BITUMEN CHEMICAL MODIFICATION BY THIOUREA: RHEOLOGICAL BEHAVIOUR AT LOW IN-SERVICE TEMPERATURES AND MICROSTRUCTURE

Antonio Abad Cuadri[1], Pedro Partal[1], Francisco Javier Navarro[1], Moisés García Morales[1], Críspulo Gallegos[1], Antonio Pérez Lepe[2], Antonio Páez[2]
[1]Departamento de Ingeniería Química. Facultad de Ciencias Experimentales. Campus 'El Carmen'. Universidad de Huelva. 21071 Huelva (Spain)
[2]Technology Centre REPSOL YPF. Road N-V, Km 8, 28931, Móstoles (Spain)

ABSTRACT

As bitumen is the only deformable component in asphalt mixtures and constitutes the continuous phase, pavements performance mainly depends on this binder rheological properties. However, when these are not good enough, some road distresses may arise at both high and low in-service temperatures (namely, permanent deformation and thermal cracking, respectively) as a consequence of the combined action of traffic loads and weathering. In order to mitigate their effects, improved modified binders have been developed by the paving industry over the last decades. As an alternative to classic bitumen modification with polymers, we propose the use of thiourea which, at a concentration of 9 wt.%, has proved to efficiently enhance the binder resistance to thermal cracking at low in-service temperatures. Thus, glass transition temperature, determined by dynamic flexural tests was significantly seen to decrease. As a result, modification by thiourea would result in an economical and sustainable paving practice, which may lead to prolong asphalt pavements life-time in harshly cold weather. In addition, this research emphasizes the use of the Time-Temperature-Superposition (T-T-S) principle to study the evolution with temperature of the linear viscoelasticity functions (E', E'') through master curves obtained from frequency sweep tests at selected temperatures. This approach leads to glass transition temperature values which do not depend on the selected heating rate, in contrast to those derived from isochronal temperature sweep tests.

Keywords: Bitumen, thiourea, rheology, low temperature, 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]. Regarding 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].

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 [3] to waterproof membranes for the roofing industry [4]. 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 [5]. 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 the lack of flexibility) [6,7]. 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.) [8].

As an alternative to the above modifying agents, this work evaluates a novel bitumen modification through the use of a chemical agent: thiourea. It has shown to induce benefits on the binder properties, by enhancing its rheological properties at low in-service temperatures. As a result, modification by thiourea would result in an economical and sustainable paving practice, which may lead to asphalt pavements with prolonged life-time, as it increases resistance to thermal cracking under loading in harshly cold climates.

2. EXPERIMENTAL

2.1 Materials

Bitumen with a penetration grade of 40/50 has been used as base material for the modification. Results of technological tests (penetration grade and R&B softening temperature, according to ASTM D5 and D36, respectively) and chemical composition, in terms of "SARAs" fractions, are shown in Table 1. Thiourea (Th) is the selected chemical agent used for bitumen modification. It melts at around 175-179 ºC, and has a molecular weight of 76.12 g/mol.

Table 1. Penetration, Ring & Ball softening temperature, "SARAs" fractions and colloidal index for the neat bitumen studied.

	Neat bitumen
Penetration (dmm)	47
R&B soft. point (ºC)	52.5
Saturates (wt.%)	5.1
Aromatics (wt.%)	52.6
Resins (wt.%)	23.9
Asphaltenes (wt.%)	18.4
Colloidal Index (C.I.)	0.31

2.2 Modified bitumen processing

A blend of bitumen with 9 wt.% Th was prepared for 1 h, at 180ºC, in a cylindrical vessel (60 mm diameter, 140 mm height). A low-shear mixer IKA-RW20 (Germany), equipped with a four-blade impeller, was used at a rotating speed of 1200 rpm. Just after processing this binder was poured onto aluminium foil, forming a thin layer which was exposed to ambient conditions for 60 days before being tested. Interestingly, this storage ("curing") period has shown to produce a significant enhancement in the binder performance. Additionally, a reference bituminous binder containing 3 wt.% commercial SBS Kraton D-1101 was prepared (same processing set-up, for 2 h, at 180 ºC and 1200 rpm).

2.3 Tests and measurements

Dynamic Mechanical Thermal Analysis (DMTA) tests were performed on 50 mm × 10 mm × 3 mm specimens of both neat and modified bitumens, with a Seiko DMS 6100 (Seiko Instruments Inc., Japan) in double cantilever (bending) mode. Liquid nitrogen was used as cooling system. Frequency sweep tests, from 10^{-2} to 10^{2} Hz, were carried out in the linear viscoelasticity region (LVR), at five different temperatures (-40, -30, -15, 0 and 15 ºC).
Simultaneous DTG/DTA measurements, using a Seiko TG/DTA6200, were carried out on 5-10 mg samples of Th, neat bitumen and Th-modified bitumen, under inert atmosphere. A T-ramp at the rate of 10 ºC/min between 40 and 600 ºC was applied.
All tests were carried out at least twice, in order to ensure the repeatability of the results.

