Bitumen modifiers for reduced temperature asphalts: a comparative analysis between three polymeric and non-polymeric additives

A.A. Cuadri, V. Carrera, M.A. Izquierdo, M. García-Morales✉, F.J. Navarro

Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro²TecS), Campus de 'El Carmen', Universidad de Huelva, 21071, Huelva (Spain)

✉ Author to whom correspondence should be addressed:

Dr. Moisés García-Morales

E-mail: moises.garcia@diq.uhu.es

Phone: +34 959 21 82 07

Fax: +34 959 21 93 85

1

ABSTRACT

This study presents three bitumen modifiers which may find successful application in the fabrication of binders for warm mix asphalt in the paving industry. In that sense, two non-polymeric additives, thiourea and thiourea dioxide, along with a reactive isocyanate-terminated prepolymer have been evaluated. Viscous flow and linear viscoelasticity tests, at 60 ℃, reveal bituminous modified binders which evolve towards highly viscous materials when subjected to ambient curing. However, at 135 ℃, they show lower viscosity than a typical 3 wt.% SBS binder used as reference. These results suggest modified binders with low viscosity which may contribute to reduce the mix asphalt temperature. On the contrary, they are expected to undergo an important increase in viscosity when the asphalt is in service, which would contribute to improve further their performance. Low temperature performance and effects of short-term and long-term aging were not considered in this study.

Keyword: modified bitumen, thiourea, thiourea dioxide, isocyanate, warm mix asphalts.

1. INTRODUCTION

Bitumen is usually defined as a dark brown to black material, mainly obtained from crude oil distillation. It is widely used as a binder of mineral aggregates in road pavements [1], as well as waterproofing material, joint sealant and for roofing applications [2,3].

Bitumen shows quite a high chemical complexity. It contains different types of molecular species, which are classified (in terms of solubility in n-heptane) into two major fractions, maltenes and asphaltenes. The asphaltenes (As) consist of highly condensed planar and heteroatom polar groups, polar aromatic ring systems and large amounts of heteroatom polar functional groups [4]. Based on differences in solubility and polarity, the maltene fraction can be further divided into three groups: saturates (S), aromatics (A) and resins (R) [5]. Thus, bitumen physico-chemical and rheological properties strongly depend on both temperature and the relative proportion of those four "SARAs" fractions [6,7].

Bitumen is the only deformable component and the continuous phase in asphalt mixtures. In this sense, the viscoelastic properties of bitumen, over a wide range of temperatures and loadings, are of major importance when predicting roads performance [8]. Any bitumen additive should improve the binder properties at high and/or low in-service temperatures, depending on the requirements demanded [9]. Consequently, it should be strong enough to withstand traffic loads at high temperature, which may cause rutting or permanent deformation. On the contrary, it may be necessary high flexibility at low temperatures, in order to avoid excessive thermal stresses.

Polymeric additives have been widely used to enhance the in-service properties of bitumen [3,10-12]. Polymers commonly used to modify bitumen include styrene–butadiene–styrene copolymer (SBS), styrene–butadiene rubber (SBR), ethylene vinyl

acetate (EVA), polyethylene (LDPE, HDPE, etc.) and waste polymers (plastics from agriculture, crumb tire rubber, etc.) [3,13-16]. The characteristics of their mixing with bitumen may significantly affect the technical properties of the resulting blend, as well as the costs of the whole operation [17]. Thus, for example, bitumens modified with high molecular weight polymers may yield a significant phase separation during their storage at high temperatures [18].

Desirably, a modifying agent of bitumen for warm climate countries should meet the following features: a) easy to incorporate; b) homogeneously dispersed during storage; c) adequate viscosity at high in-service temperatures, which increases resistance to permanent deformation; but d) low viscosity at the mix asphalt temperatures, which permits energy saving operations. In relation to this last demand, production temperatures corresponding to traditional hot mix asphalt (HMA) requires materials to be heated between 135 and 180 °C, as polymer modified bitumens present very high values of viscosity at lower temperatures. The success of warm mix asphalt (WMA) technologies, emerged over the last years, relies on the development of binders which exhibit low viscosity during the asphalt production. This allows for the adequate coating of mineral aggregates and the consequent benefit for the lay-down and compaction operations.

On these grounds, a modified bitumen with low viscosity (which facilitates the asphalt mixing and compaction) which evolves towards a highly modified bitumen by means of ambient curing may represent a promising binder for the WMA technology. With this aim, this work proposes three bitumen modifiers which, through chemical reactions involving bitumen, may result of special interest in reducing the asphalt production/application temperatures: a) two non-polymeric chemical agents, like thiourea and thiourea dioxide; and b) a low molecular weight reactive isocyanate

4

prepolymer. Out of scope of this article are the low temperature properties and the effects of short-term and long-term aging.

2. EXPERIMENTAL

2.1. Materials

Bitumen with penetration grade 150/200 was used as base material for the bitumen modification. The results of penetration grade (EN 1426:2007 [19]), softening temperature tests (EN 1427:2007 [20]) and "SARAs" fractions (procedure outlined elsewhere [21]) are shown in Table 1.

Three different chemical modifiers are proposed. The two first, thiourea dioxide and thiourea, are non-polymeric substances, whilst the last one is a polyol functionalized with isocyanate groups. Detailed information on these modifiers is given below:

1. Thiourea dioxide ("ThD," hereinafter) has been described as a reducing agent used for vat dye, reduction of ketones to alcohols and hydrocarbons, reduction of conjugated unsaturated acids to the corresponding saturated acids, etc. So, bitumen modification by ThD is expected to occur on a strong reducing action. It was supplied by Sigma Aldrich, melts between 124-127 ºC and has a molecular weight of 108.12 g/mol.

2. Thiourea ("Th," hereinafter) has been previously used as an additive to improve coating quality and to inhibit corrosion in several applications. It was supplied by Sigma Aldrich, has a molecular weight of 76.12 g/mol and its melting point lies within the interval 175-179 ºC.

Both of these substances, thiourea dioxide and thiourea, are white powders, soluble in water and polar organic solvents, but insoluble in non-polar solvents. Their structural formulae have been included in Figure 1.

3. A polypropylene-glycol functionalized with polymeric 4,4'-diphenylmethane diisocyanate (henceforth MDI-PPG). This prepolymer was synthesized by reaction of Alcupol D-0411 (polyol donated by Repsol YPF, Spain) and polymeric MDI (supplied by T.H. Tecnic, Spain). The reaction conditions were: a PPG:MDI molar ratio of 1:5; N_2 atmosphere; temperature of 40 ºC; 48 hours of mild agitation. The resulting prepolymer, with a molecular weight of 925 g/mol, is a light brownish liquid.

