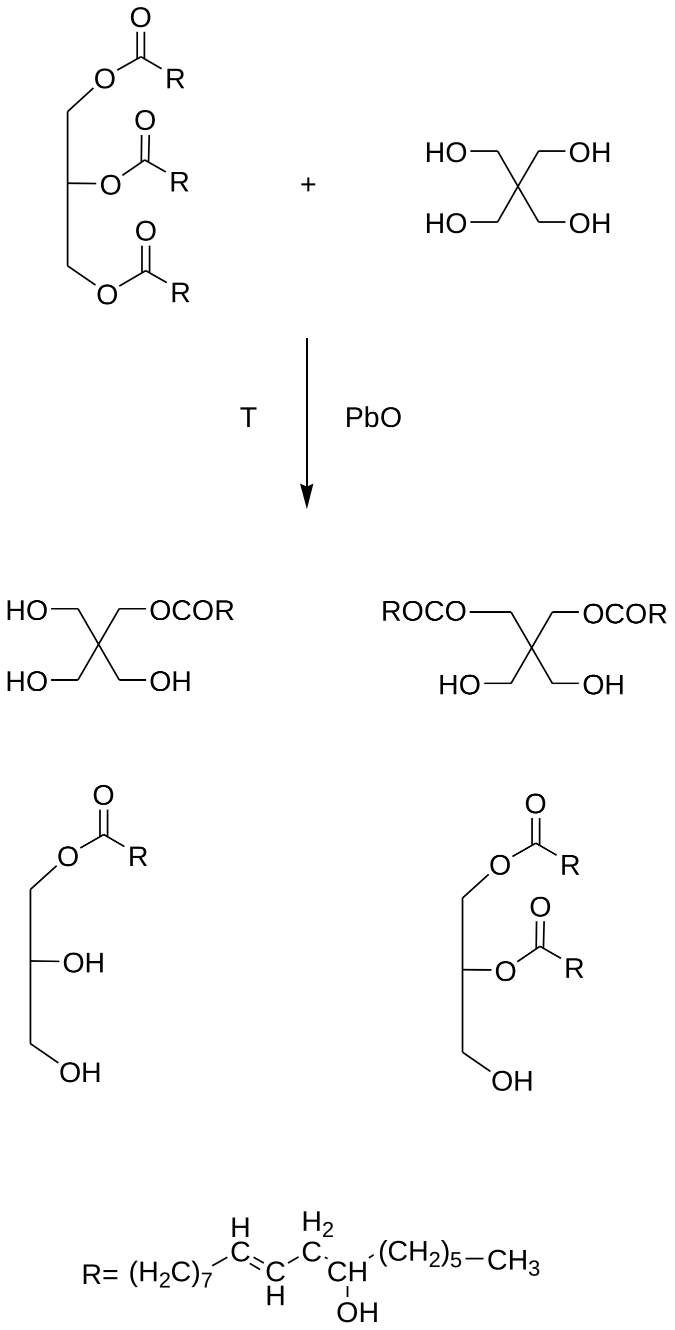


Figure 1

