Bitumen Chemical Modification by Thiourea Dioxide

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

Dpto. Ingeniería Química. Facultad de Ciencias Experimentales.

Campus 'El Carmen'. Universidad de Huelva. 21071 Huelva (Spain)

✉ Author to whom correspondence should be addressed:

Dr. Pedro Partal

E-mail: partal@uhu.es

Phone: +34 959 21 99 89

Fax: +34 959 21 93 85

ABSTRACT

This work evaluates a novel bitumen modification through the use of a chemical agent, thiourea dioxide, substance which has been traditionally used as a reducing agent. Thermogravimetric analysis demonstrated the formation of new chemical compounds, most probably originated through reactions between products from thiourea dioxide thermal decomposition and some highly polar bitumen molecules. As a result of these reactions, which continues even after 60 days, bitumen permanent deformation resistance at high temperature is enhanced, as indicated by a significant increase in its viscosity and elastic features. On the other hand, thiourea dioxide addition produces changes in the bitumen colloidal nature, which improve its flexibility at low in-service temperatures, and consequently its resistance to thermal cracking under loading. In fact, dynamic bending tests indicated a remarkable decrease in the value of binder glass transition temperature, which was further corroborated by differential scanning calorimetry. As a conclusion, thiourea dioxide can be seen as a promising modifiying agent, which can extend the in-service temperature range at which bitumen would present a satisfactory performance.

Keywords: Bitumen, thiourea dioxide, modification, rheology, product design.

1. INTRODUCTION

Bitumen, residue from crude oil distillation, is a complex mixture of different organic molecules. Its chemical composition primarily depends on both crude oil source and processing procedure involved [1]. Bitumen compounds can be separated by chromatographic techniques into four generic groups (SARAs): saturates (S), aromatics (A) and resins (R), which make up the maltene fraction, and asphaltenes (As). Their complexity, aromaticity, heteroatom content and molecular weight increase in the order S<A<R<As [2]. Bitumen behaviour greatly depends on the relative concentration of its different fractions. Thus, a variation in its composition strongly affects its mechanical properties and chemical reactivity. Concerning its microstructure, bitumen can be considered as a colloidal system in which asphaltenes are dispersed into an oily matrix of maltenes and surrounded by a shell of resins whose thickness depends on temperature [3,4].

Bitumen is widely used as a binder of mineral aggregates for paving applications [5]. However, this material shows common distresses, associated to the binder phase in road, such as rutting (permanent deformation of the pavement at high temperature) and thermal cracking (fracture due to the lack of flexibility at low temperatures) [6,7]. As a consequence, bitumen performance has been traditionally improved through the addition of virgin polymers (SBS, SBR, EVA, etc.) and waste polymers (plastics from agriculture, crumb tire rubber, etc.) [8,9].

In addition, bitumen may undergo ageing processes, which also affect its performance as asphaltic binder. First, there is a rapid chemical ageing upon mixing hot bitumen with hot aggregates. Second, there occurs an in-situ ageing during the service life of the pavement. Bitumen molecules may irreversibly evolve through chemical ageing, which is mainly related to oxidation reactions and polymerisation between asphaltene molecules and, to a lesser extent, some evaporation of the lightest bitumen compounds. As a result, chemical ageing leads to a global hardening of the material, which increases the cracking probability [4].

A promising alternative to the above-commented modifiers is the use of non-polymeric reactive agents able to form chemical bonds with bitumen compounds such as sulphur, polyphosphoric acid (PPA) [10], a mineral acid [11] or organic molecules [12]. On these grounds, this work deals with the use of thiourea dioxide (ThD) as a potential chemical agent in bitumen modification. Although well-known in many other industrial applications, it may somewhat become a new approach in the asphalt industry. It is worth mentioning that ThD 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. In contrast to PPA, which promotes the development of bridging/phosphorylation/condensation reactions, bitumen modification by ThD is expected to occur on a strong reducing action.

In summary, the main objective of this research was to study binder modification degrees achieved by adding thiourea dioxide (ThD) to two different types of bitumen, with penetrations within the intervals 40/50 and 150/200. More precisely, this work seeks to assess the effect of the chemical changes induced by this reactive modifier on the complex chemistry and rheological properties of bituminous materials. In this sense, viscous and oscillatory shear behaviour, dynamic mechanical thermal analysis (DMTA), thermal behaviour (by modulated DSC and TGA) and chemical composition (by TLC/FID) of different modified bitumens were studied.

2. EXPERIMENTAL

Two different types of bitumen, with penetrations within the intervals 40/50 and 150/200, respectively, were used as base material for the modification. The results of two selected technological tests (penetration grade and softening temperature, according to ASTM D5 and ASTM D36, respectively) and the SARAs fractions corresponding to each of them are shown in Table 1. Bitumen SARAs fractions were determined by 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 [15].

Thiourea dioxide (ThD), supplied by Sigma Aldrich, traditionally used as reducing agent, has been selected for bitumen modification. It melts at around 124-127 ºC, and has a molecular weight of 108.12 g/mol. Blends of bitumen with 3 and 9 wt.% ThD were mixed for 1 h, in a cylindrical vessel (60 mm diameter, 140 mm height), at 130 ºC and an agitation speed of 1200 rpm, using an IKA RW-20 stirring device (Germany) equipped with a four-blade turbine. After processing, the modified bitumen melt was poured onto aluminium foil, forming a thin layer, and cured for up to 60 days at room conditions. The specific effects of temperature and agitation were assessed by subjecting neat bitumen, without ThD addition, to the same conditions described above (“blank”, hereinafter).

Viscous flow measurements, at 60 ºC, were carried out in a controlled-strain ARES rheometer (Rheometric Scientific, USA), using a plate-and-plate geometry (25 mm diameter and 1 mm gap). Temperature sweep tests in oscillatory shear, using a heating rate of 1 ºC/min, 10 rad/s, and 1% strain, were conducted in a controlled-stress rheometer PHYSICA MCR-301 (Anton Paar, Austria) between 30 and 100 ºC.

Dynamic Mechanical Thermal Analysis (DMTA) tests were performed on neat and modified bitumens with a Seiko DMS 6100 (Seiko Instruments Inc., Japan) in double cantilever bending mode, using 50 × 10 × 3 mm samples, and liquid nitrogen as cooling system. Frequency sweep tests from 10^{-2} to 100 Hz were carried out, in the linear viscoelasticity region, at four temperatures (-30, -15, 0 and 15 ºC). Furthermore, temperature sweeps were conducted at a constant frequency of 1 Hz and strains within the linear viscoelasticity region. The selected temperature ramp was set at 2 $^{\circ}C \cdot min^{-1}$ with a temperature range from -30 to 35 ºC.

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.

Thermogravimetric analysis (TGA) tests were conducted in a TA Q-50 (TA Instrument, USA). Temperature sweeps (10 $^{\circ}C \cdot min^{-1}$; between 40 and 600 ºC) were carried out on 5-10 mg samples of ThD, neat bitumen and modified bitumens under inert atmosphere.

