THERMAL BEHAVIOUR OF BITUMEN MODIFIED BY SULPHUR ADDITION

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ABSTRACT

The most frequent use of bitumen is as binder for pavement applications. The effect of sulphur addition on the properties of the bitumen has been extensively studied several decades ago. Recently, there is a renewed interest in researching the behaviour of sulphur-bitumen combination, because off 1.The future availability of bitumen may be limited and 2. The beneficial consumption of great amounts of sulphur compounds from petroleum refining is advisable. The addition of sulphur to bitumen provokes the beginning of chemical reactions depending on the sulphur content and heating temperature. At heating temperatures T< 140 ºC liquid sulphur reacts with naphthenic-aromatic fraction forming polysulphides. At temperatures above 150 ºC dehydrogenization reactions with emission of hydrogen sulfide take place and naphthenic-aromatic molecules are transformed into asphaltenes. Therefore, the addition of sulphur to bitumen provokes changes in the chemical structure of the bitumen. The objective of this work is to analyze, the thermal behaviour of sulphur-bitumen mixtures of different composition (0-35 %wt sulphur content) prepared at 130 and 140 ºC, by means of differential scanning calorimetry (DSC). Besides, the volatile emissions of the mixtures at high temperature have been estimated from loss weight measurements as a function of stored time.

Keywords: Bitumen modified, sulphur, thermal behaviour

1. INTRODUCTION

The study of the behaviour of sulphur–bitumen mixtures goes back several decades. Between 1980 and 1990 a number of projects were carried out in EEUU in order to evaluate the performances of sulphur modified bitumen (1, 2). Until now sulphur modified bitumen has not found a wide application range owing to the hydrogen sulphide evolution provoked by the reaction between bitumen and sulphur at high temperatures (above 140-150 ºC) (3-7) which makes the production and laying processes difficult.

Sulphur in solid state crystallizes in orthorhombic crystals which are stables up to 105 ºC, at this temperature the orthorhombic structures change to monoclinic crystals. Above 120ºC sulphur melts and leads to ring molecules composed by eight atoms. At temperatures above 130ºC the ring molecules suffer a partial decomposition and polymerize into long diradical chains.

When sulphur is blended with bitumen at high temperature these sulphur radicals react with some components of bitumen provoking two competitive reactions. These radicals may either extract hydrogen from hydrocarbon molecules with subsequent hydrogen sulphide formation by means of dehydrogenation reactions, or can be incorporated to bitumen structure as carbon-sulphur bonds by means of addition reactions. Which of these two reactions is predominant depend on temperature, sulphur content and heating rate (8). Generally, the dehydrogenation reactions predominate at high temperatures above 150ºC (5).

There are also other possibilities to find sulphur in sulphur – bitumen blends. Sulphur is readily solved in bitumen, especially in its aromatic components, been possible to reach solved sulphur concentrations up to 20 wt% (9, 10). When bitumen + sulphur mixture is cooled to room temperature a slowly recrystallization of dissolved sulphur can be observed. Therefore, the rest of sulphur that it is not dissolved in bitumen and does not take part in reactions exist in bitumen + sulphur blends as crystalline state.

In spite of the complexity presented by sulphur modified bitumen, nowadays there is a growing interest in studying its behaviour because of the need of reusing the great amounts of sulphur element produced as a consequence of petroleum refining, together with the need of improving the future availability of bitumen.

Sulphur modified bitumens exhibit changes in the properties when are compared to neat bitumen. It has been previously reported that sulphur modification decreases penetration and increases the viscosity and the softening point (3, 7, 11) when mixtures are stored several days at high temperature after preparation. Although it seems obvious that the changes observed are due to structural modifications in the bitumen, arising from the reactivity of sulphur and bitumen and also to the presence of dissolved and crystallized sulphur, there is still no single interpretation of the experimental behaviour observed in these mixtures.

The aim of this paper is double. To evaluate the emission of volatile substances such as hydrogen sulphide from bitumen + sulphur mixtures stored at high temperature, which is one of the main problems that arise in the implementation of such mixtures at industrial level and to investigate the changes in the thermal behaviour of neat bitumen produced by the presence of sulphur under experimental conditions similar to those used in the processing of the bitumen binders. The results obtained in this paper provide additional information to that existing in the literature on the structural modification of bitumen due to the presence of sulphur.

