

# Polyurethane/olefinic ionomer blends. 1: Compatibility characterization

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The compatibility behaviour of melt-mixed blends of a polyester-type polyurethane (PU) with the  $Zn^{2+}$  ionomer of poly(ethylene-*co*-methacrylic acid-*co*-isobutylacrylate) terpolymer (Ion.,  $Zn^{2+}$ ) was investigated in the complete composition range. The techniques applied were tensile testing, dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.), Fourier transform infrared (FTi.r.) spectroscopy and optical microscopy. Tensile properties were typical of a compatible system and d.m.a. results indicated a miscible blend. FTi.r. results failed to reveal the nature of the specific forces involved in bringing about compatibilization. Analysis of the thermal data obtained allowed the determination of a polymer–polymer interaction parameter which had a near zero value at the elevated temperatures where it was determined. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: ionomer blends; polyurethane blends; blend miscibility)

## INTRODUCTION

Polymer blending leading to a miscible system or a polymeric alloy is an established route to polymer property diversification<sup>1,2</sup>. To obtain a compatible blend, components are chosen so that their functional groups are ‘complementary dissimilar’<sup>3</sup>, or a third component is added to act as a compatibilizer<sup>4,5</sup>.

Among the various compatibilizers used ionomers have been particularly effective<sup>6,7</sup>. In previous work we have used<sup>8</sup> the sodium salt of poly(ethylene-*co*-methacrylic acid) to modify the properties of poly(ethylene terephthalate) (PET) and compatibilize PET/LLDPE blends<sup>9</sup>. Compatibilization of the ternary was attributed to interfacial PET/ionomer transreactions and to the mixing of the polyolefin with the ionomer due to structure similarity. In later work<sup>10</sup> the zinc salt of poly(ethylene-*co*-methacrylic acid-*co*-isobutylacrylate) (Ion.,  $Zn^{2+}$ ) was employed to compatibilize poly(vinyl alcohol) (PVOH) and the incompatible PVOH/HDPE blends. The results were attributed to complexation reactions of  $Zn^{2+}$  with the acidic hydroxyls of PVOH. Analogous findings were reported<sup>11</sup> for the poly(ethylene-*co*-vinyl alcohol) (EVOH)/Ion.,  $Zn^{2+}$  and the compatibilization of the incompatible EVOH/HDPE using the same ionomer as a compatibilizer.

In this work reported in two parts, the compatibility behaviour of a polyester-type polyurethane (PU) with Ion.,  $Zn^{2+}$  is examined. Once their compatibility was established the study was extended to the application of the ionomer as a compatibilizer for the incompatible PU/HDPE blend. These last results will be the subject of another report<sup>12</sup>. The choice of this compatibilizer was based on the fact that amide groups may interact with the ionomers via hydrogen bonding, ion–dipole interactions and/or metal–ion coordination<sup>6,13,14</sup>. Other electron-donating groups of PU that may in principle coordinate with the metal  $Zn^{2+}$  are the carbonyl moieties.

Of relevance to the binary PU/Ion.,  $Zn^{2+}$  blends is the work of Rutkowska and Eisenberg<sup>15,16</sup> on PU/sulfonated

polystyrene ionomers examining the effect of PU structure and counter ion content on blend miscibility.

In Part 1 of this work melt-mixed PU/Ion.,  $Zn^{2+}$  blends were investigated in the complete composition range. The characterization techniques applied were tensile testing to assess large deformation behaviour, dynamic mechanical analysis (d.m.a.) and differential scanning calorimetry (d.s.c.) to evaluate the degree of mixing, Fourier transform infrared (FTi.r.) spectroscopy to detect possible intermolecular interactions and optical microscopy to characterize blend morphology.

## EXPERIMENTAL

### Materials and preparation

Polyurethane (Desmopan 359) was donated by Bayer A. G. It is a polyester-type PU with hard segments formed by the addition of butanediol to diphenyl methane-4-4'-diisocyanate (MDI). The soft segment with an  $\bar{M}_n$  of about 2000 g mol<sup>-1</sup> consists of polyester chains formed by polycondensation of adipic acid and butanediol-1,4. The density was 1.23 g cm<sup>-3</sup>. The zinc ionomer (Surlyn 9020) was donated by DuPont de Numerous Co. It is a random terpolymer of ethylene–methacrylic acid–isobutyl acrylate with a molar composition 78–10–12, respectively, and a degree of neutralization of 70%:  $\bar{M}_n = 25\,000$  g mol<sup>-1</sup>, density = 0.74 g cm<sup>-3</sup> and MFI = 1.0 g/10 min.

