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Blends of bitumen with polyethylenes

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Abstract

Blends of a 100 penetration grade bitumen with four different polyethylenes having up to 40 pph or 29% of polymer by weight were prepared using a Z-blade mixer at more than 160°C. The blends were studied by fluorescence optical microscopy, differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The optical measurements indicated the presence of bitumen-rich and polymer-rich phases. The DSC showed that the melting point of the crystallites was lowered and within the polymer-rich phases, the extent of crystallinity reduced by the presence of the bitumen. Annealing made significant changes to crystallite size, suggested by the raising of the melting point of the polymer crystallites. The DMTA measurements show that these polymers lower the temperature at which the glass transition softens the material, but raises the temperature at which the blend undergoes viscous flow. When the polymer fraction is over 20% to 28% the flow starts only when the crystallites melt, so the polymer then provides an associating junction network. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Bitumen; Polyethylene; Blends

1. Introduction

Bitumen, which remains after crude oil has been processed in distillation plants and catalytic crackers [1], is a mixture of four main components–aromatics, paraffins, asphaltenes and resins. It has uses that range from the construction of the pavements of roads [2] with an aggregate and as a waterproofing agent [3], to more specialised purposes such as, when blended with a proportion of a polymer used in built-up membranes for the roofing industry [4] and in improved forms of bitumen for roads to resist adverse weather conditions [5,6]. Besides any novel blends of polymers being used for similar and new purposes [7] we may also envisage the possibility of disposing of troublesome waste plastics within road bitumens [8], especially if the properties are improved by the presence of the polymer or polymers. Blends of bitumens with polymers may thus have a number of applications.

In this paper we examine the properties of blends of a bitumen with a number of polyethylenes. Four polyethylenes were used, a high density polyethylene (HDPE) from BASF, two linear low density polyethylenes (LLDPE), one from Exxon Chemicals having an ethyl side chain, the other from Dow Chemicals having a butyl side chain, and finally a low density polyethylene from Exxon Chemicals.

Each blend of a single polymer was prepared with a Z-blade mixer, and had up to 40 pph or about 29% of the polymer by weight, a range which covers at least one common use and in which "phase inversion" with atactic polypropylene is known to take place, the polymer rich phase then being the continuous phase [4]. The blends were examined by differential scanning calorimetry (DSC) to characterise any glass transition temperatures and melting transitions, by fluorescence optical microscopy to reveal any large scale inhomogeneities, and by dynamic mechanical thermal analysis (DMTA) to characterise the bulk properties such as the modulus and mechanical loss processes.

2. Experimental

An analysis of the Nynas 100 pen. bitumen from Venezuela with an Iatroscope instrument found the following proportions of the components: aromatics 47%, paraffins 6%, asphaltenes 16% and resins 31%. The source and properties of the polymers we have used are entered in Table 1.

Blends of bitumen with the polyethylenes were made with a Winkworth 1.5 pint Laboratory 3-Wing Z-blade masticator mixer. The temperature of blending was

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Table 1
The polyethylenes used in this study

Polyethylene	Source	Grade	MFI (g/10 min)	Density (g/cm^3)
High density HDPE	BASF	LUPOLEN 5431P	16 – 20	0.943 – 0.947
Linear low LLDPE	Exxon Chemicals	ESCORENE LL1007 YB	2.8	0.918
Linear low LLDPE	Dow Chemicals	DOWLEX 2056E	1.0	0.92
Low density LDPE	Exxon Chemicals	ESCORENE LD 655	155	0.912

normally between 160°C and 180°C. Typically the first blend was made from a 200g quantity of the bitumen and 20g of the polymer, and after a weighed sample of that 10 parts per hundred (pph) mixture had been removed, second, third and fourth blends were made and sampled in turn by the addition of successive appropriate quantities of bitumen and the polymer.

Fluorescence Optical Microscopy was performed with an Olympus BHS-RFL attachment using a mercury lamp as a light source and times 125 magnification. Photomicrographs were obtained with a Polaroid camera. DSC was performed with a Perkin–Elmer model DSC-7 on 10–20mg samples sealed in aluminium containers, using heating and cooling rates of 10°C/min. Certain samples, in a DSC pan, were annealed at 100°C or a similar temperature by placing them in an autoclave furnace for a period such as 2 or 24 h. The samples afterwards were allowed to cool initially at about 0.1°C/min to ambient temperatures overnight before being re-examined.

DMTA was performed on a Polymer Laboratories dynamic mechanical thermal analyser Mark II, using the single cantilever bending mode on strip samples about 10 mm × 5 mm × 2 mm that had been cut off the end of the dumbbell samples prepared for tensile testing with a hot press. For the standard experiment we used the five frequencies of 0.3, 1, 3, 5 and 10 Hz and a heating rate of 2°C/min,

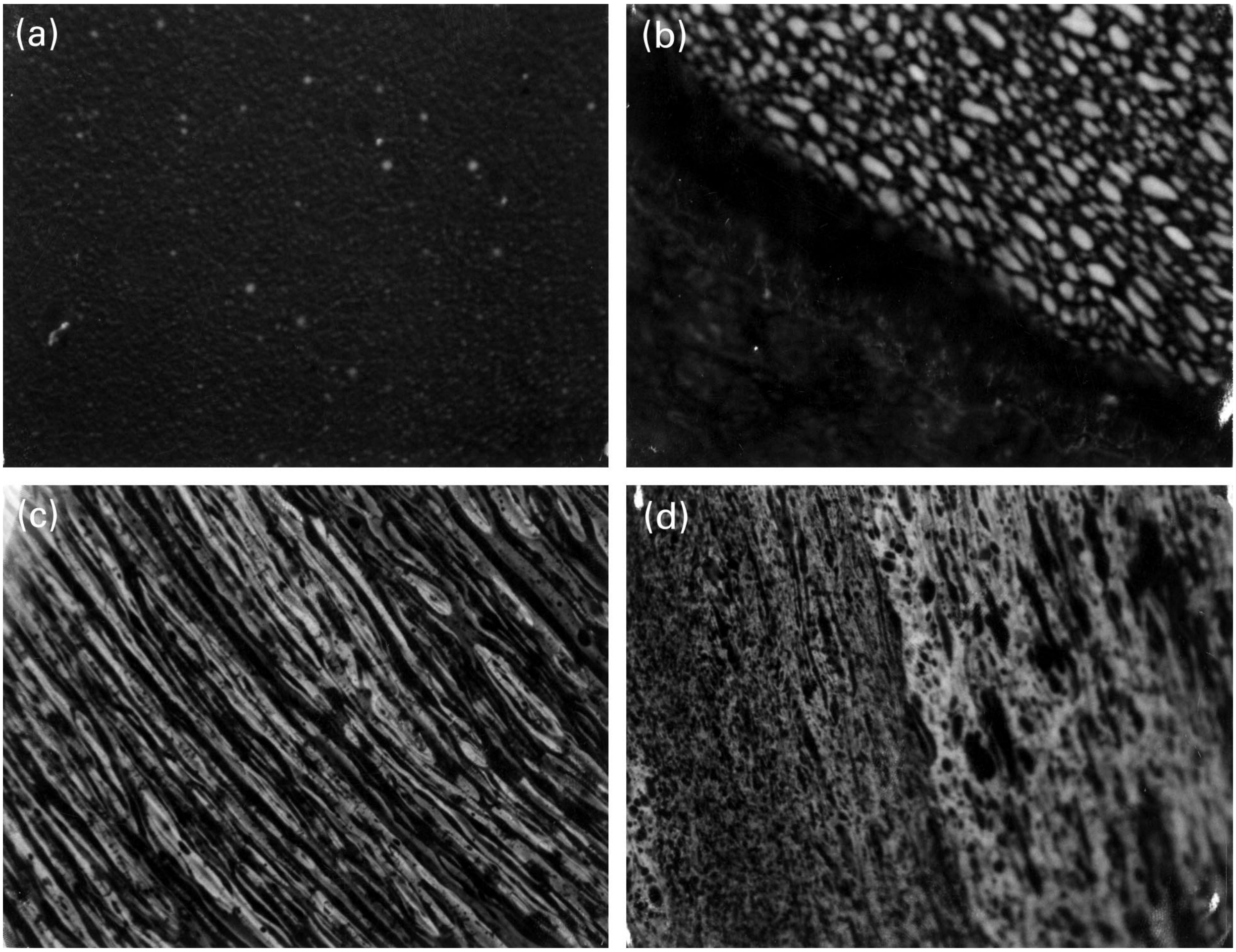


Fig. 1. Fluorescence photomicrographs of (a) 10 pph, (b) 20 pph, (c) 30 pph and (d) 40 pph blends of high density polyethylene (HDPE) with 100 pen. bitumen, (×100).