In order to establish a comparative analysis with a non-reactive additive, the commercial thermoplastic elastomer "Kraton D-1101," which belongs to the category of physical modification, has been also studied. This triblock copolymer of styrene-butadiene-styrene (SBS), provided by Shell Chemical Company U.K., is able to modify through physical dispersion in bitumen. It has a molecular weight of $1.5 \cdot 10^5$ g/mol and a styrene content of 31 wt.%.

2.2. Modified binders

Blends of bitumen with the different modifiers were carried out by means of an IKA RW-20 stirring device (Germany) equipped with a four-blade turbine, which has previously shown to produce the adequate mixing of bitumen with these three modifiers. A glass vessel (60 mm diameter; 140 mm height) containing bitumen was dipped into a bath with circulating oil and heated up to the processing temperature. Once this was reached, the modifier was added and the blend was stirred under the conditions described in Table 2. Regarding the non-polymeric substances, both of them

6

are in molten state at their selected processing temperature (130 ºC for ThD and 180 ºC for Th). As for the polymeric additive, this is a liquid with very low viscosity at the processing temperature of 90ºC. For these reasons, a four-blade turbine rotating at 1200 rpm for 1 hour is enough so that a proper dispersion can be achieved. After preparation, the binders were divided into two parts: a) one part was tested as such (referred to as "fresh" binder); and b) the another part was poured onto aluminium foil, forming a thin layer which was exposed to ambient under free access of air/moisture ("ambient cured" binder).

Regarding the SBS binder, blending was conducted with a Silverson L5M (Silverson Machines Ltd, U.K.) homogenizer under the conditions detailed in Table 2, as this rubber requires of more severe conditions to obtain a proper homogeneous dispersion.

2.3. Tests and measurements

Viscous flow measurements, at 60 ºC, were carried out in a controlled-strain ARES rheometer (Rheometric Scientific, USA). Temperature sweep tests in oscillatory shear, using a heating rate of 1 ºC/min, a frequency of 10 rad/s, and 1 % of strain, were conducted in a controlled-stress rheometer PHYSICA MCR-301 (Anton Paar, Austria) between 20 and 95 ºC. Before testing, samples were equilibrated for 30 minutes at the starting temperature. Plate-and-plate geometry (25 mm diameter and 1 mm gap) was always used. In order to ensure accurate results, at least two replicates were conducted for every sample.

Thermogravimetry tests (TGA) were conducted in a TA Q-50 (TA Instrument, USA). Temperature sweeps at 10 ºC/min, between 40 and 600 ºC, were carried out on 5-10 mg samples of pure thiourea dioxide, pure thiourea, neat bitumen and selected bituminous binders, under N_2 atmosphere.

"SARAs" fractions corresponding to neat bitumen and ThD/Th binders were determined by thin layer chromatography coupled with a flame ionization detector (TLC/FID), using an Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan). Elutions were performed in hexane, toluene and dichloromethane/methanol (95/5, in volume).

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian, USA) apparatus. Two solutions of selected MDI-PPG binders were prepared by dissolving 0.4 g of each in 25 mL of toluene and dichloromethane, respectively. Toluene was chosen because of its lack of absorbance in the spectral region of interest (-NCO band at 2275 cm^{-1}). On the other hand, the binders were also dissolved in dichloromethane, which does not show any relevant peak between 1500 and 2000 cm^{-1} (urea/urethane NH and C=O bands). The measuring cell, consisting of two KBr disks (32 mm diameter × 3 mm thickness) with a Teflon spacer in between (path length of 1 mm) placed into the appropriate sample holder, was filled with the different solutions. The spectra were obtained in a wavenumber range of 400–4000 cm^{-1} at 4 cm^{-1} resolution in the transmission mode.

The toluene-insoluble fractions were obtained by conducting a filtration test on bituminous solutions prepared by dissolving the binders in toluene (5 mg in 10 mL). Standard glass microfibre filters (Whatman 934-AH^{TM}) with a particle retention of 1.5 µm were used.

3. RESULTS AND DISCUSSION

3.1. Modified binders based on thiourea derivatives

The viscous flow behavior, at high in-service temperatures, of bituminous binders containing "ThD" or "Th" was studied by means of steady viscosity curves at 60 ºC.

This value represents the maximum temperature expected in a pavement exposed to ambient in warm climates.

Figure 2 shows the curves for neat bitumen, bituminous binders prepared by chemical modification ("ThD" or "Th"), as a function of curing time, and the reference SBS sample. Neat bitumen and chemically modified binders display nearly Newtonian behavior in the whole interval of shear rates studied. The SBS binder, instead, presents some slight level of shear-thinning. Moreover, for "fresh" ThD modified binders, an increase in the modifier content from 3 up to 9 wt.% results in increasing the viscosity from 100 up to 200 Pa·s. On the contrary, the fresh 9 wt.% Th formulation shows lower viscosity than that with 3 wt.%. This result may be attributed to a large quantity of non-reacted thiourea which, as such, would act as a "viscosity reducer." However, for both ThD and Th binders, ambient curing is seen to increase their viscosity, mainly for the largest curing time studied (60 days). This provokes that, after 20 days of curing, 9 wt.% Th leads to a binder with higher viscosity than that with 3 wt.%. Furthermore, the differences between both binders results much more important after 60 days of curing. Consequently, Figure 2 suggests two different bitumen modification pathways, referred to as "short-term" and "long-term" modification. "Short-term" modification is noticed in "fresh" binders, whilst "long-term" modification is caused by the effect of ambient curing on finished binders. In case of Th binders, addition of 9 wt.% of modifier results in a low degree of modification, with viscosity just increasing from 80 Pa·s (for the neat bitumen) up to 100 Pa·s, in the freshly prepared binder. However, after 60 days of curing, the viscosity increase observed is of about one order of magnitude, which is larger than the reference SBS-binder.

The above-mentioned enhancement in viscosity, at 60 ℃, suggests changes in the binder composition and microstructure upon addition of these non-polymeric modifiers.

In that sense, thin layer chromatography (TLC-FID) and thermo-gravimetric analysis (TGA) may provide valuable information about eventual routes of bitumen modification.

