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# Characterization of bitumen by differential scanning calorimetry

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The behaviour of bitumen was investigated by differential scanning calorimetry. It is shown that two glass transitions take place after cooling at constant rate. The magnitude and temperature of these transitions depend on the cooling rate. At low cooling rate, ($<1\,K\,min^{-1}$) the glass transition at the higher temperature vanishes and an endothermic peak is obtained. From these observations, a segregation mechanism is proposed to explain the behaviour of bitumen during cooling.

(Keywords: bitumen; glass transitions; differential scanning calorimetry)

Bitumen produced in petroleum refining is a very complex system owing to its heterogeneous nature. The use of bitumen for road-surfacing has led to the development of several characterization techniques such as dilatometry[1], penetrometry[2], differential thermal analysis[3] and differential scanning calorimetry (d.s.c.)[4]. The last of these has also been used for the study of separated fractions of bitumen[5-10]. It was established that the presence of paraffinic compounds, i.e. waxes, gives an endothermic peak in the thermogram[5-9]. However, no clear quantitative relation was found between crystallized compounds observed by thermal methods and fractions isolated by solubilization. Nevertheless it was shown that saturates, isolated by precipitation, crystallize on cooling. When added to the bitumen matrix, they decrease the glass transition temperature, $T_g$[1,10]. More generally, determination of the glass transition characteristics provides a better understanding of the molecular interactions occurring in complex mixtures, as shown for coal tars[11] and coal tar pitches[12].

The purpose of this study was to investigate the behaviour of a bitumen during thermal treatment and to provide a better understanding of the interactions between the paraffinic and aromatic fractions.

## EXPERIMENTAL

Samples obtained from the same bitumen, Elf Feyzin 40/50, by distillation were used. Paraffins were obtained by ethanol–ethyl ether precipitation at 253 K according to a method described elsewhere[13].

The samples were observed by optical microscopy using transmitted light. A small amount of material (0.5–1 mg) was placed on a glass slide at room temperature, covered with another glass slide and then heated to ~470 K. The thin layer obtained was then cooled to room temperature before observation. The presence of particles exhibiting optical anisotropy was detected with crossed polarizer and analyser. The proportion of domains showing optical activity was determined by image analysis at a magnification of 300.

Differential scanning calorimetry (d.s.c.) was performed using a thermoanalyser interfaced with a computer for data storage and processing. All d.s.c. experiments were carried out on ~20 mg of material under a flow of dry nitrogen. Samples held at 278 or 373 K in the d.s.c. cell were cooled to 153 K at a linear rate ranging from 15 to 0.5 $K\,min^{-1}$. The d.s.c. signal was subsequently recorded at a linear heating rate of 15 $K\,min^{-1}$ as described elsewhere[11].

The glass transition temperature, $T_g$, was determined as the midpoint of the heat flow shift after cooling and reheating the sample at 15 $K\,min^{-1}$. The difference in specific heat capacity between the liquid and the glass, $\Delta C_p$, was given by the thermoanalyser computer. The experimental uncertainty in the measurements of $T_g$ and $\Delta C_p$ were $\pm 1\,K$ and $\pm 0.02\,J\,g^{-1}\,K^{-1}$ respectively.

## RESULTS AND DISCUSSION

At 373 K, no optical activity could be found in the bitumen. However, after storage for 1 d at room temperature, anisotropic domains a few micrometres in size appeared, as shown in *Figure 1*. They represented 3–5 vol.% of the sample and disappeared during subsequent heating at 333 K.

D.s.c. curves for bitumen pretreated by cooling at a constant rate from 373 to 153 K are shown in *Figure 2*. It
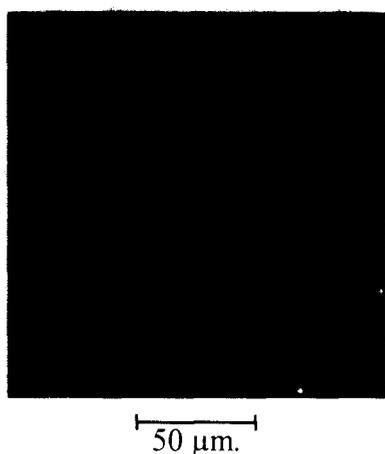
50 µm.