Table 2
DSC characteristics of the high density polyethylene (HDPE) bitumen blends

pph polymer	10	20	30	40	
% polymer	9.1	16.7	23.1	28.6	100[a]
T_m (°C)	122.3	122.9	123.9	124.4	134.4
ΔH (J/g) blend	11.4	20.1	31.1	36.3	—
ΔH (J/g) polymer	125.4	120.6	134.7	127.1	203.9
% of full ΔH	61.5	59.1	66.1	62.3	—
F_c in blend	44.3	42.6	47.6	44.9	—

[a] Crystallinity from the X-ray scattering pattern: 72%.

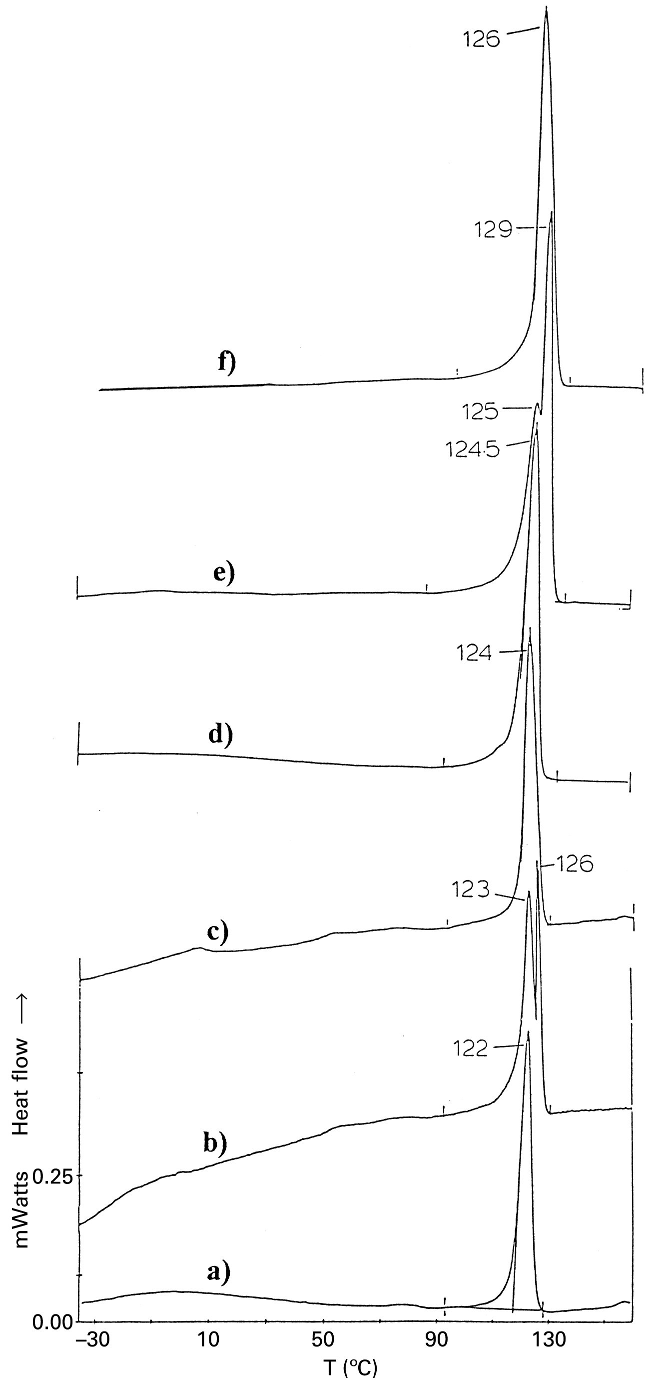


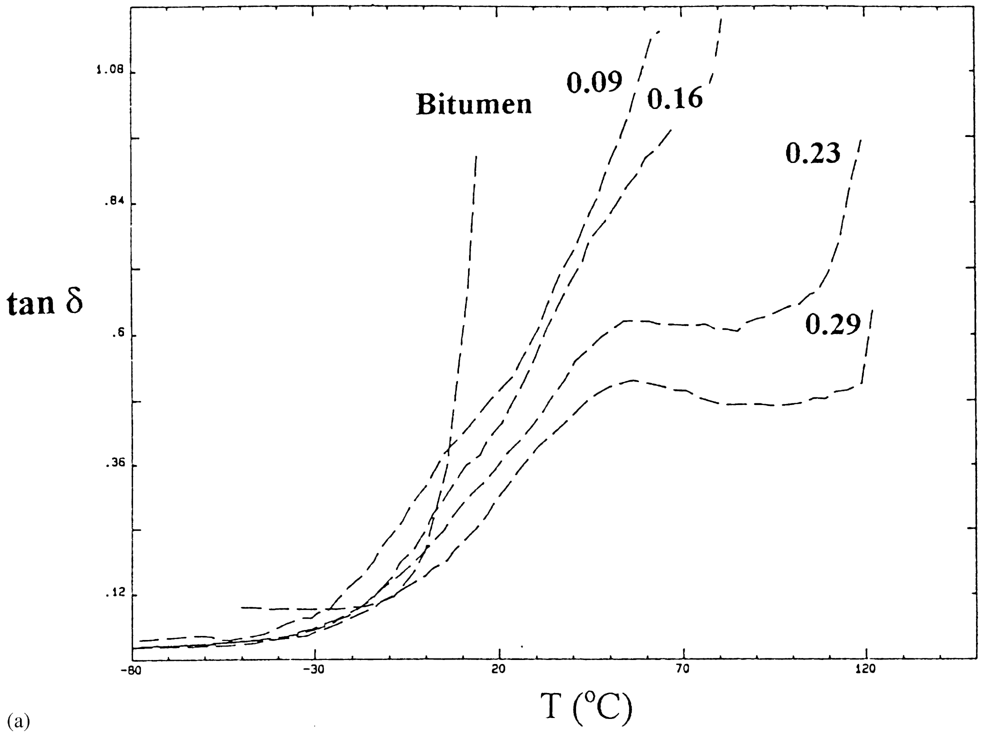
Fig. 2. DSC curves of (a) 10 pph HDPE with bitumen, (b) sample of (a) annealed for 2 h at 130°C, (c) sample of (a) annealed for 24 h at 130°C, (d) a blend of 40 pph HDPE with bitumen, (e) sample of (d) annealed for 2 h at 130°C and (f) sample of (d) annealed for 24 h at 130°C.

starting at about −80°C, and ending when the sample became too soft to measure. The instrument was calibrated on a regular basis. The bitumen itself was measured in the shear mode. For the tensile tests, samples were hot pressed to the usual dumbbell shape by applying pressure to samples placed within a mould cut in aluminium sheeting, and had a nominal thickness of 2 mm, a width of 6 mm and a length of 30 mm. The press used was capable of applying a pressure of 1 to 1.5 t on the ram. Tensile measurements were made on an Instron Tensile tester with a crosshead speed of 500 mm/min., five samples usually being used of each blend.