The thermal behaviour has been investigated by differential scanning calorimetry (DSC). This technique allows the determination of useful thermal properties by rapid and simple experimentation, and for this reason it has been widely used in the study of thermal behaviour for neat bitumen (12-15). DSC provides parameters such as glass transition temperature (T_g), melting temperature, T_m, and enthalpy of melting (ΔH_m) which supply a better understanding of phase morphology of bitumen + sulphur blends. The blends have been prepared with different amount of sulphur (0-35 wt% over the bitumen mass). The analysis of the variation of the T_g´s from blends as a function of the sulphur content, storage temperature (130 – 140 ºC) and storage time, will give information about the percentage of sulphur which is miscible with bitumen. In the same way it will be analyzed the presence of endothermal transitions, in the temperature range 100 - 130 ºC, corresponding to melting process attributed to the existence of crystalline sulphur in the blends. Besides, in order to evaluate the percentage of sulphur which is evolved as volatile fraction, loss weight measurements, at 130 and 140 ºC, as a function of storage time have been carried out.

2. EXPERIMENTAL

2.1 Materials

The bitumen and the sulphur used in the experimental work were kindly supplied by Repsol. The bitumen from Maya crude oils having the following specifications: penetration, 40 dmm, 25ºC (UNE-EN 1426); ring and ball softening point, 53 ºC (UNE-EN 1427); viscosity at 135 ºC (UNE-EN 12595:2007), 672 cP.

2.2 Sample preparation

Depending on the experiments two types of samples, with different amounts of bitumen have been prepared. For loss weight experiments the amount of bitumen used in sample preparation was 10 g and sulphur in powder was mixed with liquid bitumen under moderate stirring (200 rpm) using a magnetic stirrer. For DSC experiments the amount of bitumen used in sample preparation was 140 g and sulphur in powder was mixed with liquid bitumen under vigorous stirring (3200 rpm) using a Silverson shear stirrer. For loss weight experiments two mixing temperatures were selected 130 and 140 ºC, for DSC measurements the mixing temperature was always 130ºC. In both kinds of experiments, various percentages of sulphur ranging from 5 to 35 wt%, over the bitumen mass, were added to bitumen and, in order to obtain a good dispersion of sulphur in bitumen, the mixing time selected was 90 minutes. After mixing process the obtained blends were moved to an oven under nitrogen atmosphere for avoiding oxidation process. The storage temperature was always the same that the corresponding one to the mixing process. All the samples were measured by DSC in a period of time comprises between 24 and 48 h after their preparation.

2.3 Differential scanning calorimetry (DSC)

A Mettler Toledo mod. 82e Differential Scanning Calorimeter was used to determine the glass transition temperature, T_g, melting temperature, $T_{m,}$ and enthalpy of melting, ΔH_m of bitumen – sulphur blends. The instrument was calibrated with n-octane, indium and zinc and the measurements were conducted under nitrogen atmosphere. In all the cases pans of aluminium of 40 μl, were used and the weight of the samples was kept in the range 7 – 14 mg. The heating scans were recorded from -70 ºC to 150 ºC at a heating rate of 20 degrees min^{-1}. T_g was obtained from the inflection point of the curves corresponding to the first scan.

2.4 Gravimetric measurements

The loss weight measurements were realized with a Mettler AE200 balance with an accuracy of $\pm 1\ 10^{-4}$ g.

3. RESULTS AN DISCUSSION

3.1 Loss weight measurements

Figure 1 shows the loss weight of the samples expressed as: $\Delta m = m_t - m_0$, where m_t represents the mass of the bitumen + sulphur blend at storage time, t, and m_0 represents initial mass of the sample. Comparing the values of Δm obtained at the same storage time, it can be appreciated that the temperature is an important factor in the volatile emissions of bitumen – sulphur blends, given that the more high temperature is , the more volatile emissions is observed. The same conclusion can be obtained if it is compared the volatile emissions as a function of sulphur concentration, at constant temperature.