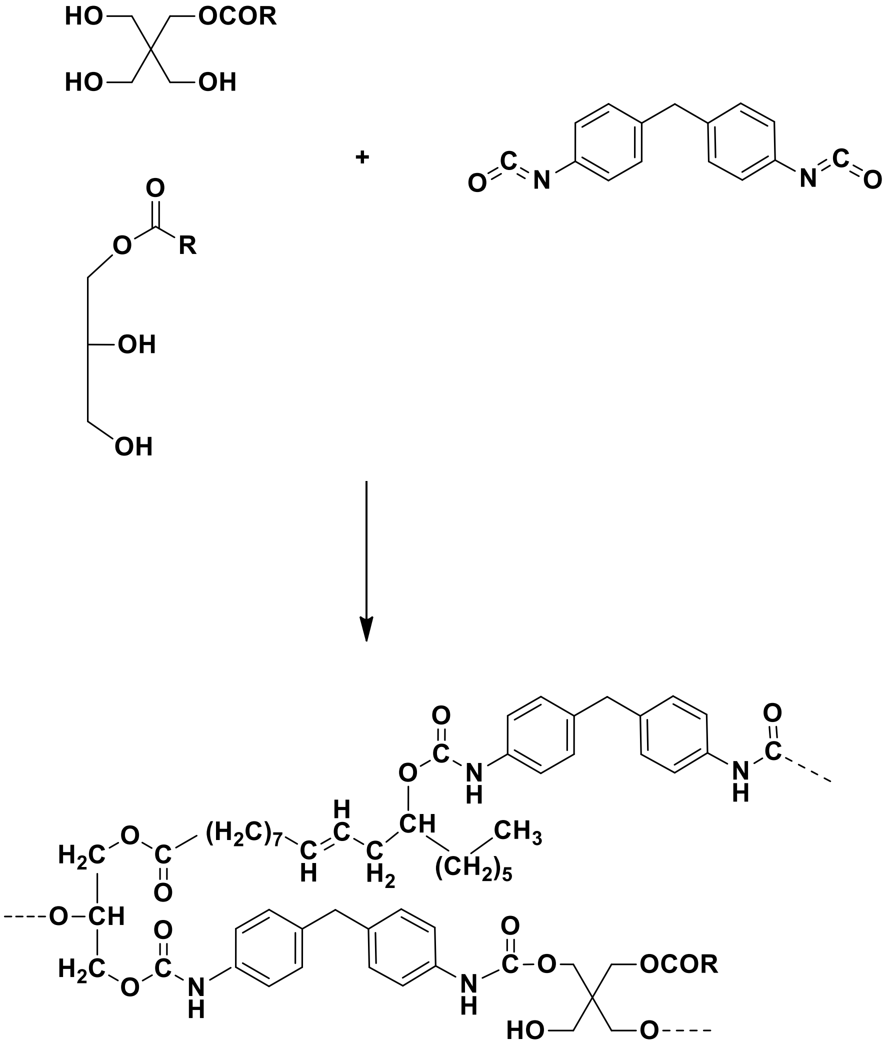
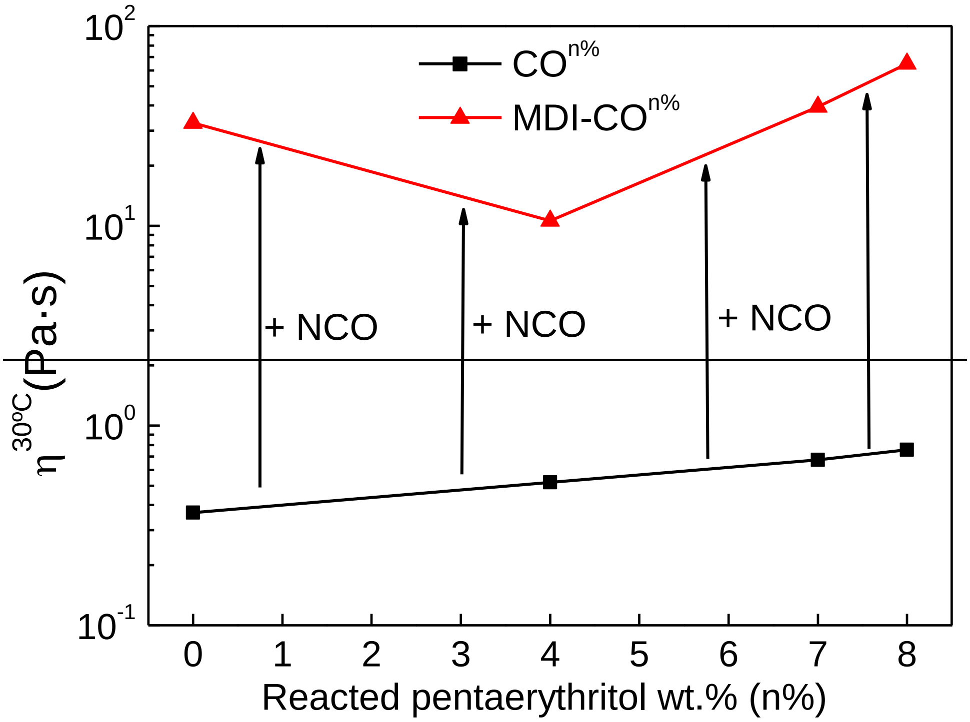


