Structural characteristics of peat bitumen and peat/petroleum bitumen blends, and consideration of their potential use as road binder materials

J. J. LEAHY, J. A. G. DRAKE, C. BIRKINSHAW
National Institute for Higher Education, Limerick, Ireland

I. L. JAMIESON
National Research Council, Strategic Highway Research Program, 818 Connecticut Avenue NW, Washington 2006, USA

Bitumen derived from peat was blended with petroleum bitumen and subjected to laboratory evaluation for use as road binder material. Standard empirical procedures used included penetration, softening point and Fraass brittle point determinations. Rheological behaviour has been assessed at low shear rate using a sliding plate microviscometer and at high shear rate using a cone and plate instrument. Thermal analysis techniques including calorimetry and dielectric thermal analysis have been used to obtain fundamental structural information. Properties have also been measured after accelerated ageing. Peat bitumen is shown to differ significantly from petroleum bitumen in having a relatively high (30%) crystal content; however, as crystal melting commences below 20° C, the initial effect obtained in blending with petroleum bitumen is that of a plasticizer, reducing blend viscosity and increasing penetration. Crystallinity in the blends is lower than expected and this is ascribed to diffusional control of the crystallization process. Peat bitumens show a marked propensity to harden on heating, presumably due to condensation reactions increasing molecular weight, and this more than compensates for the plasticizing effect. The results suggest that age hardening will limit technically useful blends to a maximum of 17% wt/wt peat bitumen.

1. Introduction
The use of bitumens derived from peat may offer economic advantage to those regions possessing substantial deposits of this raw material. Bituminous substances can be obtained from milled peat by solvent extraction; the chemical nature, and in particular the polarity, of the extraction solvent determining the type and quantity of species extracted. Only limited information is available regarding the detailed chemical structure of peat bitumen, but compared to petroleum bitumen, materials derived from peat contain significantly higher proportions of aliphatic acids, C_{20} to C_{30} alcohols, and their esters [1].

The potential of bituminous materials from peat has long been recognized in Eastern Europe [2, 3], but exploitation has been restricted in the West due to the ready availability of petroleum bitumens. Initial work [4] on extraction and characterization of bitumens from native Irish peat has suggested that detailed evaluation of these materials as constituents of road binder materials is justified. The work described here is an examination of the physical characteristics of peat bitumen, and blends with petroleum bitumen, considered potentially useful for road binder applications. In addition to standard empirical procedures commonly used in classifying these materials, thermal analysis has been used to provide more fundamental structural information.

2. Bitumen extraction and blend preparation
Peat bitumen examined in this study was obtained by extraction with SBP11 (Shell Chemicals). This solvent is known preferentially to remove aliphatic species, but is more environmentally and economically acceptable than solvents of higher aromatic content and greater extractive power. The product obtained was of a soft consistency at room temperature and therefore not suitable for direct use as a road binder material. Initial work suggested that technically useful blends should be based on a relatively hard petroleum bitumen; a standard 50 penetration grade material was considered appropriate. Blends containing 10%, 17% and 25% by weight of peat bitumen were prepared by mechanical mixing at 120° C. Microscopic examination of the blends showed them to be homogeneous.

3. Characterization
Empirical characterization procedures adopted were substantially those traditionally used with petroleum-derived materials. These included penetration, softening point and Fraass brittle point determinations, with

penetration index being calculated from the softening point nomogram of Pfeiffer and Van Doormal [5]. Long-term stability of road binder bitumens is usually assessed using the Segas accelerated test procedure [6] in which a thin film of the material is held at 55° C in oxygen for 18 h, standard empirical properties being measured before and after ageing. Whilst the validity of this test procedure with the chemically different peat bitumens can only be fully established following in-service trials, it is an appropriate starting point in laboratory evaluation.

