A Dynamic Mechanical and Thermal Study of Various Rubber–Bitumen Blends

A. H. FAWCETT, T. M. McNALLY*

School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, N. Ireland

ABSTRACT: Blends of a Nynas 100 penetration-grade bitumen with a *cis*-polybutadiene, a butyl rubber, three polyisobutylenes of different molecular weights, a chlorinated-polyethylene, polychloroprene in latex form, and a polyurethane rubber (scrap Lycra) were prepared using a Z-blade masticator mixer at a temperature of about 180°C. The blends contained between 10 and 40 pph (i.e., 9 and 29%) by weight of rubber. They were characterized by fluorescence optical microscopy, differential scanning calorimetry, and dynamic mechanical thermal analysis. The bitumen-rich phases provided the matrix in most of these systems, polymer-rich extensive phases being formed with butyl rubber, and low- and moderate-molecular-weight poly(isobutylenes) when the proportion rose above 30 pph, and for the poly(cis-butadiene) and chlorinated polyethylene system only when the proportion rose above 40 pph, according to the tan δ plots. Only glass transitions were associated with polymer-rich phases, and there were some melting transitions from paraffinic wax components ejected from the bitumen-rich phases. Below room temperature the modulus of blends of polybutadiene, chlorinated polyethylene, and the polyurethane rubber were similar to that of the bitumen; but those of the other polymers were stiffer by a factor of 50, perhaps because of a rearrangement of the asphaltenes. The softer blends, particularly the first two named above, had loss processes (with tan δ > 0.5) ranging over 200°C or more. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 586–601, 2000

Key words: bitumen; rubber; blends; dynamic mechanical thermal analysis; differential scanning calorimetry

INTRODUCTION

Bitumen and bituminous binders have been used for over five thousand years as waterproofing and bonding agents.[1] The earliest recorded use was by the Sumerians around 3800 b.c., and the Egyptians used it in their mummification processes.[2,3] However, bitumen is brittle in cold environments and flows readily at temperatures above 45°C.

Correspondence to: A. H. Fawcett.

* *Present address:* MVC Technology Research Group, Polymer Processing Research Centre, The Queen's University of Belfast, Stranmillis Rd., Belfast BT9 5AH UK.

These limitations of bitumen may be overcome and the properties significantly modified by blending a polymeric material with bitumen. Polymer–bitumen blends find widespread use in road[4–7] and roofing[5,8] applications. Improvements in low-temperature flexibility and resilience of bitumen might be achieved by incorporating a rubber into the system. In this article, we discuss the preparation and characterization of blends of bitumen with *cis*-polybutadiene, butyl rubber, with three polyisobutylenes having M_n = 40, 990, and 2100 k, chlorinated polyethylene, a polychloroprene (Neoprene latex) and with a polyurethane thermoplastic rubber (Lycra). Table I records the details of the different elastomers

Table I   The Rubbers Used in This Study

Rubber Name	Rubber Grade/Type	Supplier/Source	Molecular Weight
Polybutadiene	98% *cis*-Isomer	Fluorochem Ltd.	—
Butyl rubber	268	Exxon Chemicals	450,000[a]
Polyisobutylene	i) Vistanex LM-MS ii) Vistanex MM L-80 iii) Vistanex MM L-140	Exxon Chemicals	i) 40,000[a] ii) 990,000[a] iii) 2,100,000[a]
Chlorinated polyethylene	Hypalon CPR-6158 (36% chlorine content)	DuPont	160,000[b]
Neoprene latex	115 (35% solids by weight)	DuPont	—
Polyurethane rubber	Lycra (scrap)	DuPont	—

[a] Manufacturer literature; viscosity-average molecular weight.
[b] Determined using gel permeation chromatography at 25°C with tetrahydrofuran as a carrier solvent.

used. The second rubber, butyl rubber, a copolymer of isoprene and isobutylene,[9] had such a low isoprene content that it was essentially a polyisobutylene (PIB) with a different molecular weight. Two rubbers contained chlorine and, thus being polar, may disperse in a different manner in the colloidal bitumen, the first being poly(2-chlorobutadiene), and the second a chlorinated polyethylene with 36% chlorine content by weight. The bitumen itself was a Nynas product from the Venezuelan oil field (100 penetration grade) of a type often used in roofing membranes[5] and, by iatroscope analysis, contained aromatics, resins, asphaltenes and paraffins in the proportion of 47 : 31 : 16 : 6.[10] We have also examined systems containing an EP rubber and ethylene vinyl acetate copolymers, and these will be reported on elsewhere. The proportions of rubber used cover the range of present commercial practice, which in one case extends to about 28%.[5,11] By investigating such a wide range of concentrations, we may detect a "phase inversion," the establishment of an extensive polymer-rich phase.

EXPERIMENTAL

All blends were prepared in the temperature range of 160 to 180°C in a Z-blade masticator mixer at concentrations of 10, 20, 30, and 40 parts of polymer per hundred parts of bitumen (pph), as described in detail previously.[10] This range includes the concentrations of several useful polymer—bitumen blends.[6–9] They were examined by fluorescence optical microscopy to characterize the macroscopic phase morphology of the blends, by differential scanning calorimetry (DSC) to detect the presence of any glass transitions and melting endotherms and by dynamic mechanical thermal analysis (DMTA) at five frequencies (0.3, 1, 3, 5, and 10 Hz) to measure, *inter alia*, the variation in modulus with frequency and temperature. For this purpose, melted blends were cast in the form of 2-mm-thick slabs, from which 5 $\times$ 20 mm samples were cut.[10] Since the measurements on the bitumen alone were made in the shear mode (G'), the values were of one-third of the remainder (E') that were obtained in the bending mode[12] with a single cantilever configuration.

## RESULTS AND DISCUSSION

Polybutadiene–Bitumen Blends

The fluorescence photomicrographs for the 10- and 40-pph blends with bitumen are shown in Fig. 1(a) and (b). A grey and probably polymer-rich medium is dispersed throughout the area of the samples under view. It is possible that certain constituents of the bitumen that fluoresce (e.g., aromatics) have been absorbed by the rubber to produce a rubber-rich phase. Like certain polyolefins,[10,11] the polymer-rich phase does appear to be continuous, even when 10-pph polymer has been added; but curiously, dark and, presumably, bitumen-rich spheres of about 10 μm in size are more evident in Fig. 1(b). The nonpolar polybutadiene preferentially absorbs certain components of the bitumen and becomes swollen at elevated temperatures.
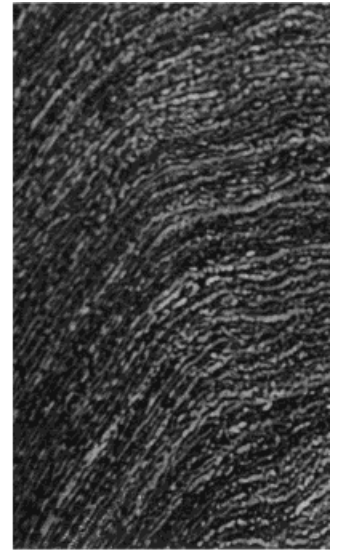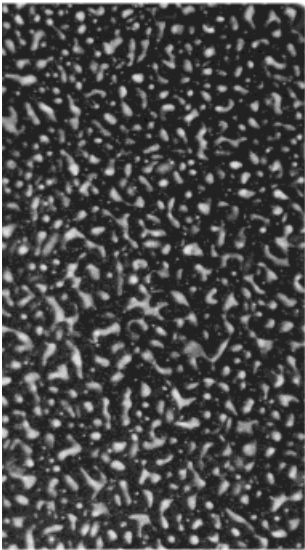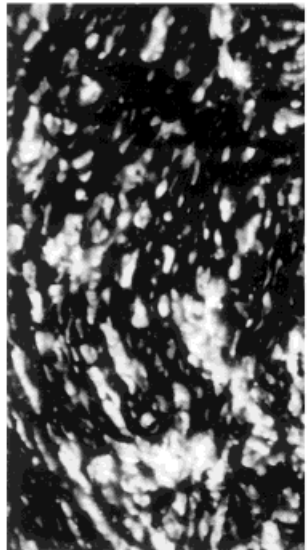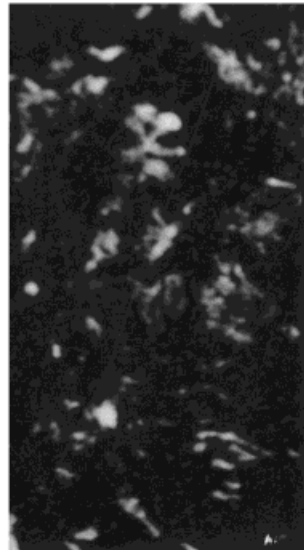
(a)