Figure 2



10^2
10^1
10^0
10^{-1}
η^{30^oC}(Pa·s)
CO$^{n\%}$
MDI-CO$^{n\%}$
+ NCO
+ NCO
+ NCO
0
1
2
3
4
5
6
7
8
Reacted pentaerythritol wt.% (n%)

~~Figure 3~~

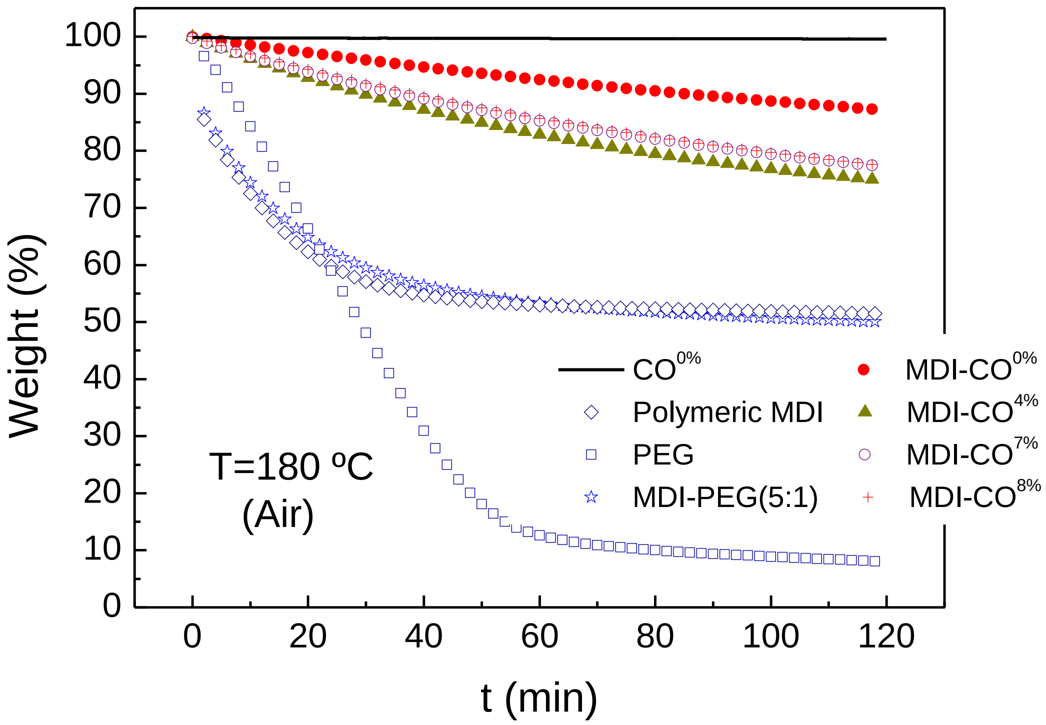
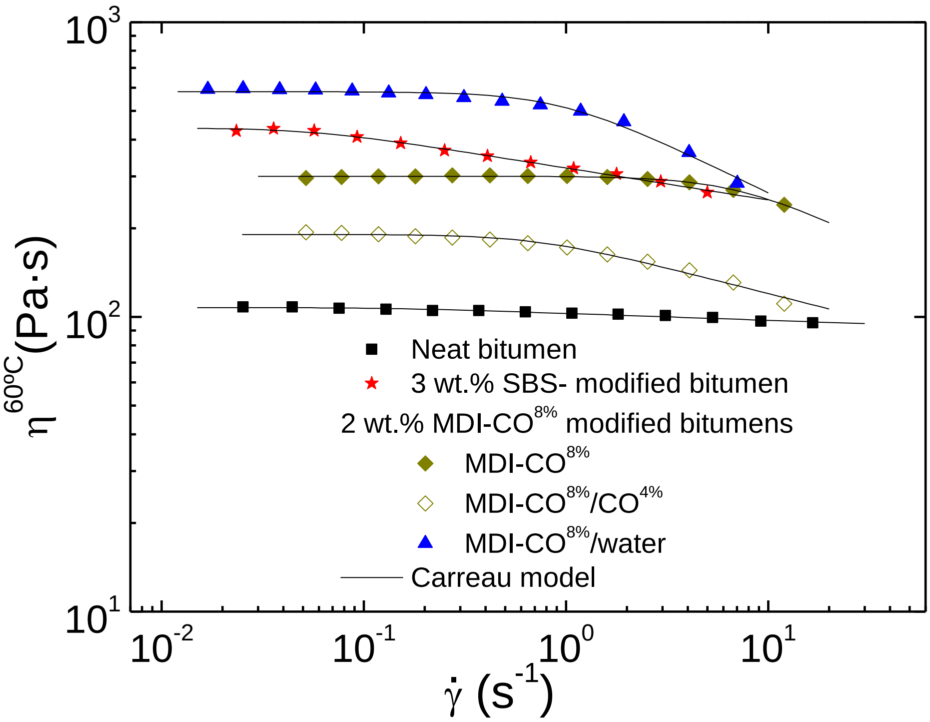

