“End-performance evaluation of thiourea-modified bituminous binders through viscous flow and linear viscoelasticy testing”

A.A. Cuadri[1], M. García-Morales[1✉], F.J. Navarro[1], G.D. Airey[2] and P. Partal[1]

[1]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)

[2]Nottingham Transportation Engineering Centre, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

✉ 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

ABSTRACT

Straight-run bitumens are no longer suitable in new asphalt mixtures. Consequently, the use of modified bitumens has become more important. In order to both improve binders mechanical properties and prevent it from phase separation whilst stored at high temperature, the paving industry is currently developing new modification routes based on reactive agents. This work studies the use of thiourea, which has proven to efficiently broaden the temperature interval over which the binder demonstrates an adequate performance. On the one hand, viscous flow and dynamic shear tests indicate an enhancement in the high in-service temperature strength, along with a reduced thermal susceptibility. On the other hand, results of dynamic flexural tests reveal a significant decrease in the binder glass transition temperature. Finally, the use of master curves and a further frequency/temperature conversion are proposed, in order to attain a suitable viscoelastic characterisation of bituminous binders at low temperatures.

Keywords: bitumen, thiourea, viscosity, viscoelasticy, time-temperature-superposition.

1. INTRODUCTION

Bitumen, by-product from crude oil refining, is a complex mixture of organic substances with a chemical composition which primarily depends on crude oil feedstock and fractionation process involved (Becker et al. 2003). By applying chromatographic techniques, bitumen compounds can adequately be separated into four generic groups, denominated SARAs fractions. The three first fractions (saturates, aromatics and resins) constitute the maltenes. The latter fraction, which shows the highest polarity and molecular weight, is called asphaltenes (Claudy et al. 1991). Thus, bitumen is considered to present a colloidal microstructure (Lesueur et al. 1996; Lesueur 2009) in which micelles of asphaltenes, peptised by a shell of resins, are dispersed in a oily phase composed of the remaining resins, low molecular weight saturates and aromatic hydrocarbons.

Bitumen presents a large set of properties (impermeability, ductility, adhesivity, resistance to the effect of weathering and chemicals, etc) which have favoured the development of numerous applications. These range from road pavements construction (Whiteoak 1990) to waterproof membranes for the roofing industry (Fawcett and Lor 1992). With regards to paving, roads performance is greatly influenced by bitumen rheological properties. In fact, bitumen is the only deformable component in asphalt mixtures and constitutes its continuous phase. Hence, determination of bitumen viscoelastic behaviour over a wide range of temperatures and loadings gains a paramount importance in order to predict its adequacy for a specific application (Vasiljevic et al. 2010).

However, these asphalt mixtures frequently show certain distresses, mainly associated to the binding agent, the most common of which are permanent deformation (or “rutting”) at high temperature and thermal cracking (fracture due to the lack of flexibility) at low temperatures (Kandhal and Cooley 2003; Lu at al. 2003). Bitumen modification may help mitigate the combined effects of traffic loading and extreme temperatures on the pavements. Two main categories of modifiers are generally considered: a) polymers, which lead to physical modification by mere dispersion in bitumen (García-Morales et al. 2004a; García-Morales et al. 2004b); and b) reactive agents, which encompass those substances producing chemical bonds through specific functional groups (Navarro et al. 2007; Polacco et al. 2004a; Carrera et al. 2010a; Carrera et al. 2010b). Nevertheless, polymers usually present very low compatibility with bitumen, and phase separation may eventually occur during binder storage at high temperature (160-200 ºC) in absence of stirring (Perez-Lepe et al. 2006). In order to provide the paving industry with bituminous binders which remain stable previously and during their application, the use of chemical additives has lately been proposed (Polacco et al. 2004a; Polacco et al. 2004b).

This work evaluates the viscous flow and viscoelastic properties of bituminous binders derived from bitumen chemical modification by thiourea, and highlights the importance of rheology in quantitatively determining the enhancement induced. Similarly to some other substances traditionally used in bitumen modification, e.g., sulphur, polyphosphoric acid (PPA) (Masson 2008), mineral acids (Giavarini et al. 2000) or organic molecules (Martinez et al. 2008), this agent is capable of chemically interact with specific bitumen fractions. Hence, viscous flow and dynamic shear/flexural tests revealed a significant increase in the binder resistance to thermal cracking and permanent deformation under loading at low and medium/high in-service temperatures, respectively.

2. EXPERIMENTAL

2.1. Materials

Bitumen with a penetration grade of 40/50, supplied by Construcciones Morales, S.A. (Spain), has been used as base material for the modification. Details of technological properties (penetration grade and R&B softening temperature, according to ASTM D5 (1997) and ASTM D36 (1995), respectively) and chemical composition (in terms of SARAs fractions) are shown in Table 1. Bitumen SARAs fractions were determined by means of thin layer chromatography coupled with a flame ionization detector (TLC/FID), using an Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan). Elution was performed in hexane, toluene and dichloromethane/methanol (95/5), following the procedure outlined elsewhere (Eckert 2001).

Two different modifying additives, a non-polymeric substance and a thermoplastic elastomer, have been employed:

a. On the one hand, thiourea (abbreviated as “Th”, hereinafter) supplied by Sigma Aldrich, is an additive which leads to chemical reactions with bitumen molecules. It has a molecular weight of 76.12 $g\cdot mol^{-1}$, and its melting point lies within the interval 175-179 ºC.

b. On the other hand, commercial SBS triblock copolymer “Kraton D-1101”, provided by Shell Chemical Company U.K., was selected for “physical modification”, through mere physical dispersion in bitumen. It has a molecular weight of $1.5\cdot10^5$ $g\cdot mol^{-1}$, and a styrene content of 31 wt.%.

2.2. Samples preparation

In relation to “chemical” modification, two blends of bitumen with 3 and 9 wt.% Th, respectively, were prepared in a cylindrical glass vessel (60 mm diameter, 140 mm height), for 1 h, at 180 ºC and mixing speed of 1200 r.p.m. Agitation was carried out by means of an IKA RW-20 stirring device (Germany) equipped with a four-bladed turbine. After being processed, both modified binders were poured onto aluminium foil (forming a thin layer), and cured for up to 12 months, exposed to the ambient. The specific effects of temperature and agitation were assessed by subjecting the neat bitumen, without addition of Th, to the conditions described above (sample referred to as “blank”, hereinafter).