(b)

(c)

(d)

(e)
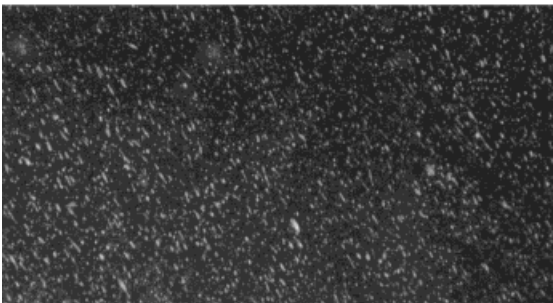

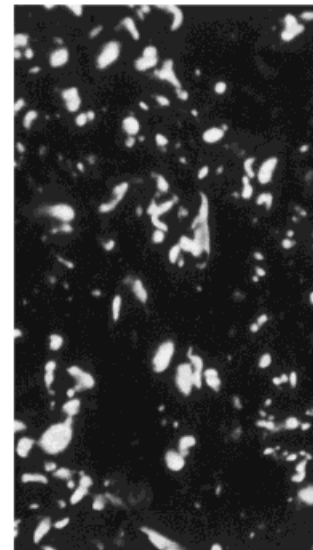
(f)

(g)

(h)

(i)
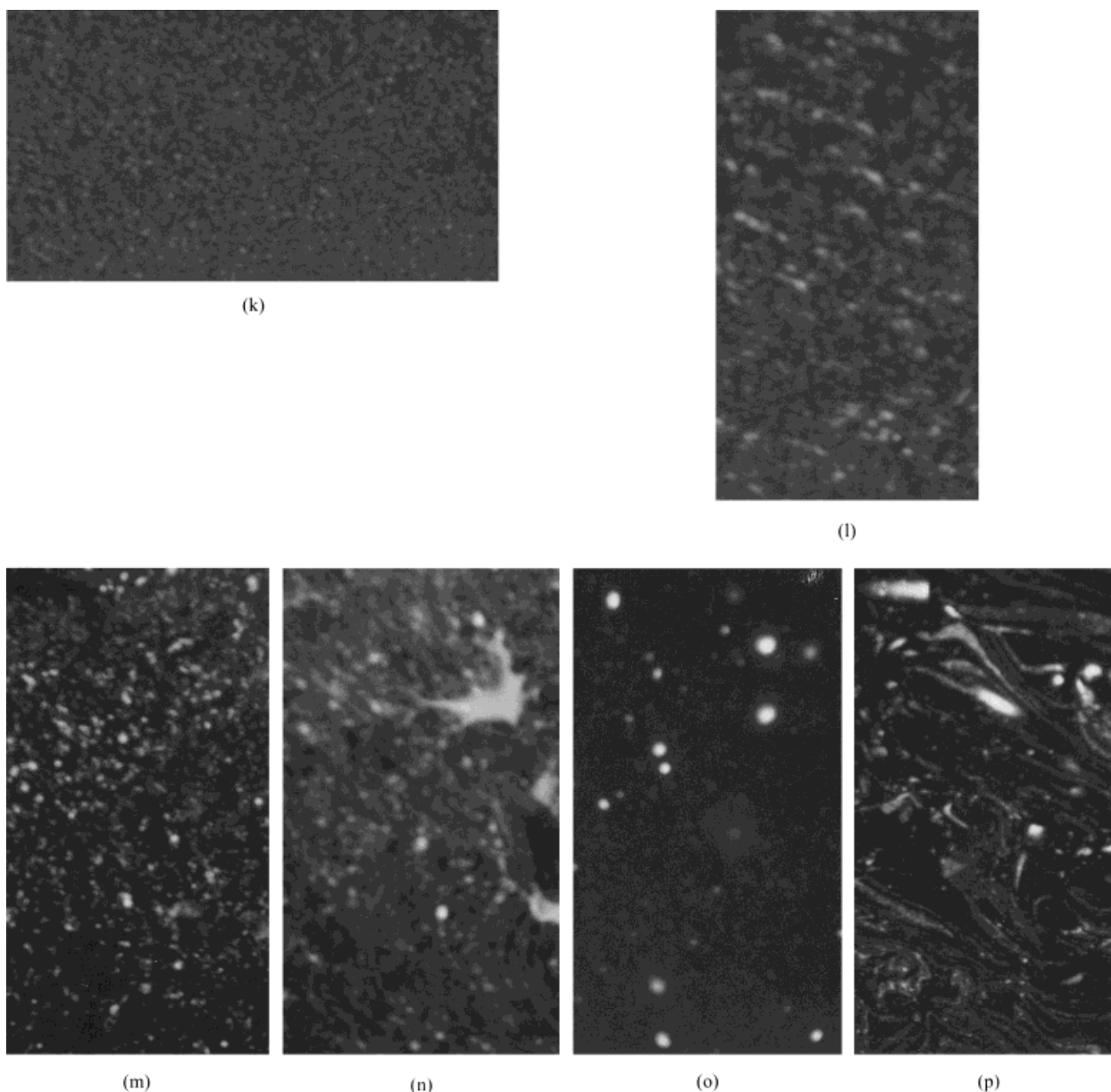

(j)

(k)

(l)

(m)   (n)   (o)   (p)
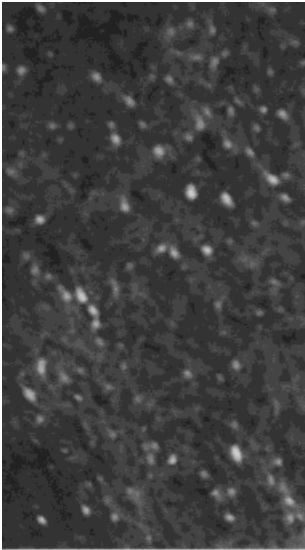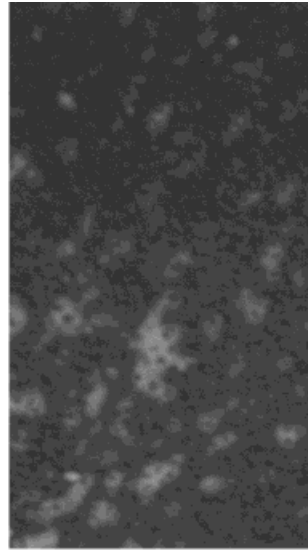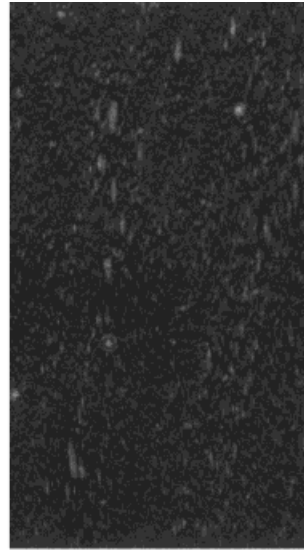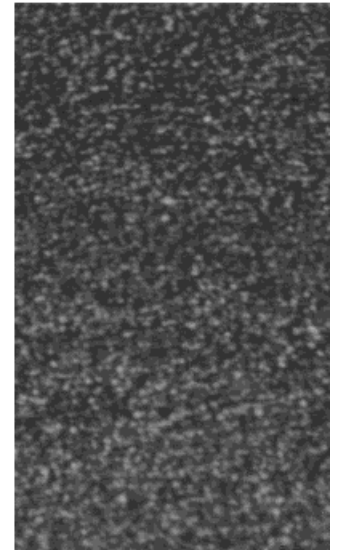
Figure 1 (*Continued from the previous page*) Fluorescence photomicrographs of blends of 100-penetration-grade bitumen wit (a) 10-pph poly(*cis*-butadiene), (b) 40-pph poly(*cis*-butadiene), (c) 10-pph butyl rubber, (d) 40-pph butyl rubber, (e) 10-pph PIB (40 k), (f) 40-pph PIB (40 k), (g) 10-pph PIB (990 k), (h) 40-pph PIB (990 k), (i) 10-pph PIB (2100 k), (j) 40-pph PIB (2100 k), (k) 10-pph chlorinated polyethylene, (l) 40-pph chlorinated polyethylene, (m) 10-pph neoprene latex, (n) 40-pph neoprene latex, (o) 10-pph Lycra, and (p) 40-pph Lycra (×97).