Weight (%)
t (min)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
T=180 ºC
(Air)
CO0%
Polymeric MDI
PEG
MDI-PEG(5:1)
MDI-CO0%
MDI-CO4%
MDI-CO7%
MDI-CO8%

Figure 3



10^3
10^2
10^1
η^{60^oC}(Pa·s)
10^{-2}
10^{-1}
10^0
10^1
$\dot{\gamma}$ (s^{-1})
Neat bitumen
3 wt.% SBS- modified bitumen
2 wt.% MDI-CO$^{8\%}$ modified bitumens
MDI-CO$^{8\%}$
MDI-CO$^{8\%}$/CO$^{4\%}$
MDI-CO$^{8\%}$/water
Carreau model

Figure 4

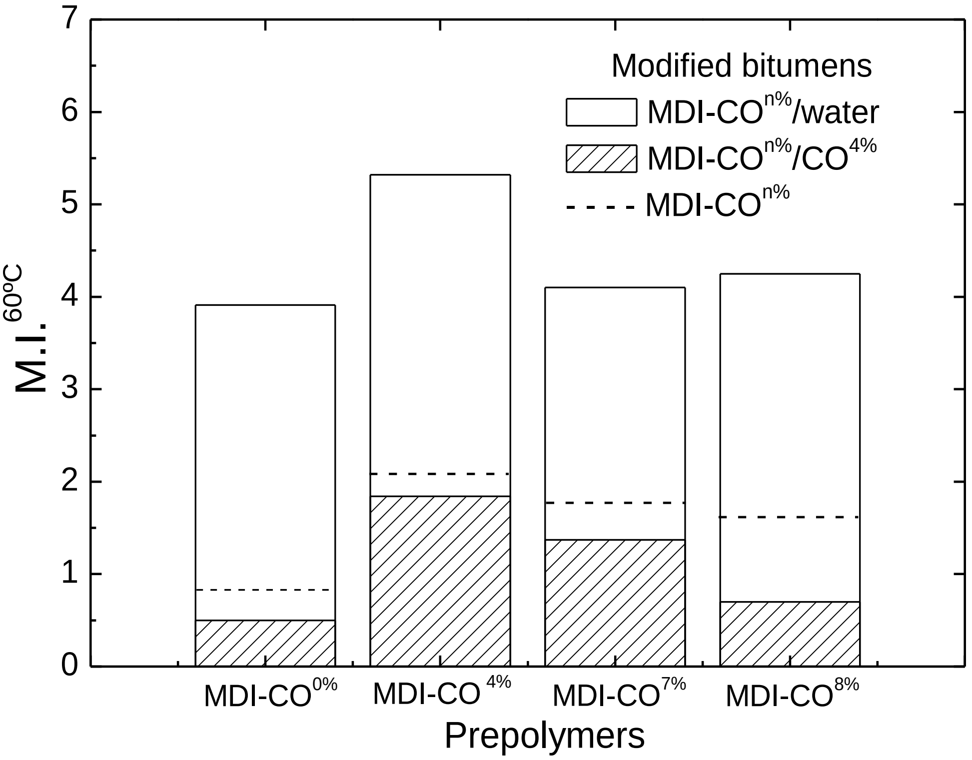

Modified bitumens
MDI-CO$^{n\%}$/water
MDI-CO$^{n\%}$/CO$^{4\%}$
MDI-CO$^{n\%}$
M.I.$^{60°C}$
0
1
2
3
4
5
6
7
MDI-CO$^{0\%}$
MDI-CO$^{4\%}$
MDI-CO$^{7\%}$
MDI-CO$^{8\%}$
Prepolymers

