Chemically modified bitumens with enhanced rheology and adhesion properties to siliceous aggregates

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ABSTRACT

Moisture damage is one of the major premature failures that worsens the performance and shortens service life of pavements. This research assesses the effect that two chemical modifiers (thiourea and an isocyanate-functionalized castor oil prepolymer) exerts on the bitumen rheology and on the resistance to potential moisture damage of asphalt mixtures based on siliceous aggregates. Both thiourea and the isocyanate-based prepolymer improve the viscous and viscoelastic behaviours of bitumen at high in-service temperatures, particularly the isocyanate-based reactive modifier. Likewise, the visual inspection of the degree of bitumen coating on loose mixtures exposed to water in a “rolling bottle” test, and further surface free energy measurements, showed that the bitumen modification by the isocyanate-based prepolymer seems to reduce moisture-induced damage on siliceous aggregates. Conversely, thiourea-based modification increases sensitivity of the bitumen-aggregate mixture to water. Different adhesion mechanisms, based on chemical or physical bonds with the aggregate surface, have been proposed for each modifier.

Keywords: asphalt mixtures, moisture damage, surface free energy, bitumen chemical modification, product design.

1. INTRODUCTION

Even the best designed and constructed road pavements deteriorate over time under the combined effects of traffic loading and weathering. The most common distresses are: rutting, or permanent deformation at high temperatures [1]; thermal cracking, or thermal fracture due to the lack of flexibility at low temperatures [2]; and fatigue cracking, due to the repetitive application of loads [3]. As a consequence, the bitumen performance has been improved by the addition of widely used virgin polymers (SBS, SBR, EVA polymers) [4,5] or reactive agents (like polyphosphoric acid [6]). Other no-common additives employed in the bitumen modification are waste polymer [7,8] (plastic from agriculture, crumb tyre rubber, etc.), sulphur [9] or polyurethanes [10-12].

In addition to them, moisture sensitivity of an asphalt mixture, generally called stripping potential, is among the most important distresses of asphaltic pavements [13]. Thus, the penetration of moisture through asphalt mixtures increases the extent and severity of the previously commented common distresses. Many variables affect the amount of moisture damage which occurs in an asphalt mixture. Some of them are related to the materials forming hot mix asphalt (HMA) such as aggregate (physical characteristics, composition, dust and clay coatings) and bitumen (chemical composition, grade, hardness, crude source and refining process). Others are related to mixture design and construction (air void level, film thickness, permeability, and drainage) or environmental factors (temperature, pavement age, freeze-thaw cycles and presence of ions in the water) [14].

On the other hand, the conventional method of identifying moisture sensitive asphalt mixes during the mixture design process is by comparing results from mechanical tests on dry and moisture-conditioned asphalt mixtures. However, these tests are not always reliable and do not provide any information regarding the causes for good or poor performance of a particular mixture [15]. To that end, the surface energy theory can explain adhesion and cohesion bonds according to both aggregate and binders physico-chemical properties [13,16,17]. Based on surface energy measurements, Cheng et al. [18] pointed out that the affinity of the aggregates for water is far greater than that for bitumen. As a result, water is able to replace (strip) the bitumen from the aggregate surface, with the rate of replacement dependent on the aggregate-bitumen bond strength in the presence of water. Consequently, the thermodynamic energy potential that drives the stripping phenomenon depends on the surface properties of the bitumen, the aggregate and water [17]. In order to prevent asphalt from experiencing moisture damage, both the surface properties of aggregates and binders can be changed. Regarding the latter, different bitumen modification routes by polymers (such as styrene-butadiene-styrene (SBS) or styrene-butadiene-rubber (SBR) [14,17]) and amine-based additives [19,20] have been widely performed. On the other hand, some experiences using epoxy resins [21] or organic-based calcium compounds [22] have been also studied in the past.

However, it is generally recognised that there is a lack of experimental data concerning the moisture damage of modified asphalt mixtures [23], which are obtained by mixing the aggregate with a modified binder. With this aim, this paper reports the effect that bitumen modification by two chemical modifying agents (thiourea and an isocyanate-functionalized castor oil prepolymer) exerts on the binder rheology and on the resistance to potential moisture damage of asphalt mixtures containing siliceous aggregates, which are well-known for their poor adhesion features. To that end, two different evaluation methods of moisture sensitivity were conducted: (i) visual assessment of the degree of bitumen coverage on loose bitumen-aggregate mixtures (the so-called “rolling bottle” test); and (ii) non-mechanical tests on mixture constitutive parts, by measurements of the surface free energy components of asphalts parts separately and assessment of the strength of adhesion bonds between binder and aggregate. In addition, the rheological characterization of the modified binders was also conducted through viscous flow curves, at 60 ºC, and temperature sweep measurements.

2. EXPERIMENTAL SECTION

2.1. Materials

Bitumen with penetration grade 70/100 was used as base material for the bitumen modification. The results of penetration grade (EN 1426:2007), softening temperature (EN 1427:2007) and "SARAs" fractions [24] are shown in Table 1 in terms of average values and their calculated standard deviations.

Two different chemical modifiers are proposed. The first one, thiourea, is a non-polymeric substance, whilst the second one is an isocyanate-functionalized-castor-oil-reactive prepolymer. Detailed information on these modifiers is given below:

1. Thiourea 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.

2. Castor oil supplied by Guinama S.L. (Spain), with hydroxyl index of 125 mg KOH/g (measured according to standard ASTM D1957), was functionalized with isocyanate groups, by its reaction with a polymeric 4,4'-diphenylmethane diisocyanate (with an isocyanate groups, -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. In order to ensure an excess of non-reacted -NCO groups in the reaction product, an equivalent ratio -NCO/-OH of 8:1 was selected. This ratio was found optimal in a previous work [12]. The resultant reactive prepolymer had an average molecular weight of 2640 g/mol, and is expected to bring about "chemical" modification of bitumen, via reaction of -NCO groups and bitumen compounds having "active" hydrogen (i.e. –OH, >NH, etc.) [10-12,25,26].

In order to establish a comparative analysis with a non-reactive additive, a commercial thermoplastic elastomer styrene-butadiene-styrene (SBS) ''Kraton D-1101'' (provided by Shell Chemical Company U.K.) has also been studied. This triblock copolymer 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.%.

Finally, acidic siliceous aggregate provided by Mountsorrell Quarry, located in Leicestershire, U.K., has been used in this research. They are composed largely of silicon and oxygen, with the addition of ions such as aluminium, magnesium, iron and calcium. Due to the acidic nature of bitumen, this type of siliceous aggregate is well known for its poor field moisture damage performance [27,28]. Before being used, the aggregates were washed with deionized water and then dried in an oven at 105 ± 5 ºC overnight.

