“Enhancing the viscoelastic properties of bituminous binders via thiourea-modification”

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ABSTRACT

Although added in a very low concentration, bitumen controls the final properties and performance of the resulting asphalt mixture. As an alternative to classic bitumen modification with polymers, we herein propose the use of thiourea, which has proved to efficiently enhance the binder thermo-rheological properties in a broad temperature interval. As revealed by thermogravimetric and chemical analysis, benefits above may derive from new structures, probably formed by the interaction between ammonium thiocyanate and bitumen most polar fraction. Thus, flexural DMTA and dynamic shear tests demonstrated an improvement in the binder flexibility and an increase in its elasticity, at low and medium/high in-service temperatures, respectively. In addition, this research emphasizes the use of isothermal frequency sweep tests (and frequency/temperature-dependence conversion) as a means of achieving glass transition temperature values which, in contrast to isochronal temperature sweep tests, do not depend on the selected heating rate.

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

1. INTRODUCTION

Bitumen, residue from crude oil distillation, is a complex material basically composed of hydrocarbons along with some other molecules which contain small percentages of heteroatoms (sulphur, nitrogen and oxygen). Bitumen compounds can be classified by chromatographic techniques into four different fractions (usually referred to as "SARAs"): Saturates, Aromatics, Resins (which make up the maltenes) and Asphaltenes. Complexity, aromaticity, heteroatom content and molecular weight increase in the order S<A<R<As [1]. With regards to its microstructure, a colloidal model is traditionally used to describe bitumen behaviour. According to this model, asphaltenes are dispersed into an oily matrix of maltenes, and surrounded by a shell of resins (which becomes thicker as temperature decreases). Thus, bitumen physico-chemical and rheological properties strongly depend on both temperature and the relative proportion of the "SARAs" fractions [2,3].

Bitumen properties (impermeability, ductility, adhesivity, resistance to the effect of weathering and chemicals, etc) have favoured the development of numerous applications that ranges from the construction of road pavements [4] to waterproof membranes for the roofing industry [5]. Bitumen is the only deformable component and continuous phase in asphalt mixtures. In this sense, the viscoelastic properties of bitumen, over a wide range of temperatures and loadings, are of major importance when predicting roads performance [6]. However, this material has proved to undergo common distresses at both high in-service temperature ("rutting", or permanent deformation due to binder low stiffness) and low in-service temperature ("thermal cracking", or fracture due to its lack of flexibility) [7,8]. Moreover, bitumen chemical ageing during its service life leads to a global hardening of the material, which increases further the thermal cracking probability [3]. As a consequence, bitumen properties have been traditionally improved through the addition of virgin (SBS, SBR, EVA, polyethylenes, etc.) and waste polymers (plastics from agriculture, crumb tyre rubber, etc.) [9,10].

As an alternative to the above modifying agents, which usually present very low compatibility with bitumen, this work evaluates a novel bitumen modification through the use of a chemical agent: thiourea. Similarly to some other substances traditionally used in bitumen modification, e.g., sulphur, polyphosphoric acid (PPA) [11], mineral acids [12] or organic molecules [13], this agent is capable of chemically interact with specific bitumen fractions. Hence, thiourea has shown to induce benefits on the binder properties, by enhancing its linear viscoelastic properties at both low and medium/high in-service temperatures: it would increase the binder resistance to thermal cracking and permanent deformation under loading in harshly cold and hot climates, 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. The results of penetration grade trials, according to ASTM D5 [14], and ring and ball softening temperature (R&B) test, determined according to ASTM D36 [15], were 47 dmm and 52.5 ºC, respectively. Chemical composition, in terms of SARAs fractions, is shown in Table 1. Bitumen (and derived binders) 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 [16].

Thiourea (abbreviated as “Th”, hereinafter) supplied by Sigma Aldrich, has been selected for bitumen modification which leads to chemical reactions with bitumen molecules. It has a molecular weight of 76.12 g·mol^{-1}, and its melting point lies within the interval 175-179 ºC.

2.2. Samples preparation

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 let cured for 20 and 60 days, 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).

2.3. Tests and measurements

Linear viscoelastic frequency sweep tests, between 0.01 and 100 rad/s (at 30 and 60ºC), and temperature sweep tests 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). A plate-and-plate geometry (25 mm diameter and 1 mm gap) was used for all rheological shear tests.

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. Liquid nitrogen was employed as cooling system.

Simultaneous derivative thermogravimetric analysis / differential thermal analysis (DTG/DTA) measurements were carried out, under inert atmosphere, on 5-10 mg samples, using a Seiko TG/DTA6200 (Seiko Instruments Inc., Japan). Temperature ramps were set at 10 $ºC\cdot min^{-1}$, between 40 and 600 ºC.

Modulated Differential Scanning Calorimetry (MDSC) tests were performed with a TA Q-100 (TA Instruments, USA) on hermetic aluminium pans containing 5-10 mg samples. Tests conditions were set to an oscillation period of 60 s, amplitude of modulation of ±0.5 ºC and heating rate of 5 ºC/min. The sample was purged with nitrogen at a flow rate of 50 mL/min. In order to provide the same recent thermal history, all the test pans were prepared 24 h before being measured.