Figure 5

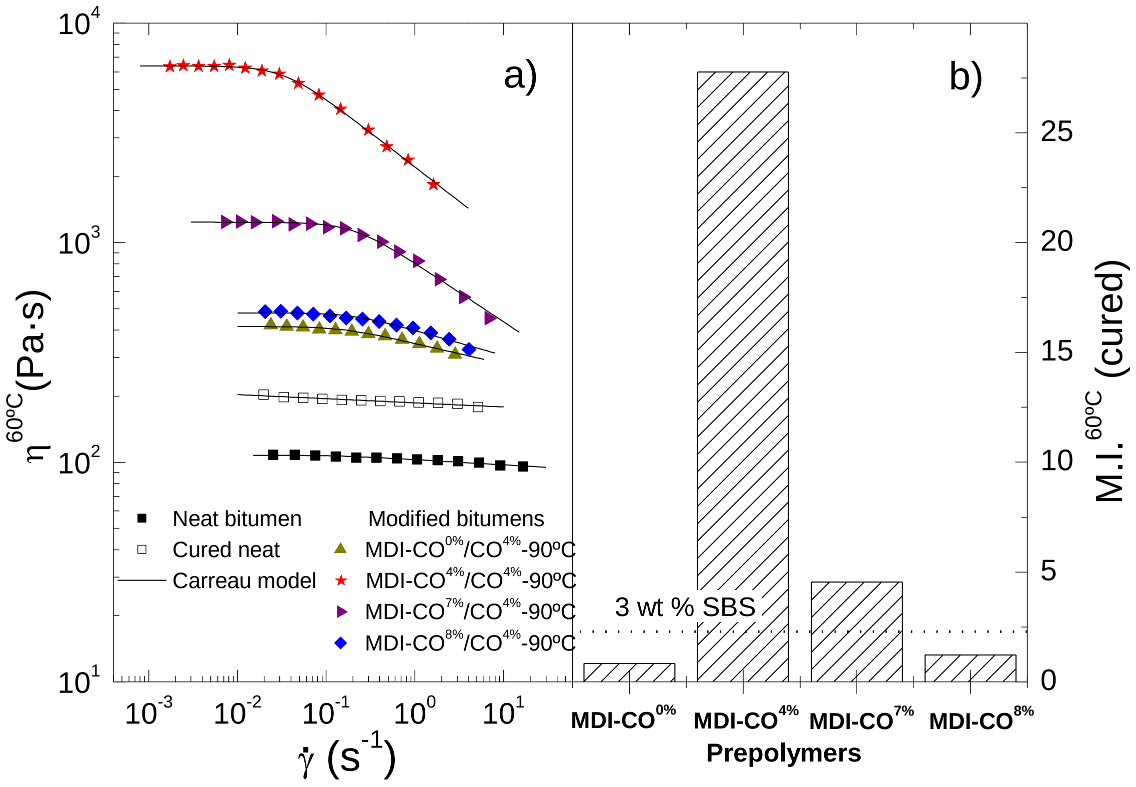

a)
b)
$\eta^{60ºC}$(Pa·s)
10^1
10^2
10^3
10^4
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
$\dot{\gamma}$ (s^{-1})
Neat bitumen
Cured neat
Carreau model
Modified bitumens
MDI-CO$^{0\%}$/CO$^{4\%}$-90ºC
MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC
MDI-CO$^{7\%}$/CO$^{4\%}$-90ºC
MDI-CO$^{8\%}$/CO$^{4\%}$-90ºC
3 wt % SBS
0
5
10
15
20
25
M.I.^{60ºC} (cured)
MDI-CO$^{0\%}$
MDI-CO$^{4\%}$
MDI-CO$^{7\%}$
MDI-CO$^{8\%}$
Prepolymers