Figure 3 shows the evolution of the "SARAs" fractions, obtained by TLC-FID, with curing time for 9 wt.% ThD binders. Neat bitumen has been included as the control sample. As observed, the asphaltenes and aromatics concentrations decrease with increasing the curing time, the resins fraction increases as curing time does, whilst the saturates remain almost constant. The contribution of every single "SARAs" fraction to the overall colloidal structure of the binders can be evaluated through a colloidal index (C.I.), which can be written as follows [7]:

$$C.I.=\frac{\text{saturates+asphaltenes}}{\text{aromatics+resins}} \quad (1)$$

Equation 1 indicates a decrease in the values of this parameter, which is more important for the largest curing time studied (60 days). Thus, C.I. goes from 0.37, for neat bitumen, down to 0.22, after 60 days of curing. However, these results do not support the viscosity increase observed in Figure 2, as lower values of C.I. are normally associated with less viscous binders. With this regard, Equation 1 defines the C.I. in terms of the "SARAs" fractions, which are determined through a chromatographic method whose starting point, previous to the subsequent elutions, consists in dissolving the binder in toluene (5 mg in 10 mL). So, it may fail in providing information about chemically modified binders, where complex reactions involving bitumen and modifier may occur.

The results derived from a filtration test conducted on a solution of 5 mg of the 9 wt.% ThD binder (60 days-cured) in 10 mL of toluene seems to shed some light on this issue. Thus, Figure 4 presents TGA tests (in the form of DTG plots) carried out on the residue

obtained after filtration of the above solution, as well as on samples of the neat bitumen, pure thiourea dioxide and pure thiourea. Neat bitumen presents a large thermal decay process, extending over a wide temperature interval from 250 to 500 ºC (with a DTG peak at 455 ºC), which involves decomposition/volatilization of chemical compounds with very different molecular weights. Regarding the thiourea dioxide, its thermal decomposition consists of two stages [22]. The first and largest one is located between 121 and 144 ºC (with a DTG peak at 135 ºC), and is related to the production of SO_2 from thiourea dioxide, involving a significant mass loss of 17 wt.%:

$$NH_2(NH)CSO_2H \text{ (s)} \rightarrow CO(NH_2)_2 \text{ (s)} + 0.5\ S \text{ (s)} + 0.5\ SO_2 \text{ (g)} \quad \text{(R1)}$$
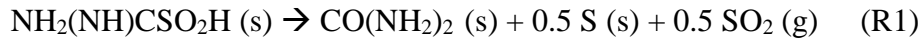
The second stage of the thiourea dioxide decomposition (DTG peak located at around 240 ºC) is governed by continuous melting, vaporization, and decomposition of urea produced during the first stage:

$$CO(NH_2)_2 \text{ (s)} \rightarrow NH_3 \text{ (g)} + HNCO \text{ (g)} \quad \text{(R2)}$$
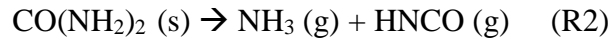
However, reaction R2 is not expected to occur during the blending of bitumen and ThD (carried out at 130 ºC).

Finally, the main interest is focused on the thermal decomposition of the 9 wt.% ThD binder residue. It can be observed a first peak, at about 120 ºC, attributed to unreacted thiourea dioxide (reaction R1), followed by a second peak, at about 240 ºC, due to the decomposition of the urea previously formed (reaction R2). Interestingly, a new peak arises at temperatures between those corresponding to R2 and neat bitumen degradation. This peak most probably corresponds to adducts derived from the interaction between bitumen asphaltenes and urea, which are proposed to be the responsible for the viscosity increase observed. Hence, we may assume a slow but progressive diffusion of moisture into the binder during its ambient curing, which would promote the decomposition of

11

residual unreacted ThD into more urea. And this, through formation of new urea-asphaltene adducts, would be the responsible for the evolution of viscosity with curing time [23]. In fact, the asphaltene fraction is seen to decrease as curing time increases. However, a fraction of these new adducts would present a reduced solubility in toluene, and this makes no possible their detection by the chromatographic method. On the contrary, another fraction of those adducts may be soluble in toluene, but with lower polarity than the asphaltenes, as demonstrated by a progressive increase in the resins content. These observations confirm that the colloidal index parameter, expressed in terms of the "SARAs" fraction, may fail in determining the "sol-gel" character of reactive systems.

Analogously, the thiourea-bitumen modification is expected to occur as a result of adducts derived from interactions between products of thiourea thermal decomposition and bitumen compounds. According to Wang and co-workers [22], thiourea thermal decomposition involves two overlapped processes. The first one, between 170 and 190 ºC, is dominated by the melting of thiourea, hardly involving mass loss. The isomeric reaction R3, with the production of NH_4SCN (ammonium thiocyanate), is suggested to occur during this first endothermic process:

$$SC(NH_2)_2 \text{ (s)} \rightarrow NH_4SCN \text{ (s)} \quad (R3)$$

In contrast to that, the second stage involves NH_4SCN (derived from R3) thermal decomposition into CS_2, HNCS and NH_3. As shown in Figure 4, this reaction leads to a significant mass loss associated to the DTG peak found at 210 ºC. Hence, NH_4SCN decomposition is not expected to occur at the processing temperature used (180 ºC). We may assume that bitumen modification and the consequent viscosity increase observed at 60 ºC is most probably related to the adducts formed from the interaction of NH_4SCN and the asphaltenes. With this regard, Figure 5 shows TLC/FID chromatograms for

selected samples. On the one hand, four peaks corresponding to the so-called "SARAs" fractions are shown in Figure 5A for the neat bitumen. Interestingly, the peak corresponding to the asphaltenes fraction splits into two new peaks in the 9 wt.% Th binder after 60 days of curing. These new peaks will be referred to as low and high polarity asphaltenes, LPAs and HPAs, respectively. Hence, the largest of them (LPAs) is thought to be the result of the interaction between NH_4SCN, from R3, and the most polar bitumen compounds. Moreover, these new adducts, which progressively form during the ambient curing of the binder, would be the responsible of the viscosity increase observed in Figure 2B. In order to confirm this result, two different solutions of neat bitumen in toluene were prepared. Then, ammonium thiocyanate ("neat bitumen + NH_4SCN" sample in Fig 5B) or thiourea ("neat bitumen + Th" sample in Fig. 5C) were added to the first and second solution, respectively. Solutions were then maintained under agitation at 25 ºC for 5 h. Results of TLC/FID analysis shown in Figures 5B and 5C reveal that separation of asphaltenes into LPAs and HPAs peaks only occur if ammonium thiocyanate is added. So, ammonium thiocyanate derived from the blending of thiourea and bitumen at 180 ºC, instead of thiourea itself, is the actual substance producing modification by means of the new LPAs fraction.

In summary, thiourea dioxide/thiourea derivatives containing N-H bonds [23,24] have demonstrated success in forming adducts which contribute to enhance the colloidal structure of bitumen by means of hydrogen-bond network. These adducts (derived from the interaction of urea/ammonium thiocyanate with asphaltenes) are responsible for the increase in viscosity at 60 ºC, and their contribution becomes more important as curing time increases.