3. Results and discussion

We start by reporting the results obtained on the most dense polyethylene and proceed to the least dense. The fluorescence photomicrographs of the high density polymer blends are shown in part in Fig. 1(a-d), where it may be seen that there is evidence for two phases in each blend, the light phase being the polymer rich phase and the dark phase being the bitumen-rich phase, from the manner in which the proportion change as the polymer is added. It is probable that some fluorescent components of the bitumen invade the polymer-rich phase to render it light to the eye and the camera. In the first two blends the polymer-rich phase is limited in extent, the droplets being barely discernible at about 1 μm diameter in the 10 pph blend, but are clearly of the order of 10 to 20 μm in size in the 20 pph blend. In the remaining two photomicrographs the polymer-rich phase extends over all the area, the bitumen-rich phase being long streaks in the 30 pph view, perhaps reflecting a lamellar structure, and being confined to droplets in the 40 pph view. As the latter blend contains only 28.6% of the polymer, and yet the polymer rich phase appears to extend over more than half of the photograph, the polymer-rich phase must contain elements from the bitumen such as the paraffinic and aromatic components, as well as the species responsible for the fluorescence. It is a gel in the sense that Flory uses the term [9] to describe the polymer-rich phase that separates during a molecular weight fractionation, and which is likely to contain a higher molecular weight fraction than the solvent-rich phase.

The DSC results shed some light on this issue. The DSC traces for the polymer had peaks that extended upwards from about 70°C. For the blends the peaks developed at about 90°C as may be seen in Fig. 2. The peaks of the DSC traces of the blends are 10°C below those for the pure polymer (134.4°C), their values rising slightly with



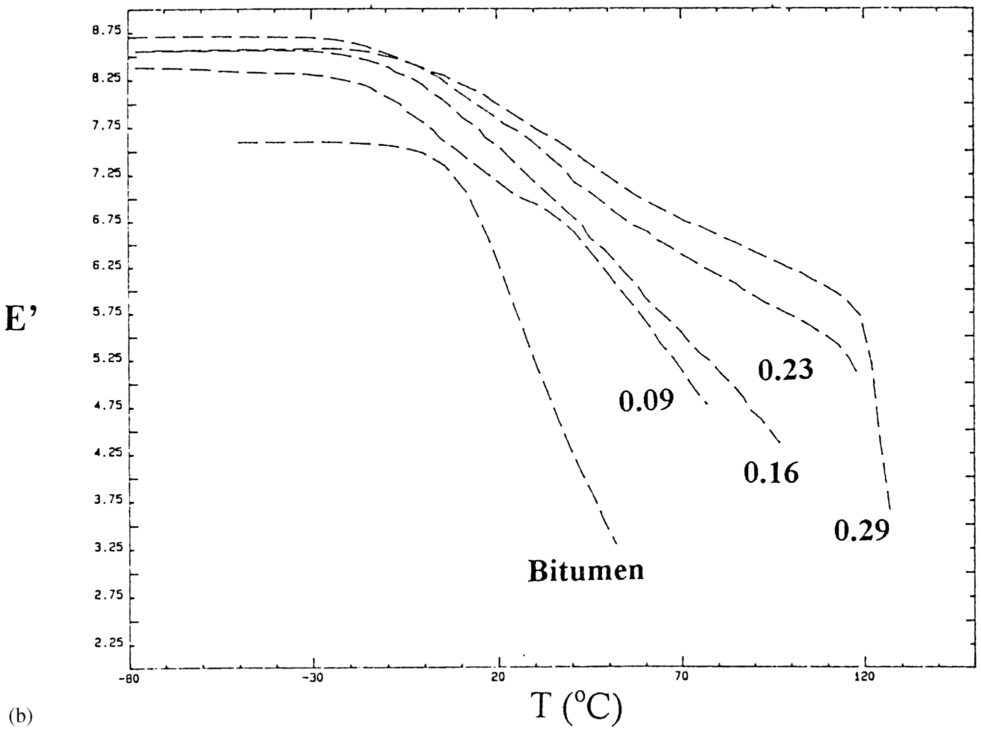


Fig. 3. Variation in (a) tan δ, (b) storage modulus (stiffness) with composition for blends of HDPE with 100 pen. bitumen, from DMTA studies at 1 Hz. Bitumen was measured in the shear mode at 1 Hz. The numbers 0.09, 0.16, 0.23 and 0.29 are the weight fraction of polymer in the blend.

polymer content from 122.3°C to 124.4°C, as is recorded in Table 2. By the time the temperature had risen to 130°C, the polymer crystallites had melted in the blends, though in the pure polymer the peak lay above that temperature. The depression of the polymer melting point by the presence of the bitumen may be attributed to the crystallites having a smaller size, an effect described by the well-known Thompson equation [10] and examined in studies on lamella in polypropylene and polyethylene [11]. In these dispersions of polymers in bitumen a lamella morphology may not be as

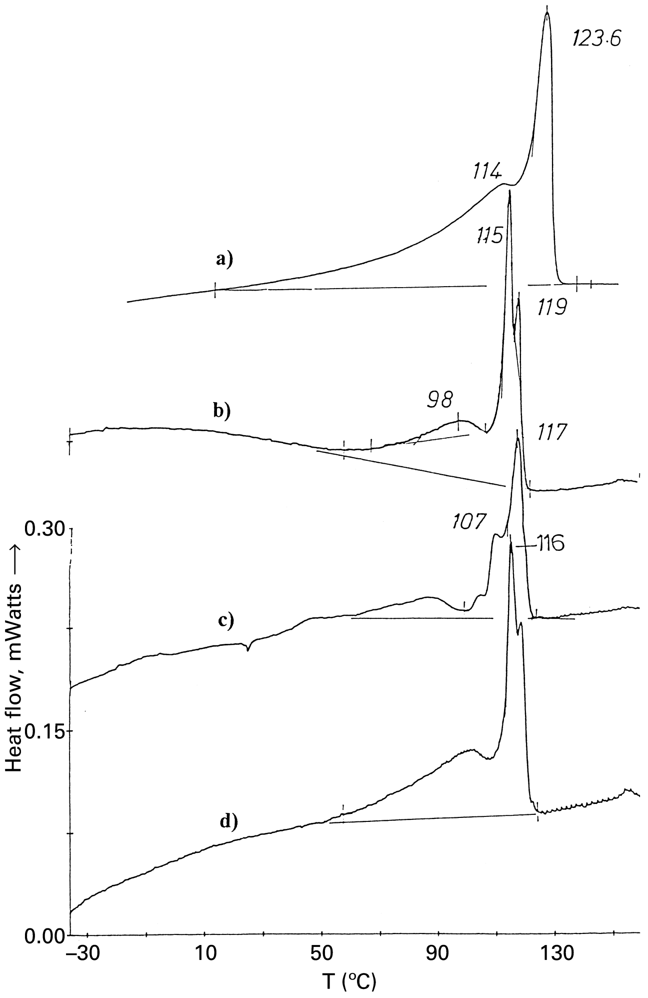


Fig. 4. DSC curves for (a) LLDPE (Exxon sample), (b) 20 pph blend with bitumen, (c) as in (b) annealed for 24 hours at 100°C and (d) rerun of (c).

appropriate as a fringed micelle model, each micele containing parallel portions of many chains. And, of course, we neglect considering the interfaces and imperfections within crystallites.

The area under the curves were used to provide the values of the heat of melting of polymer crystals per gram of blend. When these values are divided by the fraction of polymer in the blend, the result may be taken as a measure of the proportion of the polymer that melts on heating, or the fraction that is crystalline. For the pure polymer the powder X-ray scattering pattern was obtained and it was found that 72% of the scattering area belonged to peaks, and so was assigned to the crystalline content. Had the pure polymer been completely crystalline the ΔH would have been 283 J/g. This value is in good agreement with that determined by other workers (293 J/g) [12]. By combining this figure with the observed ΔH values for the blends and their weight fractions of polymer content, f_p, the fraction of polymer within the blend that is crystalline, F_c, may be calculated from

$$F_c = \Delta H/283\, f_p \tag{1}$$

When these values are considered (Table 2), it may be seen that only about 45% of the polymer has crystallised when each blend has cooled to room temperature from its temperature of preparation. The F_c values do not change significantly with the polymer/bitumen ratio. For each blend the bitumen thus lowers the extent of crystallisation of the polymer by retaining a proportion within the amorphous bitumen-rich phase and it lowers the melting point of the crystalline regions within the polymer-rich phase by making the crystallites smaller [10,13].