3. RESULTS AND DISCUSSION

3.1. RHEOLOGICAL BEHAVIOUR AT HIGH IN-SERVICE TEMPERATURES

Figure 1 shows the viscous flow curves, at 60ºC, of selected ThD modified binders prepared from two different bitumens, as a function of curing time. As can be seen, neat and 3 wt. % ThD modified binder from bitumen 150/200 display Newtonian behaviour in the whole shear rate range studied, even when ThD content is increased up to 9 wt.% (results not shown here). On the contrary, neat and 9 wt.% ThD modified binder from bitumen 40/50 show a Newtonian behaviour in the low-intermediate shear rate range studied, followed by a shear-thinning region when shear rate is increased further. It can also be observed that ThD addition to neat bitumen leads to a first slight increase in viscosity after one hour of processing, which continues during storage (curing time). However, such a time-dependent evolution of viscosity is strongly influenced by the neat bitumen used. Thus, bitumen 150/200 undergoes a very significant increase between 20 and 60 days of curing, much more apparent than that observed for bitumen 40/50 (Figure 1).

The estimation of a modification index (M.I.) from the values of the zero-shear-rate limiting viscosities of the binders may be considered as a useful parameter to quantify bitumen modification at high in-service temperatures. This modification index has been defined as follows:

$$\text{M.I.}=\frac{\eta_{0,\text{mod}}-\eta_{0,\text{proc}}}{\eta_{0,\text{proc}}}\times 100 \qquad (1)$$

where $\eta_{0,\text{mod}}$ is the zero-shear-rate-limiting viscosity of the ThD modified bitumen, and $\eta_{0,\text{proc}}$ is the zero-shear-rate-limiting viscosity of the “blank” sample, both of them at 60ºC.

Hence, this parameter quantifies viscosity changes due to the addition of the modifying agent (ThD), regardless of the expected bitumen oxidation produced during binder processing. Figure 2 displays the evolution of the modification index (M.I.) with curing time for three selected samples. As commented above, the addition of ThD leads to a first increase in the M.I. values just after processing (0 days) that, for bitumen 150/200 samples, becomes much more important as modifying agent concentration is raised from 3 to 9 wt.%. This fact suggests the existence of chemical reactions between bitumen and modifier during blending. Moreover, such a viscosity enhancement continues after 20 and, even, 60 days of curing, mainly for bitumen 150/200. These results lead to establish two different bitumen modification pathways: a) a “short-term” modification, during blending of bitumen and ThD, at 130ºC; b) a “long-term” modification, as a consequence of curing, at room temperature. As a result, bitumen viscosity may increase up to more than 500 % its original value (see bitumen 150/200, in Figure 2).

Temperature sweep tests in oscillatory shear (10 rad/s and 1ºC/min heating rate), from 30 to 75 ºC, were carried out on neat bitumen 150/200 and their corresponding modified bitumen samples (3 and 9 wt.% ThD). Figure 3 shows the evolution with temperature of the loss tangent (ratio of viscous, G", and elastic, G', moduli), as a function of curing time. A predominantly viscous character (tan δ >1), which is more apparent as temperature rises, is noticed for all samples. Still, ThD addition produces a decrease in tan δ values (enhancing binder elastic properties), mainly for those systems with the highest concentration of modifier, and which is favoured by long curing times. On the other hand, the average slope of the curve of the loss tangent vs. temperature, within the interval 40-60 ºC, can be related to binder thermal susceptibility at high in-service temperatures. Thus, this average slope decreases from 0.024 for neat bitumen 150/200 down to 0.013 for its corresponding 9 wt.% ThD modified binder, after 60 days of curing at room temperature. This result would suggest a lower thermal susceptibility, in the temperature range considered, and, consequently, an improved thermal resistance would be expected for these modified binders [16].

In summary, the modification of bitumen with ThD seems to yield an improvement in bitumen behaviour at high in-service temperatures, since it increases binder viscosity (at 60 ºC) and enhances both its elastic properties and thermal resistance. However, the kinetics of this modification appears to be quite slow, as may be deduced from the evolution of the rheological properties with curing time. Thus, it takes up to 60 days to obtain a modified binder with significantly improved properties.

3.2. BITUMEN BEHAVIOUR AT LOW IN-SERVICE TEMPERATURES

Frequency sweep tests, performed in bending mode, have been used to assess the linear viscoelastic response, between -30 and 15 ºC, of a selected modified binder (bitumen 40/50 containing 9 wt. % ThD, after 60 days of curing). The experimental results obtained at the different temperature studied demonstrate that the mechanical spectra of both binders show predominantly elastic characteristics (E' > E") at low temperatures (i.e. up to around 0ºC).

The experimental frequency sweep curves have been superposed onto a master curve by using a shift-factor, a_T (see Figure 4). The reference temperature, T_{ref} , was arbitrarily chosen to be 0ºC. In addition, neat bitumen behaviour is presented for the sake of comparison. Within the temperature range studied in this work, the temperature dependence of the shift factor may be described by the Williams-Landel-Ferry (WLF) equation fairly well:

$$\log a_T = \frac{-C_1 \cdot (T - T_{ref})}{C_2 + (T - T_{ref})} \qquad (2)$$

The parameters C_1 and C_2 are presented in Table 2, showing similar values of C_1 for both neat and modified bitumen, but slightly higher values of C_2 for the modified bitumen. The fitting of this equation is shown in the inset of Figure 4B for both types of binders.

In addition, frequency sweep tests results in dynamic bending, at the different temperatures studied, have been combined in the form of “Black” diagrams. Thus, phase angle (δ) vs. complex flexural modulus (|E*|) curves for neat bitumen 40/50 and its corresponding 9 wt.% ThD modified bitumen are shown in Figure 5. In order to shed some light on binder rheological behaviour in a wider temperature range, complex shear modulus (|G*|) values, from oscillatory shear tests performed at 30 and 60 ºC, have been also included. Phase angle is a relative measure of binder viscoelasticity, i.e. Newtonian liquids and Hookean solids are characterised by phase angles of 90 and 0º, respectively. The ability of the samples to store deformational energy at high in-service temperatures and to dissipate it through flow at low temperatures is called elasticity and flexibility, respectively [17]. As can be seen, at a fixed value of the complex modulus of 10^9 Pa (within the low temperature region), the modified bitumen presents a slightly higher phase angle value than the neat bitumen, suggesting that the addition of ThD may slow down the approach to an ideal elastic solid (i.e. to a more brittle material). On the other hand, for relatively low complex modulus values (down to 10^2 Pa), that is, in a temperature range comprised between 30 and 60ºC, the trend seems to be reversed. Lower values of phase angle are found for the ThD modified bitumen, with the consequent increase in its elastic features. As a result, an enhanced material performance is expected because the addition of ThD leads to improved elasticity and flexibility, at high and low in-service temperatures, respectively.