3. RESULTS AND DISCUSSION

3.1 Rheological behaviour at low in-service temperatures

The rheological behaviour at low in-service temperatures of a selected Th-modified binder, containing 9 wt.% Th and cured for 60 days, has been evaluated in this study. For the sake of comparison, neat bitumen and the reference sample (3 wt. % SBS) results have also been included. Figure 1 shows the results of isothermal frequency sweep tests, performed in bending mode on the SBS reference sample, at 5 different temperatures between -40 and 15 ºC. Curves of the dynamic flexural moduli vs. frequency reveal prevailing elastic features, with values of E' higher than E'' at those tested temperatures below 15ºC.

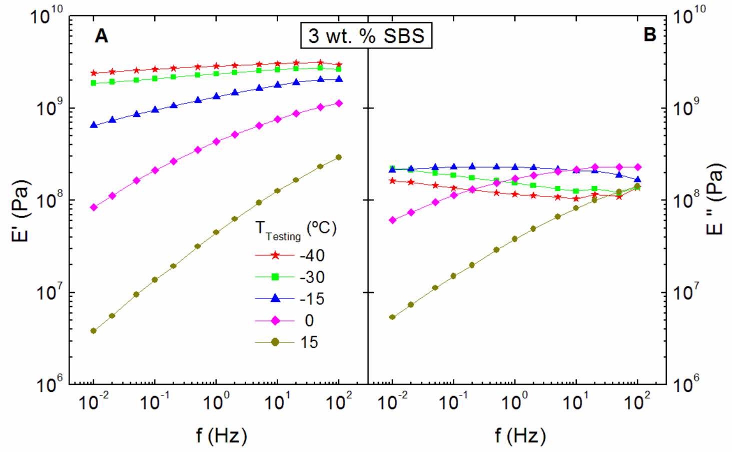

Figure 1: Evolution of the elastic (E') and viscous (E'') moduli with frequency in dynamic bending as a function of temperature, for the SBS reference sample.

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

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

The corresponding fitting of a_T to the above equation is shown in the inset of Figure 2B. 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 frequency sweep tests by following the procedure described by Martinez-Boza et al. [9], and the result for the SBS reference sample is shown in Figure 2B.

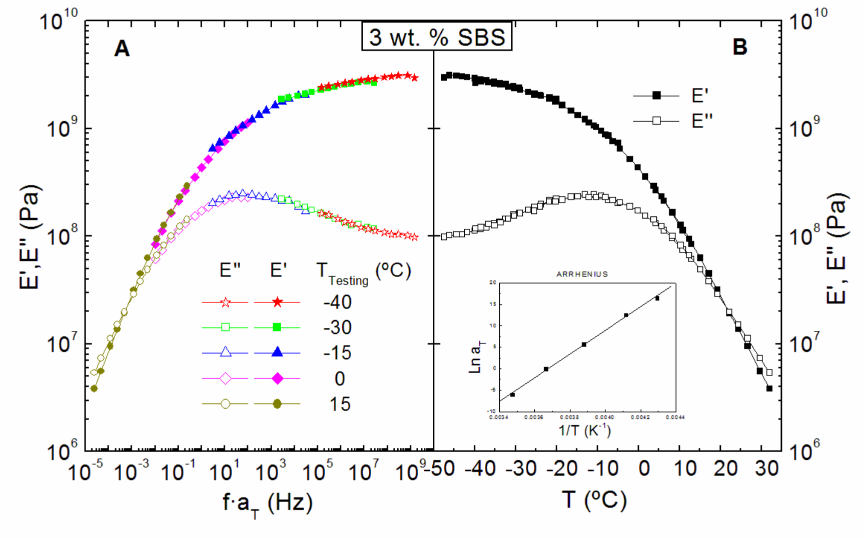

Figure 2: A) Empirical master-curve of the dynamic bending storage and loss moduli vs. reduced frequency for SBS sample. B) Evolution of E' and E'' with temperature, obtained by conversion of frequency sweep tests; Inset: T-dependence of a_T and fitting to equation (1)

Figure 2B demonstrates the classical rheological behaviour found in both unmodified and modified binders [10, 11]. As temperature increases, a clear transition from the glassy to the Newtonian region (with a crossover point between E' and E'') can be observed. No plateau is found at intermediate temperatures, which indicates the non-existence of entanglements [12].