To explore the possibilities of influencing the crystallite size, we annealed two blends of the polymer at 130°C, that is just below the melting point of the pure polymer (Fig. 2(a)), for periods of 2 and 24 h. The samples were afterwards examined by DSC, the traces being shown in the remaining parts of Fig. 2. Two hours annealing had a significant effect upon the blend, the endotherm being split into two peaks (at 125.1°C and 129.1°C, Fig. 2(c)), both at a higher temperature than the single peak of the unannealed sample (123.7°C, Fig. 2(b)). The broader low temperature peak of the pair had a tail to low temperatures, and an area of 16.7 J/g, whereas the high temperature peak was sharper and of slightly higher area (17.6 J/g). The blend annealed for 24 h displayed only one peak, at the intermediate temperature of 126.1°C (Fig. 2(d)). The material in the smaller crystallites had reformed into crystallites of a larger size. The 10 pph blend showed a similar behaviour, the two peaks for the two hour annealed sample coming at 122.9°C and 126.2°C, with areas of 9.2 and 3.5 J/g respectively, so the larger crystallites formed to a smaller extent in this case. However, in the sample annealed for 24 h the melting peak temperature (126.1°C) corresponded to that for the larger crystallites produced at the shorter period: they evidently formed after 24 h from the

Table 3
DSC characteristics of the Exxon linear low density polyethylene bitumen blends

pph polymer	10	20	30	40	
% polymer	9.1	16.7	23.1	28.6	100[a]
T_m (°C)	—	118.7 115.1 98	119 116.4 100	119.9 116.8 102	123.6 109
ΔH (J/g)	—	14	18.4	21.6	104
% of full ΔH	—	13.5	17.7	20.8	—
F_c in blend	—	29.6	28.1	26.7	—

[a] Crystallinity from X-ray scattering pattern: 53%.

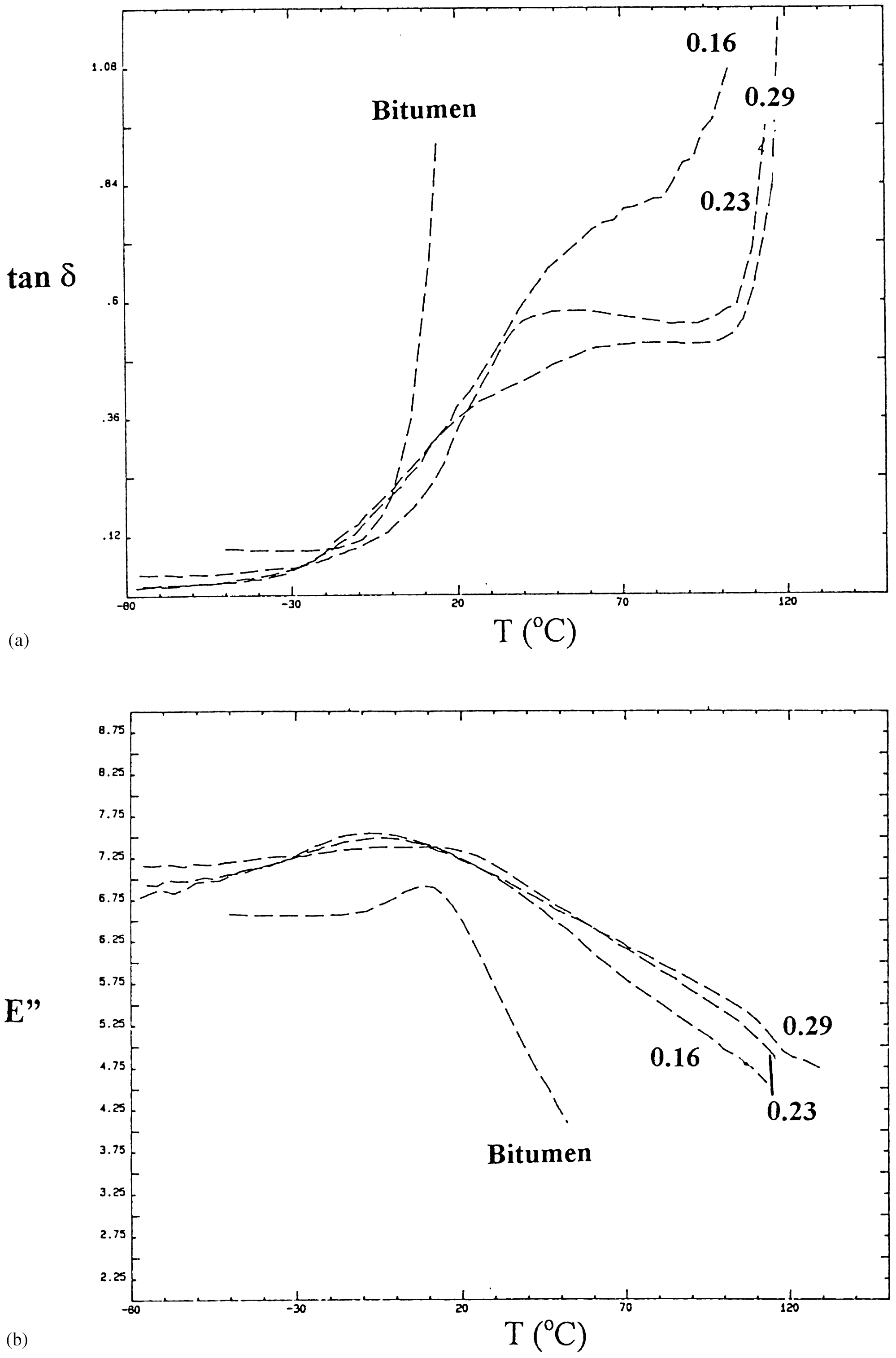


Fig. 5. Variation in (a) tan δ, (b) loss modulus with composition for blends of LLDPE (Exxon sample) with 100 pen. bitumen, from DMTA studies at 1 Hz. Bitumen was measured in the shear mode at 1 Hz. The numbers 0.16, 0.23 and 0.29 represent the weight fraction of the polymer in the blend.

smaller crystallites initially present in this blend of 10 pph polymer.

The DMTA traces obtained at 1 Hz for the bitumen itself and the four blends are shown in Fig. 3, where the storage and loss moduli and tan δ are each plotted. The measurements were made on the bitumen sample in the shear mode, and the values indicated for G' are one third of the corresponding E' value [14]. The curves all terminate when heating the samples became too soft to permit further measurement. For the bitumen itself, this was at 50°C, for