2.2. Preparation of modified binders

Blends of bitumen with the different chemical modifiers were processed in an IKA RW-20 stirring device (Germany) equipped with a four-blade turbine. A vessel (60 mm diameter; 140 mm height) containing bitumen was 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. For the non-polymeric modifier, 9 % wt.%

thiourea was processed at 180 ºC (above its melting point) for 1 h. These samples will be referred to as “Th-binder”. As for the polymeric additive, the processing of their corresponding modified binders consisted in firstly mixing bitumen and 2 % wt.% MDI-CO for 1 h at 90 ºC and, subsequently, adding 2 wt.% water for 45 min at the same processing temperature. This additive is a liquid with very low viscosity at the processing temperature of 90 ºC. For this reason, a mechanical agitation at 1200 rpm for 1h is enough to properly disperse it into the bituminous matrix. The resultant modified binders will be referred to as “MDI-binder”.

In addition, a bituminous reference sample with 3 wt.% of SBS (“SBS-binder”, hereinafter) was prepared with a Silverson L5M (Silverson Machines Ltd., U.K.) homogeneizer under the conditions detailed in Table 2, as this rubber requires more severe conditions to obtain a proper homogeneous dispersion.

3. TESTING PROCEDURES

3.1. Tests and measurements on modified binders

Different rheological tests were conducted on neat and modified bituminous samples using a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria): viscous flow measurements, at 60 ºC; and temperature sweep tests in oscillatory shear, between 30 and 100 ºC, using a continuous heating ramp of 1 ºC/min, a frequency of 10 rad/s and deformation of 1% strain (within LVE interval). Plate-and-plate geometry (25 mm diameter; 1 mm gap) was always used. In order to ensure accurate results, at least two replicates were conducted for every sample.

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian, USA) apparatus. Solutions of neat bitumen and “MDI-binder” were prepared by dissolving 0.4 g of each in 25 ml of toluene. This solvent was chosen because of its lack of absorbance in the spectral region of interest (-NCO band at 2275 cm^{-1}). 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.

3.2. Moisture damage evaluation on loose mixtures (“Rolling bottle” method)

The rolling bottle test was conducted in accordance with BS EN 12697-11 (part 11: determination of the affinity between aggregate and bitumen). This test was used to evaluate the degree of bitumen coverage on uncompacted bitumen-coated mineral aggregate particles after the influence of mechanical stirring in the presence of water. To perform the test, 6/10 mm of dust-free aggregate samples weighing 510 g were coated with 17 g of molten bitumen during the time necessary (20 min approx.) to ensure that the surfaces of the aggregates are completely covered by bitumen. Previously, the aggregate and bitumen were heated in an oven at the mixing temperature (120 ºC) for a duration of not less than 3 h. The loose mixture was then spread as individual particles on a metal plate and stored at ambient temperature for 12-64 h before testing. Each of the test bottles was filled to about half their volume with deionised water, and about 150 g of the loose aggregate–mixture was placed in each bottle. The whole assembly was put in the bottle roller rotating at a speed of 60 rotations per minute for about 6 h. At the end of the 6-h period, the aggregate particles were emptied from the test bottle into a test bowl which was then filled with fresh, deionised water to a level just above the top of the surface of the particles. At least three replicates of each sample were tested.

At the end of the test, the degree of bitumen coverage on the aggregate particles was visually estimated by two experienced technicians independently. The procedure was repeated for three more cycles (24, 48 and 72 h) with fresh water replacing the fouled water in the test bottle at the end of each cycle. For each rolling time, the mean value of each technician's recordings of the average degree of bitumen coverage obtained on the three part samples (three bottles) was calculated to the nearest 5 %, and the results were averaged to obtain the average degree of bitumen coverage for a given mixture.

3.3. Moisture damage assessment using the surface free energy method

Dynamic contact angle (DCA) tests were conducted to obtain the surface free energy of the four binders. DCA tests were performed in an analyzer Thermo Scientific CAHN Radiam DCA (USA). The surface energy components of each binder were determined from the contact angles that selected probe liquids, with known surface free energy components (Table 3), produced with the binder. The contact angles were obtained from the change in mass undergone by a bitumen-coated slide immersed in the probe liquid [29,30], as follows:

$$\cos\theta = \frac{\Delta F + V_{im}(\rho_L - \rho_{air})g}{P_t \gamma_L} \qquad (1)$$

where θ is the contact angle, ΔF is the change in force measured by the balance, V_{im} is the volume immersed in the liquid, g is the local acceleration of gravity, P_t is the perimeter of the bitumen coated plate, γ_L is the total surface free energy of the probe liquid, ρ_L is the density of the probe liquid and ρ_{air} is the density of air. According to Neumann criteria [15], the contact angle values of all the probe liquids for a given bituminous sample should lie on a smooth curve when $\gamma_L\cos\theta$ is plotted versus γ_L. If a value falls far from the curve, it should not be included in the final data for the calculation of surface energy properties. Figure 1 shows the values of $\gamma_L\cos\theta$ for the neat bitumen sample obtained using the five probe liquids. As can be observed, if the data corresponding to ethylene glycol is not considered, the other four probe liquids are well-fitted to the trend line. As a result, ethylene glycol should not be considered for the calculation of the surface free energy components. The same observations were obtained from the chemically modified and reference SBS binders.

The surface energy components of the siliceous aggregate used in this work were previously determined by Liu et al. [29] through dynamic vapor sorption tests. Their values were γ = 352 mJ/m^2, γ^{LW}=68 mJ/m^2, γ^{+}=164 mJ/m^2 and γ^{-}=123 mJ/m^2.

4. RESULTS AND DISCUSSIONS

4.1. Rheological behaviour at high in-service temperatures

Figure 2 shows the viscous flow curves for the neat bitumen and modified binders measured at 60 ºC. A nearly Newtonian behaviour over the whole range of tested shear rates is shown for the neat bitumen and “Th-binder”. On the contrary, modification with thermo-plastic elastomer SBS or reactive prepolymer leads to a non-Newtonian viscous flow behaviour, characterized by a constant viscosity, η_0, at low shear rates, followed by a shear-thinning region above a “critical” shear rate value, $\dot{\gamma}_c$. This behaviour can be described by the Carreau’s model fairly well:

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

where η_0 (Pa·s) is the zero-shear-limiting viscosity, λ (s) is a characteristic time whose inverse approximately matches the threshold shear rate mentioned above ($\dot{\gamma}_c$) and ‘s’ is a parameter related to the slope of the shear-thinning region. Table 4 includes the fitting parameters η_0 and λ for the samples studied.

As can be observed in Table 4, the "Th-binder" shows clearly higher viscosity than neat bitumen (viscosity increases from 150 up to 220 Pa·s, approximately). As reported by Cuadri et al. [31,32], the bitumen modification route through thiourea is related to adducts derived from the interaction between the asphaltenes and the ammonium thiocyanate (NH_4SCN), arising from the melting/thermal decomposition of Th during its mixing with bitumen at 180 ºC. As a result, thiourea and its derivatives containing N-H bonds contribute to enhance the colloidal structure of bitumen by developing a hydrogen-bond network. This fact leads to a higher binder viscosity at 60 ºC (Figure 2).