In addition to the empirical tests, the pure bitumens and the blends were subject to thermal characterization by differential scanning calorimetry (DSC) and dielectric thermal analysis (DETA). DSC was carried out using a Du Pont 910 instrument at a heating rate of 10° C min^{-1} between -80 and 200° C. Sample size was 7 mg and the test was carried out under oxygen-free nitrogen. DETA was performed on a Polymer Laboratories instrument over the temperature range -100 to 150° C at 4° C min^{-1}. The frequency used was 10 kHz. The DETA technique is particularly valuable in detecting thermodynamic transitions in soft materials which are not amenable to dynamic mechanical analysis and its use with peat waxes has been previously reported [7].

Samples of both the pure bitumens and the blends were cooled at a rate of 0.8° C min^{-1} as thin films between glass and were then examined at high resolution using the polarizing microscope. Dimensions and details of crystal bodies were noted.

Rheological behaviour was assessed using a SETA sliding plate microviscometer and a Haake Rotovisco cone and plate instrument at temperatures between 15 and 100° C.

4. Results and discussion

Fig. 1 shows the DSC thermograms for the pure bitumens and the blends, before and after accelerated ageing. The 50 penetration petroleum bitumen exhibits a steady endothermic drift, with change of slope around 10° C. There is no evidence, in the plot for this material, of first-order transitions such as melting. This suggests that at low temperatures the petroleum bitumen is vitreous; an observation which is consistent with generally held views as to the nature of these materials, though limited crystallinity has been reported [8] in some petroleum-derived materials. The change in slope observed here is considered to indicate the glass transition temperature.

Both the pure peat bitumen and the blends show clear evidence of a series of melting events between -20 and 72° C. Assuming that melting is associated
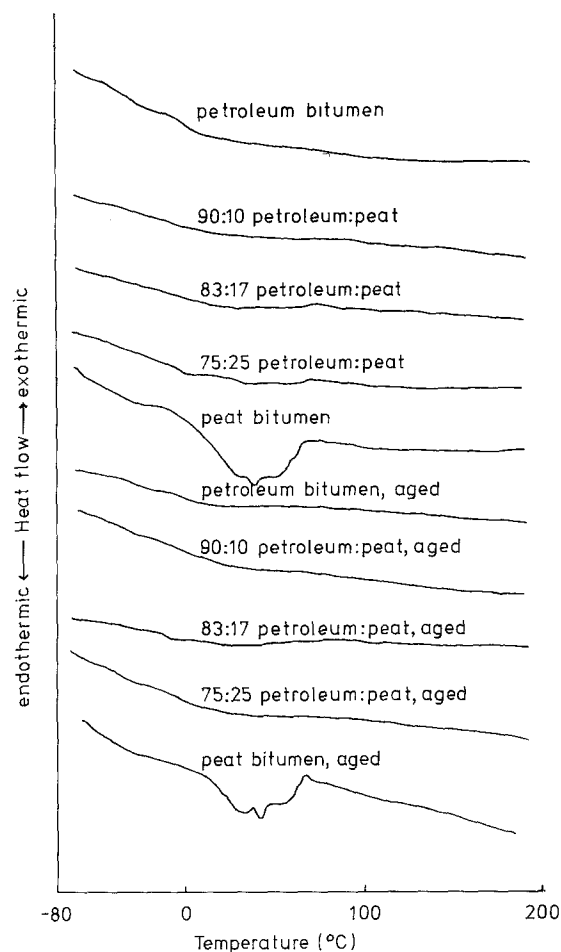

Figure 1 Differential scanning calorimetry response of petroleum bitumen, peat bitumen and blends before and after accelerated ageing.

with esters, and taking a measured heat of fusion of montan wax (69.9 mcal mg^{-1}) as being appropriate, approximate percentage crystallinity values can be calculated. These are given in Table I.