For the sake of comparison, “physical” modification was carried out by adding 3 wt.% SBS to the base bitumen (formulation commonly used in the paving industry). This blend was processed for 2 h, at 180 ºC, in a high shear mixing device.

2.3. Testing procedures

Steady state viscous flow measurements, at 60 ºC, were carried out in a controlled-strain ARES rheometer (Rheometric Scientific, USA). Additionally, temperature sweep tests in oscillatory shear, at constant frequency and strain (10 rad/s and 1%, respectively) and a heating rate of 1 ºC/min from 30 to 100 ºC, were conducted in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria). In both cases, a plate-and-plate geometry (25 mm diameter; 1 mm gap) was used.

Dynamic Mechanical Thermal Analysis (DMTA) tests were performed on rectangular samples of 50 mm length, 10 mm width and 3 mm thick, with a Seiko DMS 6100 (Seiko Instruments Inc., Japan) in double cantilever (bending) mode. Frequency sweep tests from 10^{-2} to 100 Hz were carried out, in the linear viscoelasticity (LVE) region, at four selected temperatures from -30 to 15 ºC, in 15 ºC-increments. Furthermore, temperature sweep tests, ranging from -30 to 30 ºC, were conducted at a fixed frequency of 1 Hz. Three different temperature ramps of 4, 2 and 0.2 ºC/min were selected. Liquid nitrogen was employed as cooling system.

Modulated Differential Scanning Calorimetry (MDSC) was performed with a TA Q-100 (TA Instruments, USA). Samples of 5-10 mg were always subjected to the following testing procedure: temperature range between -80 ºC and 100 ºC; heating rate of 5 ºC/min; amplitude of modulation of ±0.5 ºC; a period of 60 s; and nitrogen as purge gas, with a flow rate of 50 mL/min. In order to provide the same recent thermal history, all the samples were placed into hermetic aluminium pans for 24 h before measurement.

3. RESULTS AND DISCUSSION

3.1. Viscous flow behaviour

Figure 1 shows the viscous flow behaviour, at 60 ºC, of 3 and 9 wt.% Th-modified binders, as a function of curing time. For the sake of comparison, results corresponding to neat bitumen, blank sample and 3 wt.% SBS modified binder have been included.

It can be observed that thiourea addition induces significant increases in bitumen viscosity, mainly for the highest concentration and after a prolonged period of storage. Furthermore, all the samples present a Newtonian region, at low shear rates, followed by a shear-thinning drop beyond a threshold (or “critical”) value of shear rate. This behaviour can be described by the Carreau’s model fairly well:

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

where η_0 (Pa·s) is the zero-shear-rate-limiting viscosity, λ (s) is a time constant whose inverse approximately matches the threshold shear rate above, and ‘s’ is a parameter related to the slope of the shear-thinning region. Table 2 includes those fitting parameters for all the samples studied.

In order to more conveniently visualise the degree of modification achieved at high in-service temperatures, a modification index (M.I.), in terms of the Newtonian viscosities at 60ºC included in Table 2, has been defined as follows:

$$\text{M.I.} = \frac{\eta_{0,\text{mod}} - \eta_{0,\text{blank}}}{\eta_{0,\text{blank}}} \qquad (2)$$

This index expresses the relative viscosity increase due to thiourea addition with reference to the blank sample. It is worth mentioning neat bitumen may increase its viscosity during high temperature mixing due to oxidation processes, the so-called “primary ageing”, giving rise to the blank sample (Navarro et al. 2009). Hence, M.I. only quantifies changes due to the modifying agent, regardless of bitumen “primary ageing” that occurs during the binder processing.

Figure 2 displays the evolution of the modification index (M.I.) with curing time. Two different bitumen modification pathways, referred to as “short-term” and “long-term” modification and further tackled in subsection 3.3, have been identified. Thus, the effects of “short-term” modification are noticed in the freshly prepared (non-cured) binders and results more significant for the lowest thiourea concentration. This observation might be attributed to a larger quantity of non-reacted thiourea which, as such, would act as a “viscosity-reducing” substance.

On the other hand, the “long-term” modification, caused by curing at room temperature, yields much more significant increases in viscosity, if compared to the former pathway. Thus, for instance, bitumen viscosity increase may be of up to 6 times its original value after modification with 9 wt.% Th and curing for 12 months. Furthermore, the degree of modification attained is even larger than that corresponding to the SBS reference binder.

In addition, the fitting parameters obtained from the Carreau’s model provide information about changes in the material microstructure as a consequence of the modification. Thus, the values of λ increase with curing time, mainly for the highest thiourea concentration (see Table 2). Consequently, the “critical” shear rates which mark the onset of the shear-thinning region decrease, a fact that reveals a more complex microstructure as binder curing proceeds (Martín-Alfonso et al. 2008).

3.2. Linear viscoelastic behaviour

3.2.1. High in-service temperatures

Dynamic shear temperature sweep tests, from 30 to 100 ºC, were carried out on the neat bitumen and modified binders. Figure 3a shows the evolution with temperature of the loss tangent, as a function of curing time, for the 9 wt.% Th-modified binders. It can always be observed a prevailing viscous behaviour, with $\tan\delta > 1$ over the entire temperature interval tested, which becomes much more significant at the highest temperatures. However, $\tan\delta$ values are seen to notably decrease after addition of 9 wt.% thiourea, mainly for the two longest curing times. In consequence, this increase in elasticity 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. 2010a). On the other hand, they show a notable decrease in the average slope of their tanδ vs. temperature curves (related to thermal susceptibility at high in-service temperatures), a fact which demonstrates an enhanced resistance to temperature changes.