3.2. Modified binders based on isocyanate-terminated prepolymers

The linear viscoelastic behaviour of the neat bitumen and MDI-PPG bituminous binders was studied by means of dynamic temperature sweep tests. As can be observed in Figure 6, the storage and loss moduli (G' and G'', respectively) monotonously decrease with increasing temperature from 20 to 95 ºC. Moreover, neat bitumen shows G'' values higher than G' (and tanδ, which increases as temperature does, higher than one) in the entire temperature interval tested, which point out its prevailing viscous behaviour. However, its linear viscoelastic response is significantly changed after its modification with MDI-PPG prepolymers and by ambient curing. For the "fresh" MDI-PPG binder, even though the viscous response still prevails, the G' curve shows a shoulder at about 70 ºC which dampens the differences between both moduli in the high temperature region. In consequence, even though tanδ still remains above one, it presents a maximum at about 65ºC. This shoulder in G' has been previously described for synthetic binders containing SBS in their formulations [25]. For low SBS concentrations, the binder presents two-phases, with the shoulder in G' being the consequence of the deformation-relaxation of the dispersed polymer-rich phase [26]. In the same way, for the "fresh" MDI-PPG binder, the dispersed polymer-rich phase would arise from local reactions between –NCO groups and bitumen compounds.

Finally, after 30 days of curing, the "ambient cured" MDI-PPG binder displays quite similar values of G' and G'' over a wide range of temperature (and so, a plateau region in tanδ around a value of one), and a crossover between both curves at about 35 ºC. According to the synthetic binders' analogy, the dispersed phase may become the continuous one if the polymer concentration is increased above a critical SBS concentration. This three-dimensional polymeric network contribute to enhance the binder elastic response (G'>G''). Similarly, "long-term" bitumen modification makes

the dispersed phase in the MDI-PPG binder evolve towards an almost extended network.

With the purpose of gaining an insight into the bitumen modification route behind the MDI-PPG prepolymer, which may explain the differences in Figure 6, FTIR scans were conducted on neat bitumen and their MDI-PPG modified binders.

Figure 7 shows the variation of selected absorption bands after MDI-PPG modification, for "fresh" and 30 days-cured samples. As observed in Figure 7A, the –NCO band (located at 2275 cm^{-1}) is not detected in neat bitumen, but clearly appears in its "fresh" MDI-PPG modified binder [27]. Eventually, the height of this peak experiences an important decay for the "ambient cured" MDI-PPG binder scan. Thus, Figure 7A reveals an important consumption of free isocyanate groups as a consequence of reactions which occur during the curing period. Figure 7B also demonstrates the existence of reactions between –NCO groups in the prepolymer and –OH pendant groups in the most polar fractions of bitumen, as shown by –CO stretching mode at 1725 cm^{-1} (urethane bond). Moreover, for the "ambient cured" sample, we may assume the existence of reactions involving water (through slow diffusion from ambient), as deduced from the –CO stretching mode at 1650 (urea bond) [28-30]. Urea bonds may also come from reactions between –NCO groups and –NH pendant groups in the most polar fractions of bitumen, although in a lesser extent. Finally, the two peaks on the right of the –CO peaks, located at about 1600 and 1525 cm^{-1}, corresponds to the bending absorption modes of –NH in urethane and urea, respectively [29]. Analogously to the –CO bands, they are seen to also undergo an increase in the modified bitumens, mainly for the cured sample.

Accordingly, the results evidence a chemical modification route based on three reactions. Firstly, reaction R4 would lead to the formation of a high number of urethane

bonds (peaks at 1725 and 1600 cm^{-1}) between –NCO in prepolymer and –OH pendant groups in bitumen:

$$R^1 - NCO + R^2 - OH \rightarrow R^1 - NH - COO - R^2 \quad (R4)$$
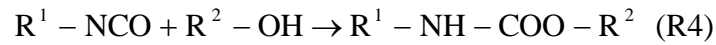
As the prepolymer functionality is higher than two, a single chain of prepolymer may connect several asphaltenes into large domains. Later, these large asphaltene domains may become even larger through the formation of urea linkages (peaks at 1650 and 1525 cm^{-1}). They come from reaction R5, between an amine group and –NCO groups yet available in the prepolymer chain previously linked to bitumen [31,32]:

$$R^2 - NCO + R^1 - NH_2 \rightarrow R^2 - NH - CO - NH - R^1 \quad (R5)$$
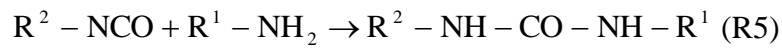
However, the primary amine above is only available when moisture from the ambient slowly diffuses into the binder and reacts with free –NCO groups, according to following reaction:

$$R^1 - NCO + H_2O \rightarrow R^1 - NH_2 + CO_2 \uparrow \quad (R6)$$
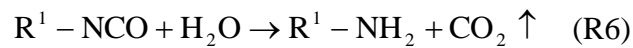
All these reactions would provide an explanation to the modification by isocyanate-terminated prepolymers and the outstanding enhancement in elasticity observed after 30 days of curing exposed to ambient.

3.3. Comparative analysis between the three chemical modifiers

In order to more conveniently visualise the degree of bitumen modification achieved at high in-service temperatures, a modification index (M.I.^{60ºC}), in terms of the zero-shear-viscosities, at 60 ºC, can be defined as follows:

$$M.I.^{60ºC} = \frac{\eta_{0,mod} - \eta_{0,neat}}{\eta_{0,neat}} \quad (2)$$

where $\eta_{0,mod}$ and $\eta_{0,neat}$ are the zero-shear viscosities of the modified binder and the neat

16

bitumen, at 60 ºC, respectively. This index expresses the relative increase in viscosity due to the bitumen modification, with respect to the base bitumen. Figure 8 indicates that, after 60 days of curing, the 9 wt.% binders derived from thiourea dioxide or thiourea present values of viscosity significantly higher than the SBS reference binder. However, for their "fresh" samples, their M.I. values at 60 ºC (and so, their viscosities at that temperature) remain quite below the SBS reference sample. This result suggests binders for which the asphalt production temperatures may be reduced down to values below those typically used for standard SBS modified bitumens. So, ThD/Th act like viscosity reducers which may facilitate the mixing and compaction of the asphalt mixture. Moreover, even though "fresh" ThD/Th binders can satisfactorily perform as such over the first weeks, they would evolve towards a better performance when in service.