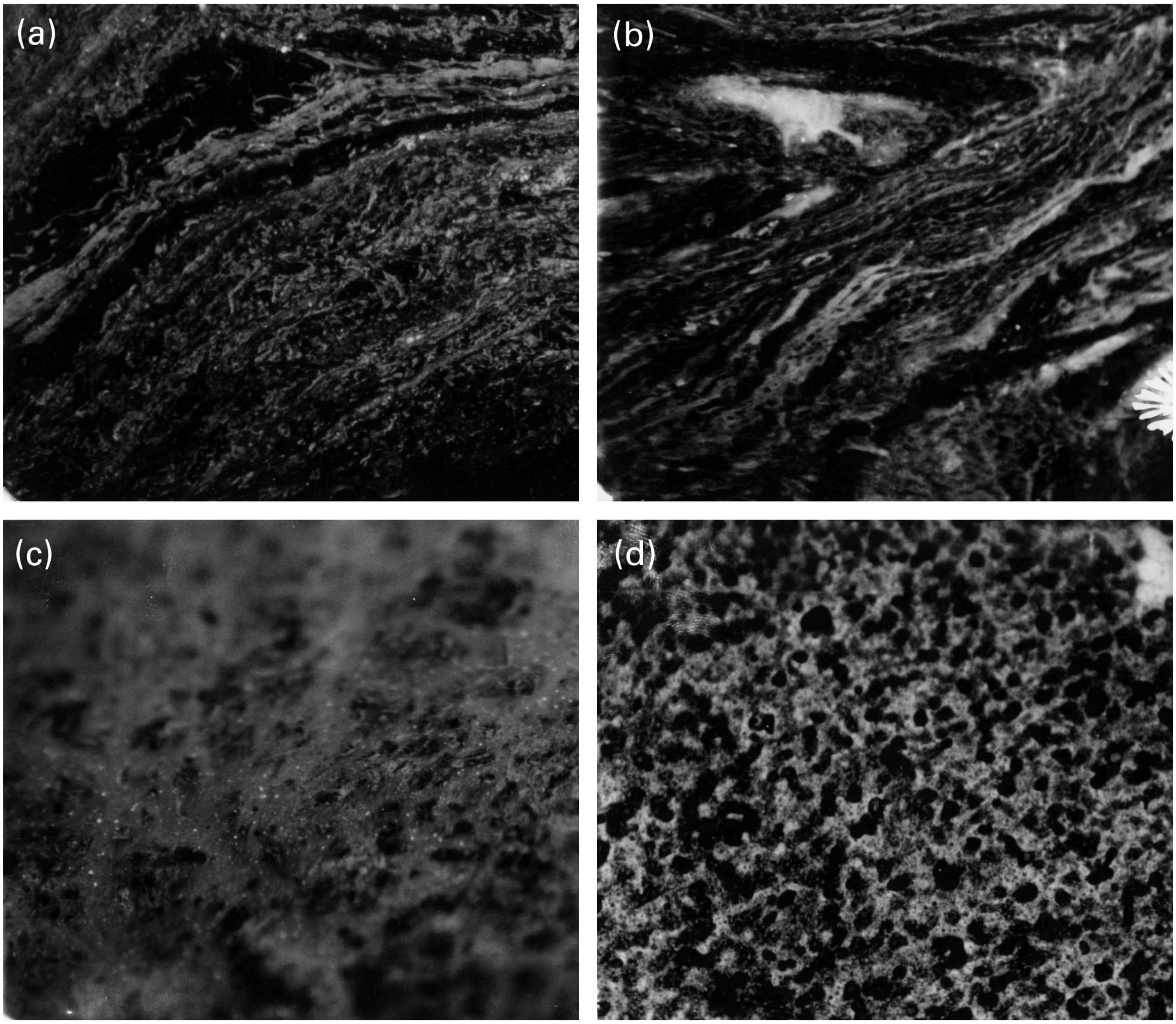


Fig. 6. Fluorescence photomicrographs of blends of (a) 10 pph, (b) 20 pph, (c) 300 pph and (d) 40 pph blends of LLDPE (Dow sample) with 100 pen. bitumen, (×102).

the 10 pph and 20 pph blends the failure took place at 80°C and 100°C respectively, but for the remaining two blends the modulus fell abruptly close to 120°C, i.e. the melting was so rapid that the instrument could not record it properly. The latter temperature coincides with the melting point obtained by DSC, indicating that when the polymer rich phase is continuous, the modulus falls abruptly when the crystallites melt presumably destroying crosslinking sites. For the blends containing 10 pph and 20 pph, the material fails before the polymer crystallites melt, consistent with the strength deriving from the continuous bitumen-rich phase, within which the non-crystalline polymer serves to increase

Table 4
DSC characteristics of Dow linear low density polyethylene bitumen blends

pph polymer	10	20	30	40	
% polymer	9.1	16.7	23.1	28.6	100[a]
T_m (°C)	120 116 98	120 117 100	121 118 102	121 118 102	123 — 108
ΔH (J/g)	12.5	21.6	26.9	30.7	101
% of full ΔH	12.4	21.4	26.6	30.4	—
F_c in blend	49	46	41	38	—

[a] Crystallinity from X-ray scattering pattern: 19.5%.

Table 5
DSC characteristics of low density polyethylene bitumen blends

pph polymer	10	20	30	40	
% polymer	9.1	16.7	23.1	28.6	100[a]
T_m (°C)	92	93	93	95	103
ΔH (J/g)	5.6	13.1	16.6	28.4	129.7
% of full ΔH	47.5	60.5	55.4	76.6	—
Fc in blend	20.3	27.7	25.4	35.1	—

[a] Crystallinity from X-ray scattering pattern: 22%.

the modulus by two orders of magnitude. Each sample shows a constant modulus at low temperatures, the bitumen itself having a value about one order of magnitude below that of the blends. Though the blends are stiffer at any temperature (Fig. 3(a)), as the temperature rises they all soften before does bitumen. They have rather broad loss processes centred on -10°C to 0°C, whereas bitumen by itself has a sharp loss process at about 15°C (Fig. 3(b)). The tan δ plots display, for the two blends rich in HDPE, a broad maximum centred upon 55°C that may be associated with the polymer-rich phase. Instead of falling smoothly beyond the maximum, however, once the temperature passes 90°C the tan δ rises again, and the storage modulus (E') continues to fall. These tendencies we associate with the melting of the smaller crystallites within the continuous polymer rich phase, which is readily apparent once the temperature rises above 90°C (Fig. 2(b)). The α-loss process of polyethylene was located at about 50°C for the pure polymer [15].

The fluorescence photomicrographs of the Exxon LLDPE or ethylene-butylene copolymer also showed the presence of polymer-rich and bitumen-rich phases. While the two low polymer content blends were almost nondescript, the 30 pph and 40 pph blends had a mottled appearance, the predominant polymer-rich phase having a nodular characteristic resembling that of the HDPE Fig. 1(d)).

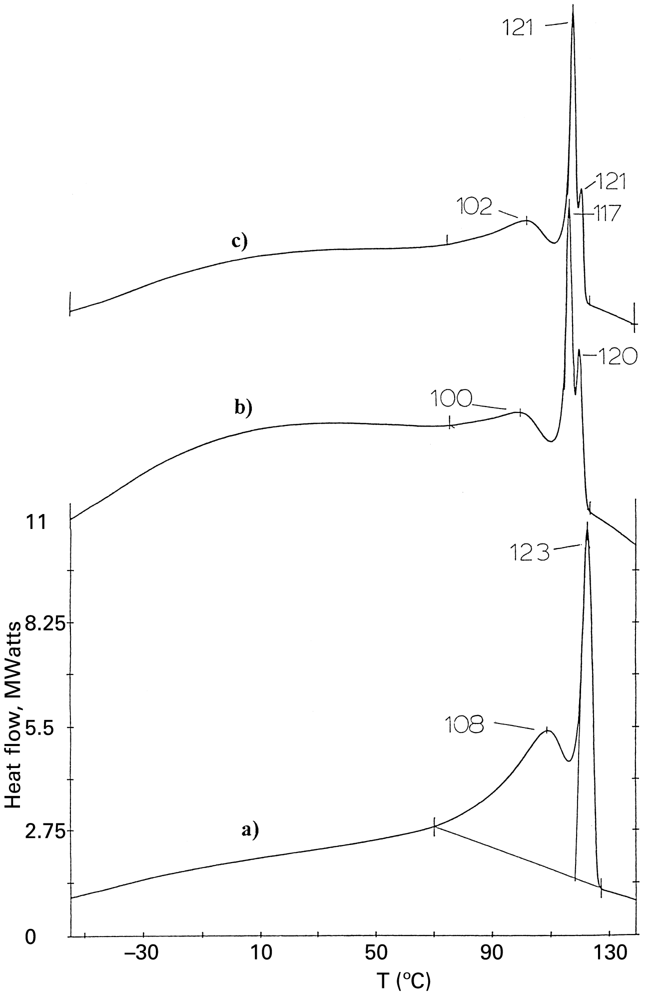


Fig. 7. DSC curves for (a) LLDPE (Dow sample), (b) blend of 20 pph LLDPE (Dow sample) with 100 pen. bitumen and (c) 40 pph blend with 100 pen. bitumen.