In the same way, Figure 6 shows the temperature sweep curves, at 1 Hz and from -30 to

35 ºC, for the 40/50 neat bitumen, and its corresponding “blank” sample and 9 wt.% modified binder. These thermo-rheological tests have widely been used to assess the end-performance of polymer modified bitumens at low temperatures [18,19]. It can be observed a clear transition from the glassy to the Newtonian region (with a crossover point between E' and E") with increasing temperature [20]. No plateau is found between both regions, a fact that indicates the non-existence of entanglements [21]. As temperature decreases, it can be observed a maximum in the loss modulus, which characterises the onset of the glassy region. The glassy state leads to brittle materials, which are more likely to undergo thermal cracking under loading. For this reason, modification should focus on shifting the above-mentioned onset temperature to lower ones. Thus, a characteristic temperature $T_{g(1Hz)}$ has been calculated (see Table 2) from the maximum value in the loss modulus curves. Despite $T_{g(1Hz)}$ depends on frequency, and should be considered as a “mechanical” glass transition temperature, it is a suitable parameter to establish a comparative analysis of the low temperature behaviour of neat and modified binders. As can be seen, the value of this mechanical glass transition temperature is reduced around 8ºC (relative to the “blank” binder) after ThD addition, which suggests enhanced mechanical properties at low in-service temperatures. Such an assertion is also in good agreement with the results obtained from Modulated Differential Scanning Calorimetry (MDSC). Thus, Figure 7 displays curves of the derivative heat capacity (dC_p/dT) for neat bitumen 40/50 and its corresponding “blank” and 9 wt.% modified binder after 60 days of curing. As may be seen, two well defined peaks are found between -40 and 20 ºC, which are related to the glass transition temperatures, T_{g1} and T_{g2}, of the binders, resulting from the overlapping of two glass transition processes corresponding to saturates and aromatics in the maltenic fraction [22,23]. Figure 7 demonstrates that ThD addition brings about a reduction in the

temperatures at which peaks T_{g1} and T_{g2} are located (see their corresponding values in Table 2).

3.3. CHEMICAL MODIFICATION

It is well known that bitumen is a colloidal system composed of two fractions: maltenes (which can be separated into three different types of compounds: saturates, aromatics and resins) and asphaltenes. In general, road paving distresses caused by bitumen ageing are related to changes in its colloidal structure. In chemical terms, it is accepted that oxidative ageing leads to a transformation among bitumen components as follows: aromatics → resins → asphaltenes. Saturates, instead, remain essentially unchanged, pointing out their low chemical reactivity. These changes result in a slightly higher glass transition temperature [4]. However, the opposite trend has been observed for the ThD modified binders studied (see, for instance, Table 2 for bitumen 40/50 with 9 wt.% ThD), a fact that hints a different type of chemical modification. On these grounds, Figure 8A shows the evolution of the SARAs fractions with curing time for 9 wt.% ThD modified bitumen 40/50 (neat bitumen is included as a reference). As may be seen, asphaltene concentration decreases as curing time increases, from 18 (for neat bitumen) down to 9 wt.% (for 9 wt.% ThD modified binder after 60 days of curing). These changes in binder colloidal nature have been assessed through the definition of a colloidal index calculated from of the SARAs fractions of the binder [4]:

$$\mathrm{C.I.}=\frac{\mathrm{saturates}+\mathrm{asphaltenes}}{\mathrm{aromatics}+\mathrm{resins}} \qquad (3)$$

Figure 8B shows a remarkable drop in the colloidal index values of both bitumens after ThD addition, more apparent for the highest concentrations and longest curing times. A lower colloidal index would suggest smaller asphaltene clusters, leading to materials with less elastic character at high in-service temperature. However, as previously discussed, binder viscosity and its relative elastic characteristics, at high in-service temperature, increase with curing time (Figures 1 and 3), which would contradict this explanation. These results can be understood by analysing the chromatographic method used to obtain the different SARAs fraction, more specifically at the stage of sample preparation. In this sense, 5 mg of bitumen were dissolved in 10 mL of toluene and, then, tested. Hence, the colloidal index (C.I.) will only take into account those compounds soluble in toluene. Since all bitumen fractions are modified in a different way with curing time, significant chemical interactions are clearly evidenced. Thus, we may assume that some new products of reaction, which are responsible for the enhanced thermo-rheological behaviour of the binder, are insoluble in toluene. Filtration tests and thermo-gravimetric analysis confirm this assumption. After filtration of a 60-day-cured sample dissolved in toluene, about 7.5 wt.% of a black-coloured residue was obtained. Instead, less than 0.5 wt.% was obtained for its corresponding neat bitumen 40/50. Figure 9 shows the weight loss and its derivative (DTG) for pure thiourea dioxide, neat bitumen 40/50 and the 60-day-cured sample residue. Neat bitumen presents a large thermal decay process, extending over a wide temperature interval (from 300 to 600ºC, with a DTG peak at 455 ºC), which involves decomposition of chemical compounds with very different molecular weights. Thiourea dioxide thermal decomposition consists of two stages [24]. The first one is located between 121 and 144º C (with a DTG maximum at 135ºC), and is related to the production of SO_2 (g) from thiourea dioxide, involving a significant mass loss of 17 wt.%:

$$NH_2(NH)CSO_2H\ (s) \rightarrow CO(NH_2)_2\ (s) + 0.5\ S\ (s) + 0.5\ SO_2\ (g) \qquad (R1)$$

The second stage of thiourea dioxide decomposition (DTG peak located at around 250ºC) is governed by continuous melting, vaporization, and decomposition of urea produced during the first stage:

$$CO(NH_2)_2\ (s) \rightarrow NH_3\ (g) + HNCO\ (g) \qquad (R2)$$

The DTG analysis of the insoluble fraction (Figure 9B) shows a first peak above 120ºC attributed to unreacted thiourea dioxide (reaction R1), and a second peak at around 240 ºC due to the decomposition of the urea previously formed in R1. Interestingly, a new peak arises at temperatures between ThD and neat bitumen thermal degradations. This event is thought to be the result of new compounds resulting from “non-identified” reactions between bitumen and products resulting from ThD decomposition at 130ºC. Those reactions would provoke the insolubilization of a part of the bitumen heaviest fractions (mainly asphaltenes), which would explain the above decrease in colloidal index. However, chemical modification also affect other bitumen fractions (except the saturates) favouring more polar compounds (aromatics → resins). In summary, these chemical changes in the bitumen give rise to an improvement of the mechanical properties of the binder at both high and low in-service temperatures and, therefore, ThD could be considered as a potential chemical rejuvenation agent for aged bitumens.

The above-commented chemically-induced changes in bitumen composition yield a modification of bitumen microstructure, as may be deduced from the non-reversing component of the heat flow curve obtained by modulated DSC (see Figure 10). According to Masson and Polomark [22,23], saturates are semicrystalline, aromatics are amorphous, and resins and asphaltenes are mesophasic, and they order in four stages upon cooling from the melt, yielding four specific thermal events in the non-reversing heat flow curve. Figure 10 shows the non-reversing thermograms for neat bitumen 40/50, as well as its corresponding “blank” and 9 wt.% ThD modified sample after 60 days of curing. Regarding neat bitumen, such events are found as a broad endothermic background which approximately extends from – 40 to 80 ºC (first event), two exotherms located at about -9 and 40 ºC (second and third event) and, finally, an endothermic peak around 50 ºC (fourth event) [22]. The second and third thermal events are caused by a time-dependent cold-crystallization of low and high molecular weight saturated segments upon cooling, respectively. Hence, above the frozen state defined by $T > T_g$, chain mobility is increased and crystallizable segments can crystallize [22,23,25]. Table 2 displays the temperatures at which the second event (T_{2nd}) appears. It can be observed similar values, of about -9ºC, for both neat bitumen 40/50 and its corresponding "blank". Instead, T_{2nd} decreases down to -11.3ºC after addition of 9 wt.% ThD and 60 days of curing. The lower T_g values seem to demonstrate that, after chemical reactions, chain mobility increases, reducing temperature at which cold crystallization begins. Consequently, low temperature properties are enhanced, which is in good agreement with the results obtained from DMTA measurements (see Table 2). On the other hand, the fourth event (endotherm located around 50ºC) is related to the diffusion of relatively large and high molecular weight structures, as those found in resins and asphaltenes, to form independent domains. In that sense, the area of this fourth event, ΔH_{4th}, also increases with the addition of ThD (see Table 2), as a consequence of the appearance of previously commented new high molecular weight compounds, which form more developed and ordered mesophasic microstructures, which require more heat during their melting process.