With regard to the MDI-PPG binder, the degree of modification attained in the fresh sample (M.I.^{60ºC} of 5.5) is larger than the corresponding to the SBS reference binder (M.I.^{60ºC} of 3.5). Moreover, changes produced in this binder during its 30 days-curing have a significant effect on its viscosity, which increases up to about 40 times the value of its parent base bitumen. Hence, this binder is expected to exhibit, after 30 days of ambient curing, an enhanced resistance to permanent deformation at high 60 ºC. However, the flow viscous behavior of this binder differs from the SBS reference sample when evaluated at the production temperatures for the asphalt mixtures. Figure 9 compares the viscous flow curves of the SBS reference sample and "fresh" MDI-PPG binder at 135 ºC. This temperature is very often reported as the limit between warm and hot mix asphalts (WMA and HMA, respectively). On the other hand, viscosity is expected to range between 200 and 300 mPa·s for the binder to be adequately mixed with the mineral aggregates and laid down [33]. Interestingly, the MDI-PPG binder

17

presents, at 135 ºC, a value of viscosity just slightly higher than 300 mPa·s, and significantly lower than the SBS reference sample. So, Figure 9 demonstrates that, in the same way as ThD/Th, the NCO-terminated prepolymer studied may constitute an alternative modifier for the production of reduced temperature asphalts.

4. CONCLUSIONS

The adequacy of three different bitumen modifiers (polymeric and non-polymeric) in the preparation of modified binders with improved high-temperature performance, to be used in reduced temperature asphalt technologies, has been evaluated. Low temperature performance and effects of short-term and long-term aging were not considered in this study. They all (thiourea, dioxide thiourea and an isocyanate-terminated prepolymer) have shown to present low viscosities at the mixing/lay-down/compaction temperatures typically used in WMA production. On the contrary, they all become highly structured and viscous materials as a consequence of ambient curing. In consequence, even though "fresh" modified binders can satisfactorily perform as such over the first weeks, they would evolve towards a better performance against the permanent deformation when in service.

Interestingly, depending on the modifier nature, two different modification routes have been identified. On the one hand, thiourea dioxide/thiourea derivatives containing N-H bonds have demonstrated success in forming adducts which contribute to enhance the colloidal structure of bitumen by means of hydrogen-bond network. On the other hand, the modification by the reactive prepolymer takes place through reactions involving – NCO groups in the prepolymer, –OH pendant groups in the asphaltenes and ambient water, as described by reactions R4, R5 and R6.

5. ACKNOWLEDGEMENTS

18

6. REFERENCES

[1] Airey GD. Rheological properties of styrene-butadiene-styrene polymer modified road bitumens. Fuel 2003;82(14):1709-19.

[2] Singh B, Tarannum H, Gupta M. Use of isocyanate production waste in the preparation of improved waterproofing bitumen. J Appl Polym Sci 2003;90(5),1365-77.

[3] Ait-Kadi A, Brahimi H, Bousmina M. Polymer blends for enhanced asphalt binders. Polym Eng Sci 1996;36(12):1724-33.

[4] Dong XG, Lei QF, Fang WJ, Yu QS. Thermogravimetric analysis of petroleum asphaltenes along with estimation of average chemical structure by nuclear magnetic resonance spectroscopy. Thermochim Acta 2005;427(1-2):149-53.

[5] Redelius PG. Solubility parameters and bitumen. Fuel 2000;79(1):27-35.

[6] Lesueur D, Gerard JF, Claudy P, Létoffé JM, Planche JP, Martin DA. Structure related model to describe asphalt linear viscoelasticity. J Rheol 1996;40(5):813-36.

[7] Lesueur D. The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification. Adv. Colloid Interface Sci. 2009;145(1-2):42-82.

[8] Vasiljevic-Shikaleska A, Popovska-Pavlovska F, Cimmino S, Duraccio D, Silvestre C. Viscoelastic properties and morphological characteristics of polymer-modified bitumen blends. J Appl Polym Sci 2010;118(3):1320-30.

[9] Zanzotto L, Stasna J, Vacin O. Thermomechanical properties of several polymer modified asphalt. Appl Rheol 2000;10(4):134-44.

[10] Fawcett AH, McNally T. Blends of bitumen with polymers having a styrene component. Polym Eng Sci 2001;41(7):1251-64.

[11] Navarro FJ, Partal P, Martínez-Boza F, Gallegos C. Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens. Fuel 2004;83(14-15):2041-49.

[12] García-Morales M, Partal P, Navarro FJ, Martínez-Boza FJ, Gallegos C, González N, González O, Muñoz ME. Viscous properties and microstructure of recycled EVA modified bitumen. Fuel 2004;83(1):31-8.

[13] Blanco R, Rodríguez R, García-Garduño M, Castaño VM. Rheological properties of styrene-butadiene copolymer-reinforced asphalt. J Appl Polym Sci 1996;61(9):1493-501.

[14] Hesp SA, Woodhams RT. Asphalt–polyolefin emulsion breakdown. Colloid Polym Sci 1991;269(8):825-34.

[15] Newman JK. Dynamic shear rheological properties of polymer-modified asphalt binders. J Elast Plast 1998;30(3):245-63.

[16] Yousefi AA. Polyethylene dispersions in bitumen: the effects of the polymer structural parameters. J Appl Polym Sci 2003;90(12):3183-90.

[17] Lu X, Isacsson U. Modification of road bitumens with thermoplastic polymers. Polym Test 2001;20(1):77–86.

[18] Garcia-Morales M, Partal P, Navarro FJ, Martinez-Boza F, Gallegos C. Linear viscoelasticity of recycled EVA-modified bitumens. Energ Fuel 2004;18(2):357-64.

[19] British Standards Institution. BS EN 1426:2007. Bitumen and bituminous binders. Determination of needle penetration.

[20] British Standards Institution. BS EN 1427:2007b. Bitumen and bituminous binders. Determination of the softening point. Ring and Ball method.

[21] Ecker A. The application of Iatroscan-technique for analysis of bitumen. Petrol Coal 2001;43(1):51-3.

[22] Wang S, Gao Q, Wang J. Thermodynamic analysis of decomposition of thiourea and thiourea oxides. J Phys Chem 2005;109(36):17281-9.

[23] Cuadri AA, Partal P, Navarro FJ, García-Morales M, Gallegos C. Influence of processing temperature on the modification route and rheological properties of thiourea dioxide-modified bitumen. Energ Fuel 2011;25(9):4055-62.

[24] Cuadri AA, García-Morales M, Navarro FJ, Gordon GD, Partal P. End-performance evaluation of thiourea-modified bituminous binders through viscous flow and linear viscoelasticy testing. Rheol Acta 2013;52(2):145-54.

[25] Martínez-Boza FJ, Partal P, Conde B, Gallegos C. Influence of temperature and composition on the linear viscoelastic properties of synthetic binders. Energ Fuel 2000; 14(1):131-7.

[26] Bousmina M, Bataille P, Sapieha S, Schreiber HP. Comparing the effect of corona treatment and block copolymer addition on rheological properties of polystyrene/polyethylene blends. J Rheol 1995;39(3):499-517.