With regards to the "MDI-binder", an apparent increase in viscosity is found by the addition of the reactive prepolymer to the neat bitumen (Table 4). In this case, viscosity undergoes an increase from ca. 150 Pa·s, for the neat bitumen, up to 835 Pa·s, for the "MDI-binder", a much higher viscosity than the reference SBS-based formulation (with about 380 Pa·s). This result can be explained by the bitumen chemical modification produced by the isocyanate reactive groups (-NCO) of the prepolymer. In this sense, during the bitumen-prepolymer blending, a fraction of the –NCO groups in the prepolymer are known to react with –OH (and >NH) pendant groups present in the most polar molecules of bitumen (asphaltenic regions) as follows:

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

Hence, the resulting urethane linkages lead to larger and more complex domains, which still have free –NCO sites available for further reaction. Then, water addition during the second stage of "MDI-binder" processing promotes two series reactions involving the mentioned excess of –NCO groups:

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

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

Consequently, reactions 2 and 3 are expected to build up a more compact microstructure, through the formation of urea linkages between smaller units which, as commented, still had reactive –NCO sites available [25,26,33,34]. In addition, the Carreau's model fittings (see Table 4) reveal the development of a more complex microstructure for the "MDI-binder", as deduced from a higher value of viscosity (η_0) along with a lower value of the threshold shear rate $\dot{\gamma}_c$ (i.e. longer times for λ) [25].

Further to the viscous flow tests, dynamic shear temperature sweeps, from 30 to 100 ºC, were carried out on these samples (Figure 3). As seen in Figure 3A, all modified binders show a significant increase in complex modulus, $|G^*|$, in the whole temperature range studied, if compared to neat bitumen. Such an increase is more important for the "MDI-binder", which considerably exceeds the modulus of SBS-modified bitumen. Moreover, Figure 3B shows the evolution with temperature of the loss tangent, a parameter that establishes a comparison of the viscous features relative to the elastic ones ($\tan \delta = G''/G'$). All the samples show a prevailing viscous behaviour in the experimental temperature range studied, with values of $\tan \delta > 1$ (mainly, at high temperatures). As can be observed, chemically modified binders present a decrease in $\tan \delta$ values (enhancing binder elastic properties), more significant for the isocyanate-modified binder ("MDI-binder"). A higher elasticity is expected to reduce the progressive accumulation of permanent deformation (the so-called "rutting") produced by traffic at high in-service temperatures [34].

4.2. Moisture damage assessment

Qualitative measure of moisture damage on asphalt mixtures prepared from the chemically modified bitumens was obtaining by means of a rolling bottle test. The binder coverage on loose bitumen-coated aggregate particles observed after 6, 12, 48 and 72 h of rolling time is displayed in Figure 4. As expected, all the loose mixtures display a decrease in bitumen coverage as rolling time increases, showing the negative effects that both mechanical agitation and water exert on bitumen-aggregate stripping. Visual observation of the samples showed that the mixtures prepared from neat bitumen and “Th-binder” follow the same trend, decreasing the bitumen coverage to nearly 10 % and 5 % after 12 and 72 h, respectively. Interestingly, “MDI-binder” produces a loose mixture with significant higher coverage of bitumen, for each rolling time, compared to the other two samples. Thus, the isocyanate sample (Figure 5B) presents a bitumen coverage of about 70 %, after 24 h, seven times higher than that corresponding to the neat bitumen sample (Figure 5A). Therefore, “rolling bottle” tests suggest moisture damage of these asphalt mixtures might be reduced by bitumen modification with an isocyanate-functionalized castor oil prepolymer.

Aiming at a more quantitative assessment, the surface free energy of the binders, aggregate and water are used as the inputs for computing the adhesive bond strength of the asphalt mixtures in dry and wet conditions. Surface free energy components of the different bituminous samples were calculated from their contact angles with three of the probe liquids as previously proposed (water, glycerol and diidomethane), which were used to solve a system of three equations generated from Equation 3, as described by Howson et al.[17]:

$$\gamma_L(1+\cos\theta)=2\sqrt{\gamma_b^{LW}\gamma_L^{LW}}+2\sqrt{\gamma_b^{+}\gamma_L^{-}}+2\sqrt{\gamma_b^{-}\gamma_L^{+}} \qquad (3)$$

where γ_L, γ_L^{LW}, γ_L^{+} and γ_L^{-} are the surface free energy components of the selected probe liquids (Table 3); γ_b^{LW}, γ_b^{+} and γ_b^{-} are the unknown surface free energy components of the bitumen sample; and θ is the contact angle between them (Table 5).

Figure 6 shows the γ_b^{LW}, γ_b^{+} and γ_b^{-} values for the bituminous samples studied. They always display the non-polar component (γ_b^{LW}), with much higher values than the other components, followed by the base component (γ_b^{-}) and the acid component (γ_b^{+}). It can be observed that the non-polar component for neat bitumen and "MDI-binder" are very similar but smaller than those observed for "SBS-binder" and "Th-binder". In addition, the three modified binders present a decrease in the acid component, γ_b^{+}, which drops about 50 % for the "MDI-binder" to zero for "SBS-binder" and "Th-binder". Regarding the base component, it is worth noting than the physical bitumen modification with SBS produces a similar value to neat bitumen. However, chemical modification leads to different outcomes depending on the modifier. The isocyanate-functionalized castor oil prepolymer leads to a significant increase in γ_b^{-} for the "MDI-binder" with respect to the neat bitumen, from 1.8 to 4.5 mJ/m^2. Conversely, the non-polymeric chemical modifier (thiourea) produces a noticeable decrease in this component (down to 0.1 mJ/m^2) for the "Th-binder".

The surface free energy components of the bituminous binders and the aggregate are used to calculate the adhesive bond energy in dry conditions, ΔG_{adh}, according to Equation A.3. As shown in Figure 7A, ΔG_{adh} values for the chemically modified binders seem to depend on their base component (γ_b^{-}) values. Thus, "MDI-binder" displays a much higher ΔG_{adh} value compared to that obtained for "Th-binder". However, the increase in ΔG_{adh} value, with respect to neat bitumen, for the physical modified binder (i.e, "SBS-binder") can be attributed to the higher value of its non-polar component (γ_b^{LW}). From a thermodynamic point of view, a higher value of ΔG_{adh} indicates that a larger amount of energy is required for a crack to propagate along the bitumen-aggregate interface. When water is present, the energy associated with the displacement of each bituminous sample by water from its bitumen-aggregate interface (ΔG_{BWA}) was calculated from Equation A.4. Interestingly, Figure 7B shows that the lowest value of ΔG_{BWA} was obtained for the “MDI-binder” which implies a lower energy potential for water to displace this bituminous binder from its interface with the aggregate and, consequently, a higher resistance to moisture damage is expected.