The ionomer was dried at 60°C and the PU at 100°C for 24 h in dynamic vacuo. Blends were prepared by melt-mixing in a home-made stainless steel bob-and-cup type of mixer described previously<sup>10</sup>. Based on tensile property optimization, in particular the ultimate elongation at break  $\epsilon_b$ , the mixing time employed was 10 min at 240°C. PU/Ionomer compositions prepared were 90/10, 70/30, 50/50, 30/70, 10/90.

To examine the effect of the metal ion on compatibility an attempt was made to replace  $Zn^{2+}$  with  $H^+$  using an ion exchange procedure<sup>17</sup>. The ionomer was dissolved in decalin and precipitated in acetone. After removal of decalin with acetone the fine white precipitate was stirred

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in 20% hydrochloric acid solution for 1 h and filtered. This batch process was repeated several times. Analysis for  $Zn^{2+}$  by fluorescence spectroscopy indicated incomplete replacement by  $H^+$ . Since acid treatment could modify the polymer chain structure as well (e.g. ester hydrolysis), it was decided not to proceed with further  $Zn^{2+}$  substitution.

Films were obtained by compression moulding between Teflon sheets at 240°C and 10 MPa, followed by pressure release and quenching to 0°C.

#### Apparatus and procedures

Tensile tests were performed at a crosshead speed of 10 cm min<sup>-1</sup> at 23°C according to ASTM D882 using a J.J. Tensile Tester type 5001 and rectangular film strips measuring 6.0 × 0.65 × 0.25 cm<sup>3</sup>.

D.m.a. data were obtained at 10 Hz with the RSA II mechanical spectrometer of Rheometric Scientific Ltd. Specimen dimensions were 2.3 × 0.5 × 0.015 cm<sup>3</sup>.

D.s.c. measurements were carried out using the SP+ instrument equipped with the Autocool accessory from Rheometric Scientific Ltd. The thermal cycling applied was 25°C → 250°C with 20°C min<sup>-1</sup> heating rate, quenching to -50°C at controlled cooling rate 50°C min<sup>-1</sup> and heating up to 250°C at heating rate 10°C min<sup>-1</sup>.

FTi.r. spectra were obtained using a Perkin-Elmer 1600 spectrometer.

Optical micrographs with phase contrast and crossed polarizer arrangement were obtained with an Olympus BH-2 microscope.

## RESULTS

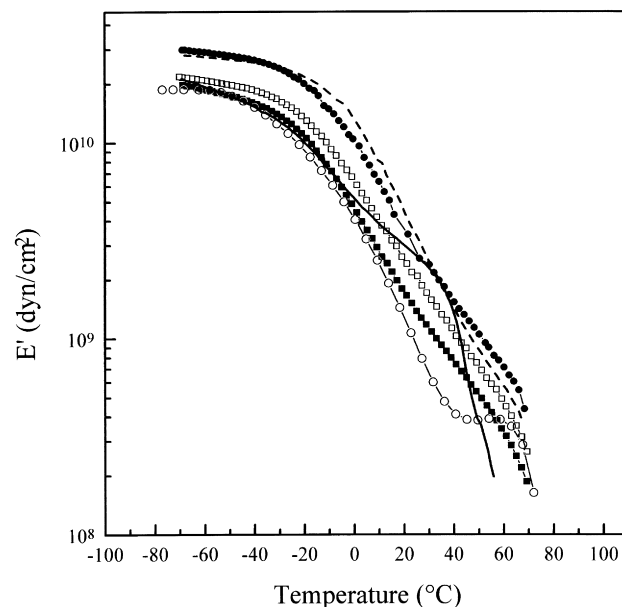
#### Tensile properties

Table 1 summarizes the results in terms of ultimate properties,  $\sigma_b$ ,  $\epsilon_b$  and  $E_b$ , ultimate strength, elongation at break and energy to tensile failure, respectively. It is evident that tensile properties are good at all compositions. In particular, data on  $\epsilon_b$ , which is a sensitive indicator of component interface adhesion in the case of polymer alloys or cohesion in miscible blends, support the view that the system is mechanically compatible or miscible. In blends, increase of PU enhances strength while  $\epsilon_b$  shows a maximum at low PU contents.  $E_b$ , usually associated with impact strength, shows a maximum at the intermediate blend composition. The decrease of  $\sigma_b$  with the addition of the ionomer may be attributed to limited disruption of hydrogen bonding in PU. It is of relevance to note some reduction in all tensile data observed of the 70/30 blend where  $Zn^{2+}$  in the ionomer was partially (30%) replaced by  $H^+$ . This may indicate the contributing role played by the metal ion in bringing about compatibilization when mixed with PU, in analogy to polyamide/ionomer blends.

