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An investigation into the behaviour of SPBT and SPBT/PC blends

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Abstract

Thermal, wide angle X-ray scattering and light microscopy studies have been carried out on sulphonated poly(butylene terephthalate) (SPBT) and its blends with polycarbonate (PC). A better understanding of the morphology and behaviour of the ionomer SPBT as well as initial information on the miscibility and level of crystallinity of the new family of ionomer blends, SPBT/PC, has been obtained. The samples with a degree of sulphonation above 7 mol.% showed the partial miscibility as well as improved optical clarity with respect to blends of non-sulphonated PBT/PC. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is always a requirement for new improved polymeric materials. The modification of existing polymers by the incorporation of ionic groups, for example, or by blending with a second polymer provides a cost efficient means of selectively improving polymer properties. Polymers containing a small percentage (typically less than 10 mol.%) of ionic groups chemically bound to a non-polar chain are termed *ionomers*. Their physical and mechanical properties are often dramatically changed with respect to the starting material [1,2].

This paper is concerned with the physical properties and behaviour of the sulphonated, (ionomeric) form of the well known engineering thermoplastic poly(butylene terephthalate) (PBT) and its blends with polycarbonate (PC) (see Fig. 1). PBT is a semi-crystalline polymer which has wide ranging applications, its blend with polycarbonate (PBT/PC), which is an ideal material for injection moulding, has good mechanical properties and chemical and solvent resistance. Due to its crystallinity this blend is opaque [3,4].

The novel ionomer sulphonated poly(butylene terephthalate), (SPBT) has been shown by Gorda and Peiffer [5] to have mechanical properties that are as favourable as its non-ionic precursor, PBT, but with greatly reduced crystallinity, leading to improved optical clarity. Hence, it is anticipated that an ionomeric blend, SPBT/PC, should have equally favourable properties as PBT/PC but with the added advantage of optical clarity and other property improvements leading to a new range of possible applications.

In order to achieve this aim, it is necessary to gain an improved understanding of the properties and behaviour of SPBT and to investigate the miscibility and physical properties of the new blend system with a view to optimising both the functionality of the homopolymer and the blend composition. In this context, ‘optimising’ means choosing the best combination of the degree of sulphonation of SPBT and its weight content in the blend to yield the minimal crystallinity, hence the highest transparency. To this end, we have carried out comprehensive studies of the PBT, SPBT and their blends with PC using a combination of thermal techniques, wide angle X-ray scattering and light microscopy. As a result, we have gained a deeper understanding of the morphology and behaviour of the ionomer, SPBT. Initial information on the miscibility and level of crystallinity of the new family of ionomer blends, SPBT/PC, has been obtained.

2. Experimental

2.1. Materials: PBT and SPBT

Samples of PBT [poly(butylene terephthalate)] and SPBT [sulphonated poly(butylene terephthalate)] were the same as

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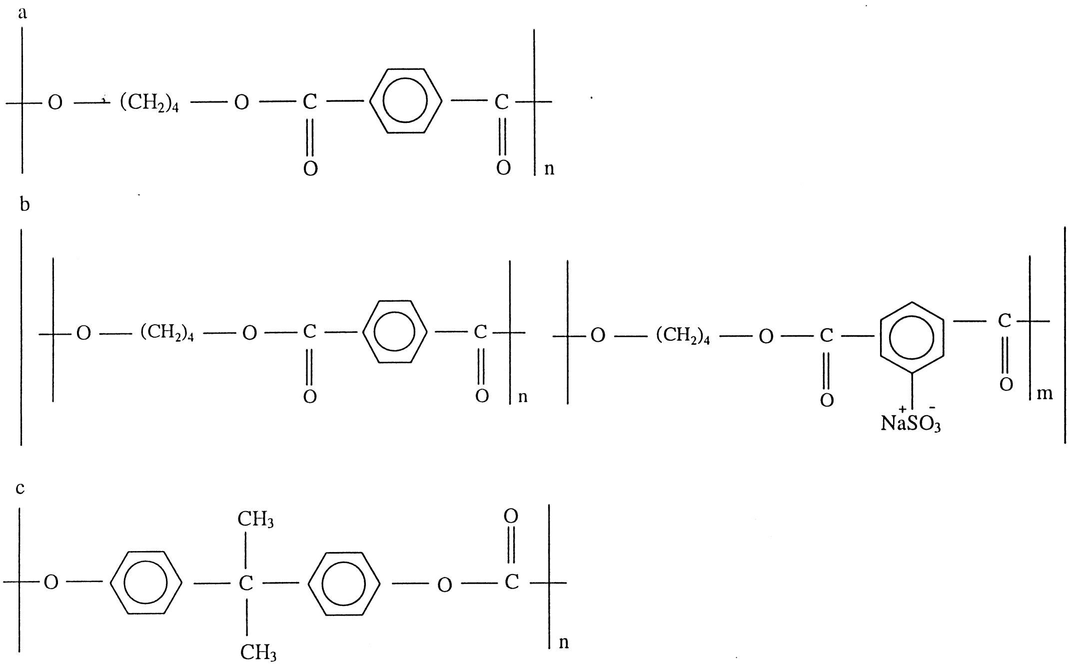

Fig. 1. The chemical formulae of (a) PBT, (b) SPBT and (c) PC.

used by Gorda and Peiffer in the previous study [5]. The SPBT samples contained sulphonation levels from 3.5 to 13.5 mol.% and were prepared by the melt condensation method described in detail in Ref. [5].

Samples were available having the following levels of sulphonation:

Powder samples (i.e. as prepared): 0.0; 3.5; 7.9; 11.1 mol.%.
Melt pressed samples: 0.0; 4.9; 8.4; 13.5 mol.%.

Polycarbonate samples were purchased from Aldrich. The chemical structure of all materials is shown in Fig. 1.

2.2. Preparation and characterisation of SPBT/PC blends

The blends were prepared by solvent and melt casting methods. Various solvents were tried in order to establish a good common solvent for SPBT and PC. Subsequently, both precipitation techniques (where the blend is precipitated out of solution) and solvent casting techniques (where the solvent is allowed to evaporate) were assessed and the resulting blends characterised using DSC. The solvent casting technique was found to be the most efficient method.

The following method was therefore adopted for all subsequent blend preparation. Two percent solutions of SPBT and PC in the co-solvent tetrachloroethane/phenol (60:40 by weight) were mixed in the appropriate proportions for the desired blend composition. Following thorough mixing, the blends were solvent cast. All samples were then baked at 353 K under vacuum for at least 8 h to remove residual water vapour and solvent. Control samples were processed by the same method in order that checks for solvent effects could be made. Samples of SPBT/PC and PBT/PC blends across the composition range and for levels of sulphonation from 0.0 to 11 mol.% were prepared.

2.3. Measuring techniques

2.3.1. Thermogravitational analysis (TGA)

Prior to carrying out any calorimetric studies, the SPBT samples were examined using TGA in order to establish the temperature at which the polymers start to degrade and also to check for signs of any trapped water. Less than 2% water was found in the as-received samples and no sign of degradation was detected within the temperature range 250–600 K and on a time scale of several days.

2.3.2. Differential scanning calorimetry (DSC)

DSC was used to investigate the melting behaviour of sulphonated PBT and its unsulphonated precursor, to measure the degree of crystallinity and to establish the glass transition temperatures, T_g, as a function of the sulphonation level. Measurements were made on a Perkin Elmer DSC7 using sample masses of 5 mg. The equipment was calibrated against indium and lead standards.