Microscopic examination showed the crystalline phase to be spherulitic in form, with approximate diameters as given in the table. In the blends the measured crystal content indicated by calorimetry, is lower than that anticipated from consideration of formulation. In the case of the blend containing 10% peat bitumen, although individual crystal bodies could be observed under the microscope, their concentration was too low to allow reliable estimation by calorimetry. This reduction in crystallinity in the blends is thought to arise from diffusional control of crystallization rate. Materials close to their glass transition temperature are characterized by extremely high viscosity, reflecting reduced molecular diffusion rates. In this case, as the system approaches the glass transition of the major constituent, the petroleum bitumen,

TABLE I Melting characteristics of bitumen blends

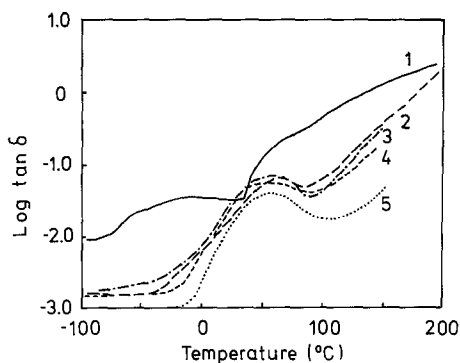| Material	Measured heat of fusion (mcal mg^{-1})	Crystallinity (%)	Spherulite diameter (μm)
Peat bitumen	21.5	30.7	5.4
25:75 blend	2.3	3.2	4.6
17:83 blend	0.6	0.8	4.4
10:90 blend	<0.3	<0.4	3.9
Petroleum bitumen	0	0	none observed
Peat bitumen after ageing	18.5	26.4	not observed

Figure 2 Variation in tan δ for petroleum bitumen, peat bitumen and blends. Curve 1, peat bitumen; curve 2, 25:75 blend; curve 3, 17:83 blend; curve 4, 10:90 blend; curve 5, petroleum bitumen.

Figure 4 (a) Rheological characteristics of bitumen blends before accelerated ageing, and (b) after accelerated ageing. (O) Petroleum bitumen, (□) 25:75 peat bitumen:petroleum bitumen blend, (Δ) 17:83 blend, (x) 10:90 blend.

the diffusion rates of dissolved species such as esters must become very low, with consequent hindrance to full crystal development. This proposal is supported by the observed reduction in crystal dimensions with increasing petroleum bitumen content. The crystallinity reduction mechanism may effectively limit the high sensitivity to temperature change often exhibited in the mechanical properties of materials with a T_m close to ambient temperature.