3. RESULTS AND DISCUSSION

3.1. Linear viscoelastic behaviour of thiourea-modified binders

In order to characterise the LVE behaviour of the different Th-modified binders studied, oscillatory shear temperature sweeps and dynamic bending tests in the medium/high and low temperature interval, respectively, have been carried out. Regarding the medium/high in-service temperature interval, Fig.1 shows the evolution with temperature of the oscillatory shear linear viscoelastic functions, G' and G", for the 9 wt.% Th-modified binder, as a function of curing time. Neat bitumen has been included as reference. As can be appreciated, both storage and loss moduli monotonously decrease as temperature increases, for every sample studied. Moreover, G" remains above G' over the entire temperature interval tested (30-80 ºC), which indicates a prevailing viscous behaviour. Also, no significant increase in the shear moduli and so, in binder strength, is observed by solely adding 9 wt.% Th (non-cured sample). Thus, the resulting binder needs to be subjected (treatment referred to as “curing”) to ambient conditions before an increase in G' and G" is observed, with modification being enhanced by a prolonged curing period. In that sense, although 20 days of curing slightly increases the values of G' and G", a more significant improvement is seen after 60 days of curing. Thus, this selected sample results in a modified binder which exhibits improved elastic properties, and so, better resistance to permanent deformation at high in-service temperatures. From the results we perceive the existence of two different, and well defined, types of modification: a) “short-time” modification, which occurs during the mixing of bitumen and thiourea, and which does not seem to produce any significant change in the binder rheology; b) “long-time” modification, which takes place during storage of the sample at ambient conditions, after being prepared, and which brings about a remarkable increase in the material strength. In addition, the viscoelastic functions for a thiourea content of 3 wt.% (not shown in Fig.1) presented lower values than those corresponding to 9 wt.%.

On the other hand, the evaluation of the linear viscoelastic response at low in-service temperatures for the 9 wt.% Th-modified binder, after 60 days of curing, is shown in Figs.2 and 3. Figure 2A presents the results of isothermal frequency sweep tests, performed on the selected binder in dual cantilever mode, at 4 different temperatures between -30 and 15 ºC. Curves of the dynamic flexural moduli, E' and E", vs. frequency reveal prevailing elastic features, with values of E' higher than E", in the entire frequency interval tested, at those testing temperatures below 15ºC. Although not presented in Fig.2A, same tests were carried out on the reference sample, that is, neat bitumen. As illustrated in Fig. 2A, E’’ behaviour is shown to be very sensitive to temperature variations at the low temperature region, and presents positive and negative values of slope in a log-log plot, above and below the material glass transition temperature, respectively.

The experimental values of the linear viscoelasticity functions may be “empirically” superposed onto a master-curve (see Fig.2B) by applying a shift-factor, a_T. Reference temperature (T_{ref}) was arbitrarily chosen to be 0 ºC. Within the temperature interval studied, the temperature-dependence of a_T is fairly well described by an Arrhenius-type equation (1):

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

where E_a is the activation energy, T_{ref} is the reference temperature and R is the gases constant.

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. [17]. The values of the frequency sweep master curve have been converted using the Arrhenius-like relationship between the shift factor and temperature as follows:

$$T = \frac{E_a T_{ref}}{R T_{ref} \ln(\omega_{exp}/\omega_R) + E_a} \tag{2}$$

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. As a result of this frequency/temperature-dependence conversion, isochronal E" curves for the neat bitumen and 60 days-cured 9 wt.% Th-modified binder are shown in Fig.3A.

Thus, in order to establish a comparative analysis on the effect of modification on the low-temperature performance of the different bituminous binders, a “mechanical” glass transition temperature ($T_{g,DMTA}$), taken as the value of temperature at the maximum in E" curve [18], has been obtained for every sample studied (shown in Table 2). This parameter accounts for the onset of the glassy region, at which the binder is expected to be affected by thermal cracking under loading. Consequently, modification should focus on shifting T_g to lower values.

Interestingly, application of Time-Temperature-Superposition principle 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 2 were obtained by conversion of frequency sweep tests on specimens which were let achieve thermal equilibrium at every selected temperature.

As can be observed, modification with thiourea brings about an improvement in the binder behaviour at low in–service temperature, as the value of $T_{g,DMTA}$ is reduced about 5 ºC when bitumen is mixed with 9 wt.% thiourea and cured for 60 days. If compared to the “blank” sample, which presents a value of -11.2 ºC, a further decrease of 2 ºC is noted.

In addition, Fig.3B shows the activation energy (E_a) values for the different binders studied. E_a, only fitting parameter in Eq.(1), has been elsewhere related to the binder thermal susceptibility [9]. Thus, Fig.3 demonstrates that, in the temperature range selected, the Th-modified bitumen presents the lowest value of activation energy (and consequently, lowest thermal susceptibility).

The linear viscoelastic behaviour of non-modified and modified bituminous binders in a wide temperature range can also be studied by means of Black diagrams, which represent phase angle (δ) vs. either complex shear (medium/high temperature) or complex flexural (low temperature) moduli. Black diagrams for the 9 wt.% Th-modified binder (60-days-cured) and neat bitumen are shown in Fig. 4. On the one hand, it can be observed that, for the highest values of $|E^*|$, which correspond to the lowest temperatures, the selected Th-binder presents slightly higher δ-values (so, enhanced viscous behaviour) than the neat bitumen. On the other hand, for relatively low $|G^*|$ values, that is, over a temperature range comprised between 30 and 60 ºC, lower δ-values for the Th-modified binder are found (with the consequent increase in its elastic features). Therefore, an enhanced performance material is expected because Th-modification leads to improve elasticity and flexibility, at medium/high and low in-service temperatures, respectively [19].

3.2. On the chemistry behind bitumen modification via thiourea

The above enhancement in the viscoelastic behaviour of the Th-modified binder suggests changes in its microstructure, as a consequence of the interaction between thiourea and some bitumen fractions. Thermal and chemical analysis (DTG/DTA, MDSC and TLC/FID) may shed some light on this issue.

The thermal decomposition of the pure components (neat bitumen and thiourea) was studied by simultaneous measurements of DTA (Fig. 5A) and DTG (Fig. 5B). DTG curve for neat bitumen presents a broad peak located at 455 ºC, which involves mass loss due to volatilization/decomposition of chemical compounds with very different molecular weights from 300 up to 500 ºC (Fig. 5B). Likewise, DTG profile for Th shows a major peak located at 210ºC, which ranges from 170 to 300 ºC.