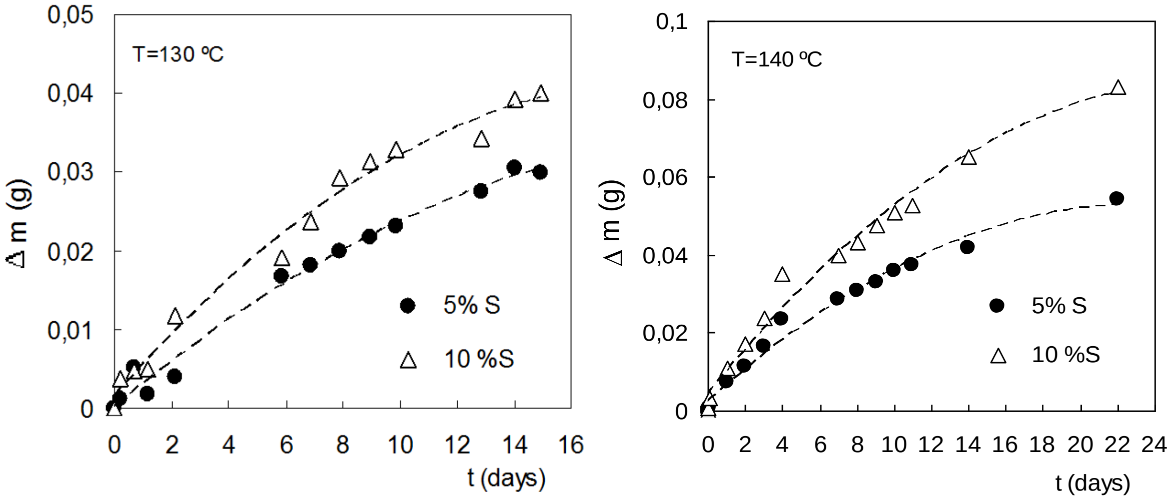

Figure 1: Loss weight, Δm, for bitumen + sulphur blends as a function of the storage time, t.

A more detailed observation of Figure 1 allows appreciating that, in any case, the slope of the curves is higher in the interval of time corresponding to the first week of the experiments, which means that the volatile emissions are more significant at the beginning. Table 1 shows the values of the slope calculated from the fitting curves.

Bibliographical results (3-7) allow confirming that the volatile emission observed in bitumen – sulphur blends are related mainly with the hydrogen sulphide evolution provoked by the reaction between bitumen and sulphur at high temperatures. However, at these temperatures, it is necessary to consider also, the evaporation of the non- reactive liquid sulphur phase that remain mixed with the bitumen. Actually in the experiment, it was detected the appearance of a yellow solid placed in the window of the oven, where the samples were stored at high temperature. The analysis of this solid phase by DSC allows confirming that it was crystalline sulphur.

Supposing that all of volatile emissions came from the sulphur, and taking as reference the loss weight data showed in Figure 1 it is possible to obtain the percentage of sulphur evolved by the blends at t= 15 days for T=130 ºC and at t=22 days for T=140 ºC. Table 2 shows the obtained results.

Table 1: Slope values of fitting curves for experimental data showed in Figure 1.

	Slope value (g.day^{-1}), T=130 ºC		**Slope value (g.day^{-1}), T=140 ºC**	
Sulphur (wt%)	**1-7 days**	**8-15 days**	**1-7 days**	**8-22 days**
5	$2{,}6\ 10^{-3}$	$1{,}5\ 10^{-3}$	$3{,}3\ 10^{-3}$	$1{,}6\ 10^{-3}$
10	$3{,}1\ 10^{-3}$	$1{,}4\ 10^{-3}$	$6{,}0\ 10^{-3}$	$2{,}8\ 10^{-3}$

Table 2 Percentage of evolved sulphur by bitumen – sulphur blends stored at T=130 ºC and T= 140 ºC

	Bitumen + sulphur (5 wt%)	**Bitumen + sulphur (10 wt%)**
T (ºC)	**Sulphur evolved* (wt%)**	**Sulphur evolved* (wt%)**
130	3,3	3,6
140	10,9	9,3

*The percentage of sulphur has been calculated over the initial amount of sulphur in the blends

Data in Table 2 shows that the percentage of sulphur evolved by the blends depends significantly of the storage temperature, being possible to appreciate a considerable increase from T=130 ºC to T=140ºC. Consequently during preparation, handling and storage of sulphur + bitumen mixtures, temperature should be stable and as close as possible to T = 130 ° C, in order to minimize the health hazards. In order to avoid as much as possible the H_2S production, the study of the blends by DSC technique has been carried out using blends prepared and stored at T=130 ºC.