Initial investigations confirmed the behaviour of all samples to be highly dependent on their thermal history. The following heating sequences were therefore adopted:

'Pretreatment' (to remove any water):

Sample heated to 393 K at 20 K min^{-1}.
Maintained at 393 K for 5 min.
Rapidly cooled to room temperature (RT) in situ.

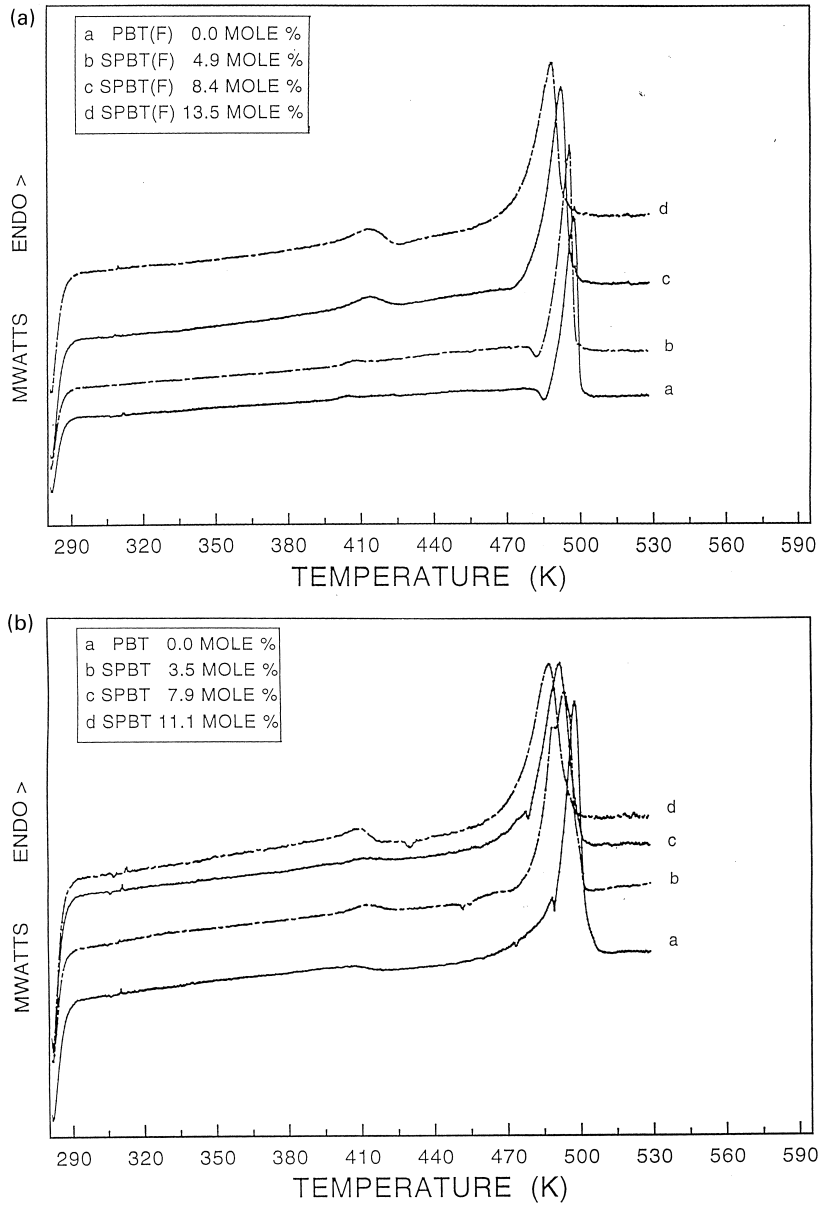

Fig. 2. Typical DSC scans for four SPBT samples: (a) film; and (b) powder.

'First scan':

Sample heated to 553 K at 20 K min^{-1}.
Maintained at 553 K for 5 min.
Rapidly cooled to RT in situ.

'Second scan':

Heated to 553 K at 20 K min^{-1}.
Maintained at 553 K for 5 min.
Quenched in liquid nitrogen.

'Post quench scan':

Heated from RT to 553 K at 20 K min^{-1}.

Typical thermal scans for four samples of different degrees of sulphonation are shown in Fig. 2. The melting temperature was identified with the maximum in the main endothermic peak and enthalpies of fusion determined from the DSC thermograms were converted to degrees of crystallinity using a value of 142 J g^{-1} for perfectly crystalline PBT [2]. The degree of crystallinity was obtained from the area under the melting endotherm to an estimated accuracy of ±5%. The results summarised in Table 1 reflect the conclusions drawn from at least three sets of data on each sample.

2.3.3. *Wide angle X-ray scattering*

Wide angle X-ray scattering (WAXS) experiments were carried out using a Philips XRG-3000 generator with Ni filtered CuK$_\alpha$ radiation ($\lambda = 1.54$ Å) which operated at an applied voltage of 36 kV and a current of 25 mA. The

Table 1
Percentage crystallinity and melting temperature for SPBT samples determined from DSC scans as described in the text. No T_g were determined for these samples

x = mol.% S	Thermal scan	Crystallinity (%)	T_m (K)	V_{amorph}	v^2 ($v = 0.01x$)
0.0	First	38.9	498	61.1	0
0.0	Second	31.5	497	68.5	0
0.0	Post quench	30.1	496	69.9	0
3.5	First	44.0	496	56.0	0.00123
3.5	Second	30.7	493	69.3	0.00123
3.5	Post quench	40.0	491	60.0	0.00123
7.9	First	28.6	493	71.4	0.00624
7.9	Second	25.7	492	74.3	0.00624
7.9	Post quench	25.8	492	74.2	0.00624
11.1	First	27.0	489	63.0	0.012321
11.1	Second	25.9	488	74.1	0.012321
11.1	Post quench	25.9	487	74.1	0.012321

samples, held in place by a teflon tape, were mounted vertically on the spinning stage of a diffractometer. Diffraction patterns were recorded at a scanning rate of 0.021° s^{-1} over an angular range $7° < 2\theta < 50°$. The amount of sample in the beam was the same for each specimen, to facilitate comparison of the spectra. Both the film and powder samples were measured. After instrumental corrections and background subtraction, data was transferred to a PC where further evaluation was performed.

2.3.4. Light microscopy

Measurements using TGA, DSC and wide angle X-ray diffraction were further complemented by light microscopy. This technique has the advantage of good spatial resolution and polarised light can provide information on large-scale structures formed in the material under investigation. Polarised light was used to visualise the crystalline phase.

3. Results and discussion

3.1. SPBT

3.1.1. Thermal measurements

3.1.1.1. DSC — melting behaviour of PBT and SPBT samples SPBT samples with 0.0, 3.5, 4.9, 7.9, 11.1 and 13.5 mol.% sulphonation have been investigated using DSC. Of these samples, the 4.9 and 13.5% had been formed into films, whilst the remaining were used as prepared. The results for the latter samples are listed in Table 1. All the samples exhibited main melting endotherms peaking in the range 487–499 K (214–226°C). The melting temperature, T_m, will be taken to be the temperature at the maximum of this main endotherm. The melt temperature was found to *decrease* with increasing sulphonation level and with thermal cycling, as will be discussed later.

3.1.1.2. Main melting endotherms For the 0.0 and 3.5 mol.% material, second endotherms merged with the low temperature side of the main melting peak were indicated, as seen in Fig. 2(b). In the case of the pure PBT, the second peak was apparent during both the first and second scans, whilst for the 3.5 mol.%, evidence of a second peak was only seen during the first scan.