In order to assess the moisture damage of asphalt mixtures by means of a single value, the ratio between the adhesive bond energy in dry conditions (ΔG_{adh}) and in the presence of water (ΔG_{BWA}) was proposed by Bhasin [15]. Furthermore, wetting/coating process between bitumen and aggregate is not only affected by the surface properties of the two materials, but the viscosity or cohesion of the bitumen itself play a significant role [35]. In order to take it account, an energy parameter [15,17,36] (ER), including a wettability relationship, has been defined as:

$$ER = \left| \frac{\Delta G_{adh} - \Delta G_{coh}}{\Delta G_{BWA}} \right| \qquad (4)$$

Therefore, a higher value of the ER parameter indicates a better resistance to moisture damage for that bitumen-aggregate combination. Figure 8, which displays ER values for the neat bitumen and modified binders studied, indicates that the bitumen modification by the isocyanate-prepolymer is expected to improve the asphalt mixture’s resistance to moisture-induced damage, whilst thiourea-bitumen modification will worsen its performance with respect to neat bitumen. In addition, similar ER values were observed for the neat bitumen and reference-SBS bituminous sample. Therefore, the conclusions derived from the surface free energy component, based on the ER parameter, are in good agreement with those obtained from the “rolling bottle” test.

4.3 Proposed adhesion mechanisms

The different moisture resistance exhibited by “Th-binder” and “MDI-binders” seems to arise from a different aggregate-bitumen interaction, which depends on the chemical reactions induced by these modifiers within the binder and on the type of aggregate (i.e. on its chemical composition). Regarding the siliceous aggregate used here, Petersen and Plancher [37] indicated that actives sites on these surfaces range from hydroxyl groups of varying acidities to hydrogen bonding sites of high acidity.

As aforementioned, thiourea bitumen modification contributes to enhance the colloidal structure of the bitumen by means of a hydrogen-bond network through the interactions of ammonium thiocyanate (NH_4SCN) and asphaltenes. Similarly, it would expected that there will be the development of hydrogen bonds between NH_4SCN and the oxygen of the silanol groups located on the surface of the siliceous aggregate, similar to the well-known bond mechanism observed for carboxylic acids and siliceous aggregate surfaces [38]. Likewise, as with other widely used anti-stripping agents, thiourea has two amine-end groups which physically bond with the siliceous surface. However, an amine anti-stripping agent for this type of aggregate should have a hydrocarbon chain with 14 to 18 carbons [39] a requirement not met by thiourea derivatives. Moreover, thiourea and NH_4SCN have low molecular weight, if compared to hydrocarbon-derived agents, and high solubility in water. Although authors think that the hydrogen-bond network between “Th-binder” and aggregate, which can be easily displaced by water [40], could be the responsible of its poor resistance to moisture, a firm answer still need further studies.

Regarding “MDI-binders”, it is accepted that the bitumen-aggregate adhesion strength could be enhanced through chemical reactions between bitumen functional groups and “active sites” present in the aggregate. For example, calcium carbonate (major component of limestone aggregates) reacts with the carboxylic acid forming a water-insoluble salt at the temperature at which hot mix asphalt is produced [40]. Based on the chemistry behind bitumen modification by isocyanate-based reactive prepolymer (reaction 1), reaction 4 illustrates a proposed chemical mechanism that would be responsible for the improvement in resistance to moisture damage observed in the “MDI-binder” asphalt mixture based on siliceous aggregates:

$$\mathrm{Agg - Si - OH + NCO - binder \rightarrow Agg - Si - NH - COO - binder} \qquad \text{(reaction 4)}$$

where Agg-Si-OH represents the bulk aggregate structure exhibiting hydroxyl groups (-OH) available to react with –NCO remaining groups, according to reaction 1. In this sense, FTIR scans conducted on this chemically modified binder (Figure 9) reveal the existence of the -NCO band, located at 2275 cm^{-1}. Thus, after the processing, which involves the consumption of free isocyanate groups as a consequence of reactions 1-3, “MDI-binder” still has –NCO groups available for further reactions with active groups on the aggregate surface. Therefore, according to reaction 4, new urethane bond linkages could be created between the free isocyanate groups present in the “MDI-binder” and the hydroxyl groups of the aggregate, improving its asphalt mixture resistance to moisture damage.

5. CONCLUDING REMARKS

The potential moisture damage of two chemically modified asphalt mixtures, obtained by bitumen modification with thiourea and an isocyanate-functionalized castor oil prepolymer, was evaluated. In addition, their rheological behaviour at high in-service temperatures was also studied.

Bitumen chemical modifications lead to higher binder viscosity, at 60 ºC, and to enhanced elastic characteristics in the experimental range of temperatures. The observed enhancement is more important for the MDI-binder, which clearly exceeds the rheological properties of both reference systems (neat and SBS-modified bitumens). Regarding the resistance to moisture damage, the “rolling bottle” tests showed higher bitumen coverage values for the modified binder with the isocyanate-based reactive prepolymer. Based on the surface energy theory, an energy parameter ER (which was calculated from the surface free energy components of both constituents of asphalt, namely aggregate and bitumen, separately) was used as a screening tool to compare the bituminous sample in terms of its resistance to moisture damage. Interestingly, the bitumen modification by the isocyanate-prepolymer displays the highest ER value. A reactive adhesion mechanism has been proposed, in which new urethane bond linkages could be created between the free isocyanate groups present in the “MDI-binder” and the hydroxyl groups of the siliceous aggregate, improving the asphalt mixture resistance to moisture damage. On the other hand, thiourea bitumen modification would worsen binder-aggregate resistance to water, if compared to neat bitumen. This fact could be due to the development of a hydrogen-bond network established between “Th -binder” and aggregate surface. However, this assumption needs further studies in order to be checked.

6. APPENDIX A

The Good-Van Oss-Chaudhury theory has been widely used to obtain the surface free energy components of various materials [41-42]. According to this theory, the surface free energy of a material is calculated by means of three components: Lifshitz-van der Waals, γ^{LW}; monopolar acid, γ^{+}; and a monopolar basic, γ^{-}. As a result, the total surface free energy of a material, γ, is obtained from these components as follows:

$$\gamma = \gamma^{\mathrm{LW}} + 2\sqrt{\gamma^{+}\gamma^{-}} \qquad (A.1)$$

Crack initiation can take place at two possible locations: through the bulk of a material or along the interface between the bitumen and aggregate. The cohesive bond energy, ΔG_{coh}, or work of cohesion, is the energy required for a crack to propagate through the bulk of a material and is twice the total surface free energy of the material:

$$\Delta G_{\mathrm{coh}} = 2\gamma = 2(\gamma^{\mathrm{LW}} + 2\sqrt{\gamma^{+}\gamma^{-}}) \qquad (A.2)$$

On the other hand, the adhesive bond energy, ΔG_{adh}, or work of adhesion, is the energy required for a crack to propagate along the bitumen-aggregate interface, and depends on the surface free energies of both the binder and aggregate (identified with the subscripts "B" and "A", respectively):

$$\Delta G_{\mathrm{adh}} = 2\sqrt{\gamma_A^{LW}\gamma_B^{LW}} + 2\sqrt{\gamma_A^{+}\gamma_B^{-}} + 2\sqrt{\gamma_A^{-}\gamma_B^{+}} \qquad (A.3)$$

In addition, when water is also present at the bitumen-aggregate interface, the energy required for the crack to propagate is a function of the surface free energy of the bitumen, aggregate and water. The energy associated with the displacement of bitumen by water from such an interface, ΔG_{BWA}, or work of debonding, is expressed as:

$$\Delta G_{\mathrm{BWA}} = \gamma_{\mathrm{BW}} + \gamma_{\mathrm{AW}} - \gamma_{\mathrm{BA}} \qquad (A.4)$$

where the subscript "W" represents the water. For practically all bitumen-aggregate combinations, the displacement of bitumen on the aggregate surface by water is a thermodynamically favourable process, so that the energy required for water to displace bitumen from the aggregate surface always has negative values.