The DSC traces for polybutadiene and its four blends with bitumen are shown in Figure 2. The curve of the rubber itself shows a sharp crystalline melting endotherm at about −9°C, with a shoulder feature at −13°C, which extends upwards from about −50°C. The T_g of this rubber is below this temperature but is typically between −95 and −118°C for the *cis*-isomer.[13] The DSC curves obtained for the blends displayed two general processes, a low-temperature glass transition temperature between −23 and 28°C, and a small endotherm at about 120°C for all the blends. It is thought that wax-like paraffinic constituents of the bitumen are not absorbed by the polymer-rich
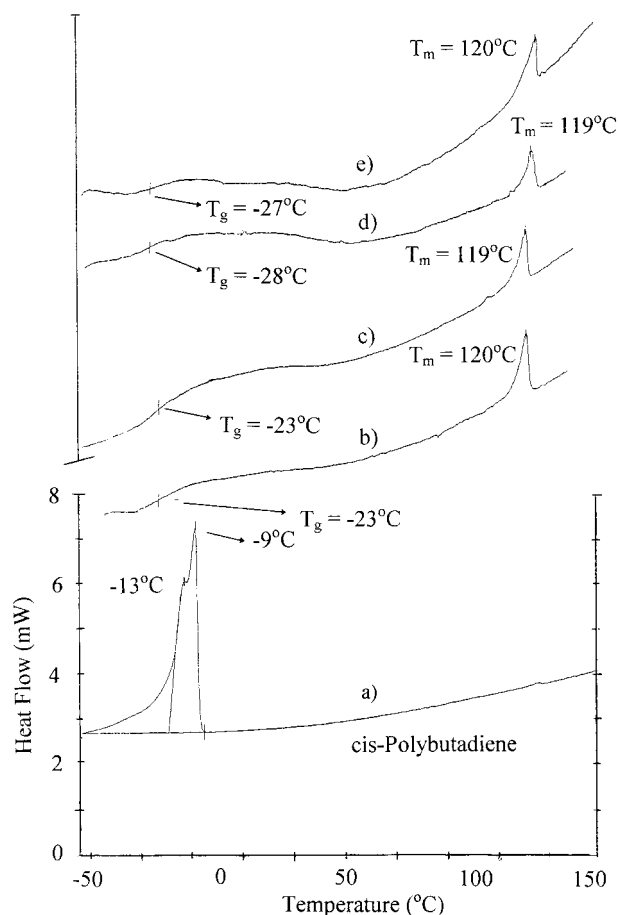
Figure 2 DSC curves for (a) poly(*cis*-butadiene), (b) 10-, (c) 20-, (d) 30-, and (e) 40-pph blends of polybutadiene with 100 bitumen.

phase and, hence, are excluded from the main blend matrix, giving rise to a separate transition in the DSC curve.[14] These waxes have some crystalline order but are present in small amounts. The large crystalline transition seen for the rubber itself is not seen in the DSC curves of the blends, indicating that the crystalline component of the rubber has been dissolved within the bitumen. Table II lists the DSC characteristics of

these blends.

The variation with temperature of loss angle (as tan δ) and storage modulus and loss modulus at 1 Hz for the blends of the polybutadiene with bitumen are shown in Figures 3 and 4. The data for the bitumen are also plotted. (The values of E' for the bitumen were multiplied by 3, after being measured in the shear mode, for comparison with the rest of the values measured in the bending mod).[12] It can be seen that even an addition of 10-pph polybutadiene reduces the storage modulus at 0°C below that of bitumen itself and that the effect is progressive with the rubber content, in keeping with the low T_g of the polymer. However, at 40°C, the order in the moduli is reversed, with the blends being about 20 times stiffer than the bitumen, because the bitumen properties change considerably with temperature and, unlike the blends, the bitumen flows readily above that temperature. Even at 200°C, each blend may be measured, with the modulus rising significantly with rubber content, but diminishing in each case as the temperature rose. At about −20°C, the blends become more flexible with increasing rubber concentration in the blend, as the E'' plot in Figure 4(b) shows. This behavior is also reflected by an increase in tan δ for the blends and by the development of a peak in the loss modulus plots having a maximum at temperatures below that of bitumen alone. Peaks just more resolved than that seen here for the 40-pph blend have been associated with the development of polymer-rich phases in other systems.[10] The T_g at peak maximum in the E'' plots for bitumen is about 9°C, but the T_g's of the blends are some 25 to 40°C below this temperature. Once the rubber content rose to 40 pph, the E'' maximum was found at −26°C, which in good agreement with the DSC value of −27°C for the T_g. A peak was also clearly seen at 10°C in the tan δ plot, the resolution of which in other polymer systems has been associated with a phase inversion, the development of an extensive polymer-rich phase.[15] A second pro-

Table II   DSC Characteristics of the Polybutadiene–Bitumen Blends

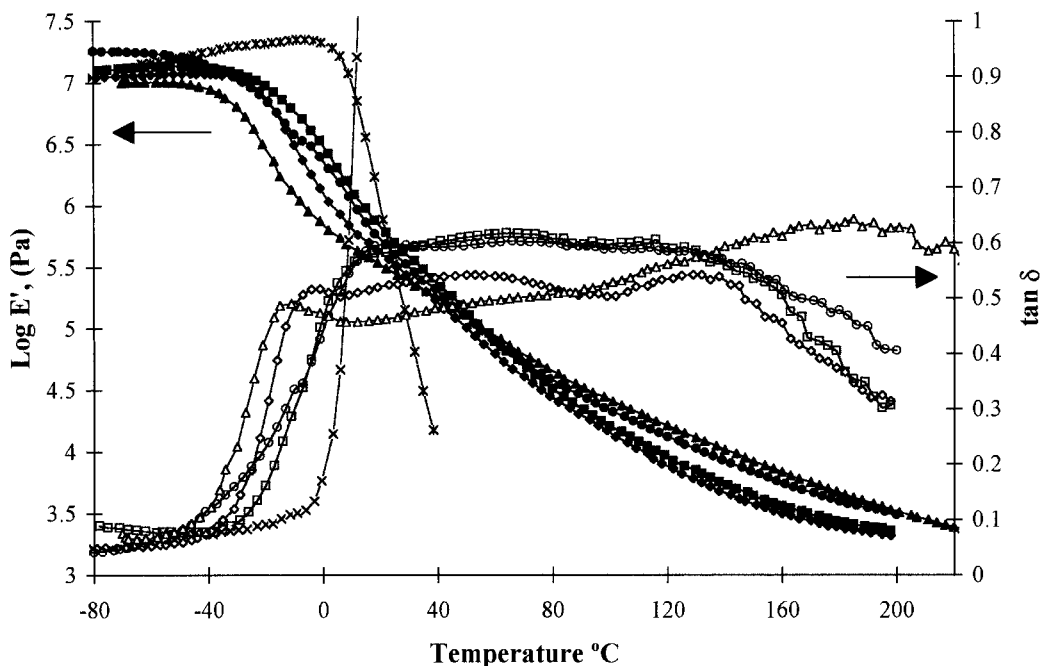| Elastomer (pph)	10	20	30	40	—
Elastomer (%)	9	16	23	29	100
T_g (°C)	−23	−23	−28	−27	<-60
ΔC_p (J g^{-1} deg^{-1})	0.06	0.09	0.08	0.03	—
T_m (°C)	120	119	120	120	−9 & −12
ΔH (J g^{-1})	0.89	0.58	0.39	0.37	41.72

Figure 3 Variation in tan δ and storage modulus, E' (stiffness) with composition for blends of poly(*cis*-butadiene) with 100-penetration-grade bitumen, from DMTA studies at 1 Hz. Bitumen was measured in the shear mode at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph; triangles, 40 pph.

cess may also be seen in the tan δ curves, at about 50 to 60°C, and in the E'' curves in the same region. A third is present at higher temperatures in the tan δ plots, with the very broad maximum moving upwards from about 120°C in all the blends to 160°C as the rubber content rose from 10 to 40 pph. The latter blend on inspection at 200°C had not melted within the measuring system, and it was possible to continue to 230°C. This result is similar to that seen for the mechanical behavior of a swollen rubber due to chain entanglements. High *cis* 1,4-polybutadienes degrade to an extent at 180°C (the temperature at which the blending process was performed), creating free radicals; and on occasions, commercial blending of SBS rubber has been known to form a gel by such reactions when stabilizers have been exhausted. Free radicals may thus have induced crosslinking in the blends and even reactions with the graphitic asphaltenes, to be reflected in a levelling off of the modulus curves at high temperatures.