In addition, the DTA curve for thiourea displays two overlapped endothermic processes. The first one, between 170 and 190 ºC (with DTA minimum peak located at 175ºC), is dominated by the melting of thiourea, hardly involving mass loss. The isomeric reaction R_1, with the production of NH_4SCN (ammonium thiocyanate), is suggested to take place during this first endothermic process [20]:

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

In contrast to that, the second stage involves NH_4SCN (derived from R_1) thermal decomposition, into CS_2, HNCS and NH_3 (between 190 and 270 ºC, with DTA minimum peak at 228 ºC) and leads to the significant mass loss associated to the DTG peak found at 210ºC. Hence, such a NH_4SCN decomposition is not expected to occur at the temperature at which mixing of bitumen and thiourea was carried out (180 ºC).

Aiming to confirm NH_4SCN formation from thiourea, the thermal decomposition of this substance has been also included in Fig. 5. As expected, DTA curve presents an endothermic peak at around 149 ºC, which corresponds to the ammonium thiocyanate melting point (lower than thiourea's, at 175-179 ºC), and another peak at 228 ºC, which stands for its decomposition. The small endothermic peak observed at 90 ºC is due to a reversible phase transition from monoclinic to orthorhombic structure [21].

Consequently, we will assume that bitumen modification and the resulting improvement in the binder mechanical behaviour over a broad in-service temperature interval is attributed to NH_4SCN arisen from R_1, and new compounds derived from its interaction with bitumen. In this regard, chemical analysis further confirmed such an assumption and may provide valuable information on the colloidal natural of binders studied. Figure 6 shows chromatograms, obtained by TLC/FID, for neat bitumen, pure thiourea and the 9 wt.% Th-modified binder after 60 days of curing. On the one hand, four peaks (which stand for the so-called “SARAs” fractions) corresponding to saturates, aromatics, resins and asphaltenes, respectively, are shown by neat bitumen. On the other hand, thiourea presents a single signal, located at the bitumen resins peak position, and no peak was found for NH_4SCN due to its insolubility in the selected chromatographic solvents. In contrast to the neat bitumen, asphaltenes in the modified binder split into two new peaks, which will be referred to as low and high polarity asphaltenes, LPAs and HPAs, respectively. Thus, the largest of them (LPAs), which was partially eluted by dichloromethane/methanol solvent and would be associated to bitumen compounds less polar than “standard” asphaltenes, is thought to be the result of the interaction between ammonium thiocyanate (from R_1) and bitumen, and is assumed to be the responsible for the enhancement in the linear viscoelastic properties of the resulting binder after modification. In addition, saturates and aromatics remain essentially unchanged (pointing out a lower chemical reactivity), whilst resins increase. In order to confirm this, two different solutions of neat bitumen in toluene were prepared. Then, thiourea or ammonium thiocyanate was added to each solution, respectively, and kept at 25ºC for 5 hours under agitation. TLC/FID analysis conducted on them demonstrated that separation of asphaltenes into two new peaks only occur when ammonium thiocyanate is added, revealing this specie (derived from R1 during processing of the binder at 180ºC), instead of thiourea itself, is the actual substance producing the new LPAs fraction.

Graphic integration of the chromatogram peaks allowed for the quantification of the different SARAs fractions. In this way, Table 1 shows the weight percentage of every fraction for the neat bitumen, its corresponding blank, and modified binders, with 3 and 9 wt.% thiourea, as a function of curing time. First of all, it can be observed that bitumen oxidation occurred during mixing causes an increase in the asphaltenes and resins fractions, whilst aromatics decrease. This transformation of aromatics into resins and these into asphaltenes is known as "bitumen primary ageing" [25]. Interestingly, both Th-modified binders show an increase in the resins concentration, which might be attributed to "standard" asphaltenes which are transformed into less polar compounds after thiourea addition and, in a much lesser extent, to non-reacted thiourea. Thus, as shown in Fig. 7, LPAs can also be eluted by the solvent used to separate the resins fraction (95/5 dichloromethane/methanol), although at lower rate than that, with the consequent formation on the silica rod of a new fraction in between resins and HPAs (5 rods on the left hand side). In contrast, LPAs fraction does not appear if the elution sequence is performed on the non-modified bitumen (5 rods on the right hand side).

On the other hand, high polarity asphaltenes are negligible if compared to low polarity asphaltenes, whose concentration seems to increase as curing time does (mainly for the highest thiourea content). However, the total content in asphaltenes (LPAs + HPAs) decreases in relation to neat bitumen or blank sample. Finally, it is noticeable, once again, that saturates and aromatics remain essentially unchanged (see Table 1)

On these grounds, changes in the modified binder colloidal nature may be quantified through a new index, defined in terms of the five fractions derived from the chromatographic method, which accounts for changes originated from bitumen reactive modification by thiourea. This "modified" colloidal index, which derived from that used elsewhere [3] and expressed in terms of the "standard" SARAs fractions, is defined as follows:

$$\text{C.I.}_{\text{mod}} = \frac{\text{saturates + LPAs + HPAs}}{\text{aromatics + resins}} \tag{3}$$

where LPAs and HPAs refer to low and high polarity asphaltenes, respectively. Table 1 displays the evolution with curing time of the "modified" colloidal index, for 3 and 9 wt.% modified binders, and "classic" colloidal index (in which LPAs + HPAs should be replaced by asphaltenes) for neat and blank bitumen. It can be noted a remarkable decrease in the colloidal index values after modification via thiourea, as saturates and aromatics nearly remain constant, resins increase, and the "asphaltene equivalent fraction" (that is, LPAs and HPAs) decreases. This would provide an explanation to the lowest values of the mechanical glass transition temperature measured (see Fig. 3 and Table 2).