During the second scan (i.e. after rapid cooling in situ) of the 3.5 mol.% samples, a small exotherm (presumably indicative of recrystallisation) was routinely observed at about 490 K just prior to the onset of the main melting endotherm. Such exotherms were not found during the first scan or following the liquid nitrogen quench. The 4.9 mol.% sample (film) exhibited similar exotherms during both first and second scans but not post quench [see Fig. 2(a), scan b]. The main melting endotherms for all the pre-melted film samples were consistently single narrow peaks. Indeed no indications of double melting endotherms were found for samples with greater than 3.5 mol.% sulphonation, as discussed later.

3.1.1.3. Low temperature endotherms During the first scan, for *all* samples, a low temperature endotherm was observed with its onset slightly above the pretreatment temperature of 393 K. The magnitude of this peak was typically from 5–10% of the main peak, representing 2–5% in terms of crystallinity. Following rapid cooling to room temperature, this peak disappeared in the 0.0, 3.5 and 4.9 mol.% materials, apparently reappearing at a lower temperature (onset typically at 308 K) following the liquid nitrogen quench. This temperature coincides with the expected value for the T_g of these samples. The 7.9 mol.% sample showed a rather broad feature on the second scan from approximately 308 to 413 K and, as described later, exhibited a T_g during the post quench scan. For samples with the highest sulphonation levels (11.1 and 13.5 mol.%) the small peak was found in all three scans, as seen in

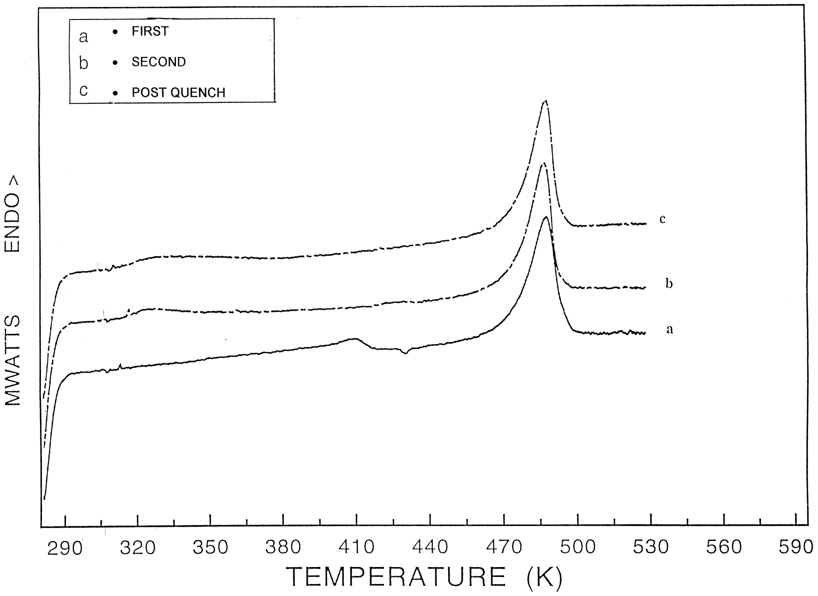

Fig. 3. DSC scans for 11.1 mol.% sample.

Fig. 3. Initially located slightly above the pretreatment temperature, the small endotherm moved, having its onset around 308 K and peaking at about 323 K during both the second and post quench runs.

3.1.1.4. Crystallinity and melting point depression Typical DSC results for the melting temperature and percentage crystallinity as a function of degree of sulphonation for the powder samples are given in Table 1 for each of the previously described thermal scans. Decreasing crystallinity with increased sulphonation was found, together with a decrease in the crystallinity after the first thermal scan. The latter is attributed to the rapid cooling following the first melt.

Crystallinity of 44% measured for the pure PBT and the 3.5 mol.% samples is slightly higher than previously reported values found in the literature for pure PBT (e.g. 40% quoted by Stein and Misra [6] and 39% obtained by Gilbert and Hybart [7]). For both samples, the crystallinity was reduced to about 30% following rapid cooling (second scan). The 0.0% sample showed a further slight reduction post quench, whereas for the 3.5% sample an increase in crystallinity was apparent. The measured value of 40% crystallinity during the third thermal scan, together with a further depression in T_m (Table 1) remains presently unexplained.

Markedly lower crystallinity of just under 30% was found in the samples with higher levels of sulphonation (Table 1). Only a small reduction in crystallinity was apparent following the rapid cooling cycles.

The melting point also showed a decrease with increasing functionality. The data obtained for the first runs exhibited smooth trends, while values obtained following the rapid cooling cycles was often scattered although still showing the initially observed trend of melting point depression, as displayed in Fig. 4.

3.1.1.5. Multiple melting endotherms in PBT and SPBT The melting behaviour of PBT is highly dependent on its thermal history, with multiple melting peaks being reported by many workers. A number of

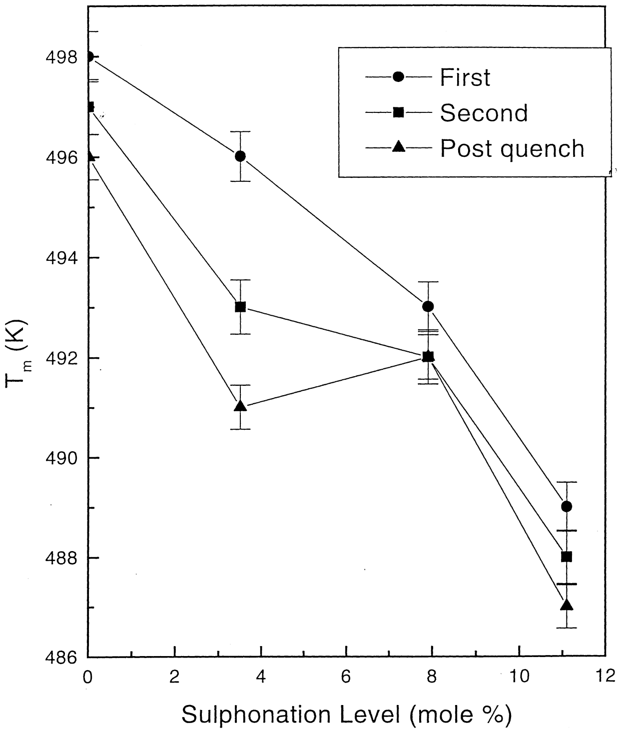

Fig. 4. Trend of melting point depression as a function of sulphonation level.