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

	Values [a]
Penetration (dmm)	82 ± 3
R&B softening point (ºC)	58.0 ± 1.5
Saturates (wt.%)	6.2 ± 0.8
Aromatics (wt.%)	56.3 ± 2.1
Resins (wt.%)	23.4 ± 1.2
Asphaltenes (wt.%)	14.1 ± 1.1
Colloidal Index (C.I.)	0.26

[a] mean values ± SD (Standard Deviation , $p = 0.05$)

Table 2. Processing conditions used for the modified binders.

Modifier agent	**Concentration (wt.%)**	**Proc. temperature (ºC)**	**Proc. time (min)**	**Agitation speed (rpm)**
Thiourea	9	180	60	1200
Reactive prepolymer	2	90	60+45[a]	1200
Styrene-butadiene-Styrene	3	180	120	2500

[a] Processing of “MDI-binder” requires two stages.

Table 3. Surface free energy components for the probe liquids (at 25 ºC).

		Surface free energy components (mJ/m^2)			
	Samples	γ^{LW}	γ^{+}	γ^{-}	γ_L
PROBE LIQUID	Water	21.8	25.5	25.5	72.8
	Glycerol	34.0	3.9	57.4	64.0
	Formamide	39.0	2.3	39.6	58.0
	Ethylene glycol	29.0	1.9	47.0	48.0
	Diiodomethane	50.8	0.0	0.0	50.8

Table 4. Carreau's model parameters for the bituminous binders studied.

Samples	**η_0 (Pa·s)**	**λ (s)**
Neat bitumen	150	--
SBS-binder	380	1.02
Th-binder	220	--
MDI-binder	835	1.85

Table 5. The contact angle values of the different bituminous binders obtained from water, glycerol and diiodomethane.

	Contact angle, θ (º)[a]		
Samples	Water	Glycerol	Diiodomethane
Neat bitumen	101.28 ± 0.17	91.80 ± 0.33	72.91 ± 0.76
SBS-binder	95.77 ± 0.69	84.12 ± 0.56	58.27 ± 0.57
Th-binder	103.28 ± 0.34	90.26 ± 0.49	57.52 ± 0.18
MDI-binder	95.55 ± 0.53	89.79 ± 0.21	72.94 ± 0.85

[a] mean values ± SD (Standard Deviation , $p = 0.05$)

Figure captions

Figure 1. Plot of $\gamma_L \cos\theta$ vs. γ_L for the neat bitumen used.

Figure 2. Viscous flow curves, at 60 ºC, for neat bitumen, SBS-reference sample and chemically modified binders.

Figure 3. Evolution with temperature of: (A) complex modulus, $|G^*|$; and (B) loss tangent, tan δ, for neat bitumen, SBS-reference sample and chemically modified binders.

Figure 4. Bitumen coverage on loose bitumen-coated aggregate particles, after 6, 12, 48 and 72 h of rolling time, obtained for neat bitumen and chemically modified binders.

Figure 5. Aggregate coating with (A) neat bitumen and (B) "MDI-binder" samples after 24 h of rolling time.

Figure 6. Surface free energy components for neat bitumen, SBS-reference sample and chemically modified binders.

Figure 7. (A) Adhesive bond energy in dry conditions ($\Delta \mathrm{G}_{\mathrm{adh}}$) and (B) energy associated with the displacement of bituminous material by water (ΔG_{BWA}) for neat bitumen, SBS-reference sample and chemically modified binders.

Figure 8. Energy parameter (ER) for neat bitumen, SBS-reference sample and chemically modified binders.

Figure 9. FTIR scans conducted on neat bitumen and "MDI-binder" samples.

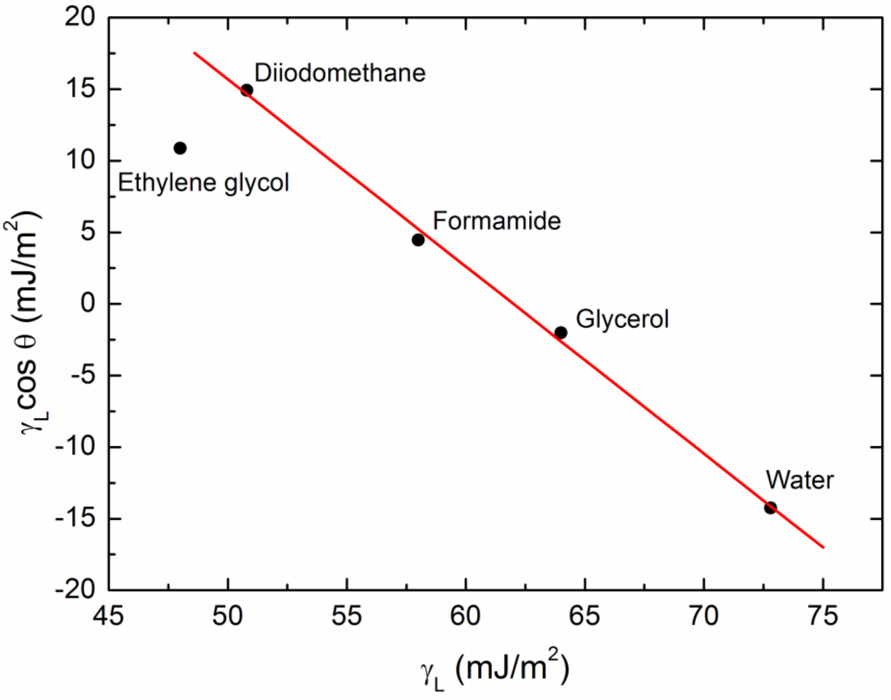
20
15
10
5
0
-5
-10
-15
-20
45
50
55
60
65
70
75
$\gamma_L \cos\theta$ (mJ/m^2)
γ_L (mJ/m^2)
Diiodomethane
Ethylene glycol
Formamide
Glycerol
Water