Butyl Rubber–Bitumen Blends

The fluorescence photomicrographs of this elastomer's blends at ambient temperatures exhibited different features [see Fig. 1(c) and (d)]. The 10- and 20-pph blends showed the presence of very small droplets of a polymer-rich dispersed medium with an average diameter of about 0.2 μm that are distributed randomly throughout the bitumen matrix. Conversely, the photomicrographs of the 30- and 40-pph blends revealed long striations of a polymer-rich dispersed medium, with this lighter feature being clearly more evident in the 40-pph blend [Fig. 1(d)]. The pattern of the features observed for these blends may have been induced by the blending method used.

Butyl rubber itself displayed one feature over the temperature range examined (−60 to 150°C) in its DSC curve, a small endothermic transition with a peak maximum at 112°C. We take the T_g of butyl rubber to be blow −60°C (i.e., below the measured range), between −67 and −75°C.[9] When we blended butyl rubber with bitumen, only one feature was obtained in the DSC curves, a glass transition process. It was difficult to recognize a T_g for the 10-pph blend; but the 20- and 30-pph blends had a T_g at −24°C, and there was a feature at −5°C for the blend containing 40-pph butyl rubber. The DSC characteristics of the blends of butyl rubber with bitumen are shown in Table III.
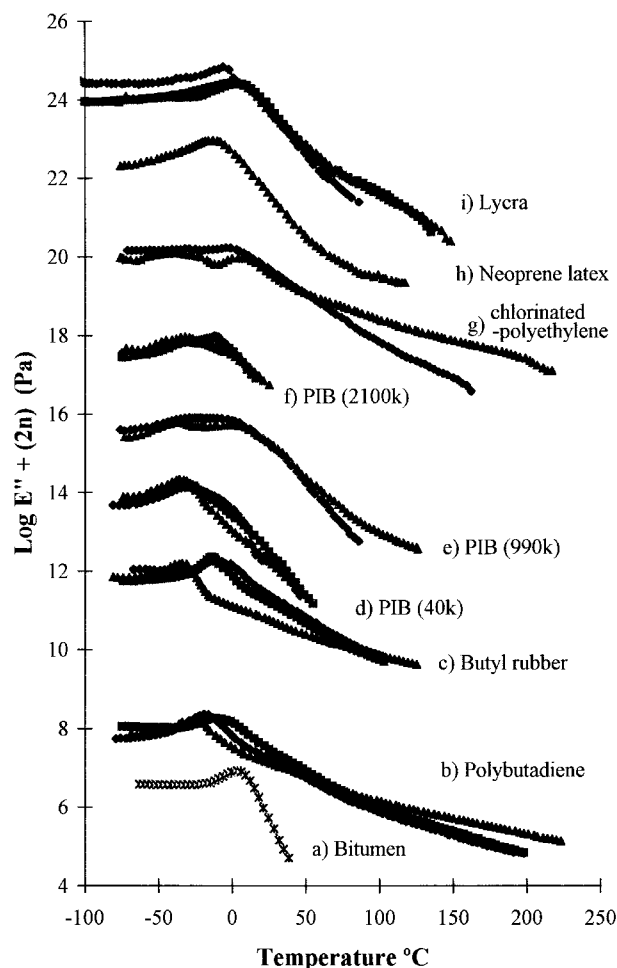
Figure 4 Variation in loss modulus E'' with composition for (a) 100-penetration-grade bitumen ($n = 0$), and blends of the bitumen with (b) poly(cis-butadiene) ($n = 1$), (c) butyl rubber ($n = 2$), (d) PIB (40 k; $n = 3$), (e) PIB (990 k; $n = 4$), (f) PIB (2100 k; $n = 5$), (g) chlorinated-polyethylene ($n = 7$), (h) neoprene latex ($n = 8$) and (i) Lycra ($n = 9$), from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; triangles, 40 pph. Bitumen was measured in the shear mode at 1 Hz.

The variation with temperature loss modulus, and tan δ and storage modulus for blends of butyl rubber with bitumen was investigated using DMTA (see Figs. 4 and 5). The following two features were obtained in the tan δ curves for these blends. The first was a small shoulder-like process between -25 and $-40°C$, which became resolved as the concentration of butyl rubber in the blend was increased to 40 pph, a characteristic of an extensive polymer-rich phase. The development of a polymer-rich phase is clear in the E' plots, for the 40-pph curve is clearly distinct from the others between -40 and $+40°C$. The second process is resolved as a peak with a maximum at $50°C$ for the 10-pph blend but is present only as a shoulder for the remaining blends. Despite the additive being a rubber, all the blends were stiffer than bitumen itself by at least one order of magnitude below $0°C$ and to a lesser extent above $0°C$; and unlike bitumen, the blends could readily be examined within the measurement system up to between 80 and $125°C$. The following two peaks were seen in Figure (c) in the loss modulus plots for these blends; one centered at about $-33°C$, which we associate with a rubber-rich dispersed medium; the second peak, having a maximum at $0°C$ derived from a bitumen-rich matrix. The intensity of the lower temperature peak appears to increase as the concentration of butyl rubber in the blends increases; concomitantly, there is a decrease in the intensity of the higher temperature process associated with the development of a bitumen-rich dispersed medium.

Polyisobutylene–Bitumen Blends

As the molecular weight of the PIB blended with the bitumen increased from 40,000 to 990,000 and then to 2,100,000, the blending time required to disperse the rubber in the bitumen matrix increased from 2 to 10 h and then to 12 h, respectively. In the latter case, blending may not have been completely successful.

PIB ($M_n = 40$ k)–Bitumen Blends

This low-molecular-weight rubber was very viscous and tacky to handle, but the blends of this rubber with bitumen did not appear to be tacky, tough, or elastic. Two fluorescence photomicrographs of the blends of this rubber with bitumen

Table III   DSC Characteristics of the Butyl Rubber–Bitumen Blends

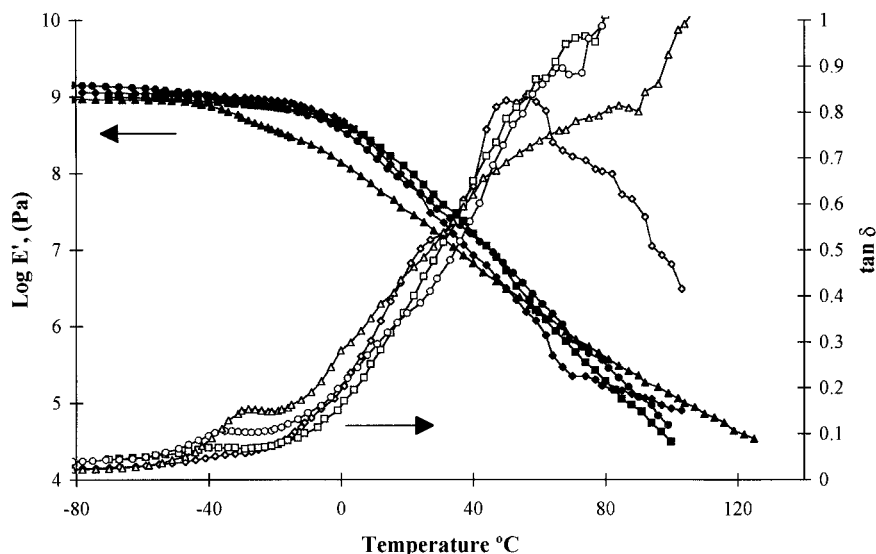| Elastomer (pph)	10	20	30	40	—
Elastomer (%)	9	16	23	29	100
T_g (°C)	—	-24	-24	-5	<-60

Figure 5 Variation in tan δ and storage modulus E' (stiffness) with composition for blends of butyl rubber with 100-penetration-grade bitumen from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph; triangles, 40 pph.

are shown in Figure 1(e) and (f), where light colored polymer-rich phases of about 10 to 50 μm are seen. As more rubber was added to the blend, it appeared to agglomerate in the bitumen matrix. The light-colored polymer-rich dispersed medium may have absorbed certain components of the bitumen, such as the paraffins and the aromatics, with the aromatic content of the bitumen contributing to the fluorescence. However, these blends phase separated readily at temperatures below the blending temperature of 180°C and gave dispersed phases, whose size increased from about 1 to 10 μm to about 5 to 40 μm. The blends were observed to sweat (i.e., to expel the rubber from the blend system) with time.