In this way, modulated DSC performed on the samples also discloses changes induced in the bitumen microstructure by the addition of thiourea. Figures 8A and 8B show the non-reversing thermograms and derivate heat capacity (dC_p/dT), respectively, for neat bitumen and its corresponding 9 wt.% Th-binders at different curing times. According to Masson and co-workers [22,23] non-reversing heat flow curves for a neat bitumen presents four clearly marked thermal events: 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. Enthalpy associated to this fourth event can be ascertained by mere integration of the corresponding peaks (see Fig. 8A). Table 2 demonstrates that enthalpy values increase with increasing curing time, what suggests the development, after thiourea addition and further curing, of 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 Fig. 1). 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 [24].

Furthermore, derivative heat capacity for neat bitumen in Fig. 8B presents two well-defined peaks (with peak maximum, T_{g1} and T_{g2}, located at -30.5 and 3.0 ºC, respectively) which, according to Masson et al. [22,23], derive from two overlapped glass transitions corresponding to saturates and aromatics. T_{g2} values were also determined for the modified binders studied, and compare with neat bitumen's. Interestingly, that temperature is seen to shift to lower temperature (from 3ºC down to 0ºC) after modification with 9 wt.% thiourea and 60 days of curing time, observation which matches with the results obtained from DMTA measurements (see Table 2) and would support the enhancement in the binders low temperature properties. Note that overlapping with a new endothermic thermal event arising at -30 ºC in Th-modified binders (see Fig. 8A) does not allow T_{g1} values to be obtained.

Moreover, the second and third (exothermic) thermal events derive from a time-dependent cold-crystallization of a certain quantity of saturates which, upon cooling from the melt, were unable to adequately crystallize. Hence, above the frozen state defined by $T > T_g$, molecular mobility increases and those saturates segments order into crystalline domains [22,23,25]. Table 2, which displays second event temperatures (T_{2nd}) confirms a decrease after addition of 9 wt.% Th and 60 days of curing, as the frozen state threshold was shifted to lower temperatures.

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 Fig. 9 allow us to conclude that the new event can be attributed to ammonium thiocyanate derived from R1, and most probably arises as a consequence of a low-temperature “non-identified” reversible phase transition, similar to that observed at 90 ºC. On the other hand, three successive cycles were conducted on the 9 wt.% Th binder (60 days-cured): i) quenching from room temperature down to -60ºC and subsequent heating at 5 ºC/min up to 100 ºC; ii) quenching from 100 down to -60ºC; iii) second heating at 5 ºC/min up to 110 ºC. In contrast to the first heating cycle, prior to which the sample was annealed at room temperature, the endothermic events at -30 and 50ºC become strongly reduced in the second heating cycle, as quenching from the melt did not provide sufficient time for the structures to adequately reorganise. This outcome points out the time-dependent ordering process of bitumen mesophases and the existence of physical interactions among bitumen molecules and Th derivatives (e.g. hydrogen bonds), instead of chemical bonds [25].

4. CONCLUDING REMARKS

The enhancement in the linear viscoelastic properties of a bituminous binder via thiourea-modification was evaluated. It was found that the addition of 9 wt.% thiourea leads to notable improvements in the thermo-rheological response of this material in a wide range of temperatures.

It was proved that, at the processing temperature (180ºC), thiourea thermally decomposes into ammonium thiocyanate, which seems to bring about interactions with the most polar compounds of bitumen. This would induce, as detected by chromatography and thermal analysis, the formation of new products and structures which evolve with time.

Consequently, chemically-induced changes above were seen to significantly enhance bitumen rheological properties. In this sense, the “mechanical” glass transition temperature was reduced, which improves both flexibility and thermal cracking resistance at low temperatures. On the other hand, at high temperatures, the storage and loss moduli are noticeably increased, and consequently, a higher resistance to permanent deformation is expected.

Therefore, the results obtained seem to support the use of thiourea as a promising chemical modifier in the manufacture of modified bituminous binders with enhanced rheological properties.

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Table 1. SARAs fractions and colloidal index values for the neat bitumen and Th-modified binders studied.

			3 wt. % Th			9 wt. % Th		
	Neat	**Blank**	**Non-cured**	**20 d**	**60 d**	**Non-cured**	**20 d**	**60 d**
Saturates (wt. %)	5.1	4.9	6.9	6.3	6.8	5.8	5.8	6.3
Aromatics (wt. %)	52.6	48.6	50.3	50.7	52.1	53.5	56.6	49.9
Resins (wt. %)	23.9	27.0	38.4	37.3	35.5	32.2	28.2	33.0
Asphaltenes (wt. %)	18.4	19.5	--	--	--	--	--	--
LPAs (wt. %)	--	--	2.6	4.5	4.8	7.1	8.4	10.1
HPAs (wt. %)	--	--	1.8	1.2	0.8	1.4	1.0	0.7
Colloidal Index (C.I., C.I.$_{mod}$)	0.307	0.322	0.127	0.136	0.142	0.167	0.180	0.206

Table 2. “Mechanical” glass transition temperatures ($T_{g,DMTA}$); glass transition temperatures obtained by MDSC (T_{g1} and T_{g2}); second event temperatures (T_{2nd}); and energy associated with the endothermic fourth event (ΔH_{4th}), for selected binders studied.

		$T_{g,DMTA}$ (ºC)	**T_{g1} (ºC)**	**T_{g2} (ºC)**	**T_{2nd} (ºC)**	**ΔH_{4th} (J/g)**
Neat bitumen		-13.3	-30.5	3.0	-9.0	2.21
9 wt.% Th	Non-cured	--	--	1.6	-9.8	2.66
	20 days	--	--	0.7	-12.1	2.81
	60 days	-18.2	--	0.0	-12.8	3.35

Figure captions

Figure 1. Evolution with temperature of the dynamic shear moduli (G' & G'') for neat bitumen and 9 wt. % Th-binders at different curing times.

Figure 2. a) Frequency sweep tests in dual-cantilever mode, at different temperatures, for the 9 wt.% Th-modified binder (60 days-cured); b) Master curves of E' & E'' vs. reduced frequency for neat bitumen and 9 wt.% Th-modified binder (60 days-cured).