4. CONCLUDING REMARKS

The effect of thiourea dioxide addition on the thermo-mechanical properties of two asphaltic bitumens with different penetration grades has been evaluated. Similar effects were found for both types of bitumen. ThD addition, at 130ºC, produces significant changes in binder chemical composition (and so, in its colloidal nature), more important as curing time increases. Results suggest the existence of "non-identified" reactions between ThD and the most polar bitumen compounds (mainly asphaltenes) forming new products, insoluble in toluene, which could not be detected by the chromatographic method followed. All these chemically-induced changes were seen to significantly enhance bitumen thermo-mechanical properties in a wide interval of in-service temperatures. On the one hand, at high temperatures, the addition of ThD leads to larger binder viscosity and increased relative elastic characteristics. On the other hand, chemical modification by ThD seems to decrease the "mechanical" glass transition temperature, improving both flexibility and thermal cracking resistance at low temperatures.

In addition to the observed enhancement in in-service properties, it is worth remarking that a part of the asphaltenes was transformed into new compounds that were not detected by the SARAs analysis. As a result, a decrease in the colloidal index values was found, which would be able to continue under environmental conditions even after asphalt laydown has finished. Such a result would suggest ThD is able to mitigate undesirable effects due to a certain primary ageing during bitumen processing and its mixing with the arid.

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Figure captions

Figure 1. Viscous flow curves, at 60 ºC, for a) 9 wt.% ThD modified bitumen 40/50 and b) 3 wt.% ThD modified bitumen 150/200, as a function of curing time.

Figure 2. Evolution of the modification index with curing time, for three selected ThD modified bitumen samples.

Figure 3. Evolution of the loss tangent with temperature, for modified bitumen 150/200 samples, as a function of curing time.

Figure 4. Master curves of the linear viscoelastic moduli in dynamic bending, E' and E", for a) neat bitumen 40/50 and b) 9 wt.% ThD modified bitumen, after 60 days of curing. (Inset: Temperature dependence of the shift factor, and WLF fitting, for both binders)

Figure 5. "Black" diagram for neat bitumen 40/50 and its corresponding 9 wt.% ThD modified binder, after 60 days of curing.

Figure 6. Evolution of E' and E'' with temperature (temperature sweep tests) for 9 wt.% ThD modified bitumen 40/50, after 60 days of curing, and its corresponding "blank" sample.

Figure 7. Evolution of C_p derivative obtained by MDSC with temperature, for neat bitumen 40/50 and its corresponding "blank", and 9 wt.% ThD modified bitumen, after 60 days of curing.

Figure 8. Evolution of a) SARAs fraction for 9 wt.% ThD modified bitumen 40/50, and b) colloidal index values with curing time, for selected modified bitumen samples.

Figure 9. Weight loss (A) and its derivative (B), between 40 and 600 ºC and under N_2 atmosphere, for thiourea dioxide, neat bitumen 40/50 and the insoluble residue in toluene from 9 wt.% ThD modified bitumen after 60 days of curing.

Figure 10. Non-reversing heat flow thermograms for neat bitumen 40/50 and its corresponding "blank" and 9 wt.% ThD modified bitumen.

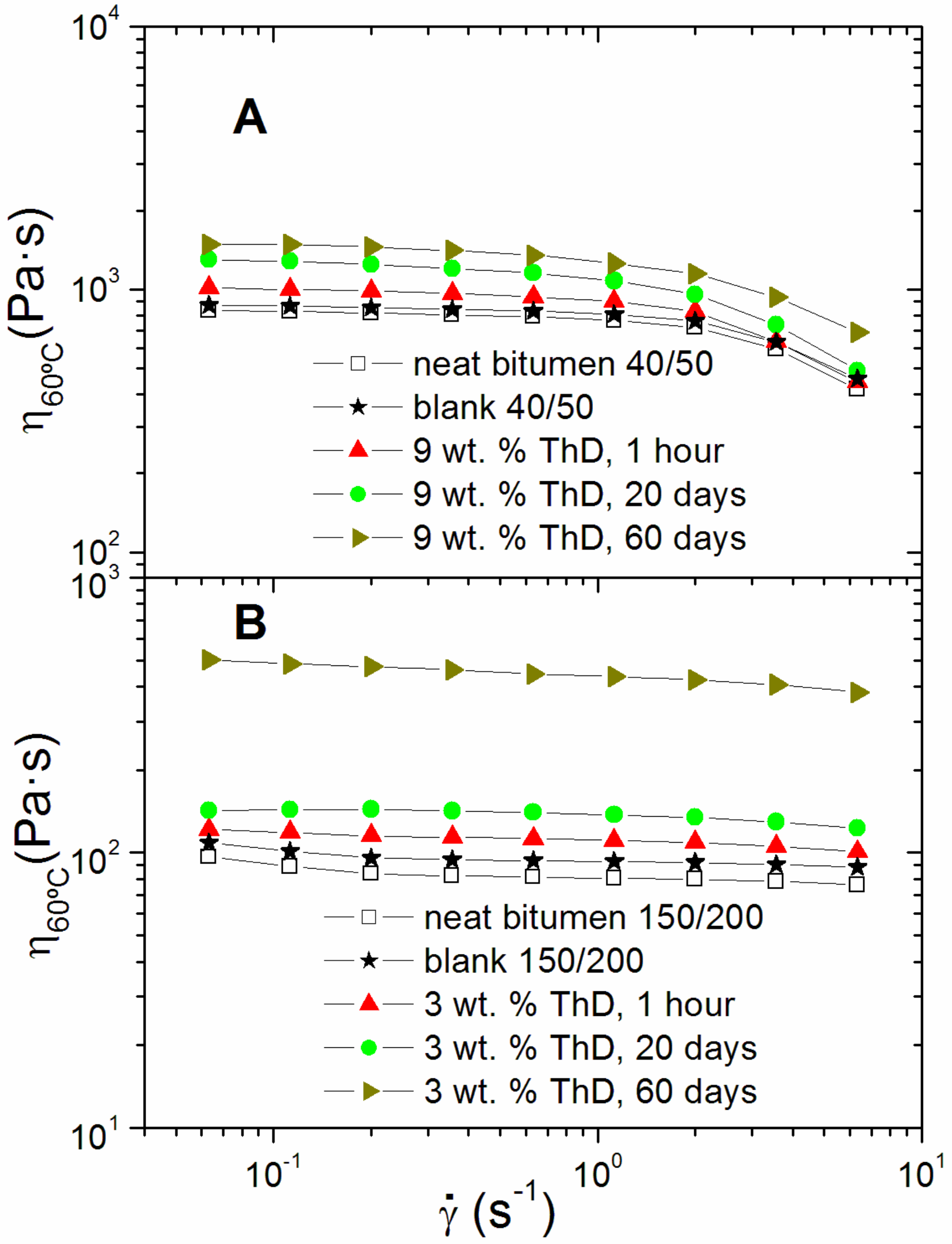

A
B
10^4
10^3
10^2
10^3
10^2
10^1
$\eta_{60°C}$(Pa·s)
$\eta_{60°C}$(Pa·s)
neat bitumen 40/50
blank 40/50
9 wt. % ThD, 1 hour
9 wt. % ThD, 20 days
9 wt. % ThD, 60 days
neat bitumen 150/200
blank 150/200
3 wt. % ThD, 1 hour
3 wt. % ThD, 20 days
3 wt. % ThD, 60 days
10^{-1}
10^0
10^1
$\dot{\gamma}$ (s^{-1})