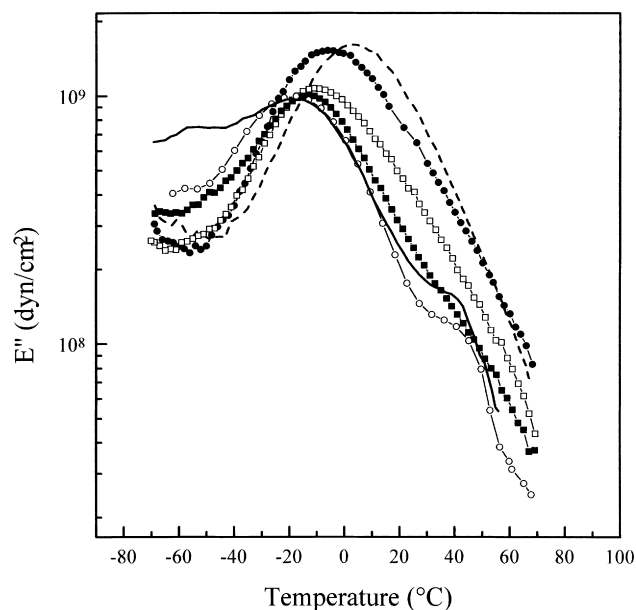
**Table 1** Ultimate tensile properties of binary blends

Binary blends PU/Ion.,Zn <sup>2+</sup>	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	$E_b$ (J cm <sup>-3</sup> )
100/0	57 ± 10	731 ± 57	220 ± 20
90/10	42 ± 7	639 ± 84	142 ± 37
70/30	28 ± 3	624 ± 75	98 ± 23
70/30 <sup>a</sup>	24 ± 3	518 ± 69	74 ± 15
50/50	32 ± 4	657 ± 66	128 ± 21
30/70	27 ± 2	743 ± 39	117 ± 13
10/90	25 ± 3	747 ± 55	106 ± 18
0/100	31 ± 3	562 ± 48	109 ± 15

<sup>a</sup>Blend with ionomer where  $Zn^{2+}$  is partially (30 mol%) substituted with  $H^+$



**Figure 1** Temperature dependence of storage modulus  $E'$  of PU/Ion.,Zn<sup>2+</sup> blends: (---) PU; (•) 90/10; (□) 70/30; (■) 30/70; (○) 10/90; (—) Ion.,Zn<sup>2+</sup>; composition 50/50 deleted for clarity



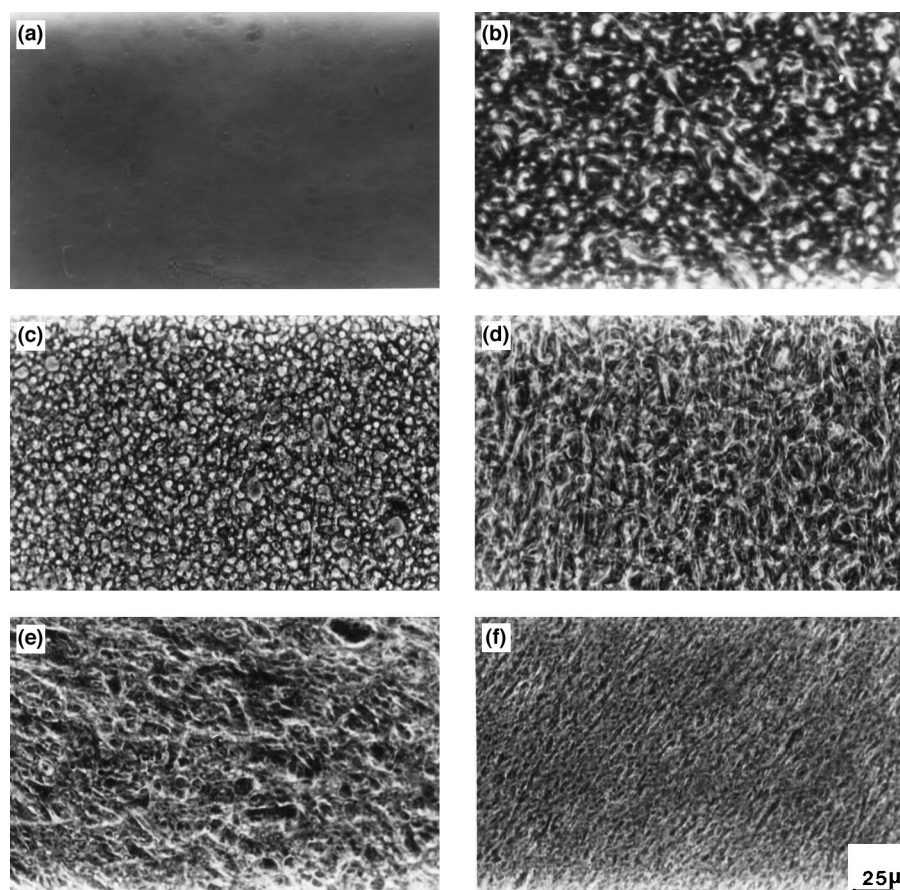
**Figure 2** Temperature dependence of loss modulus  $E''$  of PU/Ion.,Zn<sup>2+</sup> blends: (---) PU; (•) 90/10; (□) 70/30; (■) 30/70; (○) 10/90; (—) Ion.,Zn<sup>2+</sup>; composition 50/50 deleted for clarity