Figure 3. a) Evolution with temperature of the flexural viscous modulus (E'') obtained by frequency/temperature-conversion; b) Activation energy values for the different samples studied.

Figure 4. “Black” diagram for neat bitumen and 9 wt.% Th-modified binder (60 days-cured).

Figure 5. a) DTA and b) DTG curves for neat bitumen, pure thiourea and pure ammonium thiocyanate.

Figure 6. TLC/FID chromatograms for neat bitumen, pure thiourea and 9 wt.% Th-modified binder (60 days-cured).

Figure 7. Picture taken during the elution of the resins fraction with a blend of dichloromethane/methanol (95/5).

Figure 8. a) Non-reversing heat flow and b) C_p-derivate curves obtained by MDSC for neat bitumen and 9 wt.% Th-binders at different curing times.

Figure 9. Non-reversing heat flow curves for pure ammonium thiocyanate and 9 wt.% Th-binder (60 days-cured).

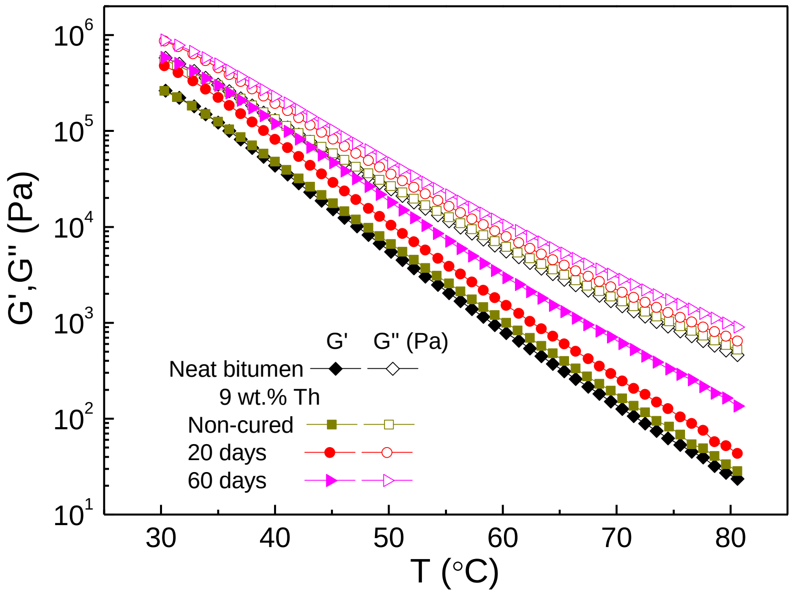
10^6
10^5
10^4
10^3
10^2
10^1
G',G'' (Pa)
30
40
50
60
70
80
T (°C)
G'
G'' (Pa)
Neat bitumen
9 wt.% Th
Non-cured
20 days
60 days

Figure 1

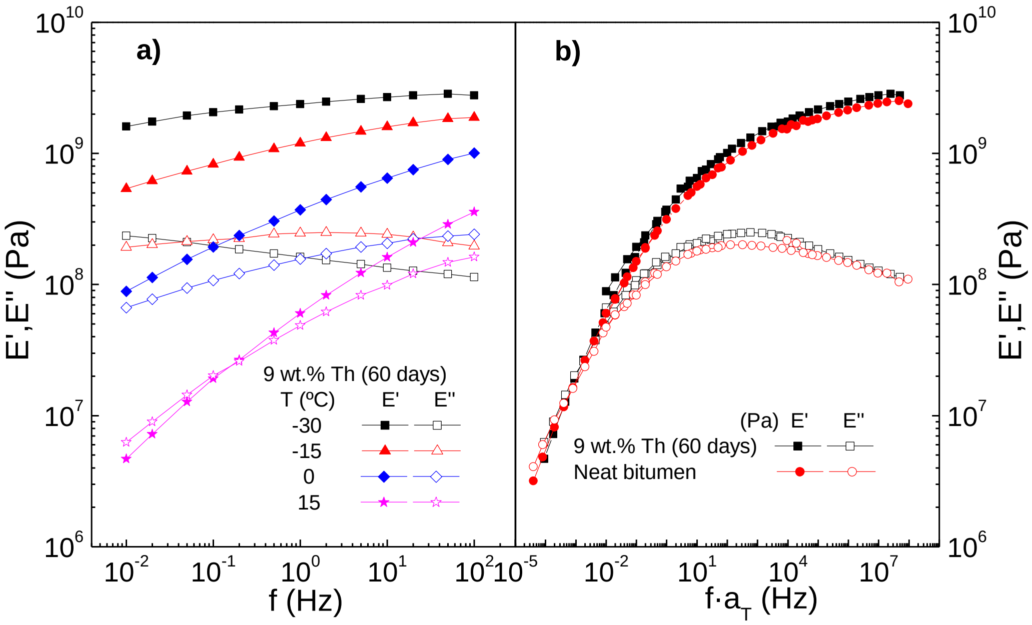
a)
b)
9 wt.% Th (60 days)
T (ºC)
E'
E''
-30
-15
0
15
(Pa)
E'
E''
9 wt.% Th (60 days)
Neat bitumen
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
E',E'' (Pa)
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
f (Hz)
10^{-5}
10^{-2}
10^{1}
10^{4}
10^{7}
$f{\cdot}a_T$ (Hz)