Figure 1

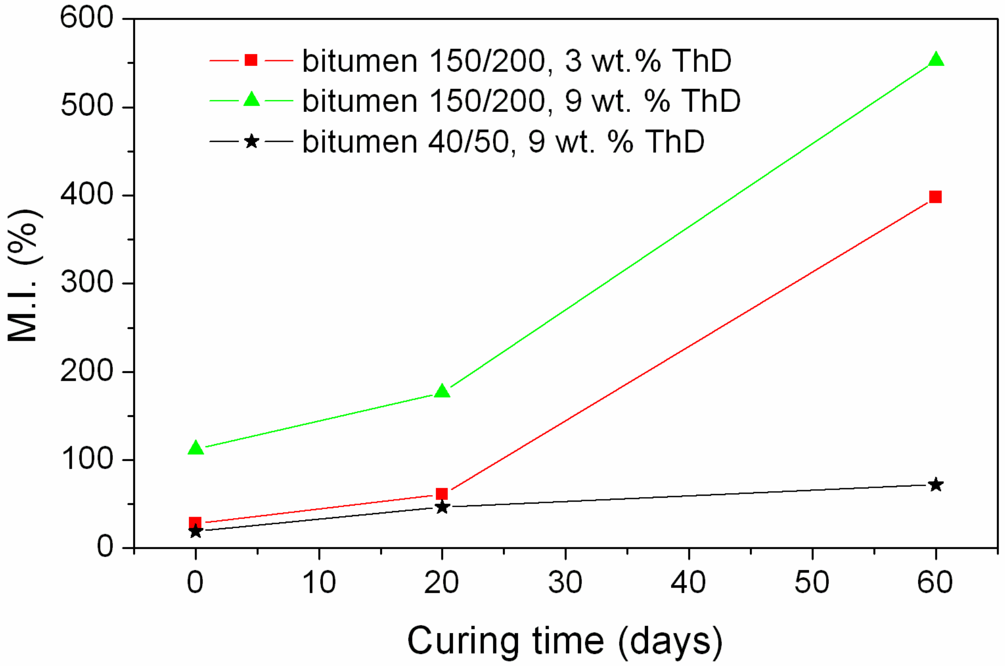

bitumen 150/200, 3 wt.% ThD
bitumen 150/200, 9 wt. % ThD
bitumen 40/50, 9 wt. % ThD
M.I. (%)
0
100
200
300
400
500
600
0
10
20
30
40
50
60
Curing time (days)

Figure 2

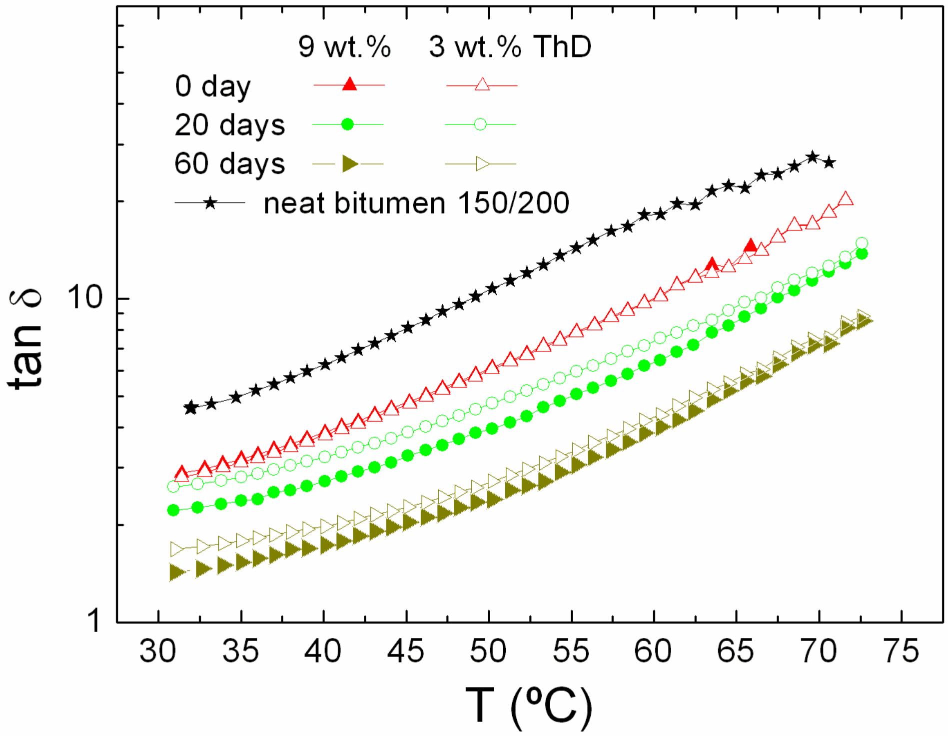

9 wt.%
3 wt.% ThD
0 day
20 days
60 days
neat bitumen 150/200
tan δ
1
10
30
35
40
45
50
55
60
65
70
75
T (ºC)