[27] Stuart, BH. Polymers. In Infrared spectroscopy: Fundamentals and applications. John Willey & Sons, New Jersey, 2004, p.113-137.

[28] Singh B, Tarannum H, Gupta M. Evaluation of TDI production waste as a modifier for bituminous waterproofing. Constr Build Mater 2004;18(8):591-601.

[29] Izquierdo MA, Navarro FJ, Martínez-Boza FJ, Gallegos C. Bituminous polyurethane foams for building applications: influence of bitumen hardness. Constr Build Mater 2012;30:706–713.

[30] Carrera V, Partal P, García-Morales M, Gallegos C, Pérez-Lepe A. Effect of processing on the rheological properties of poly-urethane/urea bituminous products. Fuel Process Technol 2010;91(9):1139-45.

[31] Mondal P, Khakhar DV. Hydraulic resistance of rigid polyurethane foams III. Effect of variation of the concentration of catalysts on foam structure and properties. J Appl Polym Sci 2004;93(6):2838-43.

[32] Segura DM, Nurse AD, McCourt A, Phelps R, Segura A. Chemistry of polyurethane adhesives and sealants. In: Cognard P, editor. Handbook of adhesives and sealants, Elsevier Ltd, Amsterdam, 2005, p. 101-162.

[33] Silva, HMRD, Oliveira JRM, Peralta J, Zoorob SE. Optimization of warm mix asphalts using different blends of binders and synthetic paraffin wax contents. Constr Build Mater 2010;24(9):1621-31.

Table 1. Penetration values, Ring & Ball softening temperatures, "SARAs" fractions and colloidal index value for the neat bitumen used.

	Values
Penetration (dmm)	168±5
R&B softening point (ºC)	41.0±2
Saturates (wt.%)	7.4±0.5
Aromatics (wt.%)	57.6±2.1
Resins (wt.%)	15.1±1.2
Asphaltenes (wt.%)	19.9±1.5
Colloidal Index (C.I.)	0.38

Table 2. Processing conditions used for the modified bituminous binders.

Modifier agent	Concentration (wt.%)	Proc. temperature (ºC)	Proc. time (h)	Agitation speed (rpm)
Thiourea dioxide (ThD)	3 and 9	130	1	1200
Thiourea (Th)	3 and 9	180	1	1200
Reactive prepolymer (MDI-PPG)	4	90	1	1200
Styrene-butadiene-Styrene (SBS)	3	180	2	2500

Figure captions

Figure 1. Structural formulae of: (A) thiourea dioxide; (B) thiourea.

Figure 2. Viscous flow curves, at 60 ºC, for (A) ThD and (B) Th binders, as a function of curing time. Neat bitumen and reference SBS binder are included.

Figure 3. Evolution of "SARAs" fractions with curing time for 9 wt.% ThD binders. Neat bitumen is included.

Figure 4. Derivative weight loss (DTG curves) for neat bitumen, pure thiourea dioxide, pure thiourea and insoluble residue in toluene from "60 days-cured" 9 wt. % ThD binder.

Figure 5. TLC/FID chromatographs for: (A) neat bitumen and "60 days-cured" 9 wt.% Th binder; (B) solution of neat bitumen in toluene with ammonium thiocyanate; (C) solution of neat bitumen in toluene with thiourea.

Figure 6. Evolution with temperature of (A) the linear viscoelastic moduli (G' and G'') and (B) tanδ for "fresh" and "30 days-cured" MDI-PPG binders. Neat bitumen and reference SBS binder are included.

Figure 7. FTIR spectra for "fresh" and "30 days-cured" MDI-PPG binders: (A) –NCO band; (B) -C=O and –NH (urethane/urea) bands. Neat bitumen is included.

Figure 8. Evolution of the modified index, $M.I.^{60ºC}$, with the curing time for the different binders studied.