#### Dynamic mechanical properties

D.m.a. data are given in Figures 1 and 2 in terms of the temperature dependence of storage  $E'$  and loss modulus  $E''$ , respectively and the main viscoelastic transition ( $T_g$ ) is recorded in Table 2. Data were obtained by scanning the temperature downwards to avoid excessive moisture absorption by PU. The results obtained give a  $T_g$  which is a few degrees higher than data obtained in the customary manner; this is a non-equilibrium effect. However, in this manner, the considerable  $T_g$  depression due to moisture pick-up is avoided and since one is interested with the effect of  $T_g$  variation with composition the non-equilibrium effect is of little consequence. The origin of the ionomer main

**Table 2** Main viscoelastic and thermal data of PU/Ion.,Zn<sup>2+</sup> blends

PU/Ion.,Zn <sup>2+</sup>	$T_g$ (°C)	$T_m$ (°C)		$T_{mb}^o$ (°C)	Slope $\eta$	$\chi_{12}$
		PU	Ion.,Zn <sup>2+</sup>			
100/0	3	205.5	–	220	0.341	
90/10	–6	204.4	86.5	221	0.276	0.036
70/30	–11	203.6	85.9	219	0.218	–0.005
50/50	–12	203.9	86.8	216	0.19	–0.008
30/70	–13	200.7	87.2	214	0.19	–0.009
10/90	–16	–	87.6	–	–	–
0/100	–16	–	87.7	–	–	–

**Figure 3** Optical micrographs of quenched PU/Ion.,Zn<sup>2+</sup> blends: (a) PU; (b) 90/10; (c) 70/30; (d) 50/50; (e) 30/70; (f) 10/90

transition at about  $-16^\circ\text{C}$  has been discussed by MacKnight *et al.*<sup>18</sup> and Yano and co-workers<sup>19</sup>. At the 10/90 composition the order–disorder relaxation due to ionic aggregate formation<sup>19</sup> is also discernible in both *Figures 1 and 2*. The main PU relaxation at  $3^\circ\text{C}$  is attributed to amorphous PU segment motion in analogy to polyamides<sup>20</sup>. A frequency–temperature scan gave an apparent activation energy for the PU relaxation of  $52.0\text{ kcal mol}^{-1}$ , a typical value for an  $\alpha$  relaxation.

In *Figure 5* the regular shift with composition of a single  $T_{gb}$  suggests a miscible blend. In calculating the PU composition the crystallinity of components was taken into account; see discussion on  $T_{gb}$ –composition correlation.

#### Thermal properties

These are summarized in *Tables 2 and 3*. In *Table 2* the melting transition  $T_m$  of each component is depressed as the