Figure 3

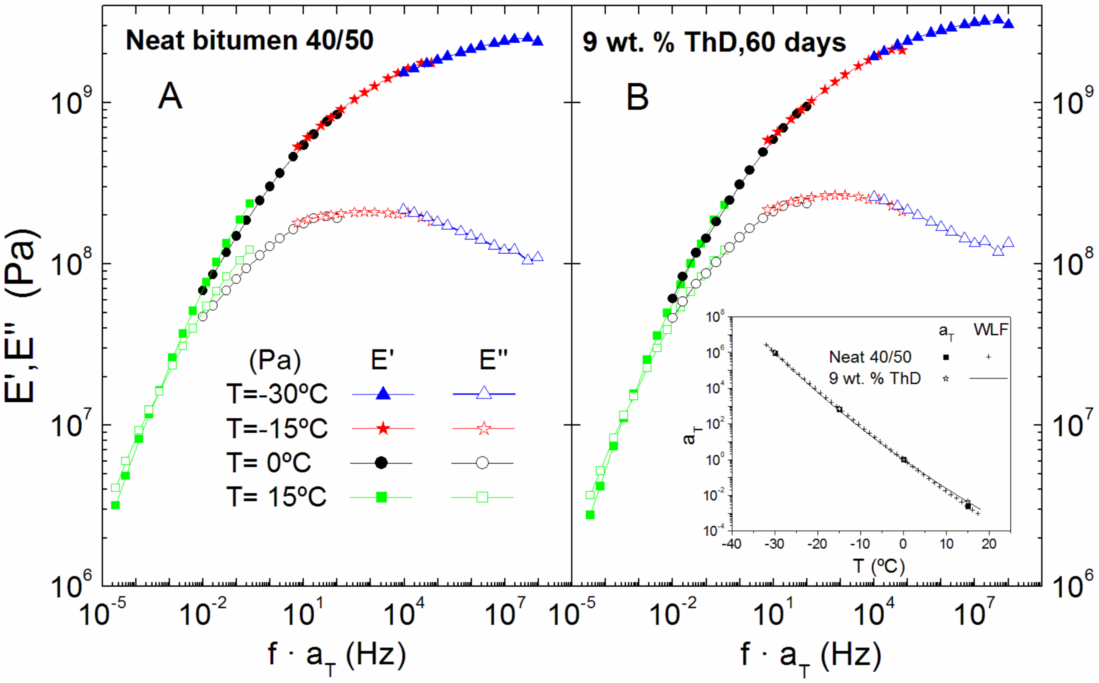
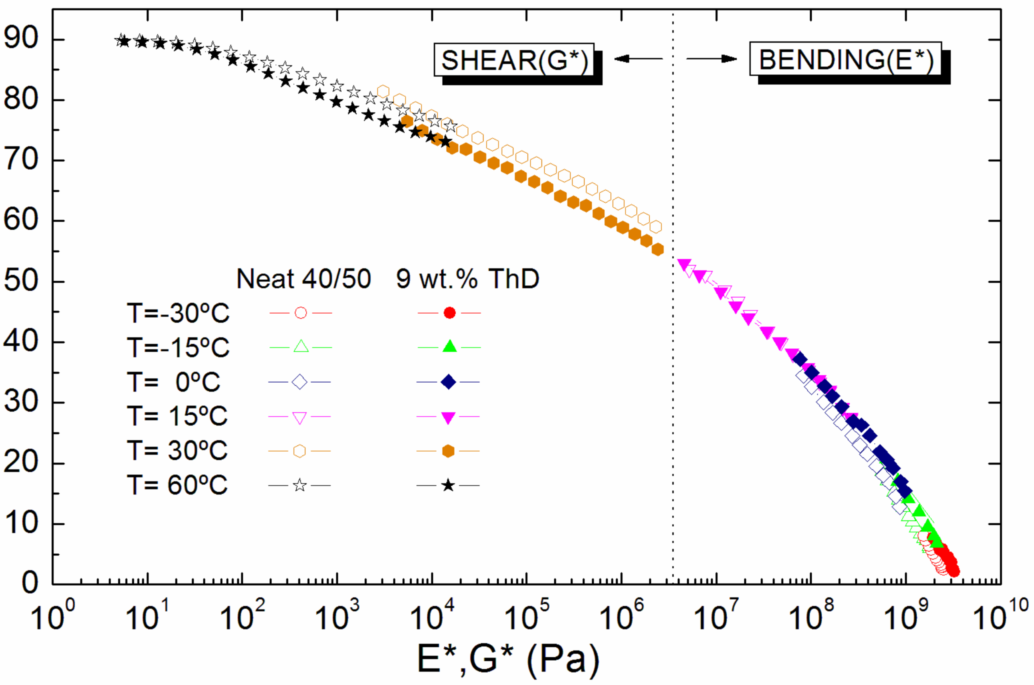

Neat bitumen 40/50
A
9 wt. % ThD,60 days
B
E',E'' (Pa)
10^9
10^8
10^7
10^6
10^-5
10^-2
10^1
10^4
10^7
f · a_T (Hz)
(Pa)
E'
E''
T=-30ºC
T=-15ºC
T= 0ºC
T= 15ºC
a_T
WLF
Neat 40/50
9 wt. % ThD
a_T
10^8
10^6
10^4
10^2
10^0
10^-2
10^-4
-40
-30
-20
-10
0
10
20
T (ºC)

Figure 4



SHEAR(G*)
BENDING(E*)
Neat 40/50
9 wt.% ThD
T=-30ºC
T=-15ºC
T= 0ºC
T= 15ºC
T= 30ºC
T= 60ºC
δ (º)
0
10
20
30
40
50
60
70
80
90
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}
E*,G* (Pa)

Figure 5

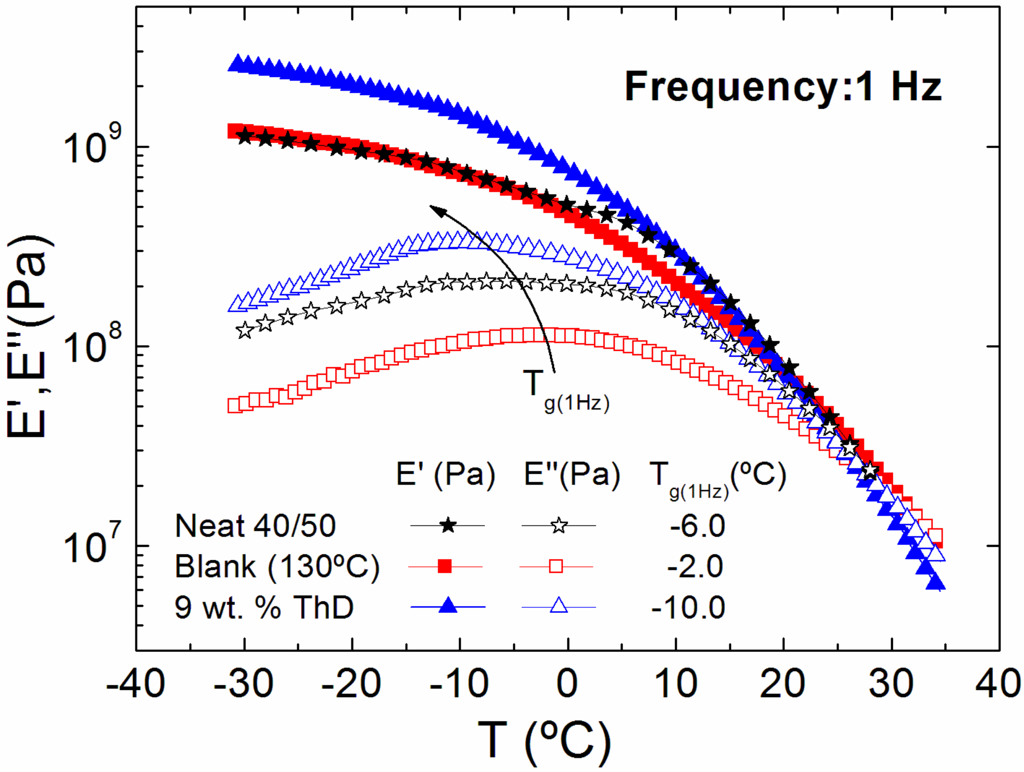

Frequency:1 Hz
E',E"(Pa)
10^9
10^8
10^7
T_g(1Hz)
E' (Pa)
E"(Pa)
T_g(1Hz)(ºC)
Neat 40/50
-6.0
Blank (130ºC)
-2.0
9 wt. % ThD
-10.0
-40
-30
-20
-10
0
10
20
30
40
T (ºC)