Figure 2

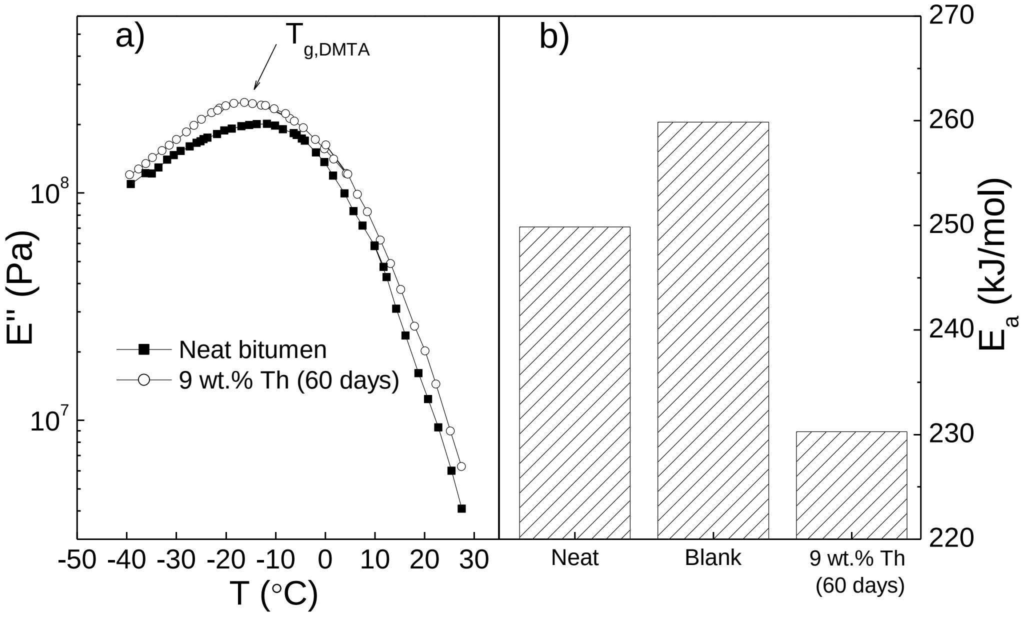
a)
$T_{g,DMTA}$
E'' (Pa)
10^8
10^7
Neat bitumen
9 wt.% Th (60 days)
-50 -40 -30 -20 -10 0 10 20 30
T (°C)
b)
Neat
Blank
9 wt.% Th (60 days)
270
260
250
240
230
220
E_a (kJ/mol)

Figure 3

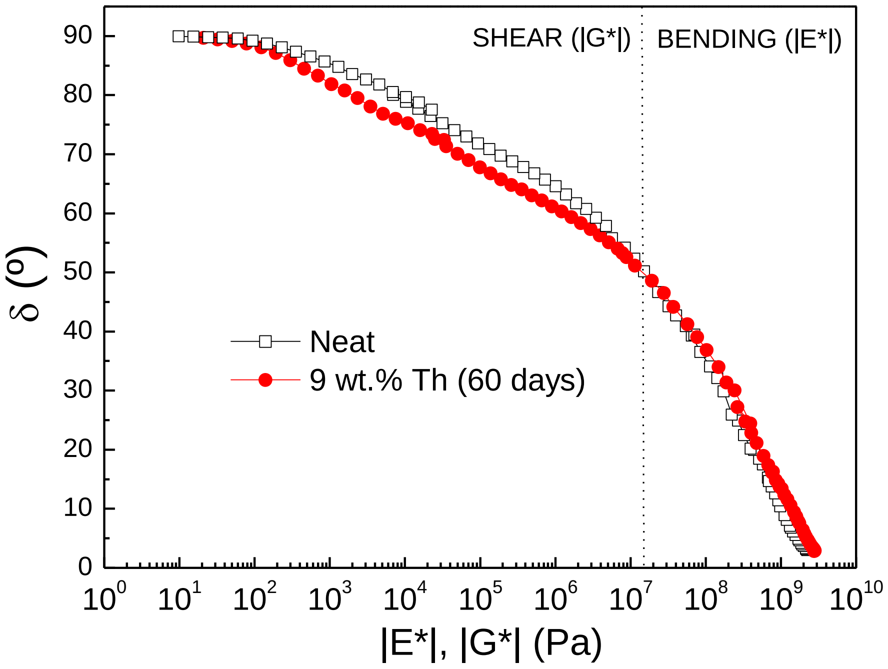
SHEAR (|G*|)
BENDING (|E*|)
Neat
9 wt.% Th (60 days)
δ (º)
|E*|, |G*| (Pa)
0
10
20
30
40
50
60
70
80
90
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}

Figure 4

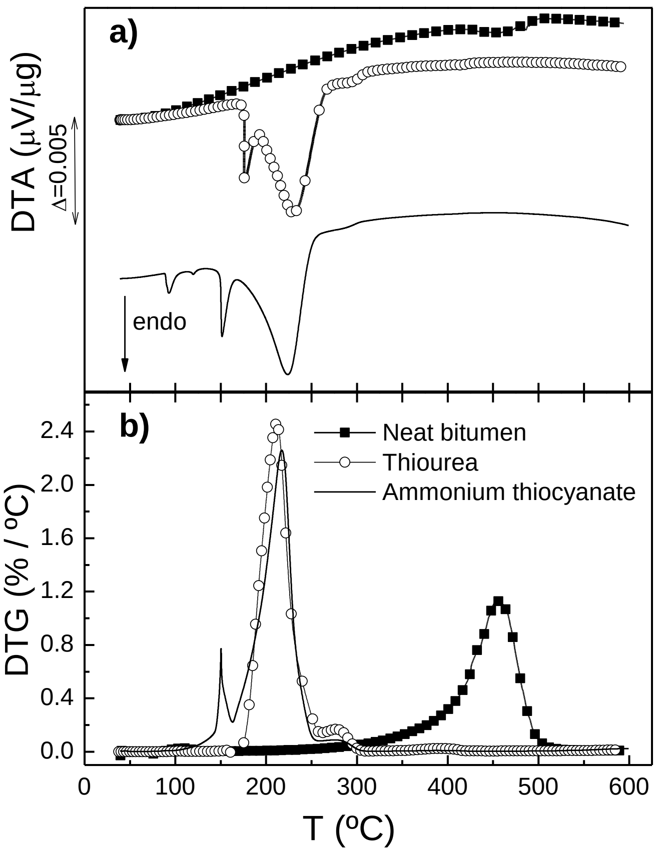
a)
DTA (μV/μg)
Δ=0.005
endo
b)
DTG (% / ºC)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
0
100
200
300
400
500
600
T (ºC)
Neat bitumen
Thiourea
Ammonium thiocyanate