Both the rubber and its blends with bitumen exhibit only one DSC feature, a glass transition at

−37°C for the rubber itself and at −15°C for the blends, a rise reflecting the stiffening effect of the asphaltenes. The value calculated for the specific heat capacity of the glass transition process approximately halved from 0.20 J g^{-1} deg^{-1} to 0.09 J g^{-1} deg^{-1} when the concentration of rubber in the blend increased from 10 to 40 pph, and so came from the bitumen-rich phase, for as the bitumen content fell, the polymer-rich phase rose in proportion. The T_g was thus a characteristic of the bitumen-rich phase. The DSC characteristics for this rubber and its blends with bitumen are listed in Table IV.

The presence of a glass transition process was also detected by DMTA [see Figs. 4(d) and 6]. In the tan δ curves, the glass transition process progresses from a shoulder feature in the 10-pph

Table IV DSC Characteristics of the Polyisobutylene–Bitumen Blends

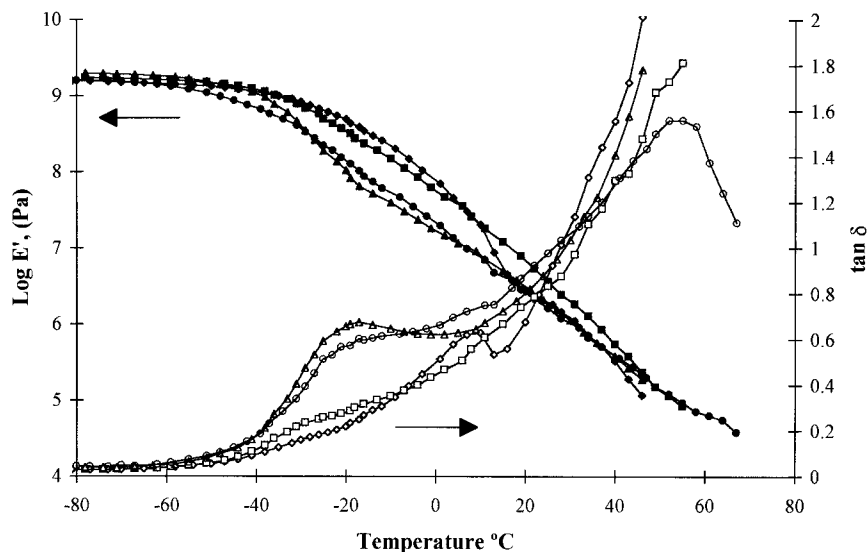| Elastomer | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Polyisobutylene | | | | | | | | | | | | | | |
| Mol wt | 40 k | | | | | 990 k | | | | | 2100 k | | | | |
| pph | 10 | 20 | 30 | 40 | — | 10 | 20 | 30 | 40 | — | 10 | 20 | 30 | 40 | — |
| (%) | 9 | 16 | 23 | 29 | 100 | 9 | 16 | 23 | 29 | 100 | 9 | 16 | 23 | 29 | 100 |
| T_g (°C) | −15 | −14 | −14 | −14 | −37 | −25 | −11 | −18 | −15 | −35 | −14 | −16 | −19 | −10 | −37 |
| ΔC_p (mJ g^{-1} C) | 200 | 940 | 790 | 190 | 40 | 150 | 90 | 110 | 90 | 20 | 200 | 190 | 180 | 110 | 90 |
| T_m (°C) | — | — | — | — | — | 119 | 120 | 119 | 119 | — | 113 & 118 | 113 & 118 | 116 | 117 | — |
| ΔH (J g^{-1}) | — | — | — | — | — | 0.24 | 0.28 | 0.58 | 0.46 | — | 2.02 | 1.85 | 1.20 | 0.85 | — |

Figure 6 Variation in tan δ and storage modulus, E' (stiffness) with composition for blends of polyisobutylene (M_w = 40 k) with 100-penetration-grade bitumen from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph, triangles, 40 pph.

blend to a resolved peak centered at about −20°C for the 40-pph blend, a distinct change in the resolution taking place between 20 and 30 pph. The blends are nearly two orders of magnitude stiffer than bitumen itself below −25°C, and the bitumen is softer than all but the 40 pph blend at 0°C. However, all the blends softened and began to flow within the measurement system between 50 and 65°C, suggesting that either the bitumen-rich phase is continuous or that the polymer-rich phase is weak, as may well be the case, for the molecular weight was low. The loss modulus curves for the blends shows one peak, which becomes more sharp with increasing rubber concentration in the blends. This behavior may result from the rubber-rich and bitumen-rich dispersed media having similar glass transition temperature ranges, so that only one peak is obtained.

PIB (M_n = 990 k)–Bitumen Blends

The fluorescence photomicrographs of two of this rubber's blends with bitumen are shown in Figure 1(g) and (h). It would appear, particularly from the photographs of the 10- and 20-pph blends,[15] that the rubber has been merely sheared and torn and is distributed randomly throughout the bitumen matrix. The photomicrographs of the 30- and 40-pph blends[15] show a more evenly dispersed polymer-rich medium within the bitumen.

The rubber itself displayed one feature in the DSC plots, a glass transition at −35°C. The blends of this rubber with bitumen showed the following two processes in their DSC curves: the first process was a glass transition at −25°C for the 10-pph blend rising to −15°C for the 40-pph blend; the second process was a small endotherm at about 119°C for all the blends, the enthalpy values of which increase from 0.24 to 0.58 J g^{-1} on increasing the rubber content in the blend from 10 to 40 pph. As polyisobutylenes are completely amorphous over a wide temperature range unless stretched, we associate this endotherm with a waxy paraffinic component, which has been ejected from the bitumen during cooling following blending. The DSC characteristics for this rubber and its blends with bitumen are detailed in Table IV.

Addition of this higher-molecular-weight rubber to the 100-penetration-grade bitumen modified its dynamic mechanical and thermal properties for they had a significant modulus value up to 120°C. The variation in loss modulus and tan δ and storage with temperature is shown in Figures 4 and 7, where the bitumen data is replotted. Three features are seen in the tan δ curves, as follows: firstly, a shoulder at about −32°C as with the previous rubber's blends but of very much reduced magnitude, so a polymer-rich phase may
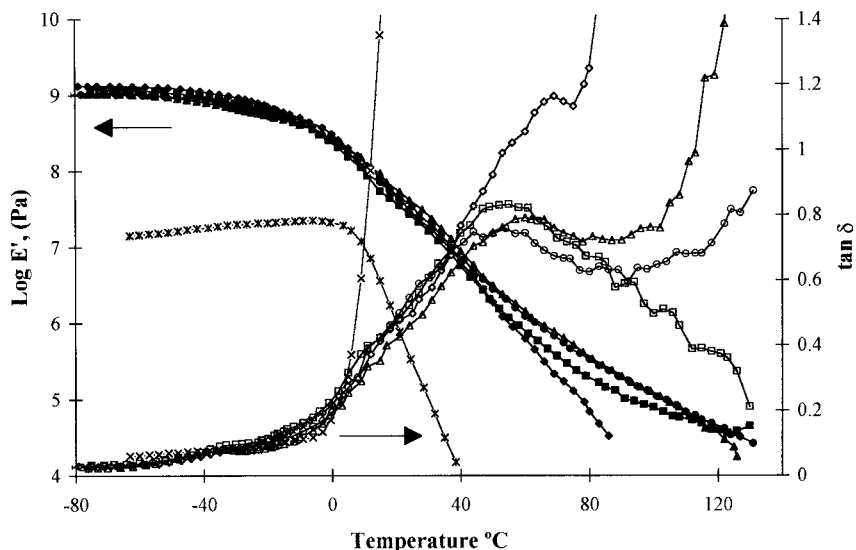
Figure 7   Variation in tan δ and storage modulus E' (stiffness) with composition for blends of polyisobutylene (M_w = 990 k) with 100-penetration-grade bitumen from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph; triangles, 40 pph.

no longer be extensive; secondly, there is a similarly reproduced small process at about 10°C; and, finally, a broad peak with a maximum between 50 and 60°C once the concentration reached 20 pph [Fig. 4(e)]. The lower-temperature shoulder process would appear to be resolved as a peak in the loss modulus plots, which we again associate with a rubber-rich, dispersed medium. The second feature appears at about 0°C in the E'' plots, a little below that of the bitumen itself, but there is also a process at about −40°C, well-resolved for the 30- and 40-pph blends. The modulus of the blends is considerably higher that the bitumen and is dependent very little on the polymer concentration. The storage modulus at 80°C was increased progressively from that of bitumen by the addition of the rubber. The blends softened and began to flow from the measurement system at 85°C for the 10-pph blend and at about 125°C for the remaining blends, some 60°C higher than that seen for the blends consisting of PIB with the lower M_n = 40 k, as is clear in Figure 4.