3.1 DSC measurements

Figure 2 show the DSC curves for the first and the second scan of neat sulphur. The first scan (Figure 2A) displays the endothermal peaks corresponding to the alloptropic forms of sulphur; the endothermal peak placed at T=104.5 ºC is related to the transition: orthorhombic sulphur (S_α)→monoclinic sulphur (S_β) ($\Delta H_{S\alpha\rightarrow S\beta}$=10.9 Jg^{-1}), and at T=119.9 ºC the fusion of S_β is observed (ΔH_m=46.2 Jg^{-1}). After fast cooling from T>120 ºC, second scan (Figure 2B) allows appreciating the glass transition temperature of sulphur (T_g=-40ºC), at low temperature region.

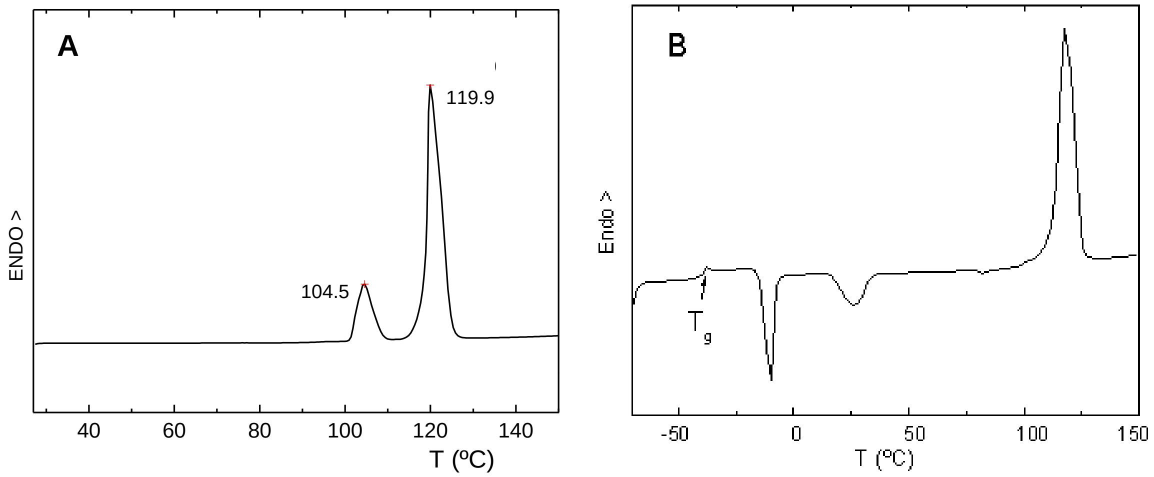

Figure 2 DSC curves for sulphur. A) first scan; B) second scan

Figure 3 shows the DSC curves corresponding to neat bitumen together with DSC curves for the blends: bitumen + sulphur (5 wt%) (see Figure 3A) and bitumen + sulphur (10 wt%) (see Figure 3B). The DSC curves for bitumen + sulphur blends have been obtained from blends stored at T=130 ºC during the period of time shown in the Figure.

The DSC curve for neat bitumen shows an abrupt change in the slope of the curve placed in the low temperature region corresponding to the glass transition temperature, T_g, of the bitumen; at temperature above T_g, a broad endothermal peak from 10 ºC to 110 ºC is observed. Paraffins are known to produce an endothermal peak in this region (12-15) and the percentage of crystallinity, X, can be calculated from the area under the peak and taken 180 Jg^{-1} as reference value for melting fusion of linear n-alkanes (13). Table 3 shows the thermal parameters, T_g, enthalpy of fusion, ΔH_m and the percentage of crystallinity, X (%) for neat bitumen and their blends obtained from Figure 3.