In that sense, the Strategic Highway Research Program (SHRP) proposed the parameter |G*|/sinδ as a manner to efficiently determine the maximum temperature below which bitumen will show a satisfactory performance. According to the criterion outlined in AASHTO MP1 (1993), that temperature is assigned to the value at which |G*|/sinδ equals 1 kPa. This has been a controversial matter of debate, as some authors (Morea et al. 2009; Biro et al. 2009) have claimed others parameters (like zero-shear-viscosity, ZSV) to be more adequate in predicting the resistance of bitumen to permanent deformation at high in-service temperatures. Anyway, if compared to the time-consuming method of the ZSV determination at several temperatures, the testing procedure presented in Figure 3b for 9 wt.% Th-modified binders stands for an easier way to establish a comparative analysis of the degree of improvement attained. As shown in Table 2, SHRP maximum temperature and so, rutting resistance, is notably increased after modification and curing. If compared with the neat bitumen, an increase of nearly 7ºC is observed after addition of 9 wt.% Th and curing for 12 months, which almost equals the value reached after SBS modification.

3.2.2. Low in-service temperatures

The rheological response at low in-service temperatures of the neat bitumen, reference sample (3 wt.% SBS) and a selected modified binder (60 days-cured 9 wt.% Th) have been evaluated. As an example, Figure 4 shows the results of double-cantilever frequency sweep tests, at four different temperatures between -30 to 15 ºC, for the neat bitumen. The experimental results show the existence of a maximum in the viscous modulus, whilst the storage modulus tends to a constant value of about 2 GPa. Additionally, a prevailing elastic behaviour deduced from values of E’ higher than E’’, at all temperatures tested, is also noted.

On the other hand, bitumen thermo-rheological simplicity, reported by different authors, has become quite controversial. Several authors have claimed that the time-temperature superposition principle (TTSP) fails at high temperature, especially for high asphaltene and/or high crystalline content materials (Lesueur et al. 1996) and is, therefore, very unlikely to apply to most polymer modified bitumens (Lesueur et al. 1998). In contrast, some others sustain that the mechanical spectrum of many modified bituminous products can be represented, reasonably well, by master curves of their linear viscoelastic material functions (Stastna and Zanzotto 1999). Anyway, the TTSP has been widely applied to both neat and polymer-modified bitumens (Becker et al. 2003; Newman 1998; Polacco et al. 2004a; Carreau et al. 2000).

Hence, the experimental values of the linear viscoelastic functions, E’ and E’’, were “empirically” superposed onto a master curve by using a shift-factor, a_T, with 273K as the reference temperature (see Figure 5a). Within the temperature range studied in this work, the temperature-dependence of the shift factor is described by an Arrhenius-type equation (Ferry 1980) reasonably well:

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \qquad (3)$$

where T_{ref} is the reference temperature (arbitrarily chosen to be 273K), E_a is the activation energy and R is the universal gas constant. Thus, the significant decrease in E_a observed for the 60 days-cured 9 wt.% Th-modified binder (see Table 3) points out a reduction in the material thermal susceptibility (Garcia-Morales el at. 2004a) in the range of low temperatures selected.

However, the most important aspect of the rheological properties of bituminous binders is their dependence on temperature. In this sense, temperature-dependence of the linear E' and E'' moduli, at a fixed frequency value of 1 Hz, was obtained from isothermal frequency sweep tests by following the procedure described by Martinez-Boza et al. (2000). The values of the frequency sweep master curves have been converted using the Arrhenius-like relationship between the shift factor and temperature as follows:

$$T = \frac{E_a \cdot T_{ref}}{R \cdot T_{ref} \cdot Ln\left(\frac{\omega_{exp}}{\omega_R}\right) + E_a} \qquad (4)$$

where E_a is the activation energy obtained from frequency sweep tests, ω_{exp} is the reduced frequency calculated from the superposition of experimental frequency sweep curves at different temperatures, and ω_R is the frequency at which the temperature sweep tests are carried out (chosen to be 1 Hz). As a result of this frequency/temperature-dependence conversion, isochronal E'-E'' curves over a wide temperature interval are obtained.

Results for the neat bitumen are shown in Figure 5b. A clear transition from the glassy to the Newtonian region can be observed, with a crossover point between E' and E'', with increasing temperature (Partal et al. 1999). Moreover, no plateau at intermediate temperatures (like that which characterises polymer melts and solutions) was detected, which demonstrates the non existence of entanglements (Ferry 1980). In addition, a maximum in E'', which characterises the onset of the glassy region is observed.

Thus, in order to establish a comparative analysis on the effect of modification on the low-temperature performance, Figure 6 shows the frequency-temperature converted master curves for the neat bitumen, the SBS reference sample and the 60 days-cured 9 wt.% Th-modified binder. For each of these three selected binders, a “mechanical” glass transition temperature ($T_{g,DMTA}$), taken as the value of temperature at the maximum in E’’ curve (Partal et al. 1999), has been obtained (see Table 3). This parameter, which accounts for the onset of the glassy region (at which the binder is expected to be affected by thermal cracking under loading), has widely been used to evaluate the end-performance of polymer modified bitumens at low temperatures (Fawcett et al. 1999; Navarro et al. 2010). In consequence, a decrease in the T_g is a highly desirable result of modification. In this sense, it has been widely reported in the literature (Yildirin et al. 2007; Airey 2004; Lu and Isacsson 1997) that SBS remarkably enhances the binders performance at low temperature. Surprisingly, enhancement in resistance to thermal cracking after chemical modification with 9 wt.% thiourea and curing for 2 months is even higher than that for SBS. Thus, a decrease of nearly 3 ºC in $T_{g,DMTA}$, from about -15 ºC for the 3 wt. % SBS sample down to -18 ºC for Th-modified binder (after 60 days of curing), was observed. If compared to the neat bitumen, which presents a value close to -13 ºC, an outstanding reduction of 5 ºC was obtained.

Interestingly, application of TTSP allowed values of T_g not affected by the selected heating rate to be obtained. Thus, in contrast to those derived from isochronal temperature sweep tests carried out by applying a certain temperature-ramp, the values of T_g in Table 3 were obtained by conversion of frequency sweep tests on specimens which were allowed to achieve thermal equilibrium at every selected temperature.