Same procedure has been followed with the remaining samples, neat bitumen and 9 wt.% Th-modified bitumen. 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 ($T_{g,DMTA}$), taken as the value of temperature at the maximum in E'' curve, 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 T-T-S 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, 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.

Table 2. "Mechanical" glass transition temperatures ($T_{g,DMTA}$) for neat bitumen, SBS reference binder and 9 wt.% Th-modified binder (60-days-cured).

	$T_{g,DMTA}$ (ºC)
Neat bitumen	-13.3
3 wt.% SBS	-15.4
9 wt.% Th	-18.2

As can be observed, if compared to the base bitumen, modification with SBS brings about an improvement in the binder behaviour at low in–service temperature (a decrease of 2 ºC in T_g). Further, the chemical modification carried out by thiourea indicates a more remarkable enhancement in performance at low in-service temperatures. In this sense, the value of $T_{g,DMTA}$ is reduced about 5 ºC after Th addition after 60 days of curing, if compared to the corresponding neat bitumen.

3.2 Chemical modification and microstructure

The above enhancement in the Th-binder viscoelastic behaviour at low in-service temperatures suggests changes in its microstructure, as a consequence of "uncertain" chemical reactions between thiourea and some bitumen fractions. Thermal analysis (TG/DTG/DTA) may shed some light on this issue.

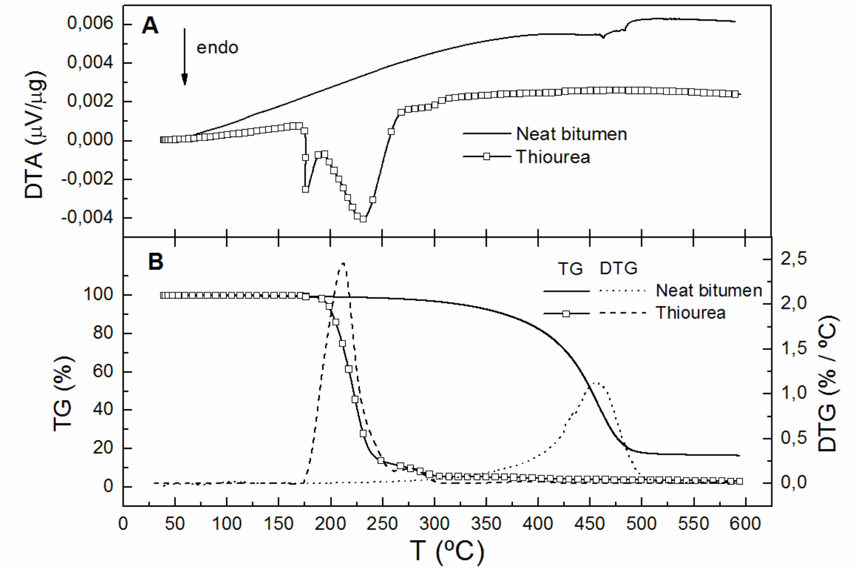

Figure 3: TG, DTG, and DTA curves for neat bitumen and thiourea.

Thermal decomposition of neat bitumen and thiourea is shown in Figure 3. Neat bitumen presents a large mass loss process which extends over a wide temperature interval (from 300 to 500 ºC, with DTG maximum peak at 455ºC). This behaviour involves the decomposition/volatilization of chemical compounds with very different molecular weights. On the other hand, 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, involving no mass loss [13]. Thus, the isomeric reaction R_1, with the production of NH_4SCN (ammonium thiocyanate), is suggested to take place during the first endothermic process:

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

In contrast to that, the second stage involves thiourea decomposition (between 190 and 270 ºC, with DTA minimum peak at 228 ºC). Hence, thiourea thermal decomposition (into CS_2, HNCS and NH_3) is not expected to occur at the temperature at which mixing of bitumen and thiourea was carried out (180 ºC).

Consequently, we will assume that bitumen modification and the resulting improvement in the binder mechanical behaviour at low in-services temperatures is due to NH_4SCN arisen from R_1, and new compounds derived from its interaction with bitumen.