Table 2
Peak positions (as equivalent Bragg spacings *d*) for SPBT film samples

Peak number	Angle 2θ (deg)	*d*-spacing (Å)	Relative intensity	*hkl*
0.0 mol.%				
1	8.78	10.06	5	(001)
2	15.88	5.58	50	$(0\bar{1}1)$
3	17.25	5.14	83	(010)
4	20.69	4.29	54	$(\bar{1}11)$
5	23.34	3.81	100	(100)
6	25.25	3.52	75	$(1\bar{1}1)$
7	29.30	3.04	14	(101)
8	31.02	2.88	15	$(\bar{1}\bar{1}1)$
4.9 mol.%				
1	8.93	9.90	7	(001)
2	15.93	5.56	49	$(0\bar{1}1)$
3	17.31	5.12	72	(010)
4	20.80	4.27	56	$(\bar{1}11)$
5	23.38	3.80	100	(100)
6	25.10	3.54	79	$(1\bar{1}1)$
7	26.84	3.32	21	(101)
8	29.09	3.06	13	$(\bar{1}\bar{1}1)$
8.4 mol.%				
1	15.93	5.56	59	$(0\bar{1}1)$
2	17.21	5.15	79	(010)
3	20.71	4.28	80	$(\bar{1}11)$
4	23.32	3.81	100	(100)
5	25.00	3.56	75	$(\bar{1}03)$
13.5 mol.%				
1	23.09	3.85	100	(100)

Table 3
DSC data for SPBT/PC 50/50 blends

Mol.% S	Thermal scan	Crystallinity (%)	T_m (K)	T_g (K)
0.0	First	41	497.2	–
0.0	Second	29	492.2	–
0.0	Post quench	30	485.7	354
3.5	First	42	492.7	–
3.5	Second	44	492.8	–
3.5	Post quench	38	490.3	–
7.9	First	31	490.4	450
7.9	Second	26	490.1	415
7.9	Post quench	26	489.6	415
11.1	First	22	488.4	403
11.1	Second	18	486.3	318/418
11.1	Post quench	19	485.9	318/421

possible explanations have been put forward to explain the observation of up to three melting endotherms in PBT [6,8–11]. Their origin was attributed either to reorganisation processes occuring during heating [8,10], melting of different spherulitic structures [6,11] or due to the effects of annealing without additional crystallisation from the amorphous regions during the scanning process [9,12]. In our study, we attempt to correlate the DSC results with those obtained by optical microscopy, but also with results obtained previously by Gorda and Peiffer [5].

In the original work on SPBT by Gorda and Peiffer [5], detailed examinations using polarised light microscopy indicated that, at the lower ion contents (less than 5 mol.% sulphonation), the so-called unusual spherulitic morphology was observed. The findings indicated that the PBT copolymers change from abnormal to normal spherulitic structure in the range of 5–8 mol.% functionalisation. It is of interest that in this current work, no double melting endotherms were observed for sulphonation levels over 3.5 mol.%, which may be indicative of the presence of only one spherulitic form at the higher levels of sulphonation.

Gorda and Peiffer [5] found the optical melting of the normal spherulites to be about 5 K *higher* than that of the abnormal spherulites. The overall *reduction* in melting temperature with increased sulphonation level observed in the current work would therefore not seem to be attributable to the spherulitic morphology of the samples, as at these higher levels of functionalisation, the normal spherulitic form has been identified.

In our investigations into SPBT, the presence of a small low temperature endotherm just above the ‘pretreatment’ temperature of 393 K is similar to the observations of peaks just above the annealing temperature in the studies reported earlier. The appearance of a similar peak at much lower temperatures following rapid cooling to room temperature (i.e. second scan) and after quenching in liquid nitrogen suggests similar effects. When this low endotherm is present, no change in C_p has been detected, therefore, it is not taken to be the ‘overshoot’ peak at the glass transition that is often observed on heating scans.

3.1.1.6. Glass transition The T_g of 323 K measured for the 7.9 mol.% sample in Table 3 is slightly higher than those reported for pure PBT in the literature, which range from 293 K [13] to 313 K [10]. No conclusions can be drawn as to the significance of this figure since we were unable to extract T_g values for other functionality levels, due to the presence of the crystalline material.

3.1.1.7. Crystallinity and melting point depression The reduction in crystallinity with increasing functionality of SPBT is in general agreement with previous measurements by Gorda and Peiffer [5]. The current work indicates the order of 30% crystallinity in the ‘as-received’ powder samples. Initial DSC scans on the 13.5 mol.% pressed film used by Gorda and Peiffer [5] indicated at least 20% crystallinity to be present. This apparent anomaly may be due to crystallisation taking place during the thermal scan.

As reported, the melting temperature of the samples decreased with increasing functionalisation. Flory’s expression Eq. (1) for the melting of random copolymers [14] has

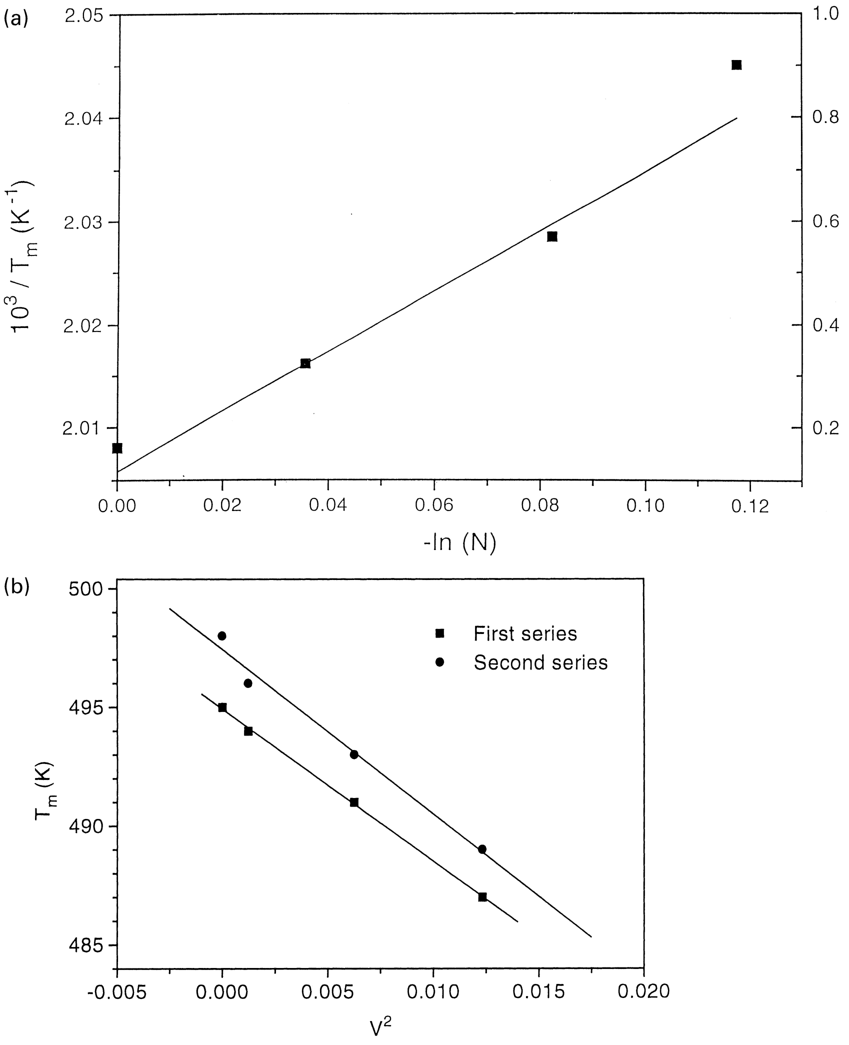

Fig. 5. (a) First scan from Fig. 4 shown as Flory's plot. (b) The melting point data (expression 3).

been used to examine the data. The theory assumes the minor component (SPBT units in our study) to be randomly dispersed within the copolymer and that this component does not enter the crystal lattice. According to this equilibrium theory, the melting temperature of the homopolymer, T_0, is related to that for the copolymer, T_m, by the following expression:

$$\frac{1}{T_m} - \frac{1}{T_0} = -\left(\frac{R}{H_u}\right)\ln N \tag{1}$$

where N is the fraction of crystallisable units, H_u is the molar heat of fusion of the homopolymer crystals and R = 8.34 J K^{-1} mol^{-1} is the gas constant.