**Figure 1** Optical micrograph of bitumen stored at room temperature. Polarized light

**Table 1** Glassy characteristics of bitumen cooled at different rates

| Cooling rate (K min⁻¹) | $T_{g1}$ (K) | $\Delta C_{p1}$ (J g⁻¹ K⁻¹) | $T_{g2}$ (K) | $\Delta C_{p2}$ (J g⁻¹ K⁻¹) |
|---|---|---|---|---|
| 15 | 251 | 0.16 | 287 | 0.21 |
| 2 | 253 | 0.19 | 287 | 0.09 |
| 0.5 | 257 | 0.21 | 295 | 0.07 |

is seen that the curve of heat flow versus temperature depends strongly on the cooling rate, but in all instances two glass transitions can be detected. The lower and upper glass transition temperatures $T_{g1}$ and $T_{g2}$, and the corresponding differences in specific heat capacity, $\Delta C_{p1}$ and $\Delta C_{p2}$, are shown for the different cooling rates in *Table 1*. It is seen that $T_{g1}$ decreases with increasing cooling rate. For a typical glass-forming system, the opposite situation is usually observed, in accordance with the kinetics of glass formation. Furthermore, the magnitude of the glass transition, as expressed by $\Delta C_p$, also varies for both transitions. Rapid cooling favours the lower-temperature transition, and at cooling rates $<1$ K min⁻¹ the higher-temperature $T_g$ vanishes. This could indicate interactions between two glass-forming systems, with mass transfer taking place between the two systems during cooling.

Bitumen samples were also submitted to d.s.c. after heat treatment at 373 K and storage at 278 K for 12 h. In that case, two different thermal signals were found (*Figure 3*). The first is located at 256 K, while the second is a broad endothermic peak of 6 J g⁻¹ centred at 323 K. The temperature of the first phenomenon decreases with the cooling rate. This behaviour is typical of a glass transition. Paraffins are known to produce an endothermic melting peak in this temperature region. The d.s.c. curve corresponding to the paraffinic fractions isolated from the bitumen is shown in *Figure 4*. A broad endothermic peak separated into two parts, located between 303 and 353 K, is observed. The width is attributed to the presence of a mixture of paraffinic compounds rather than a single compound. The addition of 9.4 wt% of this fraction to bitumen increases the
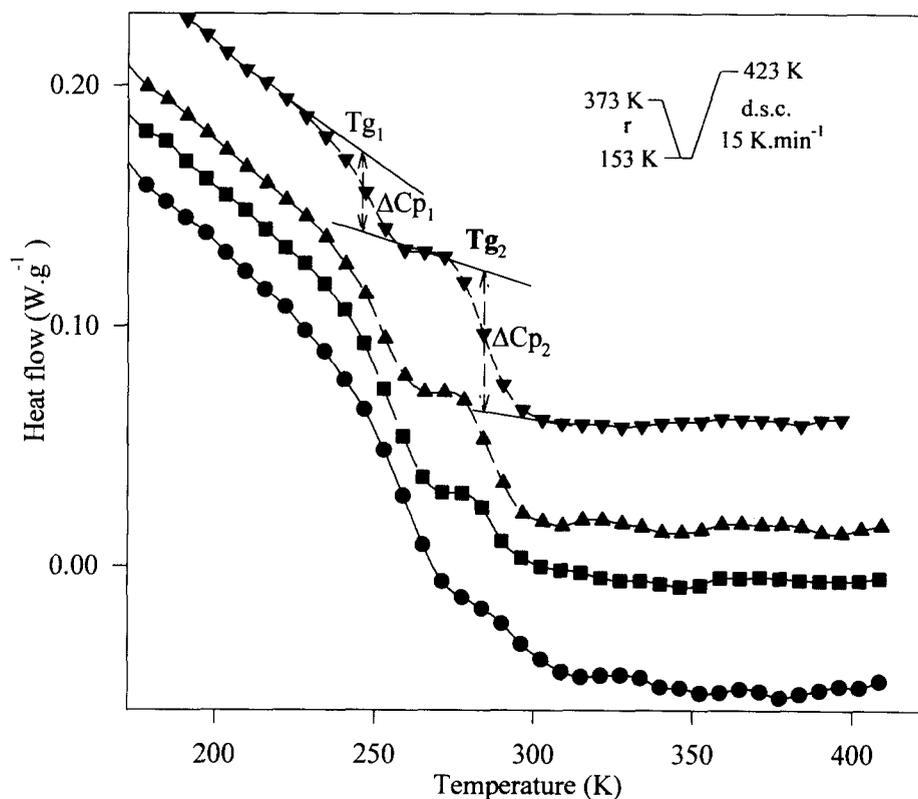