Figure 1

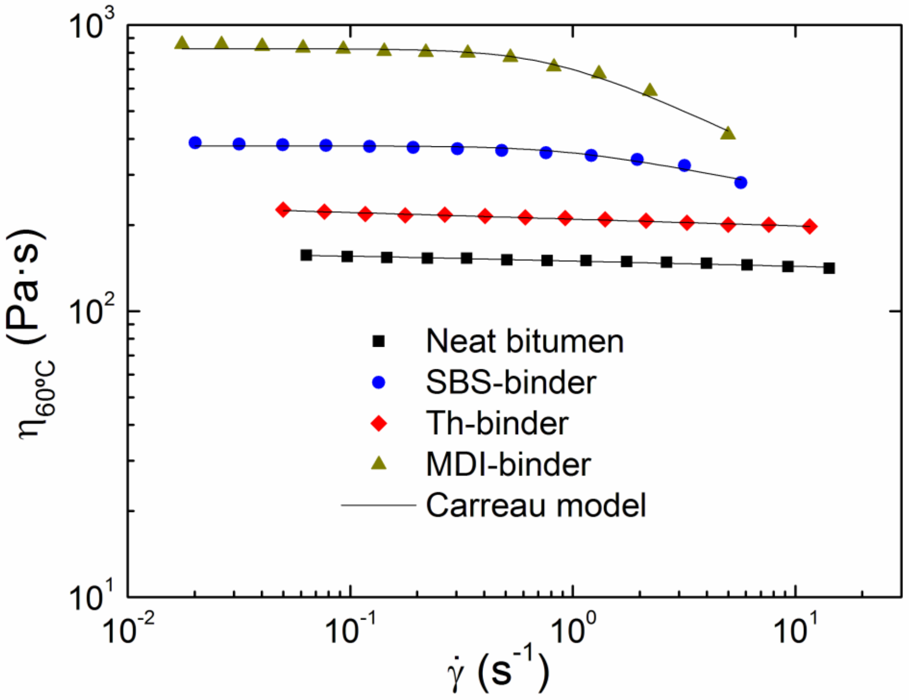
10^3
10^2
10^1
$\eta_{60^\circ C}$ (Pa·s)
10^{-2}
10^{-1}
10^0
10^1
$\dot{\gamma}$ (s^{-1})
■ Neat bitumen
● SBS-binder
◆ Th-binder
▲ MDI-binder
Carreau model

Figure 2

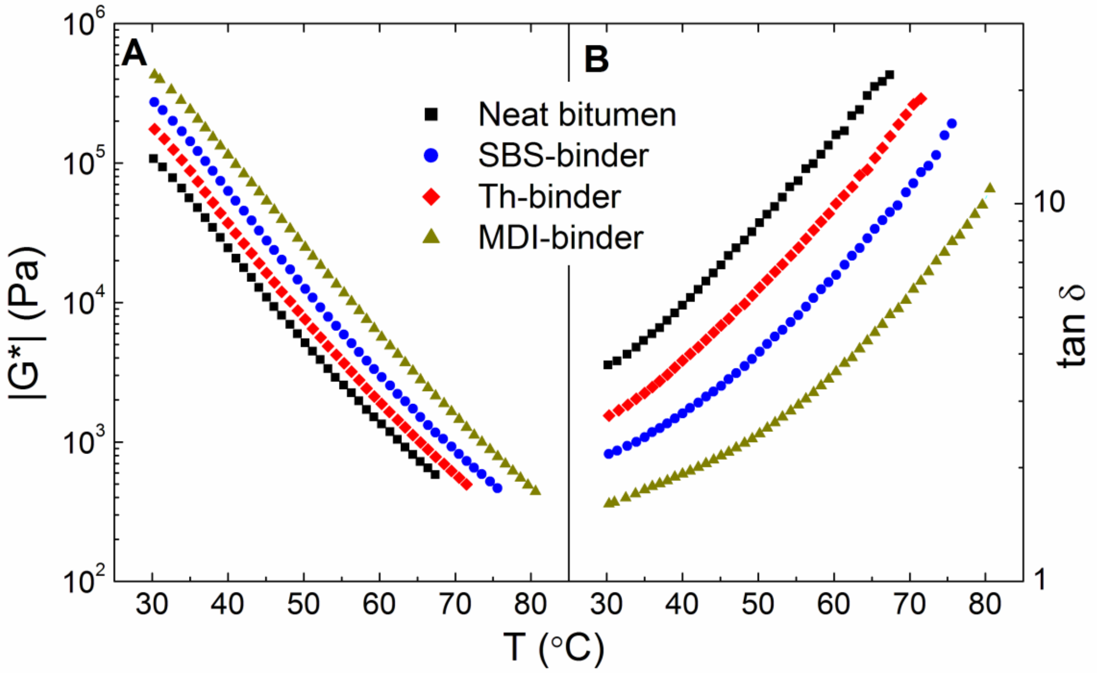
A
B
Neat bitumen
SBS-binder
Th-binder
MDI-binder
|G*| (Pa)
tan δ
T (°C)
10^6
10^5
10^4
10^3
10^2
10
1
30
40
50
60
70
80

Figure 3

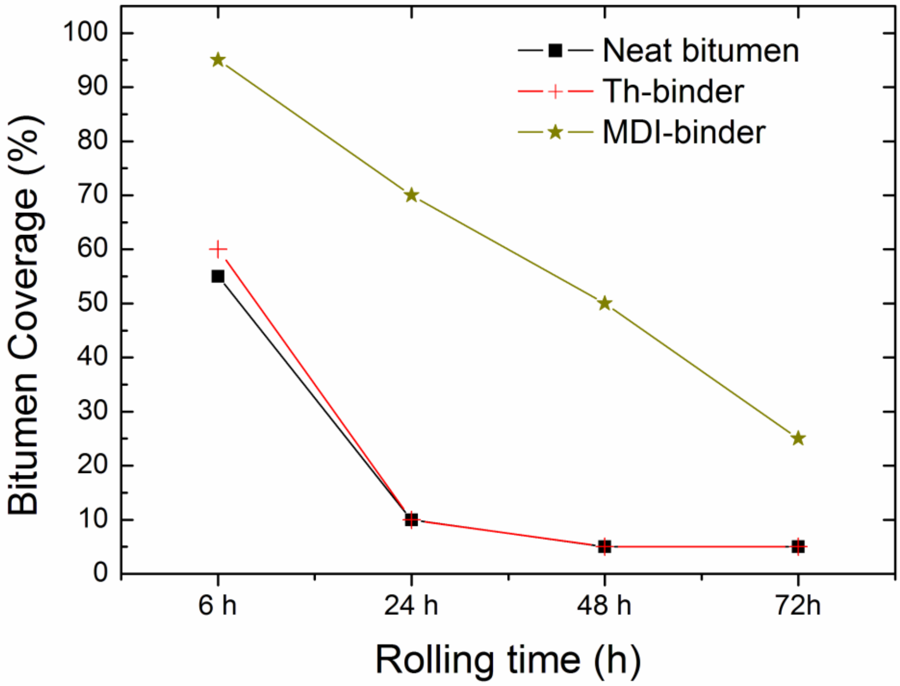
Bitumen Coverage (%)
100
90
80
70
60
50
40
30
20
10
0
6 h
24 h
48 h
72h
Rolling time (h)
Neat bitumen
Th-binder
MDI-binder