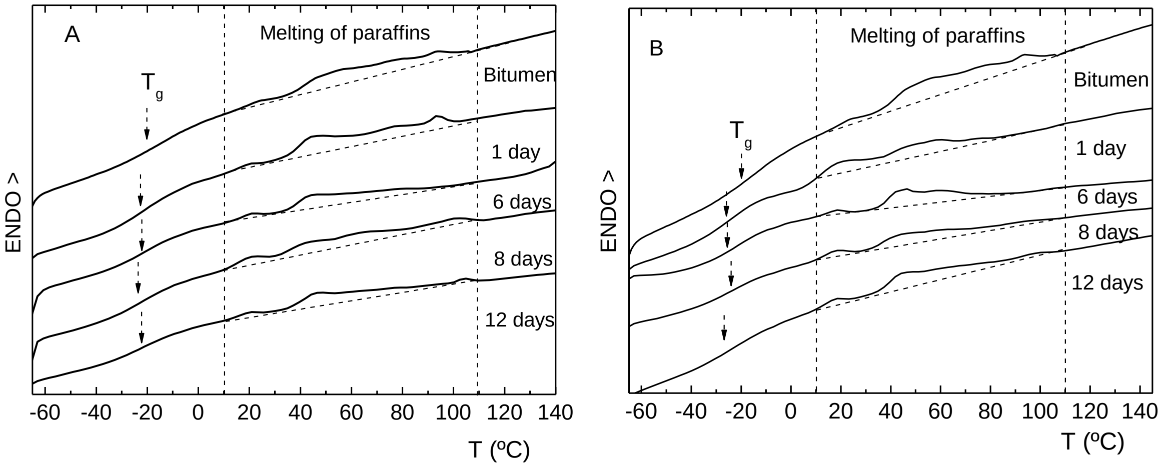

Figure 3: DSC curves for bitumen + sulphur blends stored at T=130 ºC for various periods of time: A) S (5 wt%) and B) S(10 wt%)

As it can be seen the T_g values obtained for blends containing 5 wt% of sulphur are slightly lower than those obtained for neat bitumen. This behaviour is more evident for blends containing 10 wt% of sulphur, therefore the increase in sulphur content in the blends provokes a decrease in the T_g values of bitumen + sulphur blends, that can be attributed to a certain level of miscibility between sulphur and bitumen. However it does not exist apparent relation between the T_g values and the stored time at high temperature.

Table 3: Thermal parameters, T_g, ΔH_m and crystallinity, obtained by DSC for bitumen + sulphur blends stored at 130 ºC

Bitumen	**T_g (ºC)**		**ΔH_m (J g $^{-1}$)**		**X (%)**	
	-20		8,5		4,7	
	Bitumen + sulphur (5 wt%)			**Bitumen + sulphur (10 wt%)**		
Stored time (days)	**T_g (ºC)**	**ΔH_m (J g $^{-1}$)**	**X (%)**	**T_g (ºC)**	**ΔH_m (J g $^{-1}$)**	**X (%)**
1	-23	8.0	4,7	-26	9.0	5,3
6	-22	10.0	5,8	-25	6.5	3,8
8	-23	8.5	5,0	-24	10.0	5,8
10	-23	8.0	4,7	-26	11.0	6,4
12	-21	10.0	5.8	-27	11.0	6,4

From T_g values obtained for the blends and using Fox equation it is possible to estimate the amount of sulphur miscible with the bitumen:

$$\frac{1}{T_g}=\frac{w_{bitumen}}{T_{g\ bitumen}}+\frac{w_{sulphur}}{T_{g\ sulphur}} \qquad (1)$$

where *w* refers to the weight fraction of each component in the blend and T_g represents the T_g value obtained for each blend composition.

From T_g values for bitumen + sulphur blends in Table 3 and taking $T_{g,bitumen}$= 253 K and $T_{g,sulphur}$ = 233 K the amount of sulphur miscible with bitumen estimated by Fox equation was: $w_{sulphur} \approx$ 11wt% for blends containing 5 wt% of sulphur, and $w_{sulphur} \approx$ 26 wt% for blends containing 10 wt% of sulphur. These results indicate that the decrease in T_g observed in bitumen + sulphur blends must be attributed to several effects and not only to the miscibility between sulphur and bitumen. It is known (7) that the reaction between sulphur and bitumen at T>150 ºC involves changes in molecular composition of bitumen due to the formation of polysulfides that undergo partial decomposition when sulphur modified bitumen is maintained at high temperature. These structural changes together with the partial miscibility of non-reactive sulphur in bitumen could be responsible of the decrease of T_g in bitumen sulphur blends respect the neat bitumen.