Data for the first scan from Fig. 4 is shown in Fig. 5, presented as a Flory copolymer plot of $10^3/T$ (K^{-1}) versus ($-\ln N$). The straight line represents the theoretical line for Eq. (1) using the measured value for T_0 and the accepted value of 142 J g^{-1} for H_u. Although it is appreciated that the value used for T_0 does not represent the true equilibrium melting temperature, as pointed out by Pompe et al. [4], the fit in terms of the slope and, therefore, H_u is remarkably close to the data for all except the highest level of functionality. These results additionally point to the randomness of distribution of sulphonate groups within the copolymer.

Slight deviations from Flory's theoretical curve were taken to be indicative of polymer–polymer interaction. This possibility was further investigated, as outlined later.

The thermodynamic effects of mixing two polymers was considered by Scott [15] using the Flory–Huggins approximation [14]. Using Scott's expression for crystalline polymer diluent systems, Nishi and Wang [16] derived an expression for the mixing of a crystalline polymer and an amorphous polymer, valid only under the equilibrium conditions. The expression describes the melting point depression of a crystalline/amorphous polymer pair in terms of the volume fraction of the amorphous polymer, v, the melting temperatures of the homopolymer, T_0, the polymer mixture, T_m, respectively, and the polymer–polymer interaction parameter, χ_{12}.

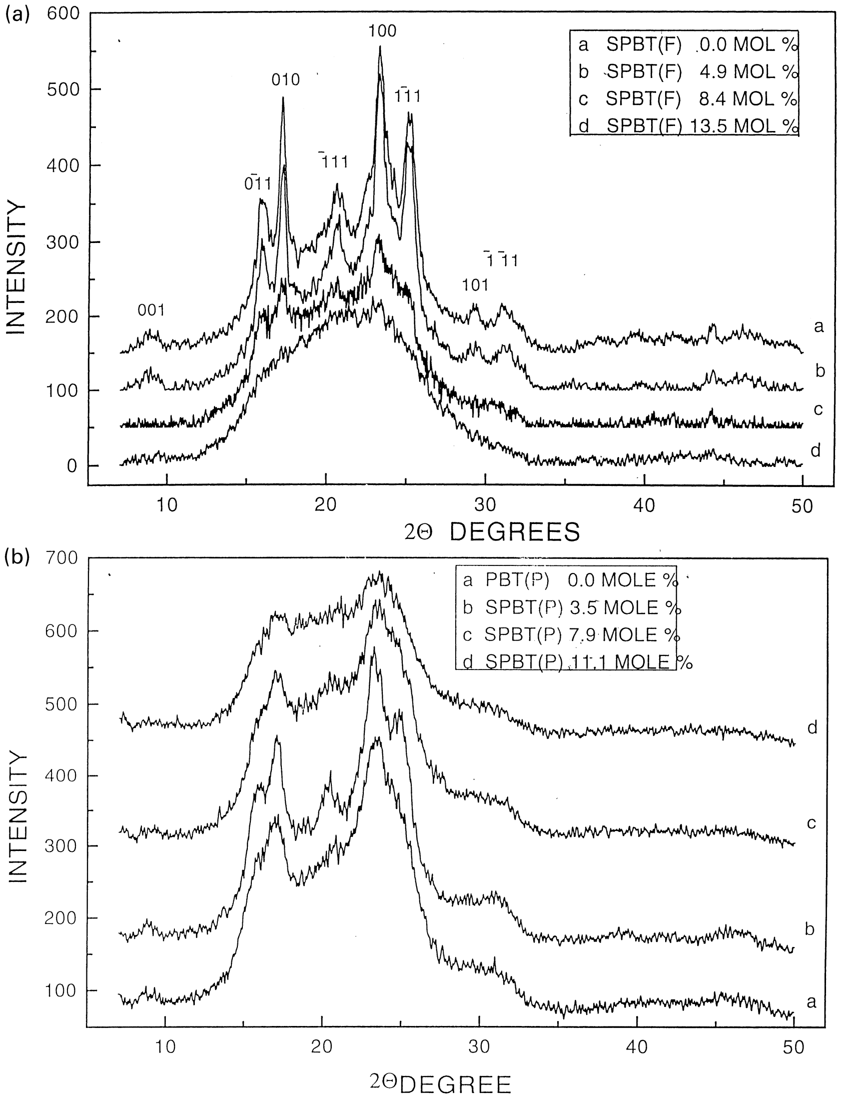

Fig. 6. WAXS data for SPBT: (a) films; and (b) powders.

$$\frac{T_m}{T_0} = 1 + \left(\chi_{12}\mathrm{R}T\frac{V_{21}}{H_u V_{1u}}\right)v^2 \quad (2)$$

where χ_{12} is the interaction parameter for the polymer pair at $T = T_m$; V_{1u} is the molar volume of the pure polymer (PBT); V_{2u} is the molar volume of the 'diluent' (SPBT); T_m is the copolymer melting temperature; and T_0 is the pure PBT melting temperature.

The molar volume of PBT, V_{1u}, is equal to 129.2 $\mathrm{cm}^3\,\mathrm{mol}^{-1}\,\mathrm{monomer}^{-1}$ [17]. Since the volume of the sulphonated polymer is not known, we assume that it is roughly equal to that of the pure polymer, $V_{1u} \sim V_{2u}$, hence Eq. (2) becomes:

$$\frac{T_m}{T_0} = 1 + \left(\chi_{12}\frac{\mathrm{R}T}{H_u}\right)v^2 \quad (3)$$

To investigate the possibility of significant interaction in the functionalised PBT samples, the melting point data were plotted as T_m against v^2 [Fig. 5(b)]. Two series of measurements gave straight lines with negative gradients, given by $\chi_{12}(\mathrm{R}T/H_u)T_0$, from which the interaction parameter $\chi_{12} = -0.04$ were obtained. (T_0 is the measured temperature of melting, $T_0 = 495$ and 498 K for these series, respectively.)

3.1.2. WAXS — wide angle X-ray scattering

WAXS data has been obtained on the melt-pressed samples of SPBT and several blends of SPBT/PC as well as SPBT powders. For SPBT, a marked reduction in the relative scattering intensity is noted with increasing sulphonation level with an absence of well-defined scattering peaks in the 13.5 mol.% sample. This does not, however, indicate a total absence of crystallinity, as can be seen by comparison with the data given by Huo et al. [17], where the scattering profile of a quenched PBT sample is compared with the quenched poly(butylene terephthalate)/polyarylate (PBT/Par) blends, which are known to be fully amorphous.

The asymmetry of the PBT profile indicates the presence of some crystallinity (Fig. 6) and is further discussed later.

The decrease of crystallinity with an increasing degree of sulphonation can be understood in terms of the destruction of the local order. This effect was extensively studied by some of us in model polysterene ionomers (Gabrys et al. [18]) using scattering of spin-polarised neutrons with spin polarisation analysis. Wide-angle neutron scattering data obtained on non-crystalline, isotactic polystyrene show that, even with a low degree of sulphonation (1.2 mol.%), the scattering pattern closely resembles that obtained for the atactic samples (Gabrys et al. [18]). The further increase of the degree of sulphonation did not bring any essential changes in the scattering pattern or the short range order parameters: the local order was already destroyed.