The Exxon LLDPE displays in its DSC curve a prominent peak at 124°C and a much broader peak at lower temperatures, the maximum being at about 108°C but the melting endotherm itself starting somewhere below 50°C, as may be seen in Fig. 4(a)). The DSC trace of each of the blends with bitumen showed three peaks, there being a broad peak at about 100°C stretching down to about 50°C, and two sharp peaks at about 118°C (see Fig. 4 and Table 3). The pattern was altered by annealing the sample at 100°C for 24 h, the low temperature peak almost vanishing and the higher temperature peaks growing in quite a different pattern, as may be seen in Fig. 4, where a small broad peak is found at 87°C, a window at the annealing temperature, and then three peaks above, at 103°C, 107°C and 116.5°C for the 20 pph sample. The changes, which reflect the different sizes of

Table 6
Tensile test results on some polyethylene bitumen blends

Polymer	Concentration of polymer in blend (pph)	Tensile strength (N/mm^2)	% Elongation at break	Elastic modulus (N/mm^2)
HDPE	10	0.38	66	1.46
HDPE	40	1.84	64	7.36
LLDPE (Exxon)	10	0.74	80	2.24
LLDPE (Dow)	10	0.44	116	1.10
LDPE	10	0.41	82	1.16
LDPE	40	1.26	22	6.24

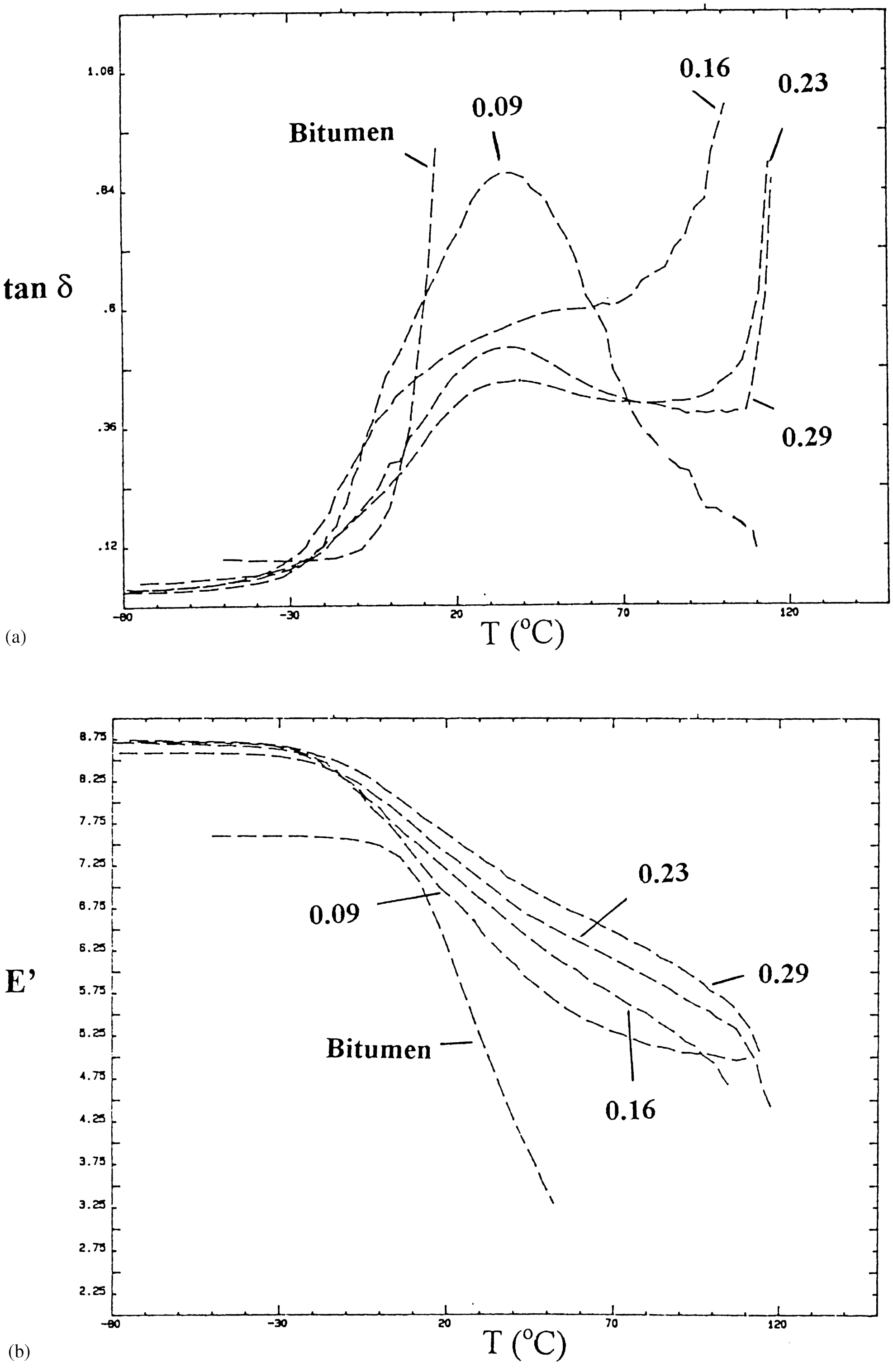


Fig. 8. Variation in (a) tan δ, (b) storage modulus (stiffness) with composition for blends of LLDPE (Dow sample) with 100 pen. bitumen, from DMTA studies at 1 Hz. Bitumen was measured in the shear mode at 1 Hz. The numbers 0.09, 0.16, 0.23 and 0.29 measure the weight fraction of polymer in the blend.

crystallites present — smaller crystallites melting at lower temperatures — were seen to be reversed when the sample was examined immediately afterwards when a trace similar to Fig. 4(b) was seen. Annealing had permitted large crystallites to form, for the enthalpy of melting is only a little less, but is concentrated in the high temperature peaks. This change was immediately reversed by a heating and cooling cycle.

DMTA curves for the Exxon LLDPE polymer blends are shown in Fig. 5. In contrast to the case of the HDPE,

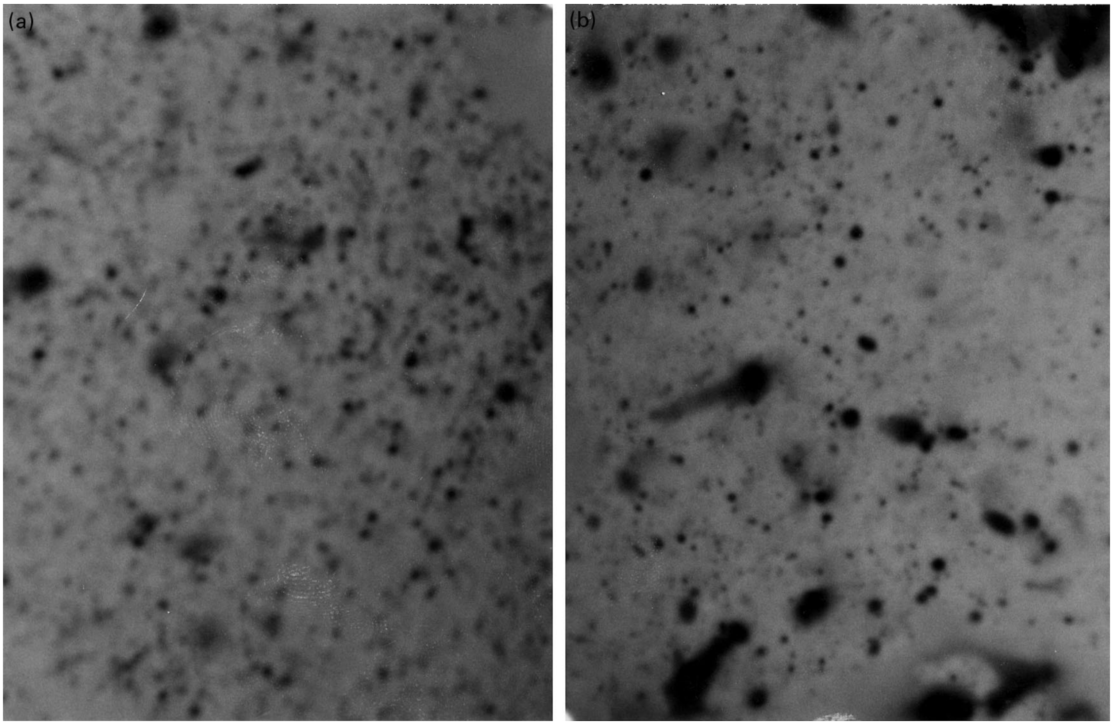


Fig. 9. Fluorescence photomicrographs of blends of 30 pph and 40 pph LLDPE with 100 pen. bitumen, (×119).

measurements could be made at temperatures above 100°C. The polymer is better able to stiffen the bitumen-rich phase at high temperatures, perhaps because more of it is dispersed within that phase.