PIB (M_n = 2100 k)–Bitumen Blends

Figure 1(i) and 1(j) shows the fluorescence photomicrographs of this rubber's blends with bitumen. The rubber component is dispersed as droplets of about 0.3 μm diameter in the 10 pph blend. In the remaining blends, the rubber appears to have agglomerated to give larger, irregularly sized objects 10 to 40 times larger. The rubber itself displayed one process in its DSC curve, a glass transition at −37°C. The DSC curves for the blends exhibited two features, typically a glass transition between −14 and −16°C and an endotherm extending upwards from about 60°C. This endotherm had two sharp peaks in the 10-pph blend at 113 and 117°C but was present as a broad feature with a peak maximum at 116°C for the remaining blends. The enthalpy value for this melting transition decreased by 58% from 2.02 to 0.85 J g^{-1} as the concentration of rubber in the blend was increased from 10 to 40 pph. As this endothermic feature is absent from the DSC curve of the rubber itself, we associate this process with some crystalline paraffinic component of the bitumen, which was ejected from the blend system on cooling after the mixing. The DSC characteristics for this rubber and its blends with bitumen are given in Table IV.

The loss modulus and tan δ and storage modulus of these blends were determined using DMTA, the results being shown in Figures 4(f) and 8. From the storage modulus curves, the blends began to soften and flow at the same temperature as the bitumen, presumably because the continuous phase is bitumen. Despite the additive being a rubber, the blends are nearly two orders of magnitude stiffer than the bitumen itself below −20°C; and when Figures 6 and 7 are considered,
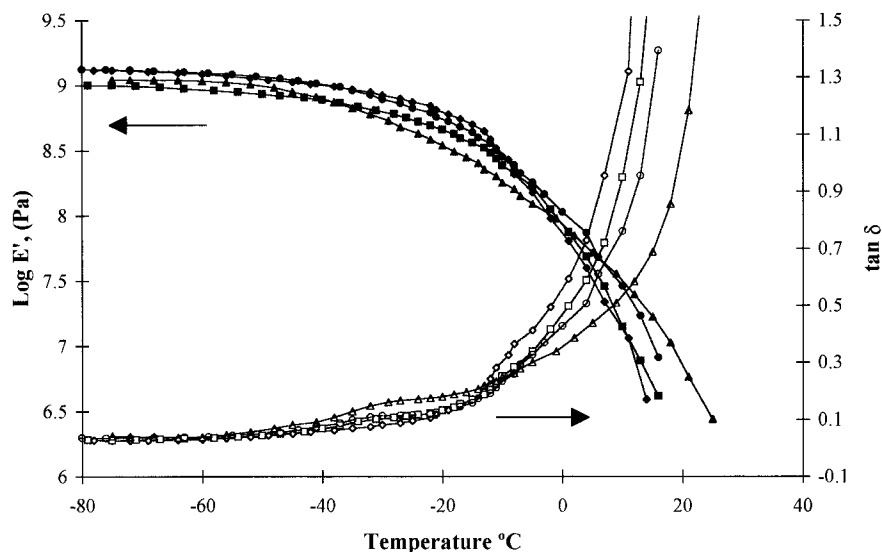
Figure 8 Variation in tan δ and storage modulus E' (stiffness) with composition for blends of polyisobutylene (M_w = 2100 k) with 100-penetration-grade bitumen from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph; triangles, 40 pph.

molecular weight is not relevant. Again, two transitions are observed in both the tan δ and loss modulus curves. In the tan δ plot, a process at about −30°C increases in intensity with increasing rubber concentration but reaches only 0.1, and a large loss process is evident similar to that seen for bitumen alone at about −10°C. Both processes in tan δ are clearly represented in the loss modulus plots by two resolved peaks, with the lower-temperature feature centered at about −32°C and being associated with a rubber-rich dispersed medium, and the higher-temperature peak with a maximum at −10°C and being derived from a bitumen-rich dispersed medium. Since the blends all failed at about 20°C, a temperature much lower than for those with lower molecular weight, we assume the high molecular weight of the rubber may have hindered the formation of the blends, for the full development of the expected rheological properties at high temperatures was not found.

Chlorinated–Polyethylene–Bitumen Blends

Characteristic features are less discernible in the fluorescence photomicrographs of blends of bitumen with chlorinated-polyethylene [see Figure 1(k) and 1(l)]. However, 1-μm-sized objects were seen in the 10-pph blend, and longer streaks of a polymer-rich dispersed medium were evident,

their shape probably reflecting the mixing process, in the 40-pph blend.

The DSC trace of this rubber showed a glass transition temperature at −16°C, followed by an endotherm at 2°C. The DSC curves of the blends of bitumen with this rubber displayed only one glass transition process between −15 and −19°C, and (with the exception of the 10 pph blend) an endotherm at about 115°C, which becomes more intense with increasing rubber content in the blends. That the endotherm for the 40-pph blend split into two peaks at 108 and 114°C and extended upwards from about 60°C was a characteristic of polymer crystallite melting behavior, as we found in blends of various polyethylene's with the same bitumen,[10] and appears only, perhaps, because the bitumen prevents entanglements, hindering crystallization. This would suggest that the endothermic transition observed for the bitumen-chlorinated–polyethylene blends may not be derived from any paraffinic, wax-like constituent of the bitumen. The feature is very small, since runs of —CH_2— groups in the polymer will be infrequent, but is observed in the blends as the fluid bitumen reduces the hindrance of entanglements on the crystallization. The DSC characteristics for blends of bitumen with chlorinated-polyethylene are detailed in Table V.

Table V   DSC Characteristics of the Chlorinated-Polyethylene–Bitumen Blends

Elastomer (pph)	10	20	30	40	—
Elastomer (%)	9	16	23	29	100
T_g (°C)	−15	−16	−17	−19	−16 & +20
ΔC_p (J g^{-1} deg^{-1})	0.11	0.13	0.10	0.10	0.38 & 5.72
T_m (°C)	—	116	118	110 & 115	—
ΔH (J g^{-1})	—	0.27	0.15	3.2	—

The variation over a wide temperature range of loss modulus and storage modulus and tan δ at 1 Hz for several blends of bitumen with chlorinated-polyethylene are shown in Figures 4(g) and 9. Until a temperature of 30°C was reached, the blends were of similar stiffness to the bitumen itself; but each sample persisted within the DMTA system until at least 200°C, whereas the bitumen became too soft to study at 50°C, even in the shear mode. The two following main processes were observed in the tan δ plots for the blends: the first occurred near 15°C, where the bitumen passes through its glass transition temperature range, but since the process became more intense with increasing rubber content, we conclude it is predominately a property of a polymer-rich phase (the process became the main feature in the tan δ plot when the rubber concentration rose to 40 pph, as if the polymer-rich phase was then extensive); the second feature was present at higher temperatures and became broader and less intense with increasing rubber content in the blends. A third minor feature was evident in the blends at about 60°C. All the blends were softer than the bitumen alone below about 25°C, the effect being most marked for the 40-pph sample at around −20°C. Above 50°C, the mechanical strength of the blends is primarily derived from the chlorinated-polyethylene, reflected by an increase in E' with rubber content and a levelling off of the modulus curve as the temperature in-
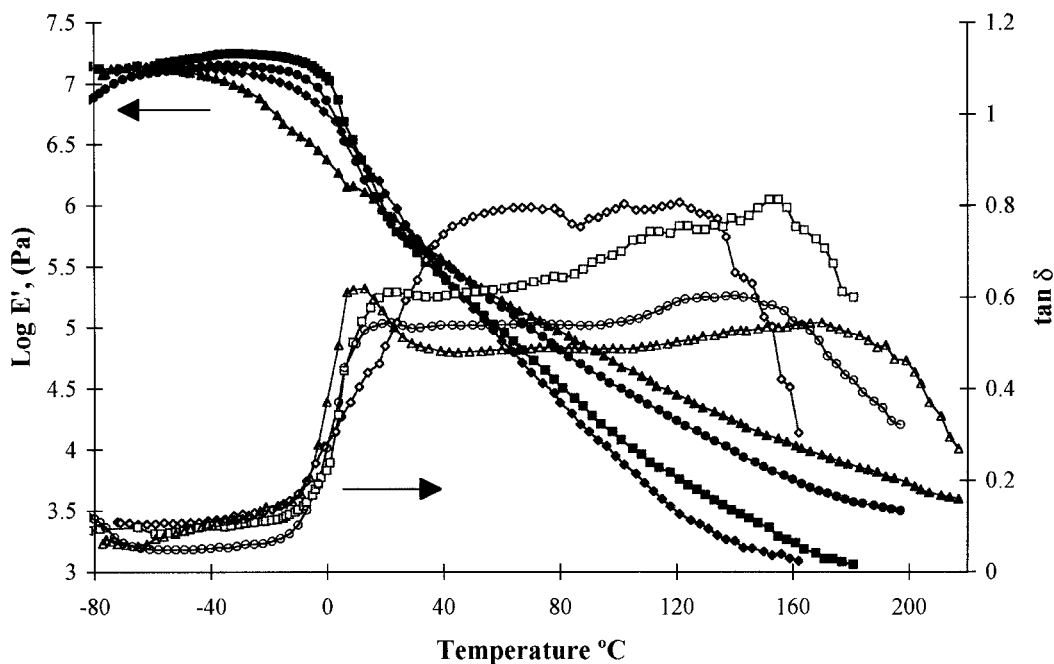