In order to validate above results, dynamic temperature sweeps within the LVE region, at a fix frequency of 1 Hz, were conducted on the 60 days-cured 9 wt.% Th-modified binder, at three different decreasing heating rates (4, 2 and 0.2 ºC·min^{-1}) from -35 to 30 ºC. Figure 7, which shows the evolution with temperature of the elastic and viscous flexural moduli, evidences the strong dependency of the viscoelastic functions with the temperature ramp selected. In fact, temperature sweeps curves only match their corresponding converted master curves at very low values of the heating rate (ideally, as heating ramp approaches to zero). As expected from the low thermal conductivity of bitumen (Whiteaoak 1990), a fast heating rate provokes big differences between the temperature programme (set temperature) and the actual value the sample presents at every measured point. Consequently, only temperature sweeps tests performed at very low rates (below 0.2 $^{\circ}C \cdot min^{-1}$) would lead to a “strictly” adequate viscoelastic characterisation of bituminous binders at low temperatures. Hence, under that condition, every measured point might be considered to be in a thermal “pseudo-equilibrium” state.

3.3. Chemical modification and microstructure

Previous improvements found in the flow viscous and viscoelastic behaviours of bitumen after modification with thiourea reveal the existence of changes in its microstructure. In order to look further into this, modulated differential scanning calorimetry (MDSC), a technique extensively applied to bituminous binders (Masson and Polomark 2001; Masson et al. 2002), has been conducted on the neat bitumen and the 60 days-cured 9 wt.% Th-modified binder. Thus, derivative heat capacity for neat bitumen in Figure 8 presents two well-defined peaks (with maximums, T_{g1} and T_{g2}, located at -30 and 3 ºC, respectively) which, according to Masson et al. (2001; 2002), derive from two overlapped glass transitions corresponding to saturates and aromatics. By contrast, the selected Th-modified binder shows clear differences compared to the neat bitumen. On the one hand, T_{g2} is shifted to lower temperatures (from 3 down to 0ºC), observation which matches with the trend derived from DMTA measurements (see Table 3) and would support the enhancement in the binders low temperature properties. On the other hand, T_{g1} cannot be identified due to its overlapping with a new endothermic thermal event arising at -30 ºC (Figure 9).

As reported by Masson and co-workers (2001; 2002), saturates are semicrystalline, aromatics are amorphous, and resins and asphaltenes are mesophasic. In consequence, as shown in Figure 9, neat bitumen presents four specific thermal events in the non-reversing heat flow thermogram: i) a broad endothermic background which approximately extends from –40 up to 80 ºC; ii) and iii) two exotherms located at about -9 and 40 ºC; iv) an endothermic peak, at around 50 ºC, being related to the diffusion of relatively large structures, as those typically found in asphaltenic micelles.

Moreover, the second and third (exothermic) thermal events derive from a time-dependent cold-crystallisation of a certain quantity of saturates which, upon a fast cooling from the melt, were unable to adequately crystallise. Hence, above the frozen state defined by $T > T_g$, molecular mobility increases and those saturates segments order into crystalline domains (Masson and Polomark 2001; Masson et al. 2002; Navarro et al. 2009). Table 3, which displays second event temperatures (T_{2nd}), confirms a decrease in that cold-crystallisation after addition of 9 wt.% Th and 60 days of curing (from -9 down to -12 ºC), as the frozen state threshold was shifted to lower temperatures.

In addition, enthalpy associated with the fourth event can be ascertained by mere integration of the corresponding peaks (see Figure 9). Table 3 demonstrates that enthalpy values increase with increasing curing time, what suggests the development, after thiourea addition and further curing, of a new structure which would require a larger quantity of energy to melt. This would relate to an enhanced resistance to permanent deformation at high temperatures (see Figures 1 to 3). In this regard, small molecules such as thiourea derivatives have demonstrated strong hydrogen bonding activity, which would contribute to a slow change (or enhancement) in the hydrogen-bond network of bitumen during its curing at room temperature (Cuadri et al. 2011).

Yet, the controversy on the origin of that new endothermic thermal event at -30ºC remains. With the purpose of shedding light on this issue, a MDSC test was carried out on a sample of ammonium thiocyanate. Results in Figure 9 allow us to conclude the new event to be attributed to ammonium thiocyanate derived from thiourea thermal decomposition during processing (at 180ºC), according to the following isomeric reaction (Wang et al. 2005):

$$SC(NH_2)_2\ (s) \rightarrow NH_4SCN\ (s) \qquad (R_1)$$

Thus, the peak at -30ºC in Figure 9 might arise as a consequence of a “non-identified” low-temperature reversible phase transition, most probably quite similar to the transformation of monoclinic NH_4SCN into orthorhombic at 90ºC reported by Mayer et al. (1997).

4. CONCLUDING REMARKS

The end-performance of modified bituminous binders via thiourea addition has been evaluated by means of viscous flow and linear viscoelasticy tests. Two different modification pathways were identified: a) “short-term” modification, whose effects are noticed in the non-cured binders; and b) “long-term” modification, caused by curing at room temperature and which, if compared to the former, yields a much larger degree of improvement. In addition, MDSC results verified the interaction between ammonium thiocyanate, most probably derived from thiourea thermal decomposition at 180ºC during the binder manufacture, and some bitumen fractions.

In consequence, modification would lead to an enhancement in the high in-service temperatures performance, as both viscosity and shear moduli increased, and thermal susceptibility was reduced. On the other hand, low in-service temperature flexibility was also improved as a consequence of a decrease in the binder glass transition temperature. Concerning this matter, this research emphasizes the use of master curves, obtained by application of the TTSP to isothermal frequency sweeps at different temperatures and further frequency-temperature conversion, in order to attain values of T_g which do not show any dependency with the heating rate selected. In this sense, bitumen low thermal conductivity limits, to very low values approaching zero, the heating rate at which temperature sweeps tests would lead to a “strictly” adequate viscoelastic characterisation of bituminous binders at low temperatures.

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Table 1. Penetration, R&B softening temperature, SARAs fractions and colloidal index for the neat bitumen used.

	Values
Penetration (dmm)[a]	47
R&B softening point (ºC)[b]	52.5
Saturates (wt.%)	5.1
Aromatics (wt.%)	52.6
Resins (wt.%)	23.9
Asphaltenes (wt.%)	18.4
Colloidal Index	0.31

[a] *According to ASTM D5.*
[b] *According to ASTM D36.*

Table 2. Evolution with curing time of Carreau's model parameters and SHRP maximum temperatures, for neat biumen, blank sample, reference SBS binder and Th-modified binders.