When comparing ΔH_m, and X (%) values obtained for the blends (see Table 3) with those obtained for neat bitumen, it can be appreciated a slightly increase mainly for blends with high content of sulphur. It could be attributed to the presence of crystalline sulphur in the blends. However, in the DSC curves of Figure 3 it is not observed the presence of any endothermal peak in the region where the thermal transitions for neat sulphur occur (see Figure 2). In order to check the existence of crystalline sulphur in the blends, a sample with a higher content of sulphur ($w_{sulphur}$=35%*)* was investigated. The results are showed in Figure 4. As it can be observed the DSC curve relating to first scan (Figure 4A) shows clearly the T_g of the blend located at -29ºC and the presence of two endothermal peaks located at T=104.0 ºC and T=116.1 ºC attributed to the presence of orthorhombic (S_α) and monoclinic (S_β) crystalline sulphur in the blend. In the second scan (Figure 4B), obtained after fast cooling of the sample, two overlapped T_g´s appear clearly visible; one of them at T_g =-40 ºC due to sulphur and the other to bitumen + sulphur blend. This behaviour is indicative of the lack of total miscibility between sulphur and bitumen.

The percentage of crystalline sulphur in the blend can be estimated by:

$$X(\%)=\frac{\Delta H_m}{\Delta H_m(sulphur)\times w_{sulphur}}\times 100 \qquad (2)$$

where ΔH_m represents the enthalpy of the endothermal peak located at T=116.1 ºC for bitumen + sulphur (35 wt%) blend, ΔH_m *(sulphur)*=46.2 Jg^{-1} is the enthalpy of fusion obtained for neat sulphur and $w_{sulphur}$ is the weight fraction of sulphur in the blend. Using equation (2) $X = 70\%$ has been obtained.

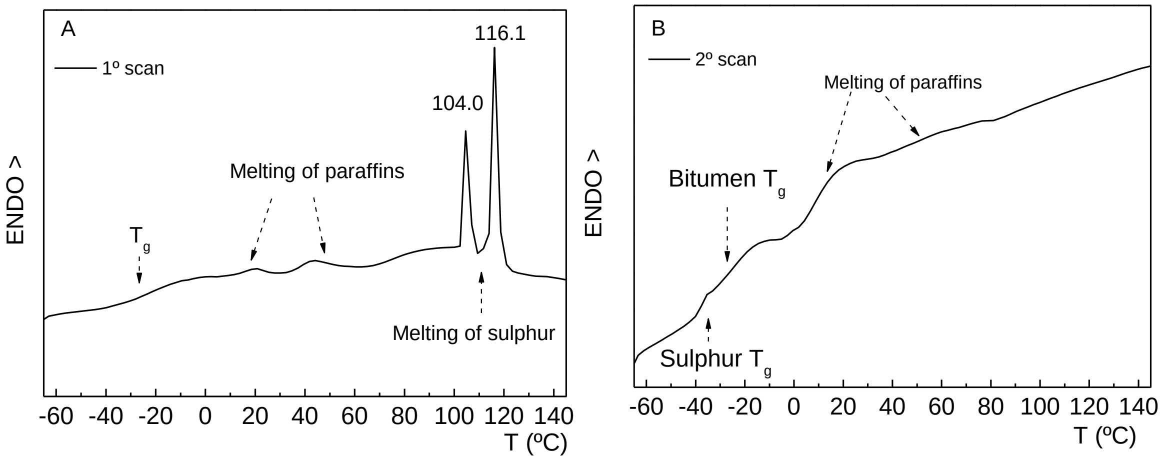

Figure 4: DSC curves for bitumen + sulphur (35 wt%) blends

Therefore these results allowed concluding that the increase of sulphur content in bitumen + sulphur blends provides evidences of immiscibility between bitumen and sulphur and indicate the existence of sulphur crystalline phase coexisting with amorphous phase formed bitumen + sulphur blend.

Bitumen + sulphur blends with low content of sulphur (5 and 10 wt%) do not show, clearly, the existence of crystalline sulphur, when they are analyzed by DSC, in a short period of time after their preparation (see Figure 3). However the little increase observed in X (%) (see Table 3) could be indicative of the presence of little amounts of crystalline sulphur. Bitumen + sulphur (10 wt%) blends were been stored during approximately one month at room temperature and during this period of time it was possible to detect the appearance of a solid phase segregated on the surface of the samples. In order to investigate the constitution of this solid phase a sample of surface was analyzed by DSC, and the results are shown in Figure 5.