**Figure 2** D.s.c. scans of bitumen cooled at (▼) 50, (▲) 15, (■) 2 and (●) 0.5 K min⁻¹; *r* refers to the cooling rate applied to the bitumen before recording the d.s.c. curve from 153 to 423 K
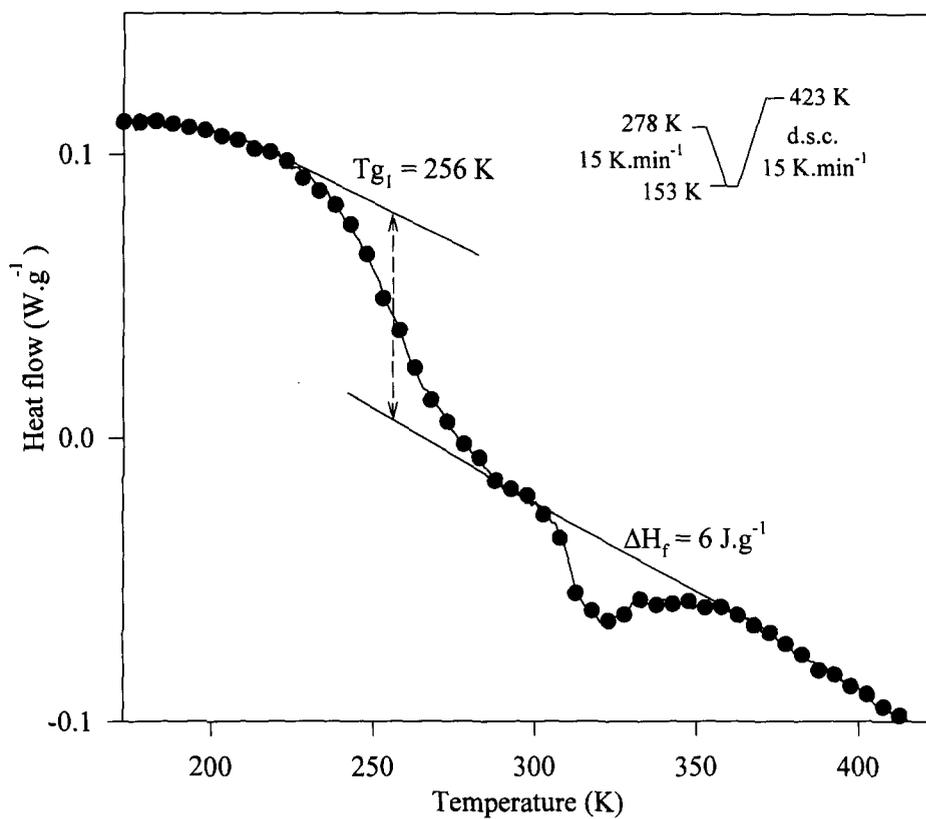
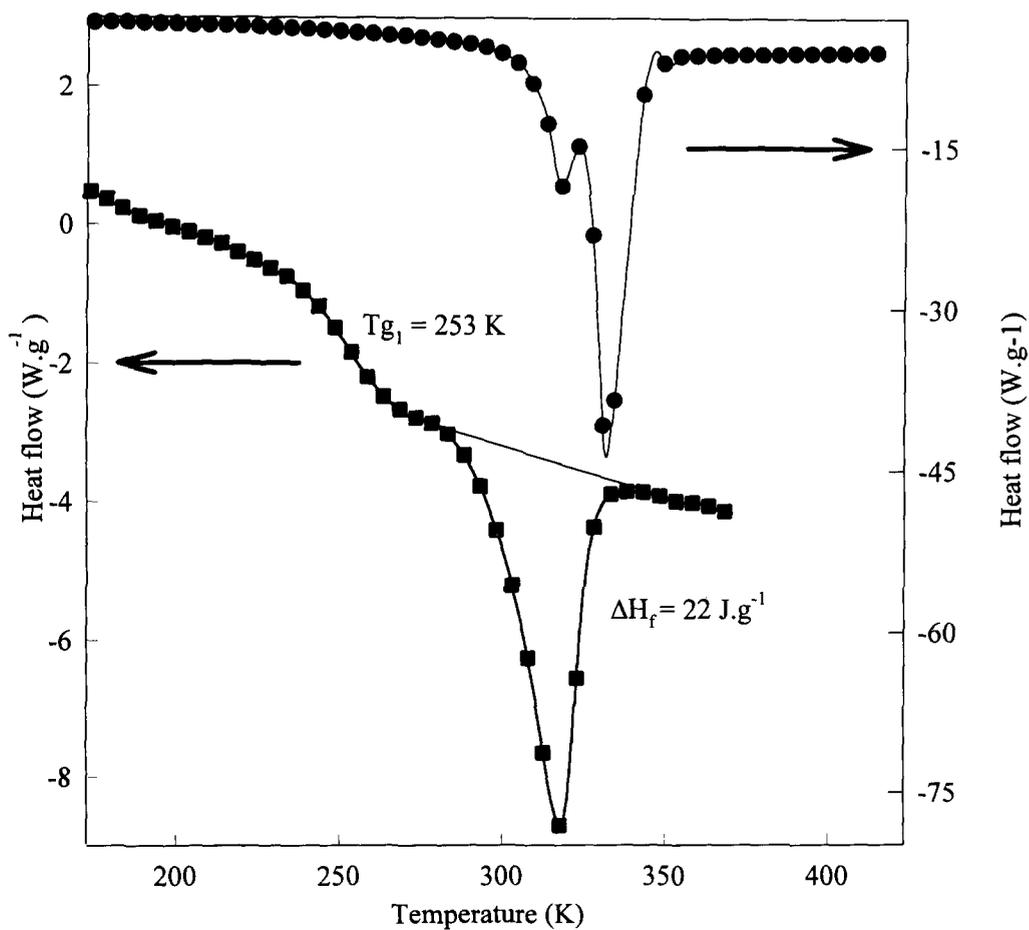**Figure 3** D.s.c. scan of bitumen stored 12 h at 278 K