		η_0 (Pa·s)	**λ (s)**	**s**	**$T_{\|G^*\|/\sin\delta=1kPa}$ (ºC)**
	Neat	553	0.23	0.39	74.0
	Blank	566	0.32	0.28	74.2
	Non-cured	722	0.34	0.40	75.8
3 wt. % Th	**20 days**	752	0.41	0.38	76.6
	60 days	825	0.41	0.41	77.1
	12 months	1374	1.00	0.34	75.6
	Non-cured	674	0.39	0.29	74.9
9 wt. % Th	**20 days**	863	0.56	0.25	76.8
	60 days	1296	0.73	0.39	80.2
	12 months	4402	2.07	0.33	80.8
	3 wt. % SBS	1883	1.04	0.27	82.4

Table 3. Activation energy values (E_a); DMTA glass transition temperatures ($T_{g,DMTA}$); modulated DSC glass transition temperatures (T_{g1} and T_{g2}); modulated DSC second event temperatures (T_{2nd}); and modulated DSC fourth event enthalpy (ΔH_{4th}).

	E_a (kJ/mol)	**$T_{g,\ DMTA}$ (ºC)**	**T_{g1} (ºC)**	**T_{g2} (ºC)**	**T_{2nd} (ºC)**	**ΔH_{4th} (J/g)**
Neat bitumen	250	-13	-30	3	-9	2.2
3 wt.% SBS	244	-15	-	-	-	-
9 wt.% Th 60 days of curing	230	-18	-	0	-12	3.4

Figure captions

Figure 1. Viscous flow curves, at 60 ºC, for a 3 wt.% Th-modified bitumen (A) and a 9 wt.% Th-modified bitumen (B), as a function of curing time.

Figure 2. Evolution of the modification index, M.I., with curing time for all Th-modified binders.

Figure 3. Evolution with temperature of loss tangent (A) and "rutting parameter", $|G^*|/\sin\delta$ (B), for selected Th-modified binders, as a function of curing time.

Figure 4. Evolution with frequency of the elastic (E') and viscous (E'') moduli in dynamic bending, as a function of temperature, for neat bitumen.

Figure 5. A) Empirical master curve of storage (E') and loss (E'') moduli vs. reduced frequency, $f \cdot a_T$, for neat bitumen (Inset: Temperature dependence of the shift factor and Arrhenius fitting). B) Evolution of the linear viscoelastic functions vs. temperature obtained by the frequency/temperature-conversion.

Figure 6. Evolution of linear viscoelastic functions (E', E") with temperature, obtained from by frequency/temperature conversions, for neat bitumen, 3 wt. % SBS and 9 wt.% Th modified bitumen after 60 days of curing.

Figure 7. Effect of heating rate on temperature sweep tests performed at 1Hz for a for 9 wt.% Th modified bitumen after 60 days of curing. Results compared with viscoelastic functions (E', E") obtained from the frequency/temperature conversion (master curve).

Figure 8. Evolution of C_p derivative obtained by MDSC with temperature, for neat bitumen and 9 wt.% Th modified bitumen after 60 days of curing.

Figure 9. Non-reversing heat flow thermograms for neat bitumen, ammonium thiocyanate and 9 wt.% Th-modified bitumen after 60 days of curing.

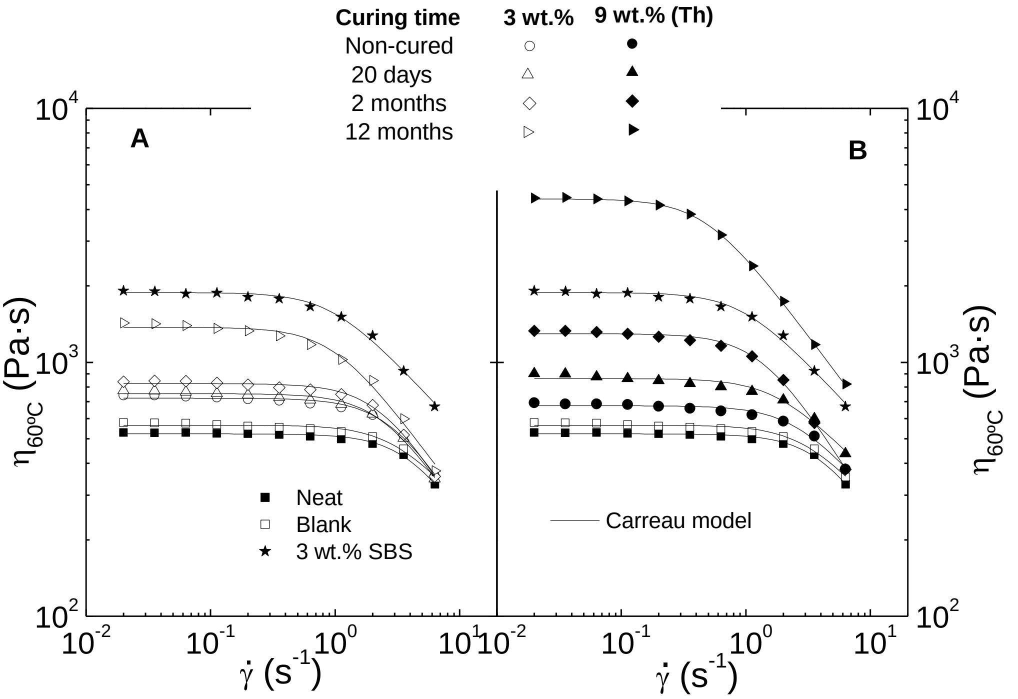

Curing time
Non-cured
20 days
2 months
12 months
3 wt.%
9 wt.% (Th)
A
B
Neat
Blank
3 wt.% SBS
Carreau model
$\eta_{60ºC}$ (Pa·s)
10^2
10^3
10^4
10^{-2}
10^{-1}
10^0
10^1
$\dot{\gamma}$ (s^{-1})