The fluorescence photomicrographs the Dow LLDPE (ethylene-hex-1-ene copolymer) blends with bitumen also showed the presence of polymer and bitumen-rich phases. The 10, 20 and 30 pph blends contained striations, which may be derived from the blending process. The 40 pph blend in similar to that seen for the blends containing 30 and 40 pph of the Exxon LLDPE in that bitumen globules are dispersed in the extended polymer rich phase (see Fig. 6).

The DSC trace of the pure Dow polymer showed two endotherms, one sharp peak at 122.6°C and a more broad peak having a maximum at 108°C. In the blends both endotherms were shifted to lower temperatures with the higher temperature sharp endotherm split into two peaks, Fig. 7(b) and (c). The enthalpy values for these blends increases with increasing polymer content, but a lower proportion of the polymer crystallises (F_c) from the blend upon cooling (Table 4).

The DMTA traces (Fig. 8.) for the blends containing the Dow LLDPE have an interesting feature: the modulus for the 10 pph sample shows the start of a plateau at about 80°C at the end of the loss process centred on 35°C. The curves of the storage and loss modulii (E' and E'') and tan δ all show the standard shapes of a single loss process, but this is terminated abruptly when the sample begins to flow at about 110°C. The breadth of the peak (about 70°C in the tan δ plot) we attribute to the presence of the five components within the system, for besides the polymer there are paraffins, aromatics, asphaltenes and resins, each of which creates an elaboration. A suitable model for this material at about 100°C would be the fringe micelle model for polyethylene itself, in the case of the blend the microcrystallite serving to bind together the continuous bitumen rich phase by linking several polymer chains to each other. When the matrix is melted, the system corresponds to a swollen rubber, and the modulus derives from the existence of the network structure. Its value, 10^5 Pa, may be used to obtain a value for the total number of crosslinks (mol kg^{-1}) with the aid of the Eq. 2 [16,17]:

$$E' = n\rho\, RT \tag{2}$$

where E' is the storage modulus (Pa), n is the total number of crosslinks (mol kg^{-1}), is the density (kg m^{-3}), R is the gas constant (8.322 mol kg^{-1} K^{-1}) and T is temperature (K). The value calculated, 0.034 mol kg^{-1} is similar to that determined by Teh et al., for a low crosslinked natural rubber (0.01 mol kg^{-1})[16]. It is the sudden melting of the crystallites that terminates the plateau. The absence of a plateau is noted from the three other storage modulus curves above 70°C: we attribute this to the melting of larger and larger crystallites over the temperature range of 50°C upwards that has the effect of progressively lowering the storage modulus.

The fluorescence photomicrographs of the low density polyethylene blends with bitumen show extensive regions of polymer rich phase even for the 20 pph blend (Fig. 9). The polymer rich phase predominates in the two higher

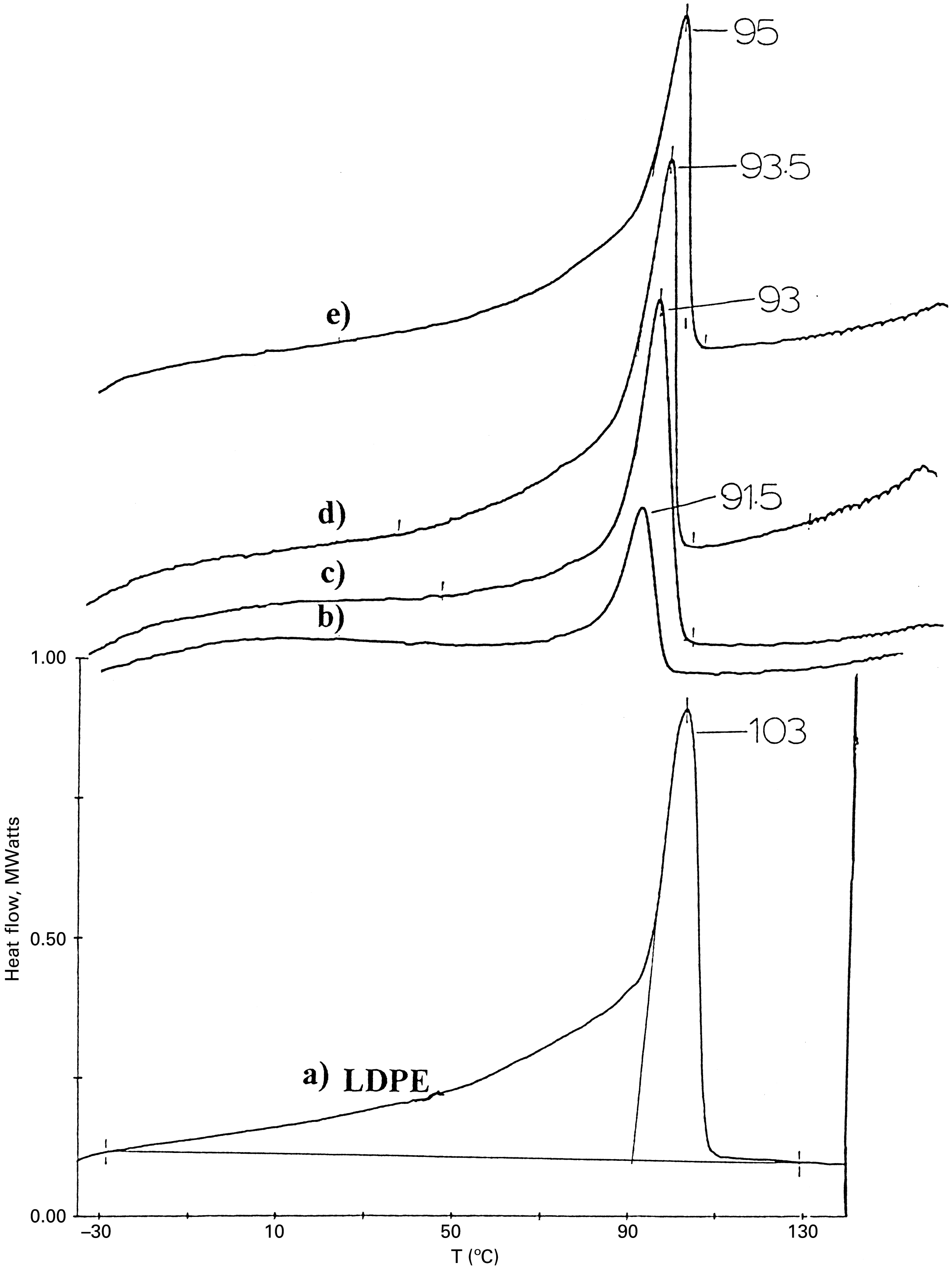


Fig. 10. DSC curves of (a) LDPE, (b) 10 pph, (c) 20 pph, (d) 30 pph and (e) 40 pph blends of LDPE with 100 pen. bitumen.

proportion samples, leaving merely droplets of 10% to 20% of the area for the bitumen-rich phase. (This phase seems to be more extensive the lower the density of the polyethylene used.)