Figure 6

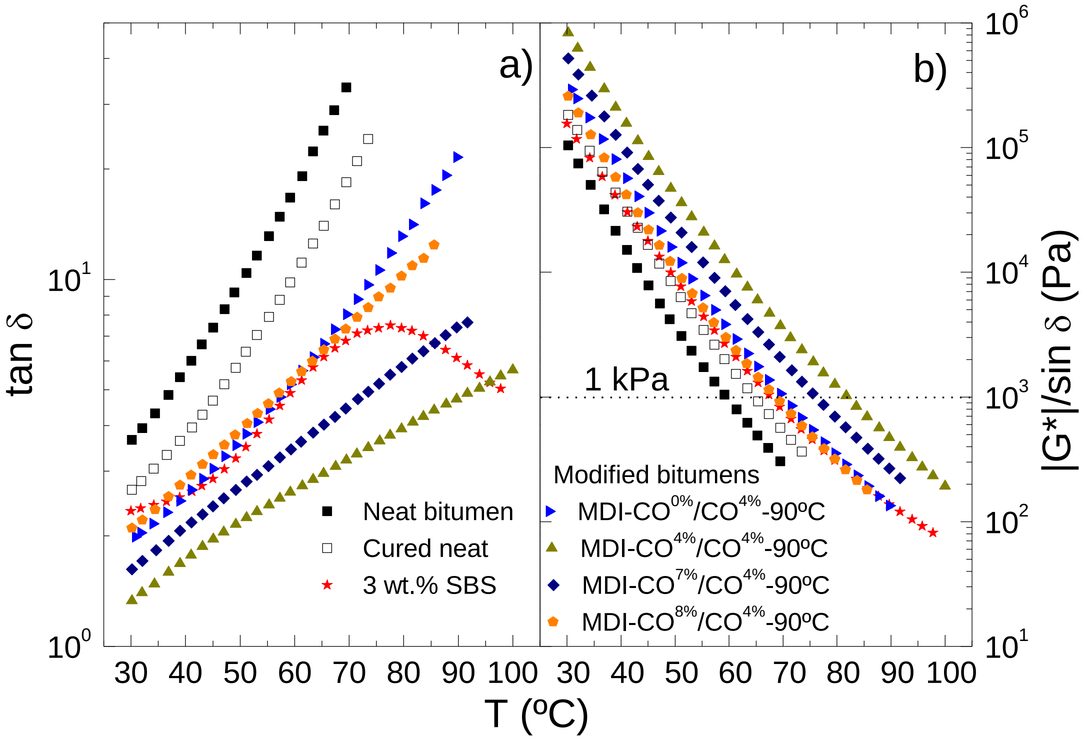

a)
b)
tan δ
10^1
10^0
30 40 50 60 70 80 90 100
30 40 50 60 70 80 90 100
T (ºC)
10^6
10^5
10^4
10^3
10^2
10^1
|G*|/sin δ (Pa)
1 kPa
Neat bitumen
Cured neat
3 wt.% SBS
Modified bitumens
MDI-CO$^{0\%}$/CO$^{4\%}$-90ºC
MDI-CO$^{4\%}$/CO$^{4\%}$-90ºC
MDI-CO$^{7\%}$/CO$^{4\%}$-90ºC
MDI-CO$^{8\%}$/CO$^{4\%}$-90ºC