Figure 1

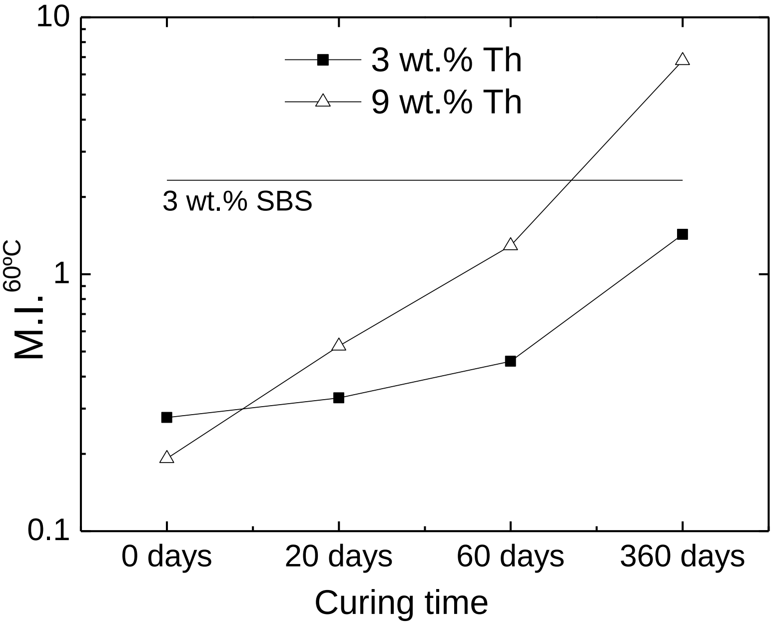

10
1
0.1
M.I.$^{60^oC}$
3 wt.% Th
9 wt.% Th
3 wt.% SBS
0 days
20 days
60 days
360 days
Curing time

Figure 2.

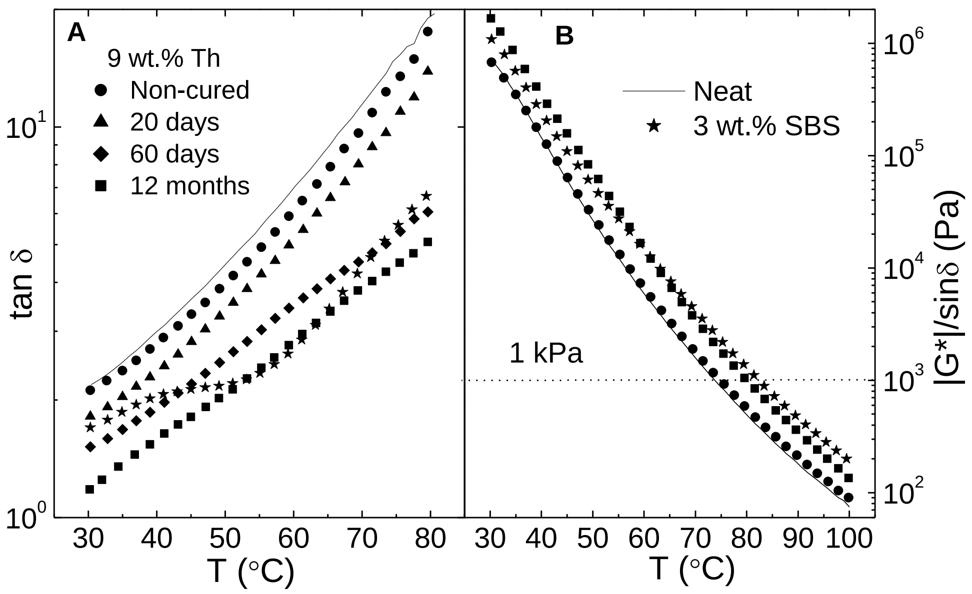

A
9 wt.% Th
● Non-cured
▲ 20 days
◆ 60 days
■ 12 months
tan δ
10^1
10^0
30 40 50 60 70 80
T (°C)
B
Neat
★ 3 wt.% SBS
1 kPa
10^6
10^5
10^4
10^3
10^2
|G*|/sinδ (Pa)
30 40 50 60 70 80 90 100
T (°C)

Figure 3

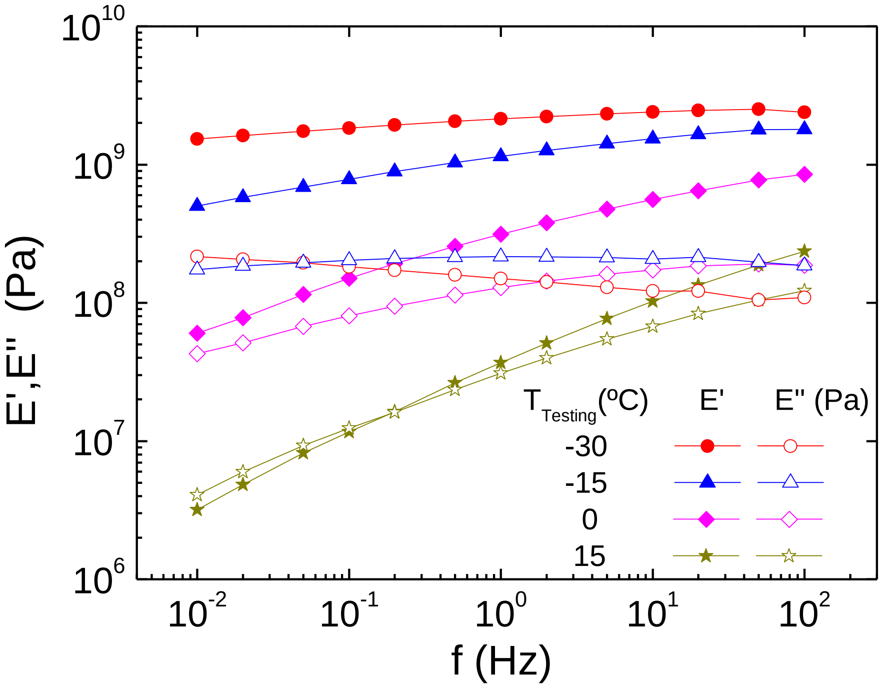

10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
E',E'' (Pa)
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
f (Hz)
T$_{Testing}$(ºC) E' E'' (Pa)
-30
-15
0
15