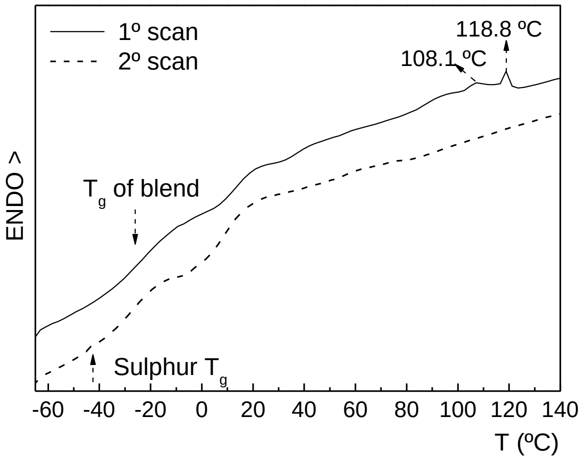

Figure 5: DSC curves for bitumen +sulphur (10 wt%) blend after aging at room temperature

As it can be seen the first scan shows the T_g of bitumen + sulphur (10 wt%) blend at -27 ºC and not being observed any significant variation of T_g sample with the storage time at room temperature (see Table 3). However in the high temperature region, after the endothermal peak corresponding to melting of paraffinic compounds constituents of bitumen, two endothermal peaks appear, located in the temperature range where sulphur thermal transitions have been observed (see Figure 1). The results confirm that crystalline sulphur is segregated from bitumen + sulphur (10 wt%) blends when these are stored a large period of time at room temperature. This behaviour could be responsible for of the decrease in the penetration and the increase in the softening point reported in the literature and must be taken into account for predicting possible changes in the behaviour of bitumen + sulphur blends at service temperatures. After fast cooling of the sample, second scan confirm the presence of segregated sulphur, by means of a T_g=-40 ºC, overlapped with bitumen + sulphur blend T_g .

4. CONCLUSIONS

Loss weight measurements and thermal analysis of bitumen + sulphur blends have allowed verifying that total sulphur added to the bitumen is divided between reactive sulphur and non reactive sulphur. At 130 ºC and 140 ºC a portion of the reactive sulphur is evolved as hydrogen sulphide. The non reactive sulphur occurs in three different forms: (1) evaporated sulphur; (2) mixed with bitumen and (3) segregated as solid crystalline sulphur.

Blends of bitumen containing several amounts of sulphur (5 wt% and 10 wt%) have been analyzed as a function of the temperature in order to determine the amount of volatile fraction evolved for the blends. The results point out that the percentage of sulphur evolved by the blends depend significantly of the storage temperature, being possible to appreciate a considerable increase from T=130 ºC to T=140ºC. It has been found that the volatile fraction lost (calculated over the total sulphur present in the blend) increase from 3.5 wt% at T=130 ºC, to around 10 wt% at T=140 ºC. It has not found considerable differences in the volatile percentage evolved by the blends as a function of sulphur content. It has been observed that the volatile compounds produced by the blends contain sulphur gas as well as hydrogen sulphide. These results warn of the need to maintain the temperature as close as possible to 130 ° C during the stages of preparation, handling and storage of sulphur bitumen mixtures, in order to reduce toxicity.

The thermal behaviour of the blends containing 5 wt% and 10 wt% of sulphur has been achieved as a function of the storage time at high temperature (T=130 ºC). It has not been observed significant changes in T_g with storage time or sulphur content. In all the blends the presence of a T_g, comprises between the T_g´s values corresponding to neat bitumen and neat sulphur, denotes the existence of partial miscibility between sulphur and bitumen. Also, changes in molecular composition of bitumen due to the reaction with sulphur could be taken into account in order to justify the decrease in T_g value compared with T_g value obtained for neat bitumen.

For blends with high content of sulphur (35 wt%), DSC curves show thermal transitions in the high temperature region (100 – 130 ºC) this indicates the presence of a solid phase in the blends formed by crystalline sulphur. In blends with low content of sulphur (10 wt%) the storage at room temperature provokes the appearance of a solid phase that it has been indentified by DSC as crystalline sulphur as well. The presence of crystalline sulphur in bitumen + sulphur mixtures as well as the observed increase of crystallinity with storage time is in accordance with the change in the macroscopic technological properties observed (decrease in penetration and increase in softening point) in sulphur modified bitumens.

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