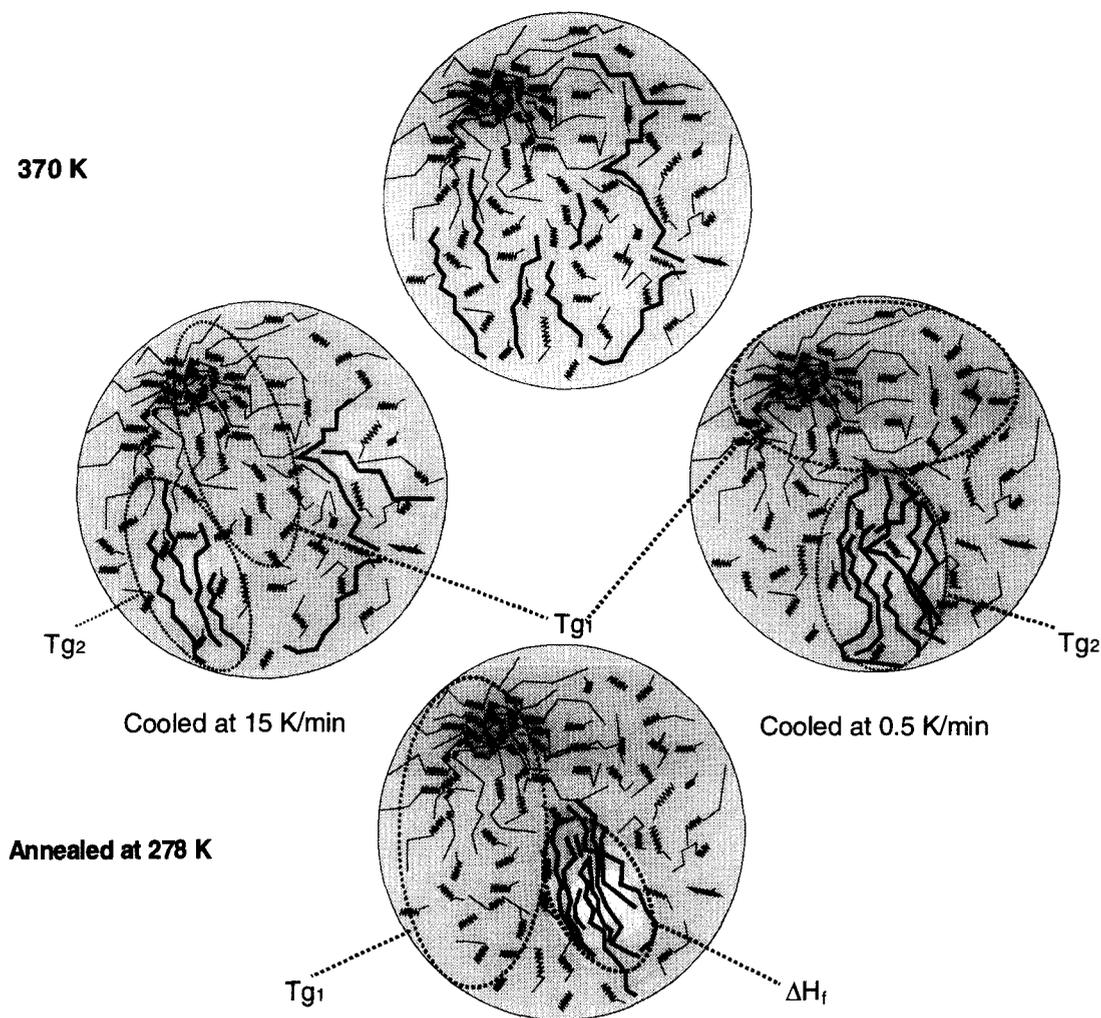**Figure 4** D.s.c. scans of paraffins (●) and bitumen with 9.4 wt% of paraffins added (■)