Figure 9. Viscous flow curves, at 135 ºC, for "fresh" MDI-PPG and reference SBS binders. Neat bitumen is included.
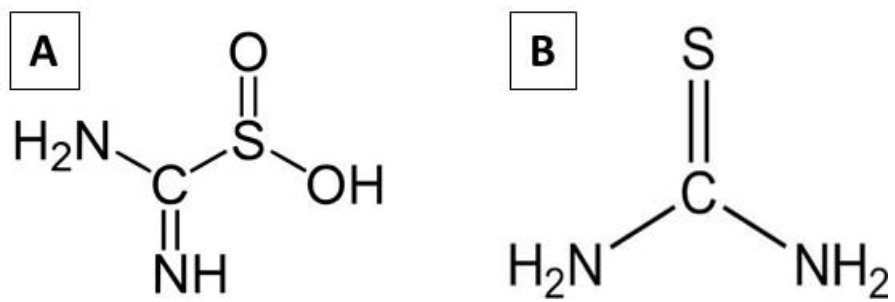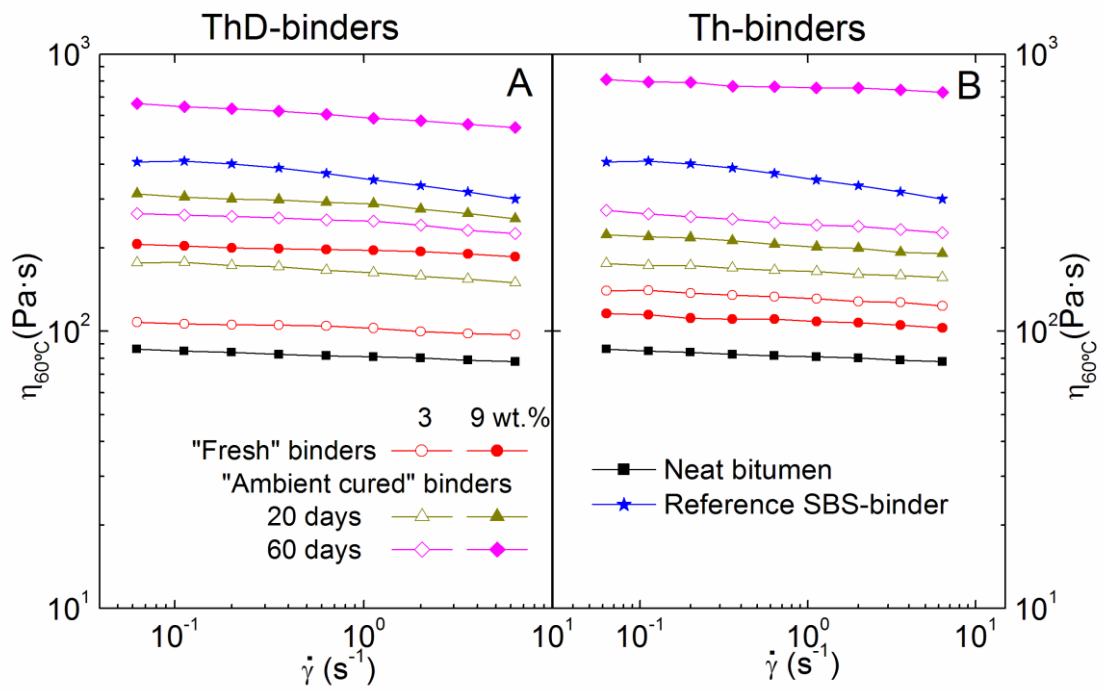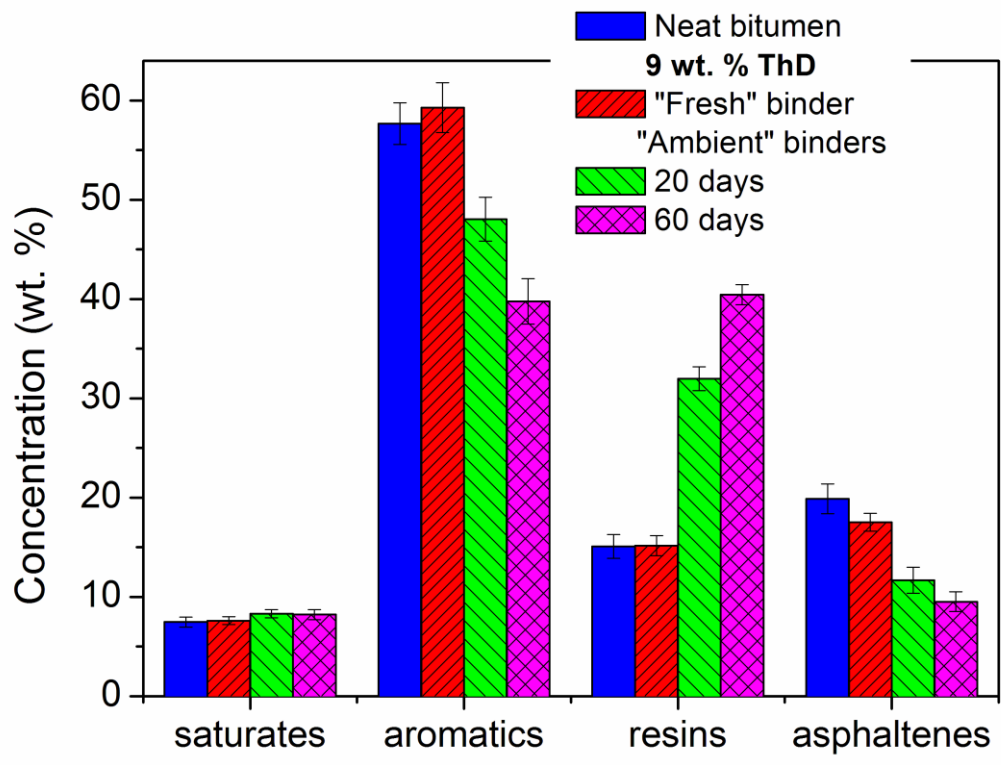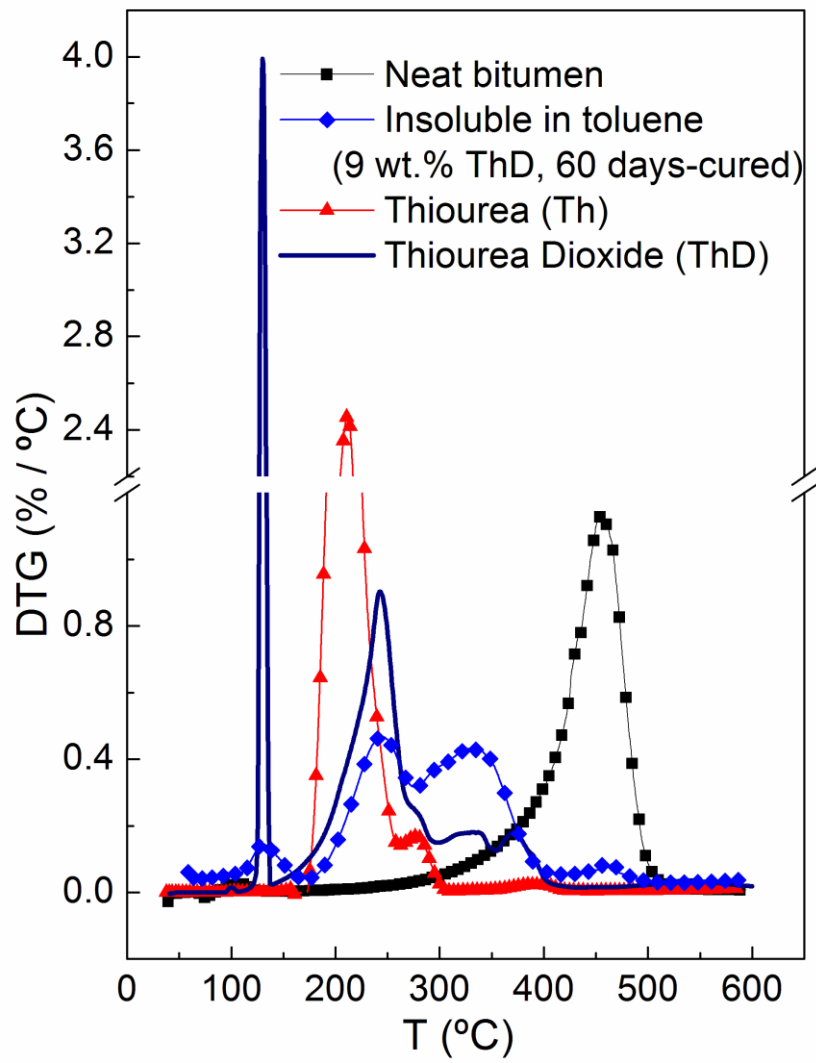
Figure 1