Figure 5

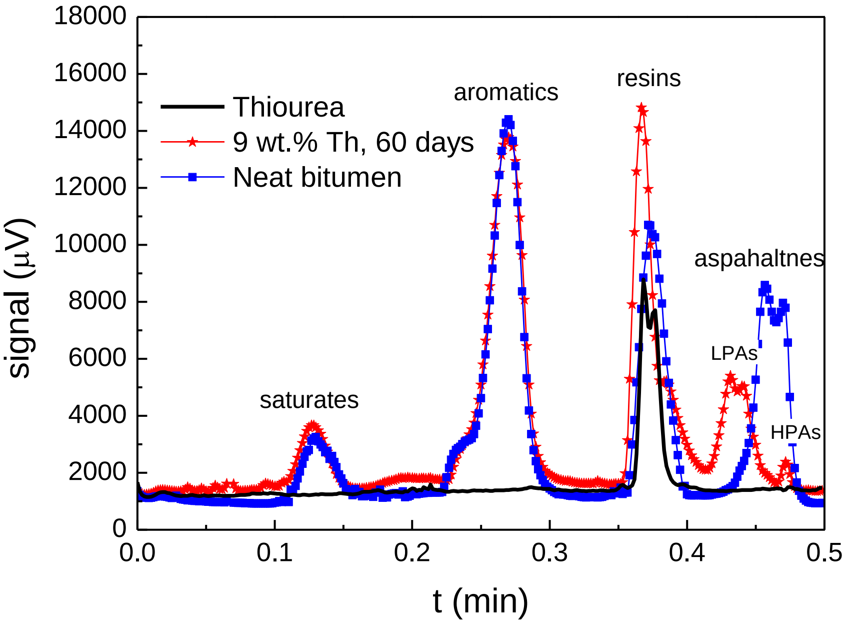
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
signal (μV)
0.0
0.1
0.2
0.3
0.4
0.5
t (min)
Thiourea
9 wt.% Th, 60 days
Neat bitumen
saturates
aromatics
resins
aspahaltnes
LPAs
HPAs

Figure 6

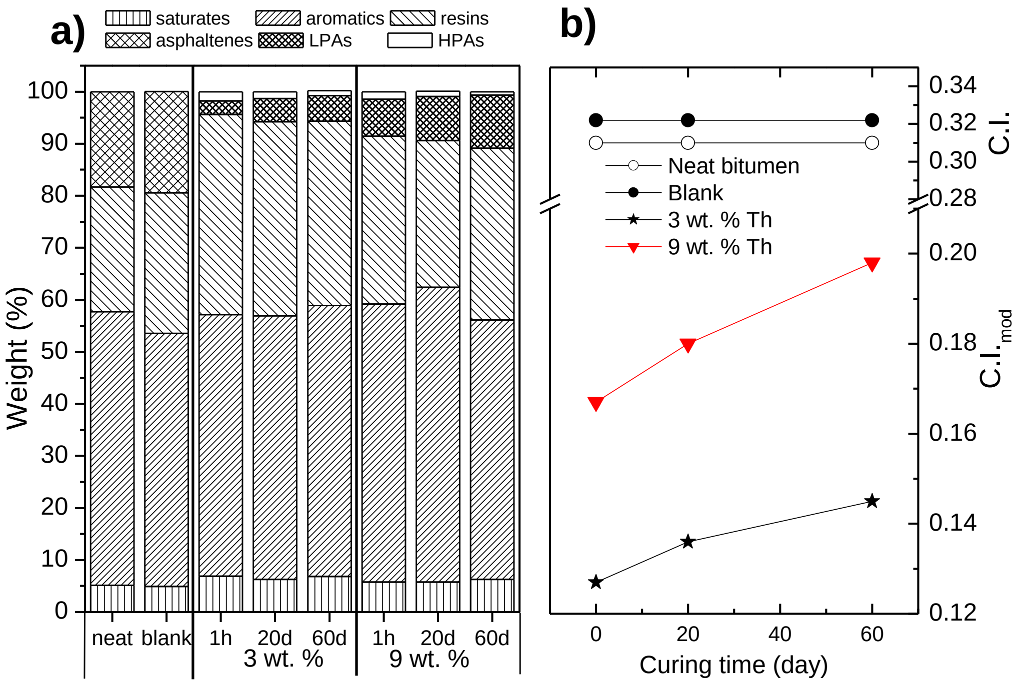
a)
saturates
aromatics
resins
asphaltenes
LPAs
HPAs
Weight (%)
0
10
20
30
40
50
60
70
80
90
100
neat
blank
1h
20d
60d
3 wt. %
1h
20d
60d
9 wt. %
b)
Neat bitumen
Blank
3 wt. % Th
9 wt. % Th
0.34
0.32
0.30
0.28
C.I.
0.20
0.18
0.16
0.14
0.12
C.I.mod
0
20
40
60
Curing time (day)