**Figure 5** Representation of bitumen structure in the course of solidification. Shaded, Aromatics, ⟶ aliphatics, ⟨ resins, 🕷 asphaltenic micelles

endothermic peak $(22\,\mathrm{J\,g^{-1}})$ observed previously. Interestingly, a decrease in the lower glass transition temperature is also observed after incorporation of paraffin, from 256 to 253 K. Hence the composition of the low-temperature glass-forming fraction has been changed. Considering the magnitude of the endothermic peak, the melting/dissolution enthalpy of incorporated paraffin can be estimated as $190\,\mathrm{J\,g^{-1}}$ paraffin, which is close to the commonly accepted values[3]. Considering that most of the crystallized compounds are of paraffinic type, this means that crystallization of 3 wt% paraffin can be detected in the bitumen sample by d.s.c. This value compares well with the microscopic observations in which 3–5 vol.% of anisotropic regions were determined.

From these observations, a description of the behaviour of bitumen during thermal treatment can be proposed, as outlined in *Figure 5*. At 370 K, local fluctuation in paraffin concentration takes place. On quenching (cooling rate $50\,\mathrm{K\,min^{-1}}$), aliphatics and aromatics tend to separate, but viscosity increases to a point where further separation is hindered. Hence two glass transitions are observed, one at high temperature $(T_{g2})$ giving material enriched in paraffinic fraction and one at low temperature $(T_{g1})$ giving material depleted of paraffins. The composition of each frozen glass fraction obviously depends on the extent of paraffin segregation, i.e. on the

cooling rate. Changes in $T_g$ and $\Delta C_p$ take place accordingly. In very slow cooling, enough time is available for total separation of the paraffins, which are then able to crystallize, giving rise to an endothermic peak in d.s.c. A similar situation can be obtained by annealing at a temperature close to the melting point of the paraffin.

## CONCLUSIONS

This study shows that differential scanning calorimetry is a powerful technique for the characterization of bitumen. During cooling, segregation of the paraffinic fraction results in the formation of two interactive glass-like fractions. After storage at room temperature or below, paraffins separate and crystallize. The glass transition of the remaining bitumen fraction is consequently hindered.

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