Figure 2

Figure 3

Figure 4
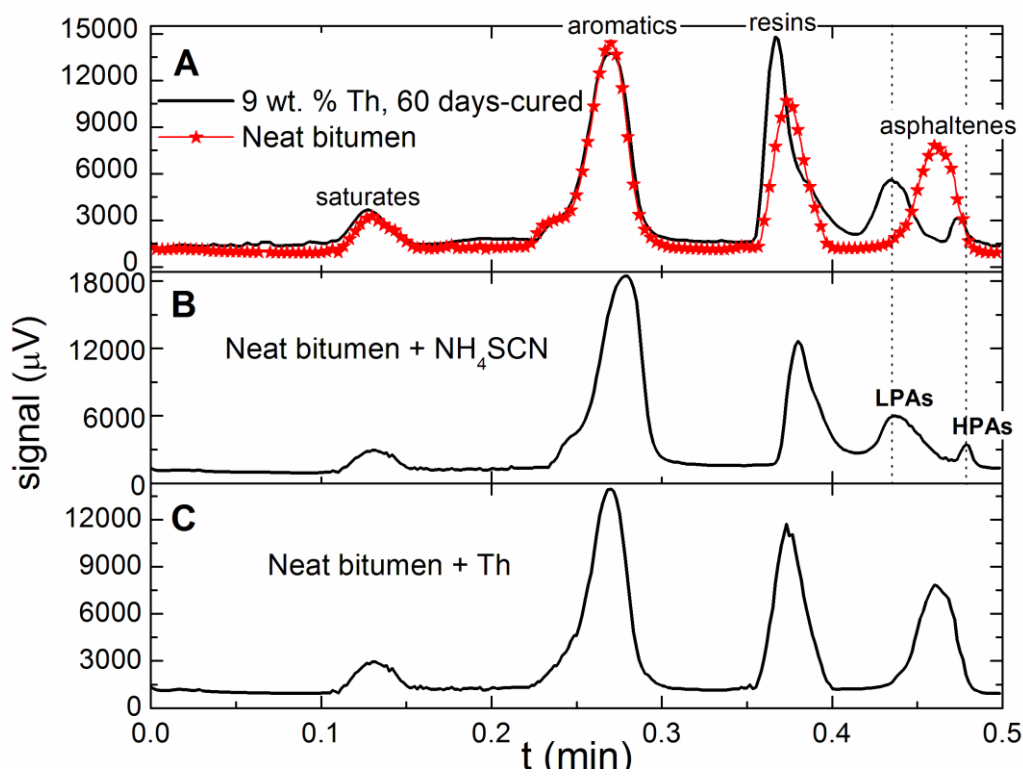
Figure 5
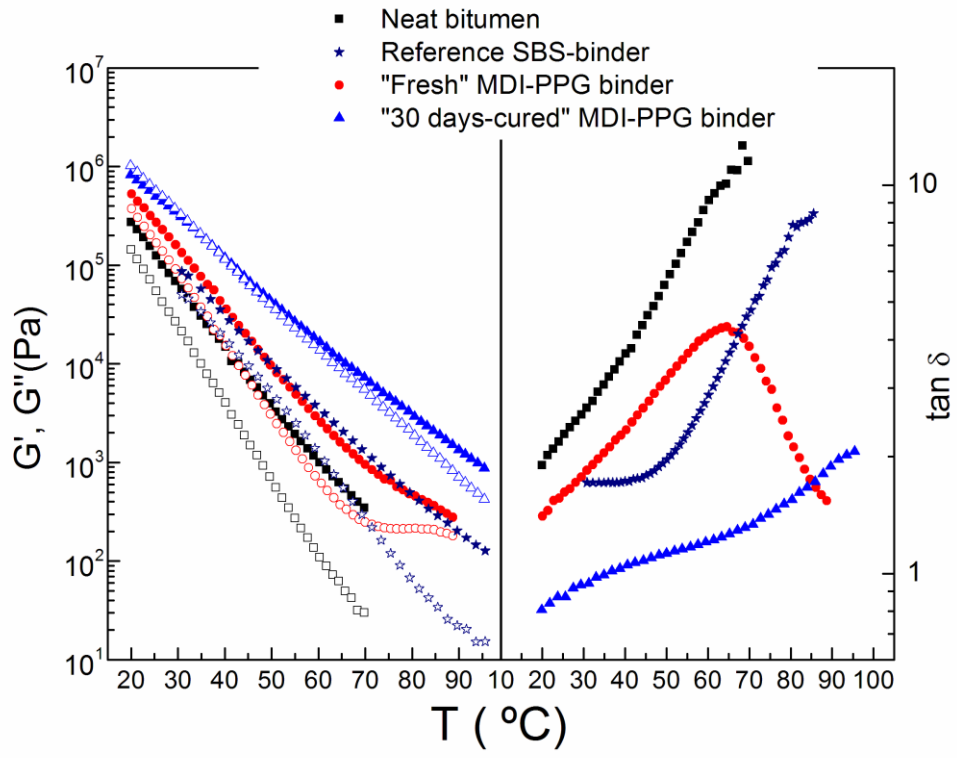
Figure 6
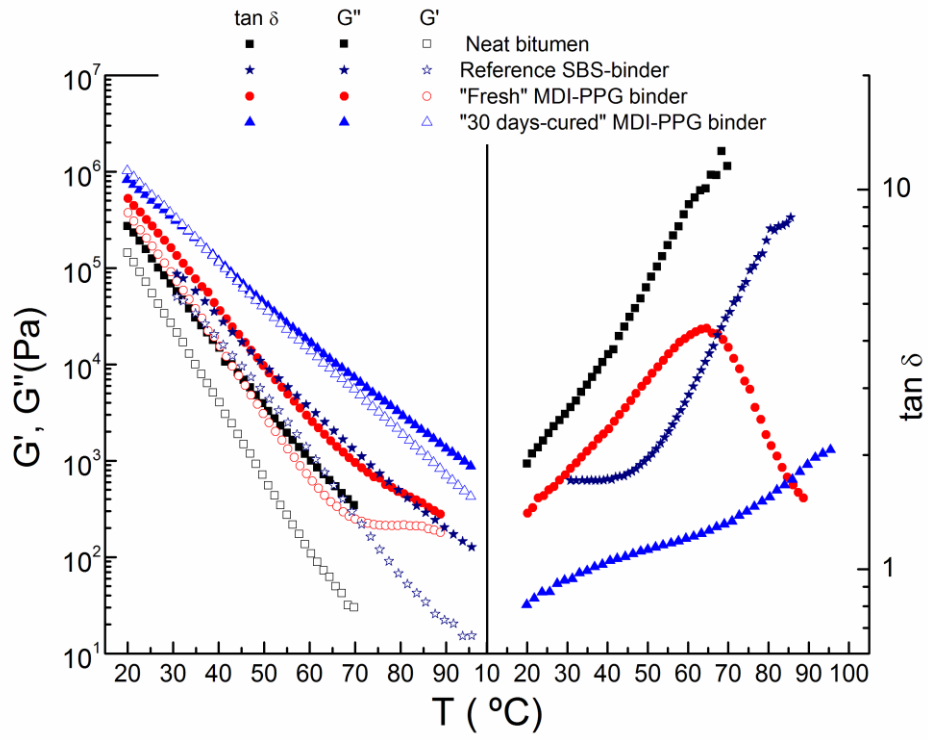
Figure 7

Figure 8

Figure 9