In the case of sulphonated PBT, the change in the scattering pattern with the increasing degree of sulphonation from 0.0 to 13.5 mol.% is more gradual, as seen in Fig. 6(a) and (b). (Hot-pressed films show much better defined crystallinity then powders, as expected.) We attribute this effect to starting with a semi-crystalline material, which is therefore more ordered locally than isotactic PS. The description of the short-range order in SPBT ionomers is beyond the scope of this paper, since we do not have the absolute coherent scattering intensity. It was this quantity which previously allowed us to describe, quantitatively, the short range order in amorphous polymers [2,18].

The observed peaks have been assigned to crystal planes as shown in Table 2 for film samples. In order to obtain an estimate of the crystal sizes in the crystallographic directions a value of the coherence length, *t*, may be obtained from the WAXS data, using the Scherrer equation [19]:

$$t = K\frac{\lambda}{\text{FWHM}}\cos\boldsymbol{q} \qquad (4)$$

where: $K = 0.9$, $\lambda = 1.54$ Å, FWHM = peak width at half maximum height, and $\boldsymbol{q}$ = scattering vector.

The crystal lattice of PBT has been reported by Yokouchi et al. [20] to be triclinic with the space group $P\bar{1}$ and the following lattice parameters for the α-form: $a = 4.83$ Å, $b = 5.94$ Å, $c = 11.59$ Å, $\alpha = 99.7°$, $\beta = 115.2°$ and $\gamma = 110.8°$.

The disposition of the crystal cell within the lamella has not been determined for PBT. However, according to Huo et al. [17], the *c*-axis lies nearly perpendicular to the lamellar crystal fold surfaces. In this case, the coherence length calculated from the (001) reflection may relate to the lamellar thickness. Unfortunately the (001) reflections in the data collected so far have been too weak to allow any sensible estimate of the coherence length and indeed have

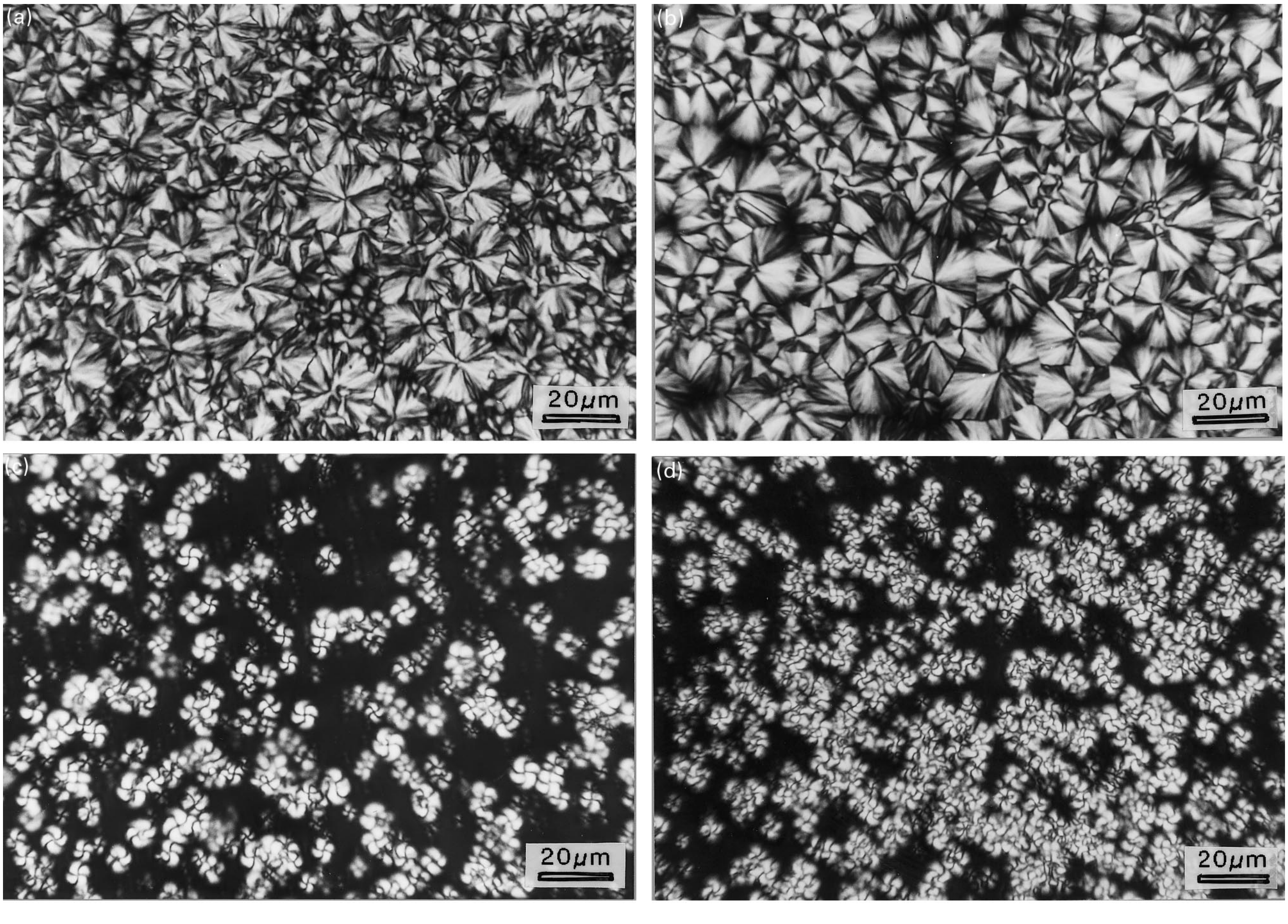

Fig. 7. Optical microscopy of SPBT and SPBT/PC blend: (a) 0.0 mol.%; (b) 3.5 mol.%; (c) 7.9 mol.%; and (d) 50/50 blend of 0.0 mol.% SPBT/PC.

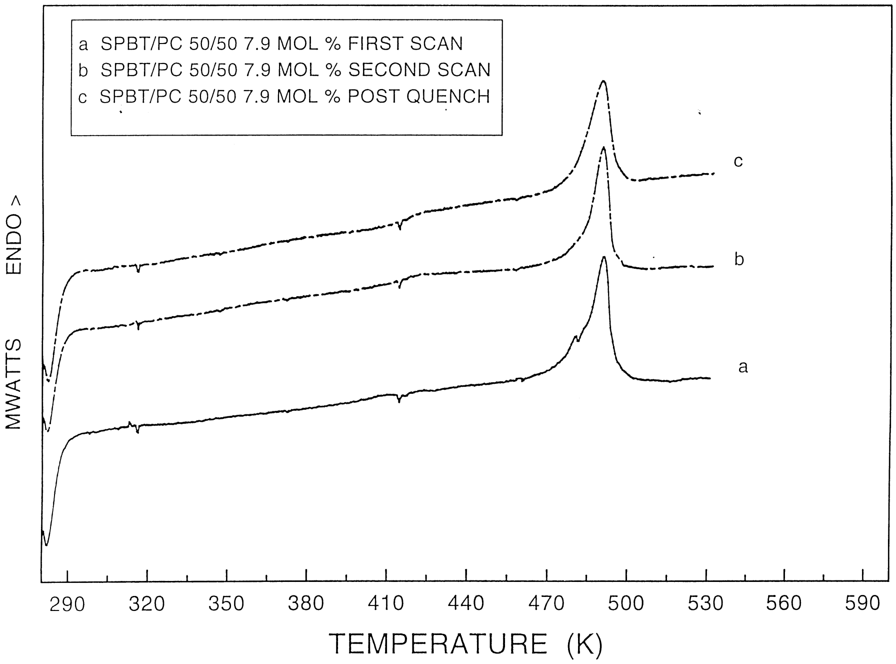

Fig. 8. DSC data for a 50/50 blend taken after varying thermal treatment.

disappeared completely by a sulphonation level of 8.4 mol.% [cf. Fig. 6(a)].