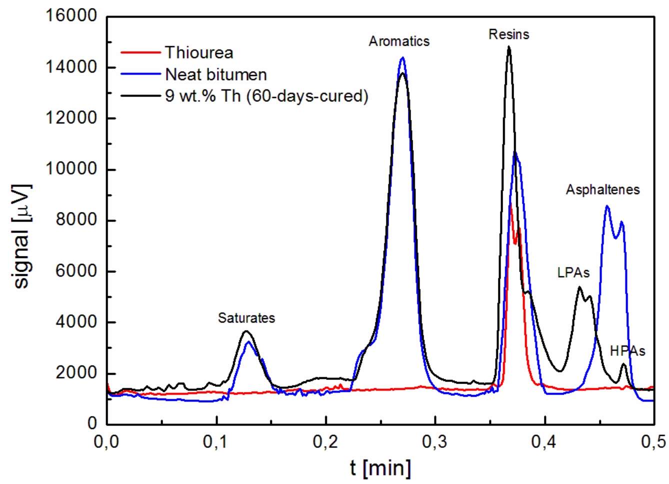

Figure 4: TLC-FID chromatograms corresponding to neat bitumen, pure thiourea and the 9 wt.% Th-modified binder (60-days-cured).

Figure 4 shows chromatograms, obtained by TLC-FID, for neat bitumen, pure thiourea and the Th-modified binder studied. On the one hand, thiourea presents a single signal (located at the bitumen resins peak position). On the other hand, four peaks (which account for the so-called “SARAs” fractions) corresponding to saturates, aromatics, resins and asphaltenes, respectively, are shown by neat bitumen. Instead, for the Th-binders, asphaltenes peak splits into two new peaks, referred to as low and high polar asphaltenes, LPAs and HPAs, respectively. Thus, the largest of them (LPAs), which 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 decrease in the “mechanical” glass transition temperature. In addition, saturates and aromatics remain essentially unchanged (pointing out a lower chemical reactivity), whilst resins increase, in part due to non-reacted thiourea.

4. CONCLUDING REMARKS

The effect of thiourea addition on the low temperature mechanical properties of bitumen has been evaluated. It was found that 9 wt.% thiourea may notably decrease in its “mechanical” glass transition temperature, which would lead to improved flexibility and thermal cracking resistance.

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 the formation of new products and structures which significantly enhance bitumen rheological properties at low temperatures.

Therefore, the results obtained seem to support the use of thiourea as a promising chemical modifier in the manufacture of modified bituminous binders with improved performance at low temperatures.

REFERENCES

[1] Characterization of paving asphalts by Differential Scanning Calorimetry. Claudy, P.; Letoffe, J.F.; King, G.N.; Brule, B.; Planche, J.P. *Fuel Sci. Techn. Int.* 1991, 9, 71-92.

[2] A structure-related model to describe asphalt linear viscoelasticity. Lesueur, D.; Gerard, J.F.; Claudy, P.; Letoffe, J.F.; Planche, J.P.; Martin,D. *J.Rheol.* 1996, 40, 813-836.

[3] The Shell Bitumen Handbook. Whiteaoak, D. Shell Bitumen U.K.: Surrey, 1990.

[4] Blends of bitumen with polyethylenes. Fawcett, A.H.; McNally, T.; McNally, G.M.; Andrews, F.; Clarke, J. *Polymer* 1999, 40, 6337-6349.

[5] Viscoelastic properties and morphological characteristics of polymer-modified

bitumen blend. Vasiljevic-Shikaleska, A.; Popovska-Pavloska, F.; Cimmino, S.; Duraccio, D.; Silvestre, C. *J. Apply. Polym. Sci.*, 2010,118, 1320-1330.

[6] Influence of polymer modification on low temperature behaviour of bituminous binders and mixtures. Lu, X.; Isacsson, J.; Ekblad, J. *Mater. Struct*., 2003, 36, 652-656.

[7] Kandhal, P.S.; Cooley, L.A. Transport Res. Board, National Cooperative Highway Research, Program Report 2003, 508.

[8] Effect of waste polymer addition on the rheology of modified bitumen. García-Morales, M.; Partal, P.; Navarro, F.J.; Gallegos, C. *Fuel*, 2006, 83, 31-38.

[9] Influence of temperature and composition in the linear viscoelastic properties of synthetic binders. Martínez-Boza, F.; Partal, P.; Conde, B.; Gallegos, C. *Energ. Fuel* 2000, 14, 131-137.

[10] Viscous properties and microstructure of recycled EVA modified bitumen. García-Morales, M.; Partal, P.; Navarro, F.J.; Martinez-Boza, F.; Gallegos, C.; González, N.; González, O.; Muñoz, M.E. *Fuel*, 2004, 83, 31-38.

[11] Bitumen chemical modification by thiourea dioxide. Cuadri, A.A.; Partal, P.; Navarro, F.J.; García-Morales, M.; Gallegos, C. *Fuel*, 2011, 90,2294-2300.

[12] Viscoelastic properties of polymers. Ferry, J.D. New York: John Wiley and Sons.1980.

[13] Thermodynamic analysis of decomposition of thiourea and thiourea oxides. Wang, S.; Gao, Q.; Wang, J. *J. Phys. Chem.*, 2005**,** 109, 17281-17289.