Figure 9 Variation in tan δ and storage modulus E' (stiffness) with composition for blends of chlorinated-polyethylene with 100-penetration-grade bitumen from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph; triangles, 40 pph.

Table VI DSC Characteristics of the Neoprene Latex–Bitumen Blends

Elastomer (pph)	10	20	30	40	—
Elastomer (%)	9	16	23	29	100
T_g (°C)	−23	−23	−24	−24	−40
ΔC_p (J g^{-1} deg^{-1})	0.17	0.16	0.13	0.16	0.28

creases. There is no change in these trends when the crystallites melted near 115°C.

Polychloroprene (Neoprene Latex)–Bitumen Blends

This latex blended very easily with this 100-penetration-grade bitumen, but rapid and even violent evaporation of water from the latex occurred during the first 5 to 10 min of the blending regime. The fluorescence photomicrographs of the blends of neoprene with bitumen are shown in Figure 1(m) and (n) and display a range of grey features. The polymer-rich dispersed medium was limited in extent in all the blends, this phase being present as droplets having diameters between 0.02 and 0.4 μm. Close examination of the photomicrograph obtained for the 30-pph blend shows the polymer-rich dispersed medium to be extended over a greater area than that seen for the other blend compositions, perhaps reflecting a phase inversion process. According to the DSC traces, the Neoprene alone had a glass transition at −41°C. When blended with bitumen in all com-

positions, only one process was obtained, a glass transition at about −24°C, halfway between the T_g's of neoprene and its blends with this bitumen. The DSC characteristics for this elastomer's blends are detailed in Table VI.

The blends were examined at 1 Hz by DMTA [see Figs. 4(h) and 10)]. One main process at about 30°C was seen in the tan δ curves for the blends, the transition becoming broader and less intense with increasing polymer content. It came at about −10°C in each E'' plot. The 10- and 20-pph blends also exhibited a curious but reproducible minor process as a shoulder to the main loss peak at about −5 and +5°C, respectively. An increase in the intensity of the tan δ peak occurred at about −30°C, representative of the low-temperature flexibility of these blends. All the blends begin to soften before bitumen itself, the peak maxima in the loss modulus curves being 20°C below that of bitumen alone. At temperatures below −30°C, the blends were more than one order of magnitude stiffer than bitumen it-
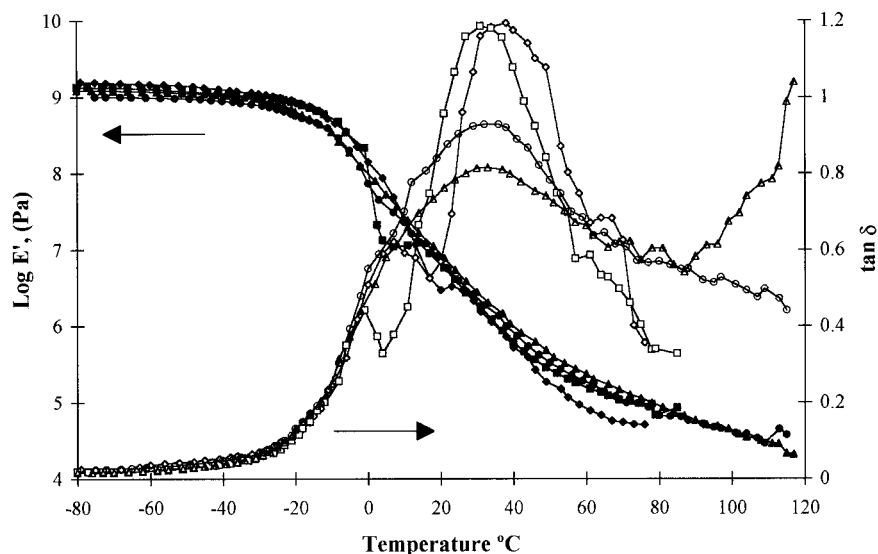

Figure 10 Variation in tan δ and storage modulus E' (stiffness) with composition for blends of Neoprene latex with 100-penetration-grade bitumen from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph; triangles, 40 pph.

self. The temperature at which the blends begin to soften and flow out of the measurement system increases with increasing neoprene content in the blends, from 70°C for the 10-pph blend to 115°C for the 40-pph blend.

Polyurethane Rubber (Lycra)–Bitumen Blends

The scrap Lycra apparently blended easily with the bitumen. The fluorescence photomicrographs of this rubber's blends with bitumen showed a random distribution of Lycra within the bitumen matrix [Figure 1(o) and 1(p)]. Droplets of a polymer-rich dispersed medium with an average diameter of between 8 and 12 μm were present in the 10- and 20-pph blends only, this medium being present as striations in the 30- and 40-pph blends. The extent of the polymer-rich environment, seen as light regions in the photomicrographs in all the blends, is less than the proportion that was added to each blend, so we examined them further to see whether a large portion of the Lycra did not dissolve in the bitumen matrix. Close visual and optical microscopic inspection of the blend samples revealed the presence of small fibers still not dispersed within the blend matrix. It may be that the mechanical properties of these blends are, in part, derived from the strengthening effect of the Lycra in fiber form at temperatures greater than 50°C.

The DSC traces of Lycra and its blends with bitumen are shown in Figure 11. The glass transition temperature (T_g) of Lycra is presumed to be below −60°C, but the Lycra displayed a small endothermic transition at about 3°C. The blends exhibited a T_g at about −21°C, having a specific heat value of 0.16 J g^{-1} deg^{-1} for the 10-pph blend and decreasing slightly to 0.12 J g^{-1} deg^{-1} for the 40-pph blend (see Table VII). Interestingly, the 10- and 20-pph blends display small endotherms at 116 and 120°C, respectively, this process being absent from Lycra itself and those blends consisting of 30- and 40-pph Lycra. This feature seen for the 10- and 20-pph blends may be associated with a paraffinic or waxy component within the bitumen,[16] a constituent of the bitumen not ejected from the system at higher loading of Lycra.