For the (100) reflection, the coherence length in the *a** direction is found to be of the order of 100 Å and that for the *b** direction from the (010) reflection is estimated at 200 Å. This data is in general agreement with that obtained by Huo et al. [17] for melt-crystallised PBT. Within experimental error, it is not possible to determine any trend in these values with functionality.

3.1.2.1. Light microscopy Samples were prepared by melt casting and by microtomy. Since the thermal history of the sample has a significant influence on the type and the nucleation density of the spherulites, all specimens of PBT, SPBT and their various blends with PC were melted at 523 K and cooled at a rate of $25\,\mathrm{K\,min^{-1}}$ to room temperature. The samples obtained were about 10 μm thick.

Polarised light was used to visualise the crystalline phase in a series of samples. Fig. 7 shows structures observed for 0.0, 3.5, 7.9 mol.% degree of sulphonation and a blend of PBT with PC which will be discussed later. In pure PBT (0.0 mol.%) there is one type of spherulites visible, with a diameter in a range of 30–50 μm. There is no visual difference between this sample and that with 3.5 mol.% sulphonation. The effect of the sulphonate group on the structure becomes visible at the sulphonation level exceeding 7 mol.%, where the spherulites are isolated in the amorphous matrix. The question of whether the amorphous phase contains sulphonate groups or if the amorphous phase can crystallise at higher temperatures will be addressed by the X-ray microprobe analysis in the near future.

3.2. SPBT/PC blend

3.2.1. DSC

All solvent cast samples, both blends and control samples, were examined using DSC following the same procedure as used for the homopolymers described earlier.

3.2.2. Crystallinity

The degree of crystallinity of the SPBT portion of the blends made from 0.0 and 3.5 % SPBT remains at the same level as found in the homopolymers (40% as prepared, reducing to 30% following melting). However, for blends produced from the higher levels of sulphonation (7 and 11%) the crystallinity of the SPBT is reduced to 20–25% following melting; as seen in Table 3.

3.2.3. Melting behaviour

The melting temperatures (defined as the maximum of the main melting endotherm) of the blends were investigated as a function of blend composition for each of the SPBT samples (i.e. sulphonation levels of 0, 3.5, 7.9 and 11.1 mol.%). No significant trend with PC concentration, which could be indicative of polymer interaction, was found for any of the ionomer blends, as seen by inspection of Table 3.

For the 0.0 mol.% sample, i.e. the PBT/PC blends, there was a dramatic reduction of melt temperature on thermal cycling, with the change in melting temperature, ΔT_m, peaking at 11.5 K at a blend composition of 50% SPBT/PC, as shown in Fig. 8.

For the other blends, ΔT_m was typically 2 K across the composition range. The behaviour in the PBT/PC sample is

Table 4
DSC data for SPBT 7.9 mol.%/PC blends

Mol.% S	Blend compositions	Thermal scan	Crystallinity (%)	T_m (K)	T_g (K)
7.9	25	First	22	489.8	403
7.9	25	Second	21	489.1	418
7.9	25	Post quench	25	487.8	419
7.9	50	First	31	490.4	405
7.9	50	Second	26	490.1	415
7.9	50	Post quench	26	489.6	415
7.9	75	First	36	490.7	316/393
7.9	75	Second	24	489.3	317/399
7.9	75	Post quench	24	488.9	316/407

taken to be indicative of transesterification which has been previously reported in PBT/PC blends [21–24].

Defined multiple melting peaks were not observed in any of the blends (cf. previous section on melting behaviour of SPBT samples) although there were asymmetries in the melting endotherms of some of the 0.0 and 3.5% endotherms which are probably the result of two unresolved endotherms.

3.2.4. Glass transition temperatures

Measurement of the glass transition temperatures of polymer blends provides a straightforward method of assessing blend miscibility. A miscible amorphous blend of two polymers will exhibit a single glass transition at a temperature between the glass transition temperatures of the homopolymers. The blends produced from the 0.0 and 3.5 mol.% SPBT showed no signs of miscibility in the as-prepared samples, but show partial miscibility following melting and quenching. Conversely the samples with higher sulphonation levels, namely the 7.9 and 11.1 mol.% SPBT, showed partial miscibility as cast but, from the T_g data, appear to have phase-separated following melting and quenching. This is recorded in Table 4.

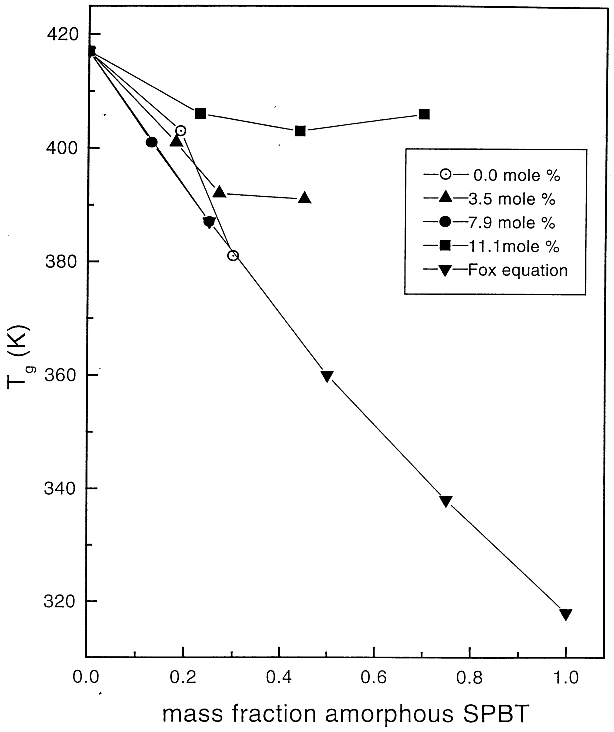

Fig. 9. Glass transition temperature as a function of amorphous mass fraction.

Fox derived the following equation for the glass transition temperature of a two-component amorphous polymer blend:

$$T_g = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{5}$$

where: T_{g1} and T_{g2} are the glass transition temperatures of component 1 and component 2, respectively. W_1 and W_2 are the weight fractions of components 1 and 2 in the miscible phase, respectively.

In considering the miscibility of blends where one component is semi-crystalline, the weight fractions (W_1 and W_2) refer to the amorphous phase. Using the data obtained from the DSC analysis on the degree of crystallinity of the SPBT/PC blends, the mass fraction of amorphous SPBT has been calculated (to an estimated ±10% accuracy). The observed glass transitions, T_g, are shown in Fig. 9 as a function of the mass fraction of amorphous SPBT for different levels of sulphonation. By comparison with the glass transition temperatures calculated from the Fox equation (also plotted in Fig. 10), the data gives an indication of the degree of miscibility of the blends as determined by DSC. We conclude the maximal miscibility is somewhere between 7.9 and 11.1 mol.%, the conclusion supported by the findings from light microscopy.