Figure 6

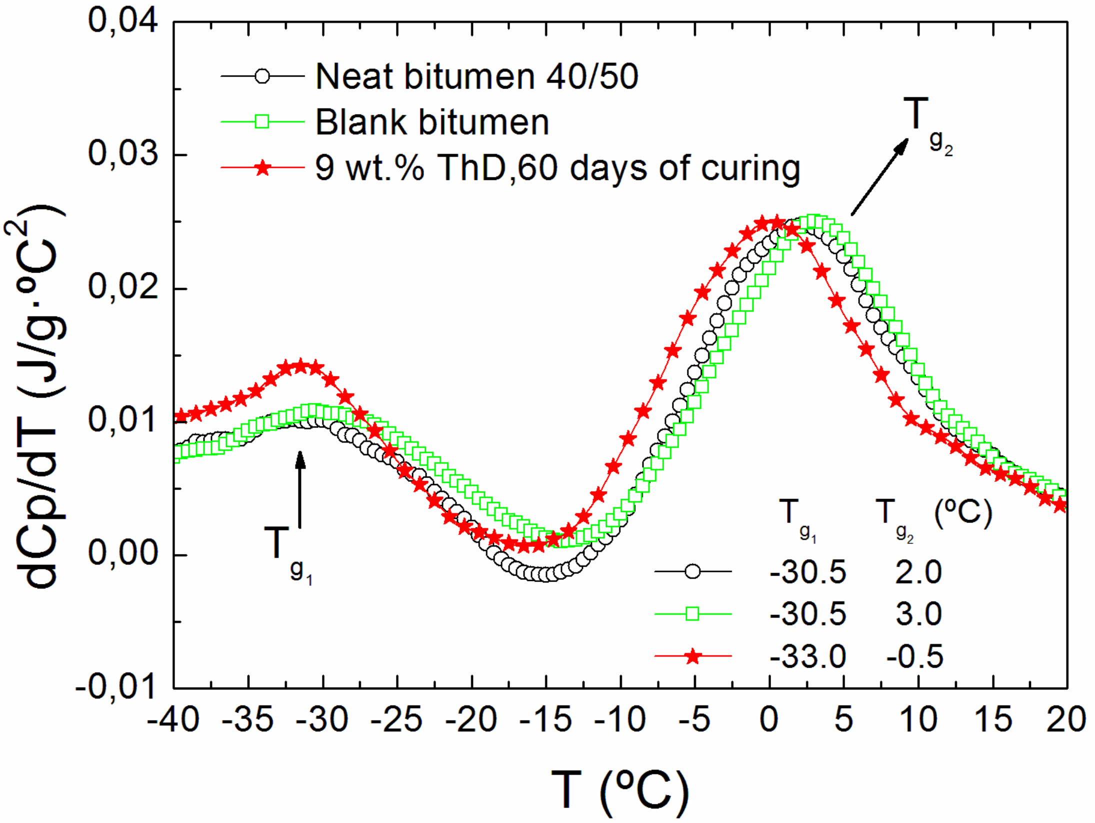

0,04
0,03
0,02
0,01
0,00
-0,01
dCp/dT (J/g·ºC^2)
-40 -35 -30 -25 -20 -15 -10 -5 0 5 10 15 20
T (ºC)
Neat bitumen 40/50
Blank bitumen
9 wt.% ThD,60 days of curing
T_{g_1}
T_{g_2}
T_{g_1} T_{g_2} (ºC)
-30.5 2.0
-30.5 3.0
-33.0 -0.5

Figure 7

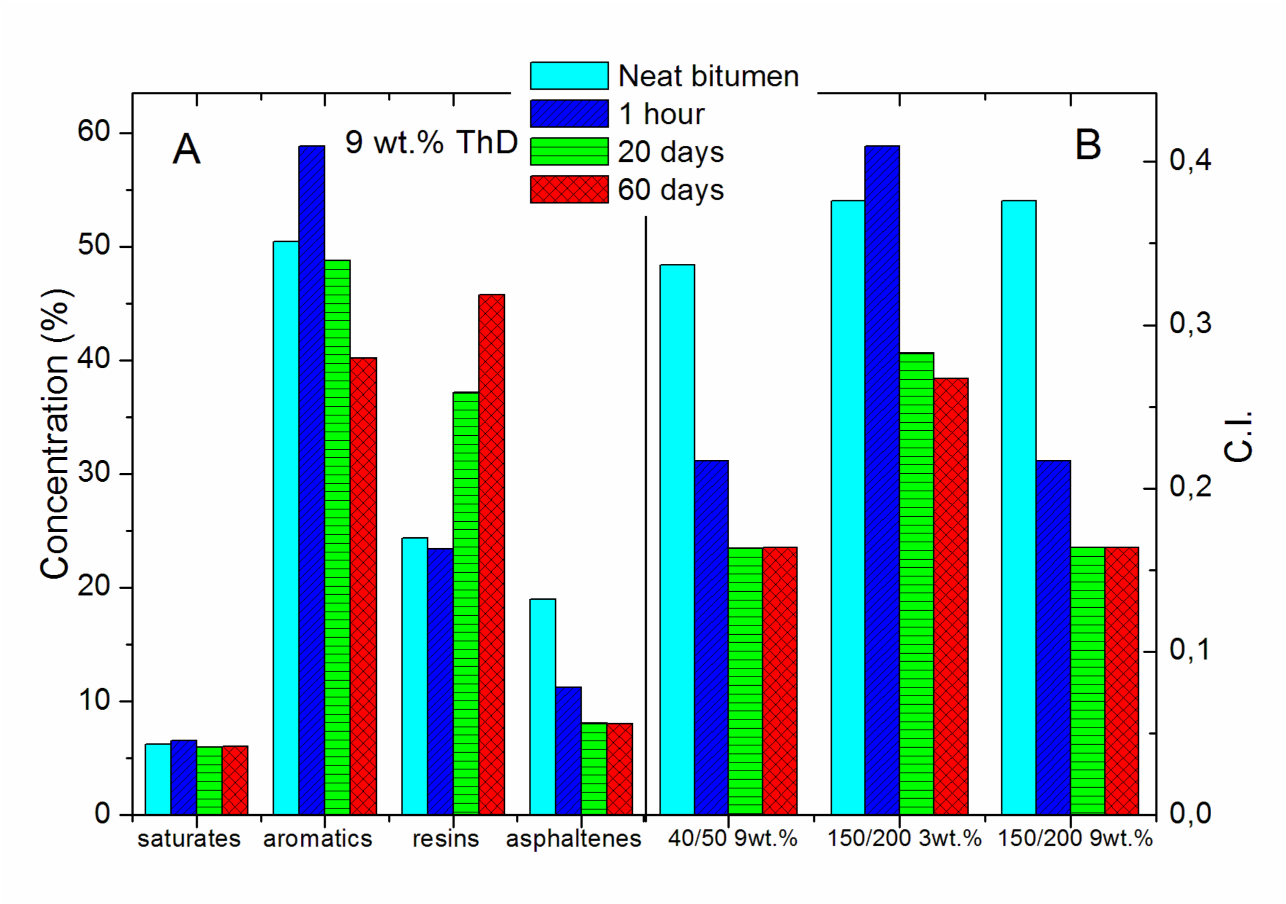

Neat bitumen
1 hour
20 days
60 days
A
9 wt.% ThD
B
Concentration (%)
C.I.
60
50
40
30
20
10
0
0,4
0,3
0,2
0,1
0,0
saturates
aromatics
resins
asphaltenes
40/50 9wt.%
150/200 3wt.%
150/200 9wt.%