The DSC traces of the pure polymer and of the blends resemble each other (Fig. 10(a),(b)) in that there is a single peak with a broad tail to the low temperature side. The peak temperature is higher for the polymer than for the blends by about 8°C, and the low temperature tail, that we associate with the melting of smaller crystallites may extend to lower temperatures. From the ΔH values of the peaks for the blends the fraction, F_c, of the LDPE that is in a crystalline phase was estimated, using Eq. 1, and is seen to be rather low in comparison with the previous forms of polyethylene, but to be greater the higher the proportion of polymer in the

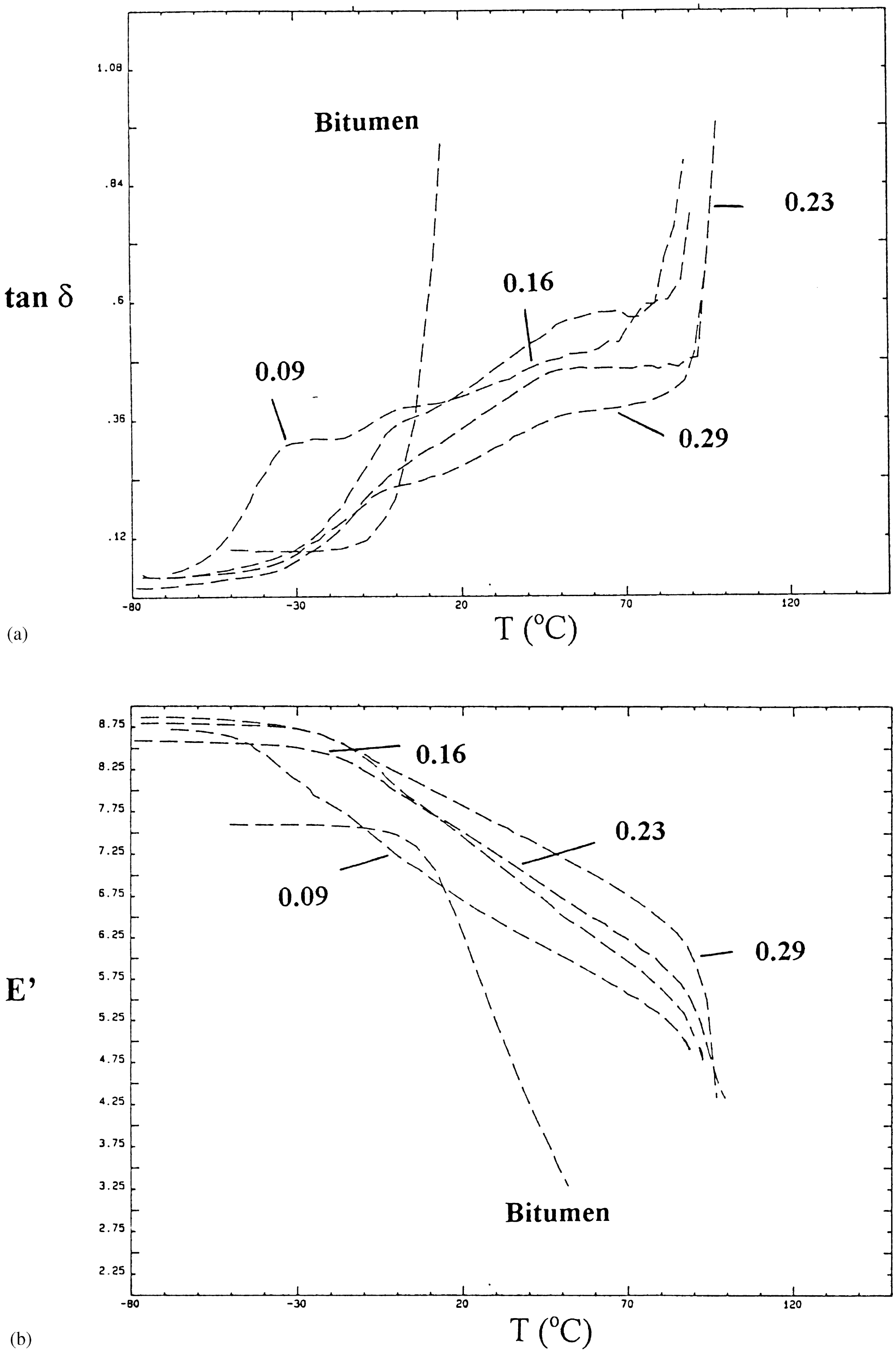


Fig. 11. Variation in (a) tan δ, (b) storage modulus (stiffness) with composition for blends of LDPE with 100 pen. bitumen, from DMTA studies at 1 Hz. Bitumen was measured in the shear mode at 1 Hz. The numbers 0.09, 0.16, 0.23 and 0.29 are the weight fraction of the polymer in the blend.

blend: the entries at the bottom of Table 5 suggest that the bitumen has a tendency to become saturated with the amorphous polymer, so that increasing the amount of LDPE leads to a greater crystalline proportion when the blends cool. The photomicrographs bear this out, as the polymer rich phases are lighter the greater the proportion of LDPE present in the blend.

The DMTA curves for this polymer's blends are shown in Fig. 11. The extensive presence of the polymer rich phase even in the 10 pph blend is responsible for the loss process at −30°C in the blend and the weakening of the material, at about 0°C the blend has a lower modulus than the bitumen itself. The blends have a higher modulus than bitumen itself at $T > 20°C$, but all four materials become impossible to study once the melting transitions start at about 90°C.

4. Tensile testing

Tensile measurements were performed on selected blends, the tensile strength, percentage elongation at break and elastic modulus were determined and are presented in Table 6. The tensile strength and elastic modulus of the blends consisting of HDPE with bitumen and LDPE with bitumen increased as the concentration of the respective polyethylene was increased in the blend. Both the tensile strength and elastic modulus of the blend containing 10 pph LLDPE (Exxon sample) are roughly twice that obtained for the blend having 10 pph LLDPE (Dow sample). Interestingly, increasing the concentration of HDPE in the blend from 10 pph to 40 pph has no effect on the value obtained for the elongation at break. However, this behaviour was not observed for the blends consisting of bitumen with LDPE, for which increasing the amount of polymer in the blend from 10 pph to 40 pph reduced the value for elongation at break by about a factor of four. The fall in ductility of this blend was observed previously in a bending mode study [4]. The blend of bitumen with the Exxon LLDPE has an elongation at break roughly 50% greater than that of the blend consisting of the Dow LLDPE with bitumen.

5. Conclusions

The four polyethylenes formed blends with 100 penetration grade bitumen, up to 40 pph (29%) polymer and displayed melting endotherms a few degrees below the melting point of the pure polymer, a behaviour we associate with the bitumen disrupting the crystalline regions of the polymer, so making them smaller. When high density polyethylene was blended with bitumen the fraction of polymer which crystallised when the blend cools remains constant at about 45% as the concentration of HDPE in the blend was increased. Different behaviour was observed when the linear low density polyethylenes were blended with the bitumen, the fraction of polymer which crystallised on cooling decreasing as the concentration of LLDPE in the blend increased. The reverse was seen when low density polyethylene was blended with the bitumen, the fraction of polymer which crystallised increased as the amount of LDPE blended increased. It would appear that the bitumen becomes more saturated with the amorphous content of the less crystalline LDPE and as such a larger proportion of the crystalline phase is present when the blend cools. This is a somewhat surprising result as this behaviour was not seen for the LLDPE (Dow sample) which has a similar crystalline content to the LDPE.

Annealing blends of bitumen with HDPE at 130°C had a marked effect on the crystallites present. Annealing resulted in the presence of two and sometimes three different crystallite size distributions in the blends. The smaller less perfect crystallites in the unannealed samples reform and attain a more stable thermodynamic state, such that the maximum point in the melting peak was greater than before annealing.

As was seen from the DMTA studies, the blends of 100 pen. bitumen with polyethylenes at all compositions were stiffer than bitumen itself, except perhaps for a small region near 0°C for blends with low polymer content. The tan δ plots all showed that the glass transition in the blends started lower than in the pure bitumen. At 50°C, when the bitumen readily flowed all the belnds had a modulus E' at least as large as 3 MPa. Increasing the HDPE proportion from 10 to 40 pph raised the temperature of onset of flow from 80°C to 120°C, a limit also reached by most blends of the LLDPEs, whether the side chains were ethyl or butyl. The onset of flow conincided with the DSC-observed melting of the crystallites, which serve to crossslink an extensive chain network at some point when weight fractions were over 20%. In contrast, the blends with LDPE flowed between 90 and 100°C.

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