3.2.5. Light microscopy

The effect of blending SPBT with PC is similar to that known for other immiscible or partially miscible polymer blends. Small separate phases are formed, and using polarised light, one can clearly differentiate between amorphous PC and crystalline PBT. In Fig. 7(d), a 50/50 blend of PBT/PC is shown. This particular sample was prepared by

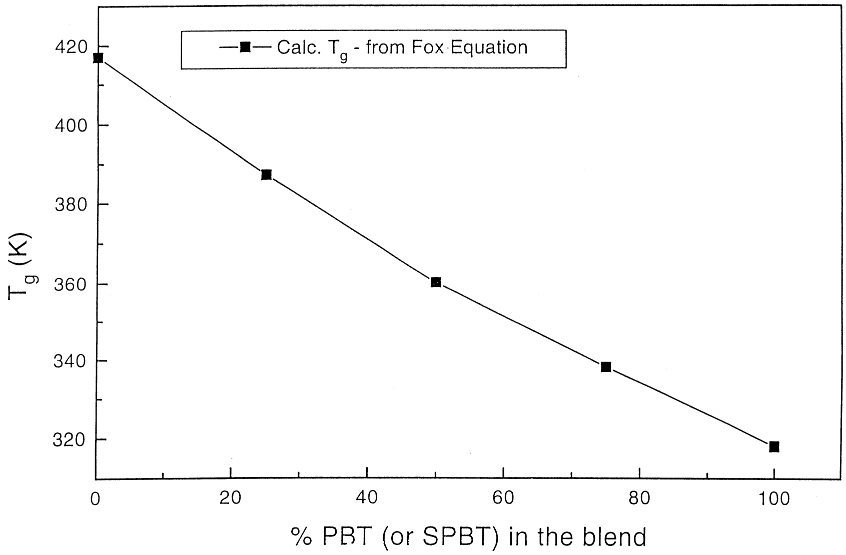

Fig. 10. Fox equation for blends.

shear mixing on a laboratory blender at 473 K for 1 min. The blending procedure can significantly affect the dispersion of phases. In our case, the structures obtained were similar to those observed in solvent cast samples.

A direct correlation between DSC results and crystallisation was not established due to the lack of availability of a hot stage.

However, it is seen by inspection of Fig. 7 that the overall loss of crystallinity with sulphonation and the subsequent dilution with amorphous polymer corresponds well to DSC results. The shift of melting temperature to lower values with the increasing degree of sulphonation can be correlated with respective changes of crystallinity. The SPBT chains, with randomly distributed, bulky sulphonate groups, are assumed to form the amorphous phase. The light micrographs indicate that phases with two different levels of sulphonation are formed, namely unsulphonated which is crystalline and a sulphonate-containing, amorphous phase. This non-random distribution of the sulphonate groups between the two phases could be the reason for the appearance of isolated spherulites. Since the X-ray diffraction patterns do not show any changes in the lattice spacings with the increasing level of sulphonation, it is unlikely that two different types of spherulites are present. The slightly different appearance of small spherulites can be attributed to the fact that a whole sphere is visible instead of a section only: the spherulite size is now smaller than the sample thickness. The thickness and defect density of the crystalline lamellae can explain the observed changes in the melting temperature.

4. Conclusions

The objective of this paper was to investigate the structural and thermal properties of a semi-crystalline ionomer poly(butylene terephthalate) (PBT), its sulphonate analogue SPBT and their blends with amorphous polycarbonate (PC). The main aim of these studies was to determine a maximally miscible composition of the SPBT/PC blends. It was found, as briefly summarised later, that the optimal composition would be made with highly sulphonated PBT, with an estimated degree of sulphonation around 9 mol.%. That was the region yielding optically clear blends, an important result for commercial applications e.g. for car windshields.

Firstly, the results obtained on SPBT samples are summarised. From DSC measurements, powder samples having sulphonation levels of 0 to 5% were found to have typically 40% crystallinity, which reduces to 30% after melting and rapid cooling (40° min^{-1}). The level of crystallinity was not significantly reduced on subsequently melting and quenching in liquid nitrogen. Samples with higher levels of sulphonation (from 5 to 11%) were found to have 25–30% crystallinity, which was unchanged on melting and rapidly cooling. Crystallinity data obtained for the melt-processed films confirmed these findings, having approximately 30% crystallinity throughout the sulphonation range. There was no significant change following rapid cooling or quenching in liquid nitrogen from the melt.

4.1. Melting behaviour

The appearance of multiple melting endotherms is well recorded [6,8–11], although their precise origin remains a subject of debate. Similar multiple endotherms have been observed in this work for SPBT samples with up to 5% sulphonation whilst only a single melting peak is found for material with higher ion content.

The melting temperature of SPBT, taken as the maximum of the main melting peak, is found to decrease with increasing sulphonation level. Data obtained have been analysed in accordance with Flory's model for the melting of random copolymers [14]. Strictly, the theory is only valid under equilibrium conditions, however the data fits the theory remarkably well, indicating the random distribution of the sulphonate groups within the copolymer and that these groups can indeed be excluded from the crystalline regions.

Slight deviations from Flory's theoretical curve were taken to be indicative of polymer–polymer interaction and were considered in terms of the Nishi and Wang model [16]. To this end, the melting point data were plotted as v^2 (v is the volume fraction of the amorphous polymer) against T_m. Negative gradients, given by $\chi_{12}(RT/H_u)T_0$, were obtained for two sets of data, hence χ_{12} was determined to be (-0.04).

4.2. Glass transition temperature (T_g)

Due to the high degree of crystallinity in the samples and the close proximity of the glass transition temperature to room temperature, it has proved difficult to obtain accurate and unambiguous values of T_g. The clearest glass transitions were observed for the melt-pressed samples, where ageing effects resulted in sharp peaks at the transition, the peaks, however, making an unambiguous determination of T_g impossible. Overall data obtained indicated a glass transition at approximately 318 K, with no defined trend in T_g with increasing sulphonation level.

4.3. WAXS

The X-ray data is in agreement with a trend in DSC data. The decrease of crystallinity with increasing degree of sulphonation inferred from thermal studies is consistent with the behaviour of X-ray spectra [Fig. 6(a) and (b)]. While eight peaks can be assigned in the spectrum of the 0.0 mol.% SPBT, the spectrum of the 13.5 mol.% sample shows only a broad halo. This happens gradually: while the 0.0 mol.% and 4.9 mol.% spectra are nearly identical, the $(\bar{1}11)$ and $(1\bar{1}1)$ peaks have disappeared, and (100) is grossly reduced in the spectrum corresponding to the 8.4 mol.% sample.

Turning to *blends*, there are distinct differences in the crystallinity, melting behaviour and glass transition temperatures compared with the PBT and SPBT samples. Although there are asymmetries present in the melting endotherms of some of the lightly sulphonated blends, well-defined multiple melting peaks were not observed. There was no single glass transition temperature observed in the as-prepared samples which indicates a lack of miscibility. However, they showed partial miscibility following melting and quenching. For the higher sulphonation levels, namely for blends prepared with 7.9 and 11.1 mol.% SPBT, the as-prepared samples were partially miscible but seemed to phase-separate following melting and quenching.

Recently, a small angle neutron scattering study of these blends was completed. The results of preliminary data analysis are in agreement with the results described above, and a paper is in preparation.

Findings from light microscopy provided crucial evidence for SPBT/PC blend miscibility. The light micrographs indicate that two phases are formed in the blend: the bulky sulphonate groups are found in the amorphous phase, and the partially crystalline SPBT chain remains in the other phase. Glass transition temperatures calculated as a function of the mass fraction of amorphous SPBT indicate that the maximal miscibility lies somewhere between 7.9 and 11.1 mol.%, supporting this conclusion.

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