Figure 4

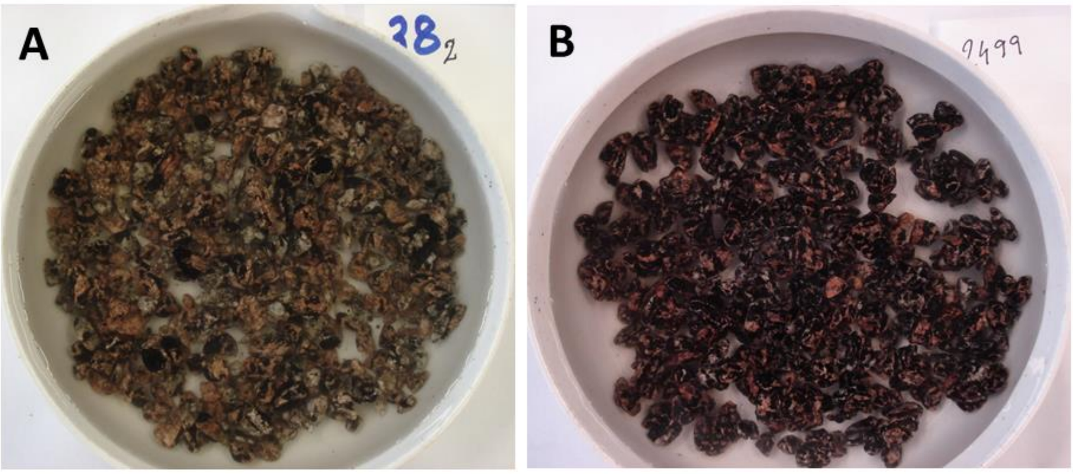

Figure 5

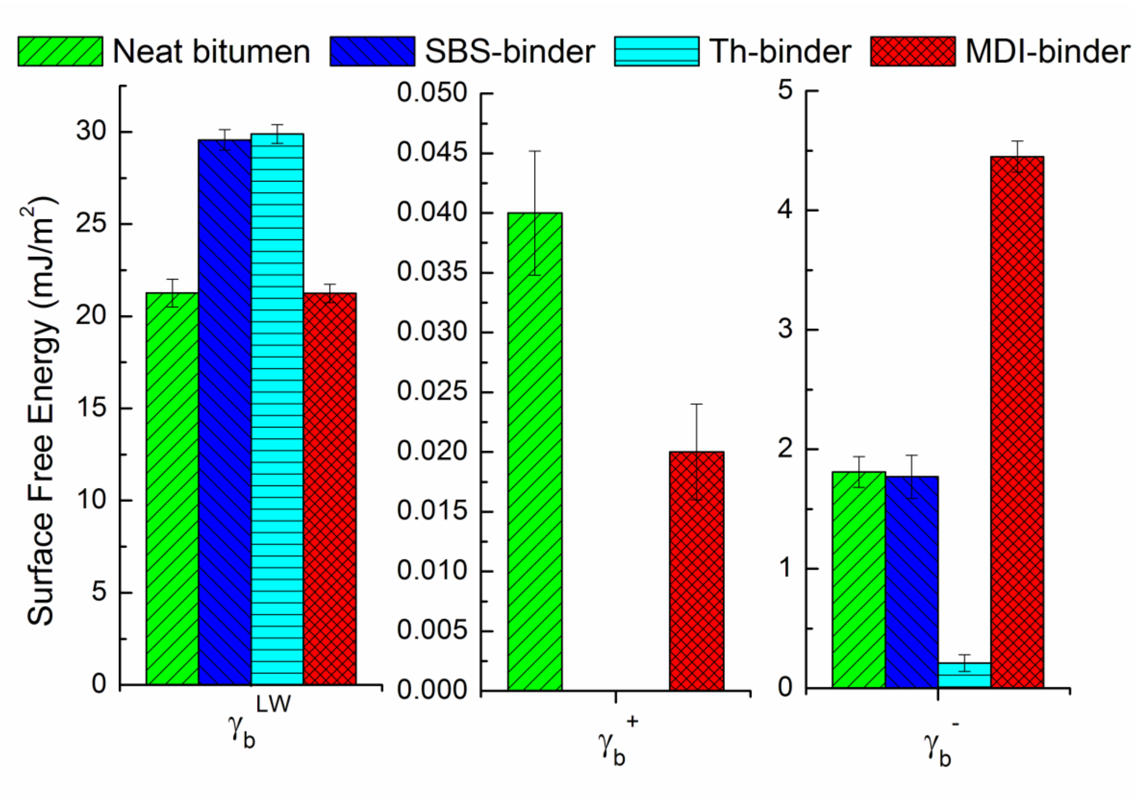
Neat bitumen
SBS-binder
Th-binder
MDI-binder
Surface Free Energy (mJ/m^2)
0
5
10
15
20
25
30
γ_b^{LW}
0.000
0.005
0.010
0.015
0.020
0.025
0.030
0.035
0.040
0.045
0.050
γ_b^+
0
1
2
3
4
5
γ_b^-