Figure 4

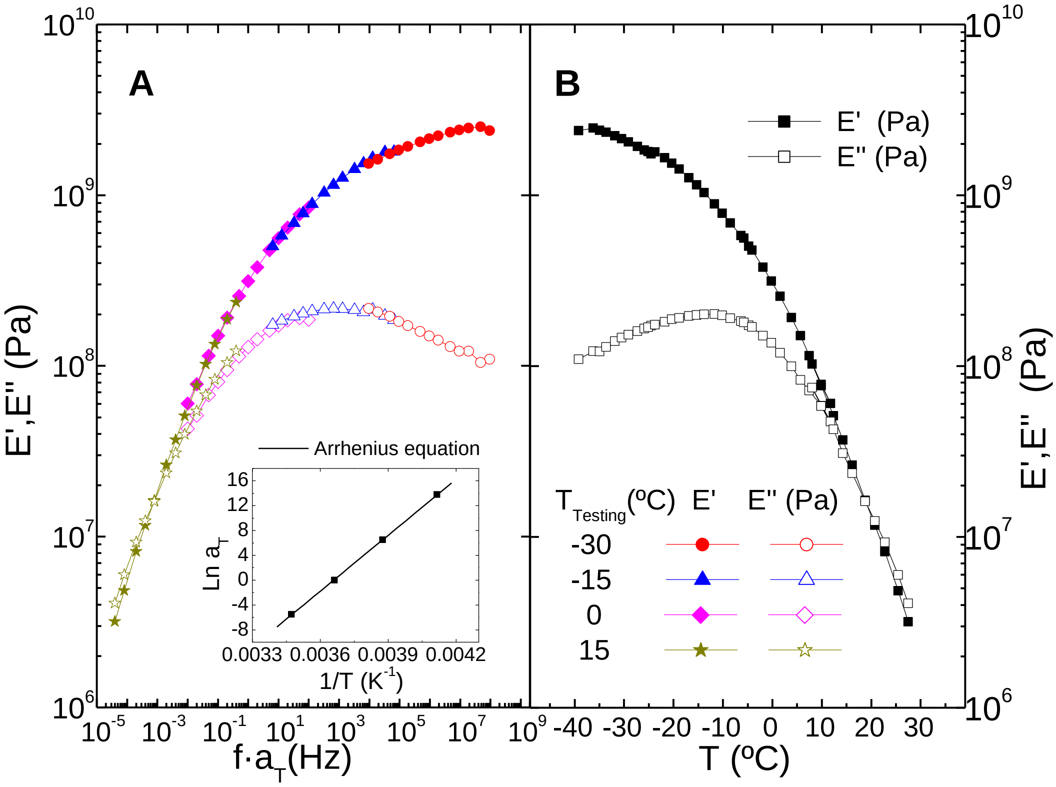

A
B
E',E'' (Pa)
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{-5}
10^{-3}
10^{-1}
10^{1}
10^{3}
10^{5}
10^{7}
10^{9}
f·a$_T$(Hz)
Arrhenius equation
Ln a$_T$
16
12
8
4
0
-4
-8
0.0033
0.0036
0.0039
0.0042
1/T (K^{-1})
E' (Pa)
E'' (Pa)
T$_{Testing}$(ºC)
E'
E'' (Pa)
-30
-15
0
15
-40
-30
-20
-10
0
10
20
30
T (ºC)

Figure 5

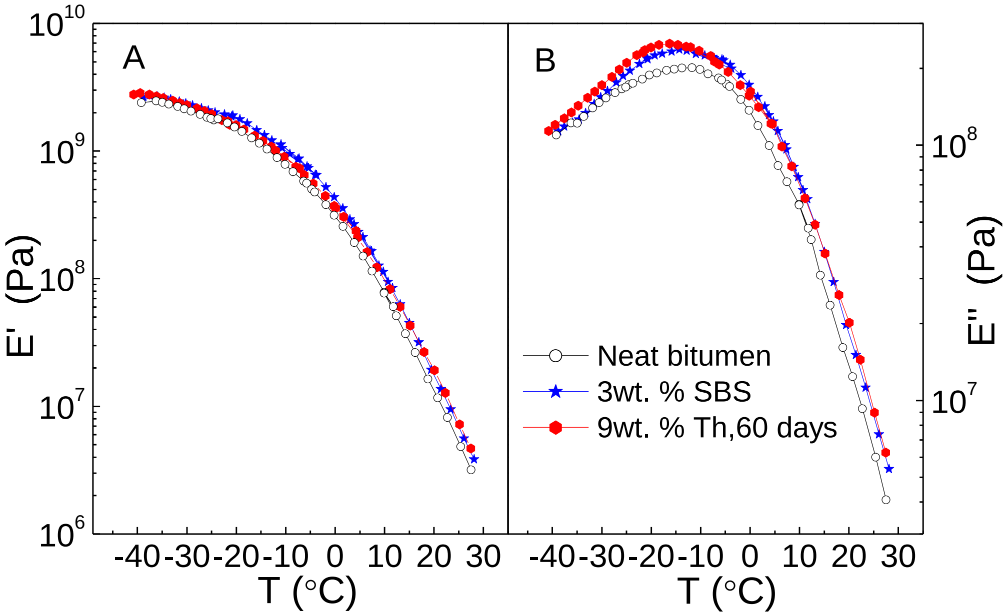
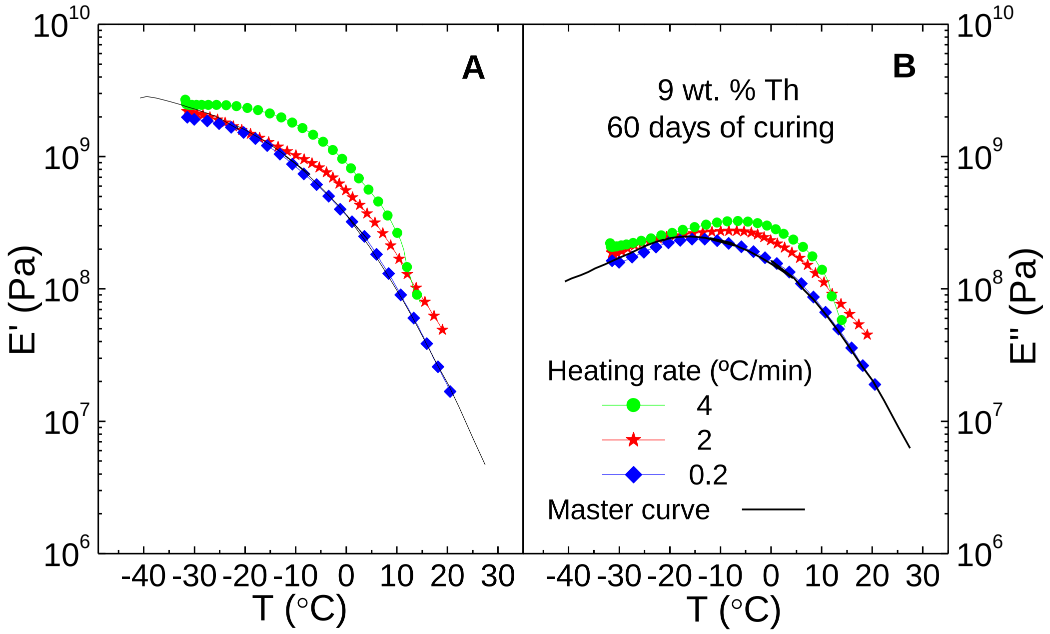