In the DETA results, shown in Fig. 2, the glass transitions of the petroleum bitumen and the blends are evident as a series of maxima around 50° C, frequency effects causing the transition to be observed at higher temperatures than in the thermograms. Both the dielectric and calorimetry results suggest that vitrification will not be an important process in peat bitumen until very low temperatures are reached.
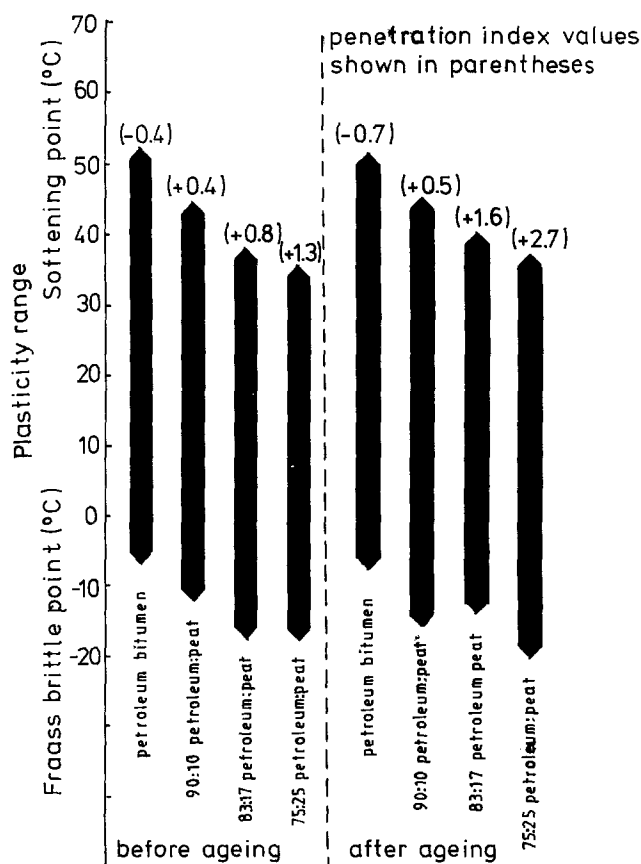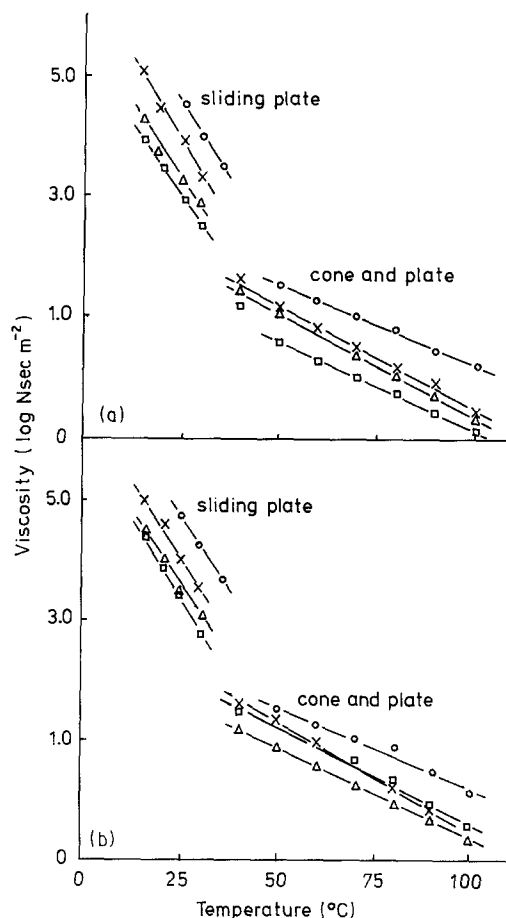
With the peat bitumen, the higher value of the loss tangent, tan δ at lower temperatures, indicates greater energy dissipation through molecular motion sympathetic to the field reversals. This is associated with the non-crystalline phase which is still liquid at low temperatures.

Fig. 3 illustrates the effect of the peat bitumen on the empirical properties of the blends. Both softening temperature and Fraass brittle point are reduced, with the greater effect on the softening temperature. This plasticizing action is consistent with the physical structures inferred from the thermal analysis results. Close correspondence exists between the observed softening points and the tan δ maxima obtained in the DETA experiments, confirming the importance of the glass transition in determining mechanical behaviour. Calorimetry results obtained after accelerated Segas ageing, and shown in Fig. 1, demonstrate that all blends have become completely amorphous, indicating chemical rearrangement in the direction of reduced structural regularity. Possible reactions include acid-alcohol condensation and oxidative coupling of aromatics; the former being more probable [9].

In the rheological plots, given in Fig. 4a, the effect of the different shear conditions on flow behaviour in the two types of instrument is apparent. Fig. 4b shows the behaviour of the same materials following ageing, where slight increases in viscosity are observed, particularly in blends of the highest peat bitumen content.

Figure 3 Empirical properties of blends based on a 50 penetration grade petroleum bitumen.

TABLE II Temperature coefficients of flow behaviour for bitumen blends

Binder	A	B
Petroleum bitumen	−0.11	8.2
90:10 blend	−0.11	7.7
83:17 blend	−0.09	6.6
75:25 blend	−0.10	6.4

TABLE III Flow behaviour indices of bitumen blends

Binder	Flow behaviour index	
	Before Segas	After Segas
Petroleum bitumen	0.95	0.82
90:10 blend	0.98	0.87
83:17 blend	0.93	0.78
75:25 blend	0.94	0.77

At the higher shear rate the increased stiffness of these materials again suggests that an increase in average molecular weight has occurred.