Figure 6

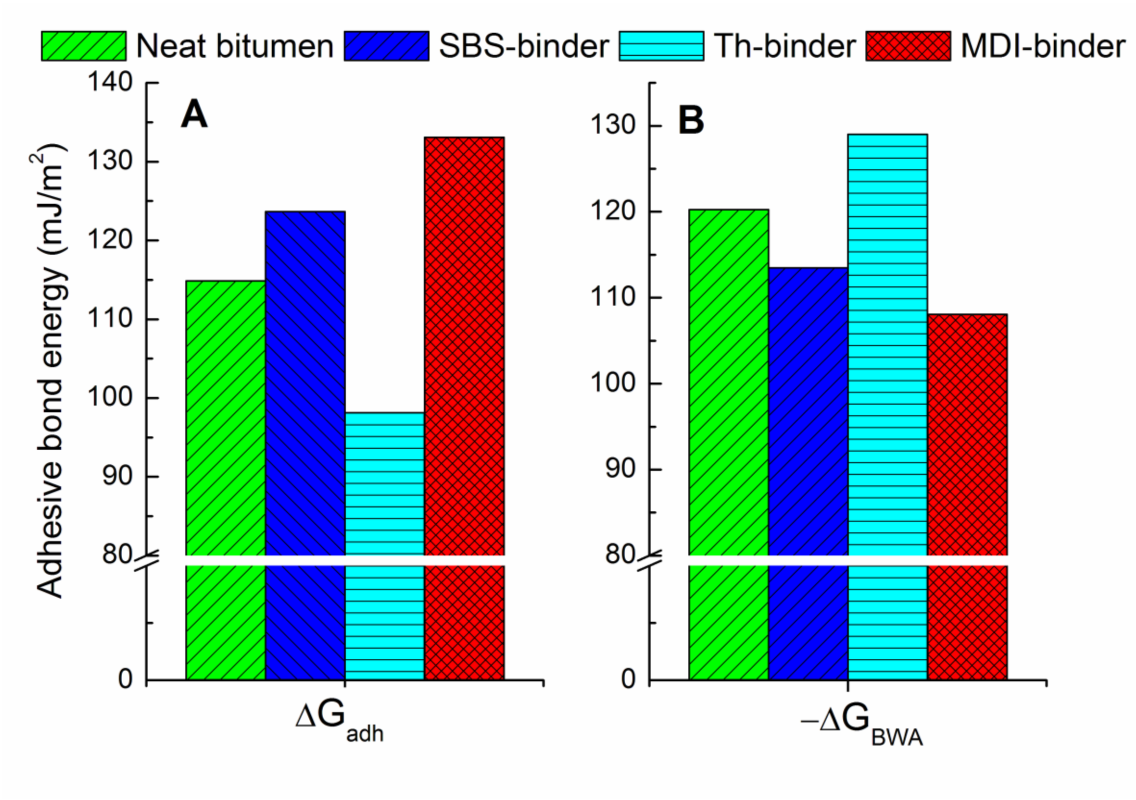
Neat bitumen
SBS-binder
Th-binder
MDI-binder
Adhesive bond energy (mJ/m^2)
A
140
130
120
110
100
90
80
0
ΔG_{adh}
B
130
120
110
100
90
80
0
$-\Delta G_{BWA}$

Figure 7

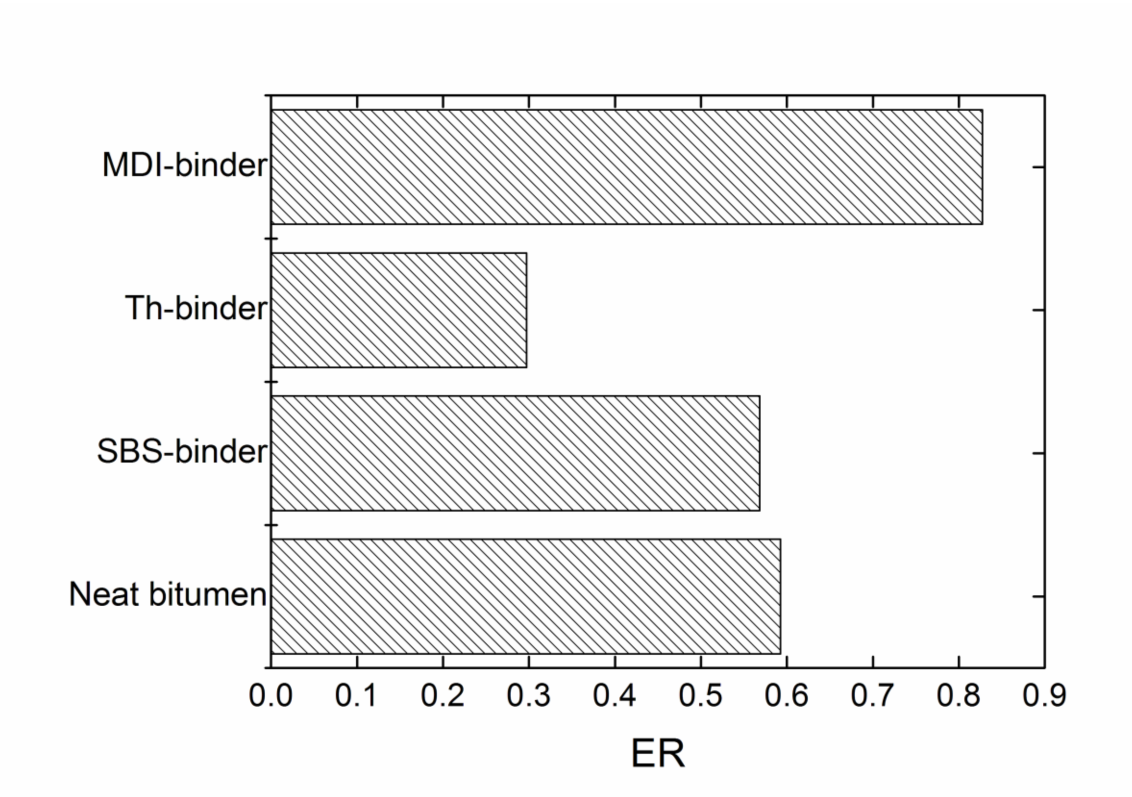
MDI-binder
Th-binder
SBS-binder
Neat bitumen
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
ER

Figure 8

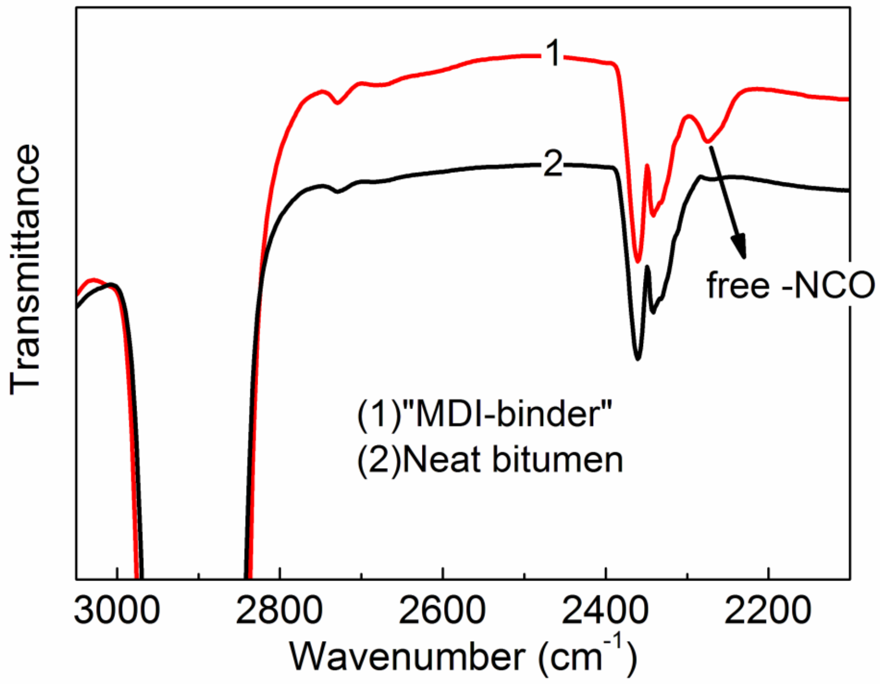
Transmittance
Wavenumber (cm^{-1})
3000
2800
2600
2400
2200
1
2
free -NCO
(1)"MDI-binder"
(2)Neat bitumen

Figure 9