A
B
E' (Pa)
E'' (Pa)
10^{10}
10^9
10^8
10^7
10^6
10^8
10^7
-40 -30 -20 -10 0 10 20 30
T (°C)
-40 -30 -20 -10 0 10 20 30
T (°C)
Neat bitumen
3wt. % SBS
9wt. % Th,60 days

Figure 6.



A
B
9 wt. % Th
60 days of curing
Heating rate (ºC/min)
4
2
0.2
Master curve
E' (Pa)
E'' (Pa)
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
-40 -30 -20 -10 0 10 20 30
T (°C)

Figure 7.

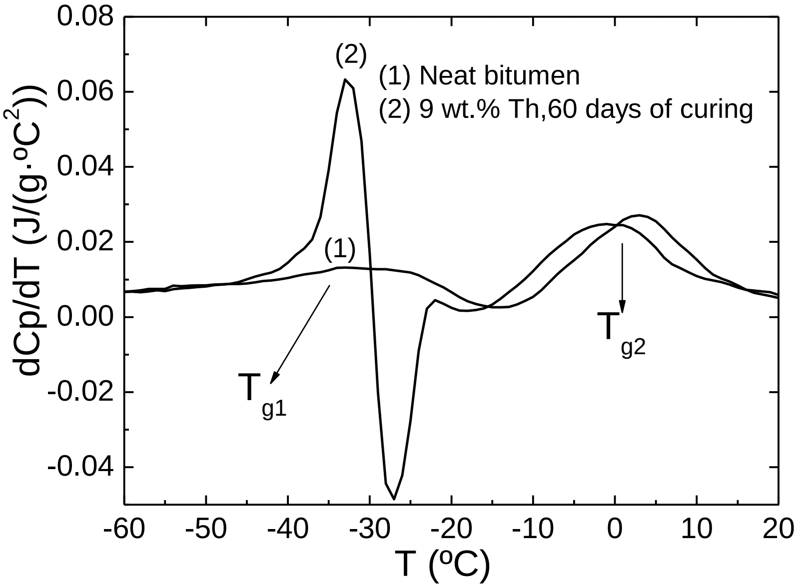

0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
dCp/dT (J/(g·ºC^2))
-60
-50
-40
-30
-20
-10
0
10
20
T (ºC)
(1) Neat bitumen
(2) 9 wt.% Th,60 days of curing
(1)
(2)
T$_{g1}$
T$_{g2}$

Figure 8.

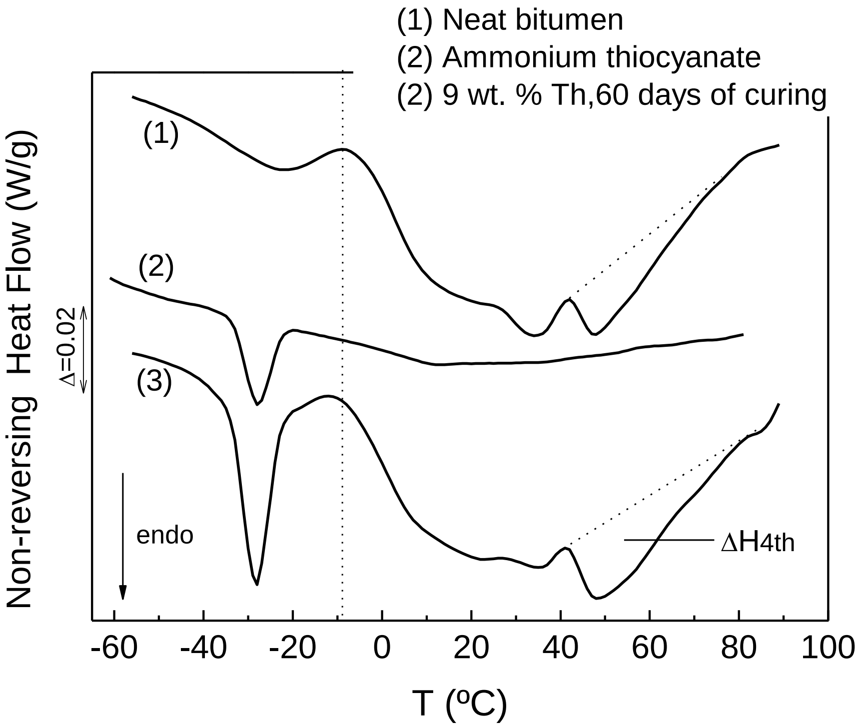

(1) Neat bitumen
(2) Ammonium thiocyanate
(2) 9 wt. % Th,60 days of curing
(1)
(2)
(3)
Δ=0.02
endo
ΔH4th
Non-reversing Heat Flow (W/g)
-60
-40
-20
0
20
40
60
80
100
T (ºC)

Figure 9.