The variation with temperature of the loss modulus and storage modulus and tan δ at 1 Hz for the Lycra–bitumen blends are shown in Figures 4(i) and 12. With the exception of the 10-pph blend, the other blends were less stiff then bitumen itself below −10°C (i.e., the T_g of bitumen).
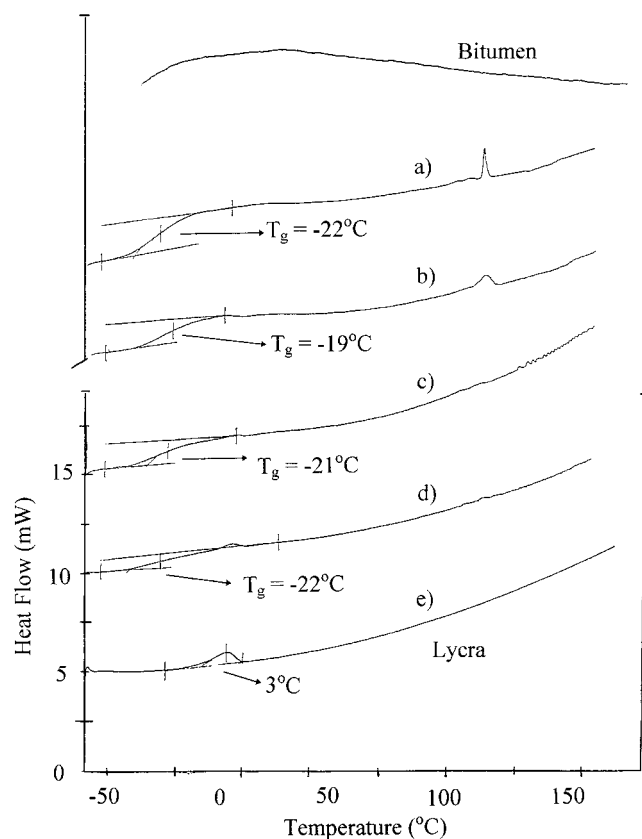

Figure 11 DSC curves for (a) 10, (b) 20, (c) 30, and (d) 40 pph blends of Lycra with 100-penetration-grade bitumen and (e) Lycra itself.

The 10-pph blend was a little stiffer than bitumen alone below 0°C. Above 0°C, the blends were stiffer than bitumen itself. There is a sharp drop in the storage modulus at 10°C for the 10-pph blend, and, at 30°C for the 20-, 30-, and 40-pph blends. This behavior, we assume, is due in part to the increased Lycra content in the blends, inducing more flexibility at lower temperatures. A slight increase in the modulus of the 10- and 20-pph blends was obtained between −50 and −10°C. We attribute this to either relaxation of the Lycra fibers in the blend, which, on reorientation, result in an increase in the modulus before the T_g of the blend is attained, or, due to internal stresses, induced in the sample during the clamping process. This phenomenon was not seen for the 30- and 40-pph blends. The blend consisting of 10-pph Lycra softened and began to flow at about 80°C, the remaining blends persisting within the measurement system up to between 120 and 140°C.

Table VII   DSC Characteristics of Lycra–Bitumen Blends

Elastomer (pph)	10	20	30	40	—
Elastomer (%)	9	16	23	29	100
T_g (°C)	−22	−19	−21	−22	<−60
ΔC_p (J g^{-1} deg^{-1})	0.16	0.12	0.13	0.12	—
T_m (°C)	120	116	—	—	—
ΔH (J g^{-1})	0.39	0.54	—	—	—

CONCLUSIONS

All the blends examined had extensive bitumen-rich phases, according to the fluorescence photomicrographs, and there was no evidence in these of a phase inversion at concentrations of up to 40-pph polymer. For these amorphous rubbers, DSC scans did not detect any transitions caused by melting of polymer crystallites in the blends, in contrast to the behavior of many bitumen–polyolefin systems.[10,17] Any mechanical property is thus derived chiefly from the bitumen-rich phase. The bending modulus was at least 10^9 Pa at low temperatures for all but the poly(*cis*-butadiene), chlorinated polyethylene, and Lycra blends. In having high moduli at low temperatures (enhanced over that of the parent bitumen), the other rubbers therefore resemble blends from many polyethylenes,[10] polyolefins,[15] and certain other polar polymers.[18] All the present blends

became softer as the rubber content rose from 10 to 40 pph, the Lycra 10-pph blend being significantly harder than those with a higher rubber component. Since these rubbers have moduli between 10^5 and 10^7 MPa, we attribute their stiffening effect to a rearrangement of the asphaltenes in the bitumen, perhaps prompted by a sequestering of the plasticizing paraffins and aromatics to the rubber-rich phases. Of the rubbers that give softer blends, the first is unsaturated, and the others contain polar groups and so may interact more with the aromatic components and even the asphaltenes in the bitumen. Supporting this is the appearance of melting peaks in the DSC scans from crystallized paraffinic components for the poly(*cis* butadiene) and some Lycra blends (Figs. 2 and 11) and for the chlorinated polyethylene blends (Table V), but such peaks were also seen for the higher-molecular-weight PIBs (Table IV). The presence of the polymer per-
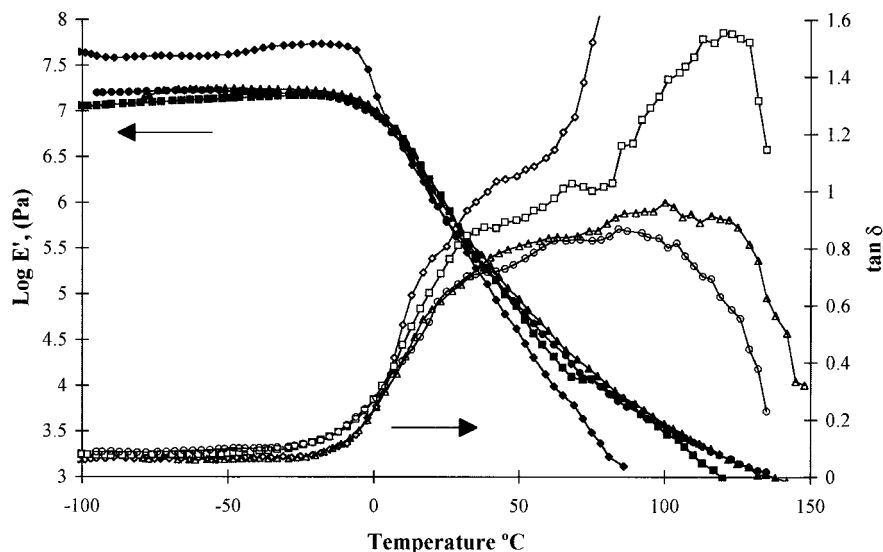

Figure 12   Variation in tan δ and storage modulus E' (stiffness) with composition for blends of Lycra with 100-penetration-grade bitumen from DMTA studies at 1 Hz. Diamonds, 10 pph; squares, 20 pph; circles, 30 pph; triangles, 40 pph.

turbs the manner in which the four components of the bitumen interact with each other.

DMTA measurements ceased automatically as the temperature rose, once the signal intensity from the transducer fell below a certain sensitivity level, as Figure 4 shows. This happened at 230°C with the 40-pph poly(*cis*-butadiene) blend when the modulus was 10^3 Pa, but as soon as 25°C for the 40-pph blend of the 2.1*M* molecular weight PIB when the modulus was still $10^{6.5}$ Pa. Blending in the latter case may have been inadequate, though the low-temperature modulus was enhanced. For the low-molecular-weight PIB mixtures, there was a large tan δ (tan δ = 0.8) at −20°C; but the higher molecular weight PIBs (and the butyl rubber) had at that temperature much lower values of tan δ, even when the weight fractions were the same. Molecular weight has controlled the dispersion into the bitumen-rich phase. The critical molecular weight lies between 40 and 450 k (if we regard the butyl rubber as thermodynamically equivalent to a PIB). In the *E″* plots for the blends of the PIBs and the butyl rubber, two features were seen, as follows: one at about −40°C from the rubber-rich phase, and the other less defined at about 5°C from the bitumen-rich phase; and the butyl rubber appeared intermediate between the 40 and 990 k PIBs, so the isoprene segments have no strong influence. From the variation of the tan δ peak with frequency and temperature for the 40-k molecular weight sample in the 40-pph blend, we obtained an Arrhenius activation energy of about 110 kJ mol^{-1}.

At −20°C the poly(*cis*-butadiene) blends of high rubber content had a larger loss feature (tan δ = 0.5); similarly, the chlorinated polyethylene blend had a distinct feature (tan δ = 0.6) at 5°C. In other blends, the appearance of such a well-resolved feature has been associated with a phase inversion, the development of an extensive polymer-rich phase, and makes a significant evolution in low-temperature properties. Polarity moves the process to higher temperatures, for the loss in the polychloroprene blends coming at about 25°C (tan δ = 1.2), even for the 10- and 20-pph blends. The blends of the nonpolar polybutadiene and the polar chlorinated polyethylene had large damping effects over temperature ranges of at least 200°C at the frequency of 1 Hz. The differences between the blends of the different rubber are clearly sensitive to factors such as molecular weight, and the manner in which the rubbers of differing chemical structure interact with the four components of the bitumen.

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