Figure 7

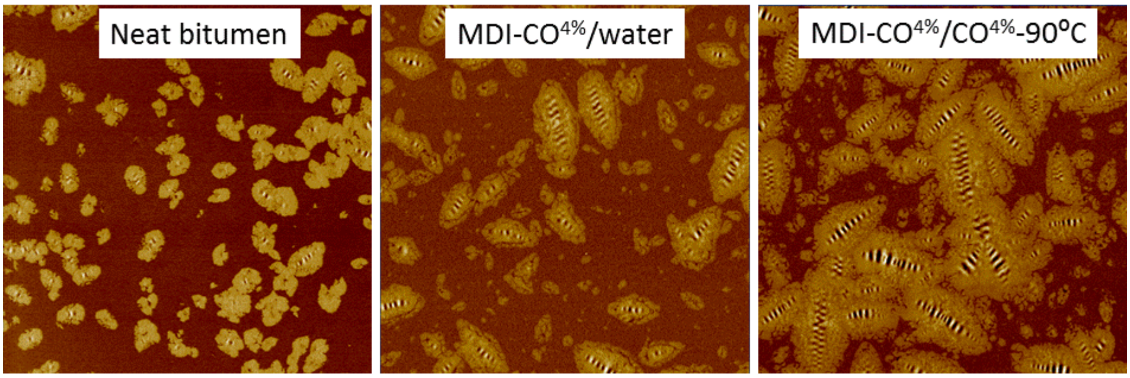


Figure 8

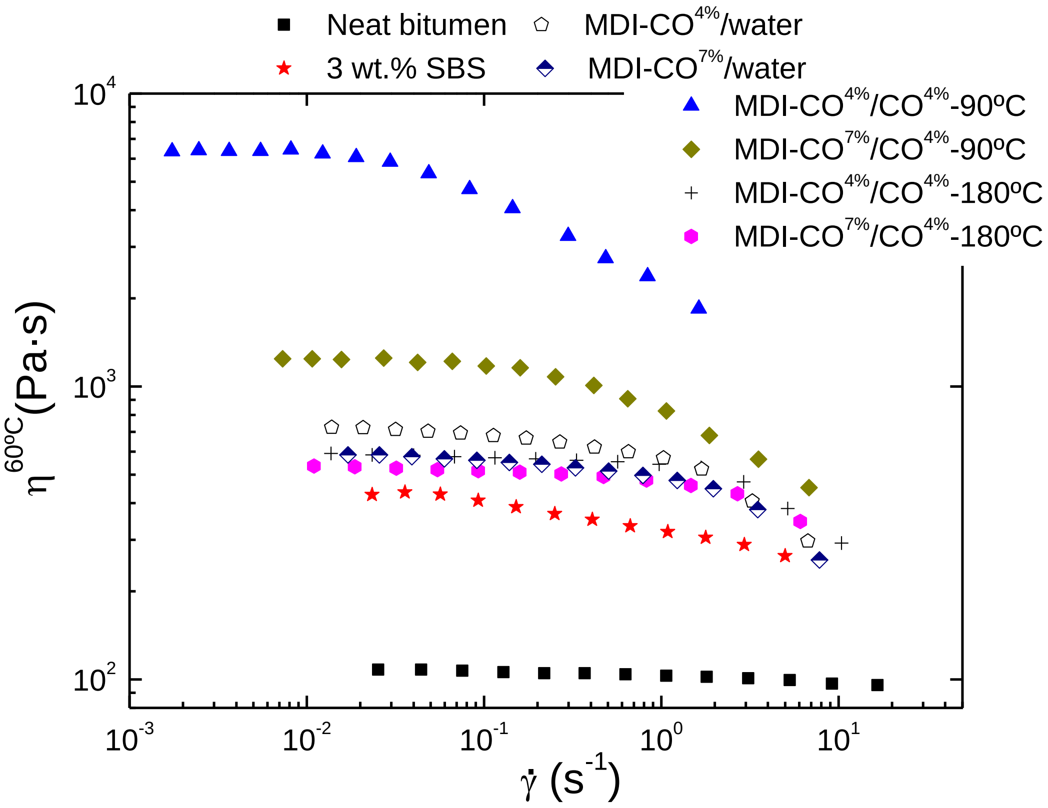

Neat bitumen
3 wt.% SBS
MDI-CO4%/water
MDI-CO7%/water
MDI-CO4%/CO4%-90ºC
MDI-CO7%/CO4%-90ºC
MDI-CO4%/CO4%-180ºC
MDI-CO7%/CO4%-180ºC
η60ºC(Pa·s)
10^4
10^3
10^2
10^-3
10^-2
10^-1
10^0
10^1
γ̇ (s^-1)

Figure 9