Previous workers [10] have found the relationship

$$\log (\text{viscosity}) = A \log (T) + B$$

to be appropriate for describing the temperature dependence of flow in bitumen systems. Application to the data obtained with the sliding plate microviscometer yields the values for A and B given in Table II. The results may be considered with the values of penetration index given in Fig. 3. A high value of penetration index is taken to indicate a reduced thermal sensitivity, suggesting that increasing peat bitumen content should reduce temperature sensitivity. Comparison of the values obtained here for the coefficients A and B, with results from earlier studies [4], indicates that the effect of the peat bitumen on temperature susceptibility is less than would be expected from the penetration tests.

Plotting log (shear stress) against log (shear rate), as shown in Figs 5a and 5b, for data obtained at 25°C with the microviscometer before and after accelerated ageing, allows calculation of the flow behaviour indices, given in Table III. The initial effect of the peat bitumen on this aspect of flow behaviour is small, even at the highest blend concentration, but significant increases in pseudoplasticity occur following ageing. This behavioural change probably arises from a
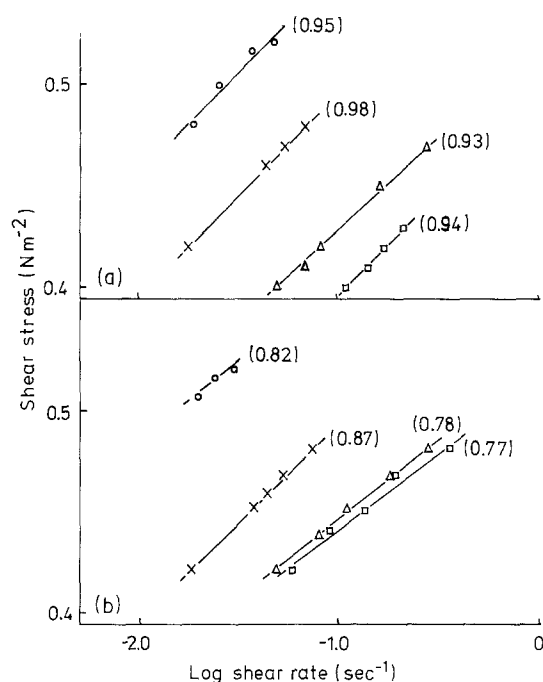
broadening of the molecular weight distribution, consequent on the condensation or coupling processes mentioned previously. Whether reaction is limited to the species from the peat bitumen or involves combination between species from both components of the blend remains uncertain.

5. Conclusion

The behaviour of both peat bitumens and petroleum bitumens, around the temperatures of practical interest for road binder useage, is dominated by thermodynamic transitions. In petroleum bitumens this is a glass transition, whilst in peat-derived materials, crystallization is the most significant event. Accelerated ageing reduces the ability of peat bitumen to crystallize, implying a high level of reactivity in these materials.

The coincidence of T_g of the petroleum bitumen and the T_m of the crystal fraction of the peat bitumen effectively suppresses the latter's ability to crystallize in blends. This may have implications for in-service behaviour, in suggesting that the thermo-mechanical characteristics of the blends, at ambient temperatures, may be substantially dominated by the vitreous character of the major constituent.

The initial rheological effects of blending peat bitumen with petroleum bitumen are relatively small and can be explained as a plasticization process. However, a significant observation is the tendency to age hardening in the blends, a process which becomes of particular importance at the highest blend concentration evaluated. Considered in conjunction with the calorimetry results, this behaviour suggests that reactions leading to both an increase in average molecular size, and an increase in polydispersity are occurring. The resulting increased resistance to flow more than compensates for any reduction in crystallinity which may occur.

The high susceptibility of the peat bitumens to age hardening, compared with the petroleum bitumen, suggests that there is a relatively low optimum level for the inclusion of these materials in blends if long-term stability is to be ensured. It is considered that blends containing 17% peat bitumen may represent the limit of acceptability.

Figure 5 (a) Flow behaviour index plots for bitumen blends before accelerated ageing, and (b) after accelerated ageing. (○) Petroleum bitumen, (□) 25:75 peat bitumen:petroleum bitumen blend, (△) 17:83 blend, (×) 10:90 blend.

Acknowledgement

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