Figure 7

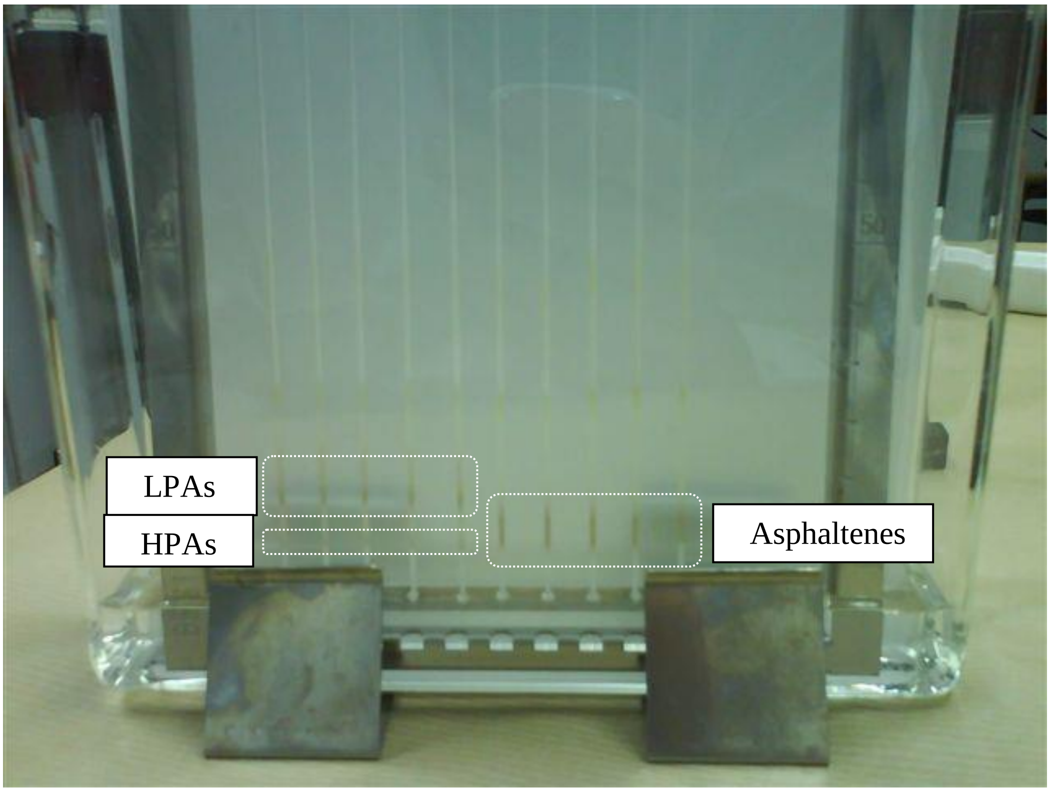

Figure 8

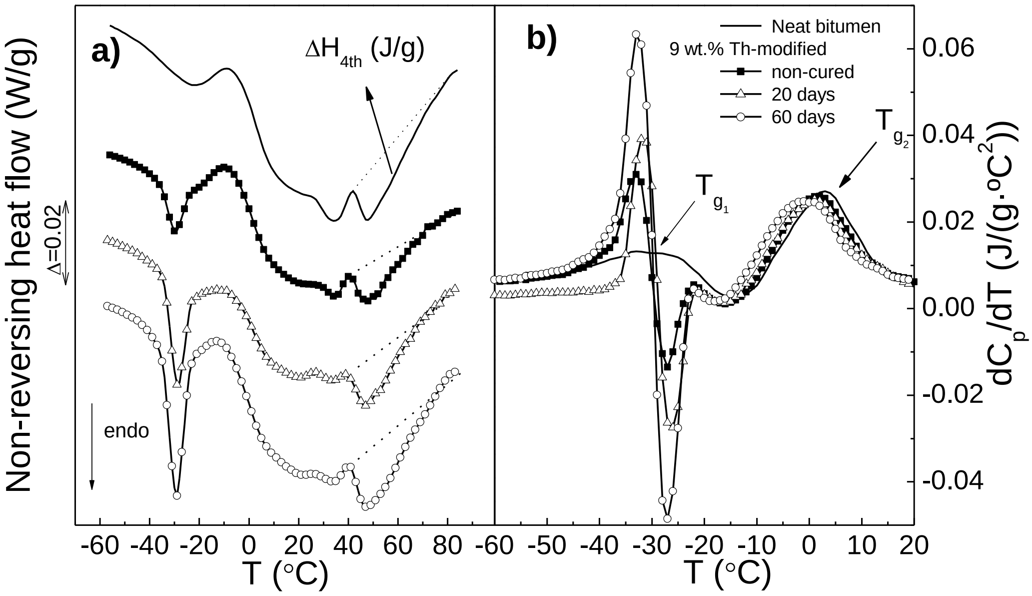
a)
ΔH4th (J/g)
Non-reversing heat flow (W/g)
Δ=0.02
endo
-60 -40 -20 0 20 40 60 80
T (°C)
b)
Neat bitumen
9 wt.% Th-modified
non-cured
20 days
60 days
Tg2
Tg1
0.06
0.04
0.02
0.00
-0.02
-0.04
dCp/dT (J/(g·°C²))
-60 -50 -40 -30 -20 -10 0 10 20
T (°C)

Figure 9

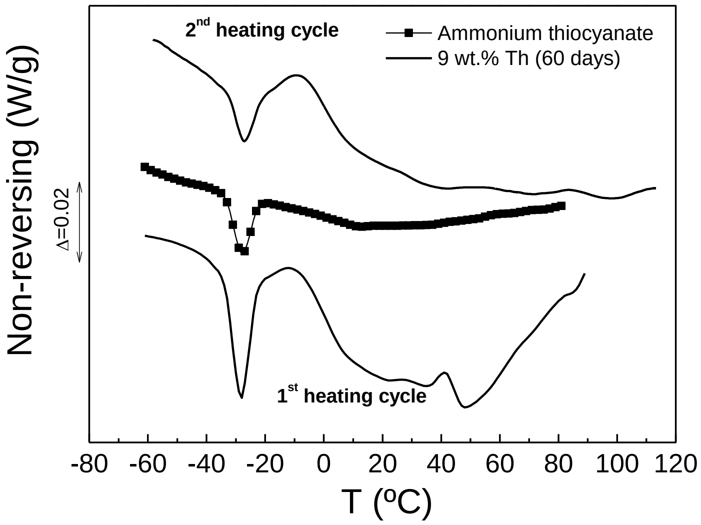
2nd heading cycle
Ammonium thiocyanate
9 wt.% Th (60 days)
1st heating cycle
Δ=0.02
Non-reversing (W/g)
-80
-60
-40
-20
0
20
40
60
80
100
120
T (ºC)

Figure 10