Figure 8

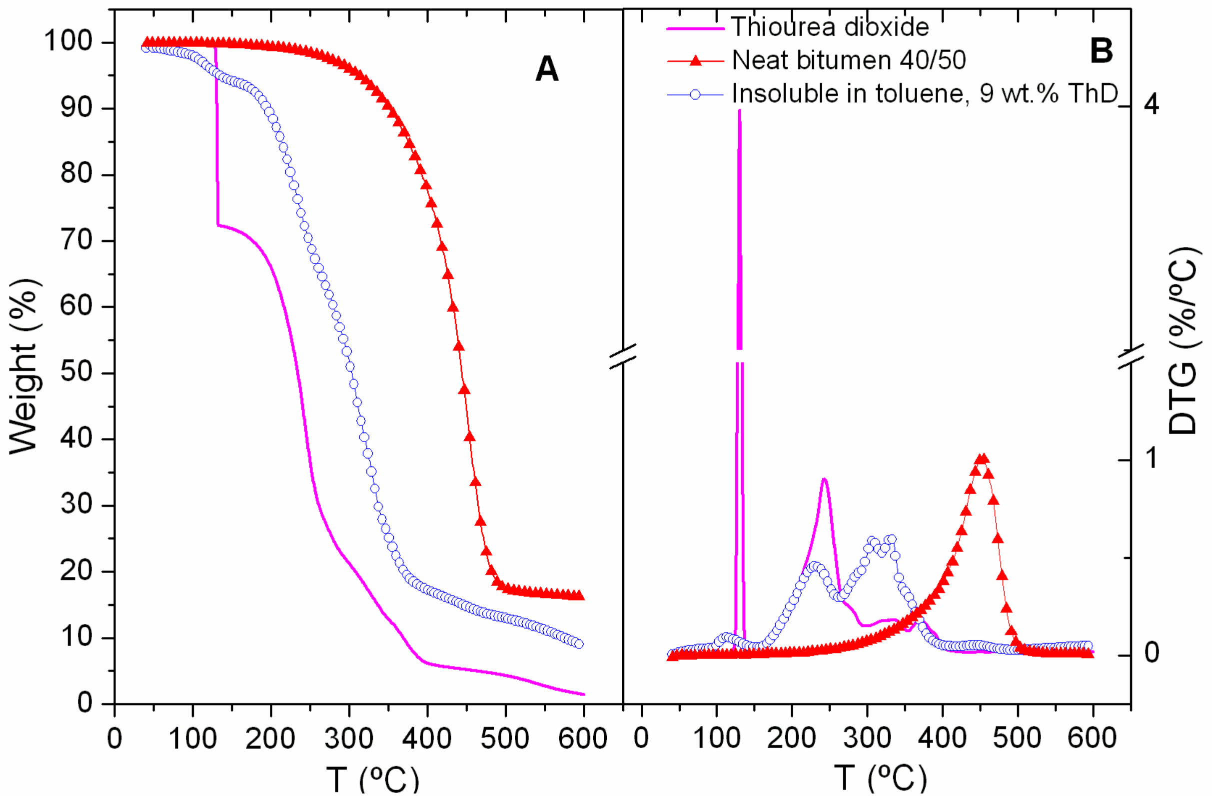

A
B
Weight (%)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
T (ºC)
Thiourea dioxide
Neat bitumen 40/50
Insoluble in toluene, 9 wt.% ThD
DTG (%/ºC)
4
1
0
0
100
200
300
400
500
600
T (ºC)

Figure 9

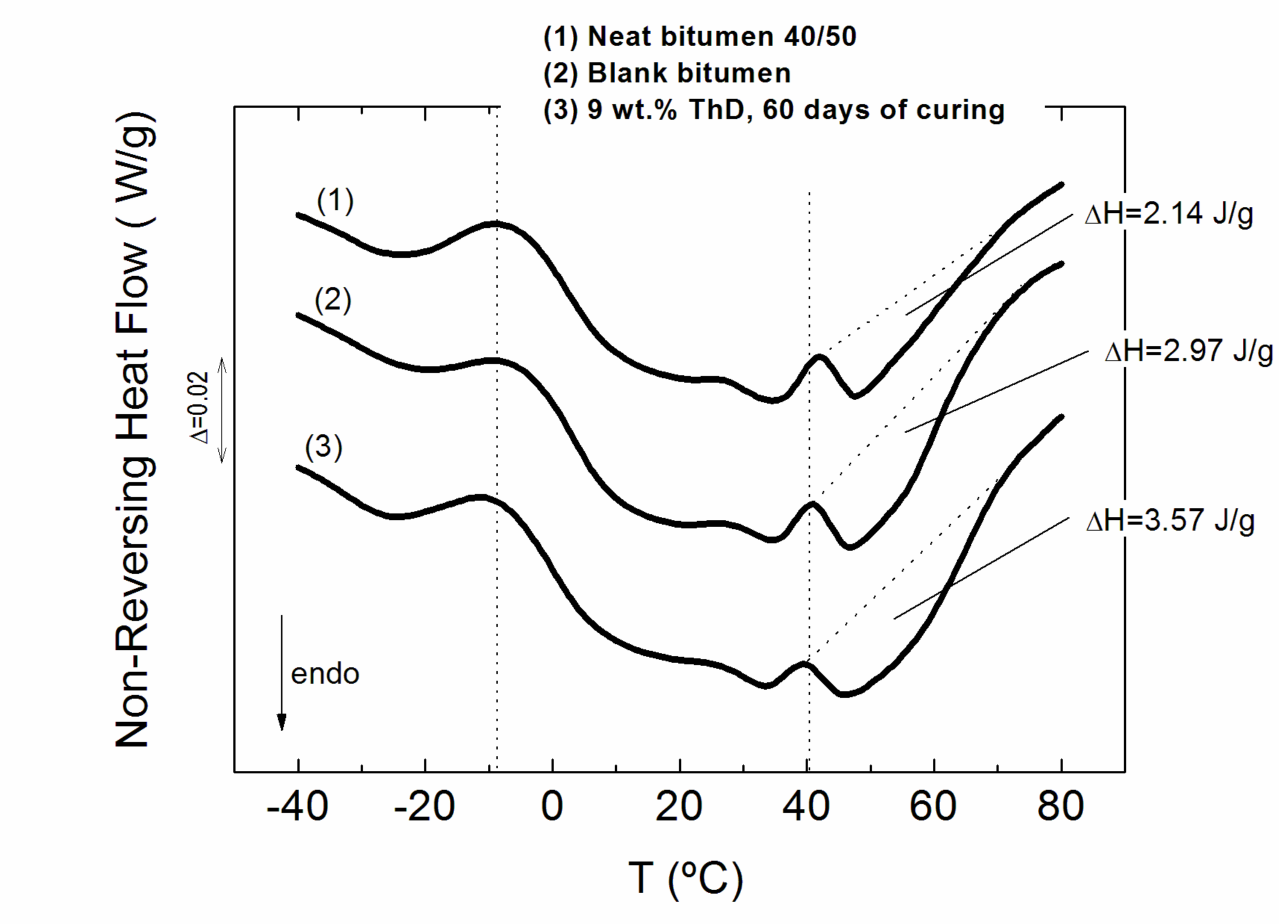

(1) Neat bitumen 40/50
(2) Blank bitumen
(3) 9 wt.% ThD, 60 days of curing
(1)
(2)
(3)
ΔH=2.14 J/g
ΔH=2.97 J/g
ΔH=3.57 J/g
Δ=0.02
endo
Non-Reversing Heat Flow (W/g)
-40
-20
0
20
40
60
80
T (ºC)

Figure 10