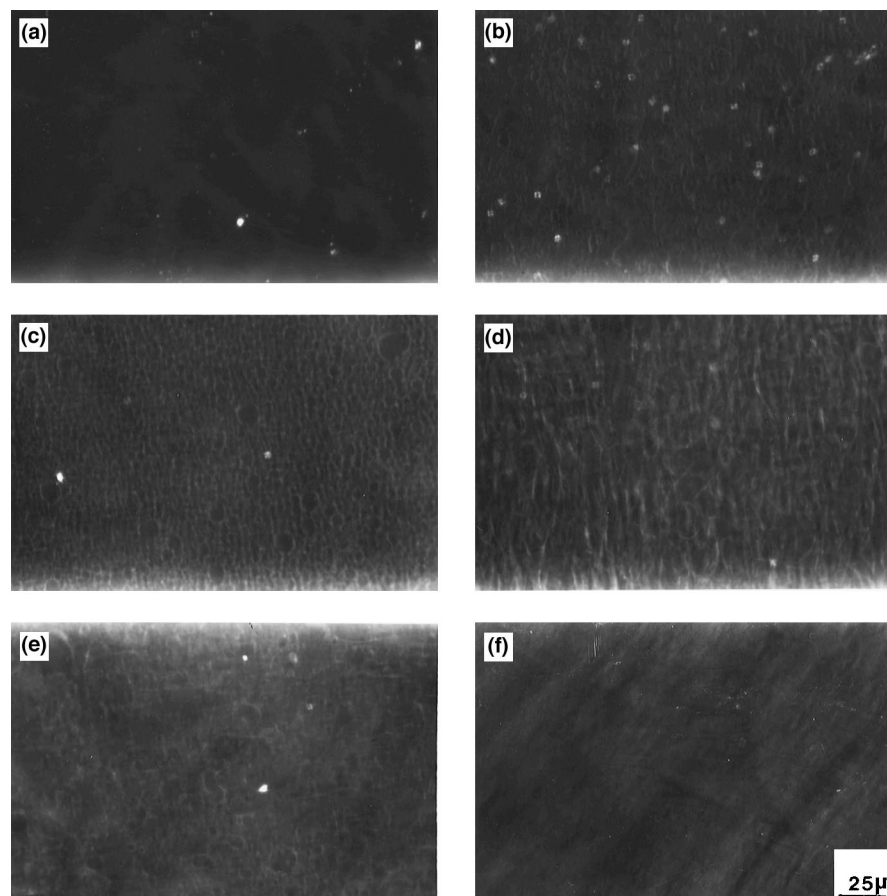
content of the other component increases. This may sometimes be an indication of component interaction in a miscible system and allows the determination of polymer–polymer interaction parameter  $\chi_{12}$ <sup>21</sup>, if morphological effects are taken into account. In *Table 3* data obtained by d.s.c. are summarized. The temperature of the Ion.,Zn<sup>2+</sup> crystallization  $T_c$  is depressed in the presence of PU—a consequence of limited PU interference with its crystallization. Similar findings were reported by Willis *et al.*<sup>22</sup> for the related polyamide/Ion.,Zn<sup>2+</sup>. This may suggest participation of PU segments in the ionomer cluster formation. This is further corroborated by the variation of the enthalpy of the ionic cluster dissociation  $\Delta H_i$  and of the temperature of the ion cluster transition  $T_i$ , both increasing in the presence of the other blend partner; see *Table 3*. Half-time  $t_{1/2}$  for the Ion.,Zn<sup>2+</sup> crystallization was determined according to ref. 22 and is also reported in *Table 3*. Its composition dependence shows that the presence of PU

**Table 3** Thermal and crystallinity data of PU/Ion.,Zn<sup>2+</sup> blends

PU/Ion.,Zn <sup>2+</sup>	$T_{\text{ons}}$ (°C)	$T_c$ (°C)		$T_i$ (°C)		$X_c$ (%)		$\Delta H_i$ (cal g <sup>-1</sup> )	$t_{1/2}$ (s)
		PU	Ion.,Zn <sup>2+</sup>	Ion.,Zn <sup>2+</sup>	Ion.,Zn <sup>2+</sup>	PU <sup>a</sup>	Ion.,Zn <sup>2+</sup> <sup>b</sup>		
100/0	197.2	–	–	–	–	33.8	–	–	–
90/10	206.8	60	51	39.3	6.7	0.1	24		
70/30	203.5	54	53	41.1	7.4	0.6	30		
50/50	200.1	54	50	39.2	12.2	0.8	36		
30/70	206.9	52	52	18.7	11.7	1.5	54		
10/90	204.6	57	52	–	11.1	1.9	48		
0/100	–	60	49	–	8.8	1.0	66		

$$^a \Delta H_{\text{fPU}}^0 = 5.825 \text{ cal g}^{-1}$$

$$^b \Delta H_{\text{fIon.,Zn}^{2+}}^0 = 66 \text{ cal g}^{-1}$$

**Figure 4** Optical micrographs with crossed polars of quenched PU/Ion.,Zn<sup>2+</sup> blends: (a) PU; (b) 90/10; (c) 70/30; (d) 50/50; (e) 30/70; (f) 10/90

accelerates the ionomer bulk crystallization. This may be due to a nucleation effect caused by the presence of the PU crystallites already formed. This factor also explains the increase of the percentage bulk crystallinity  $X_c$  of the ionomer, reported in *Table 3*. It is submitted that the variation of  $X_c$  for PU is the result of two competing factors. Low amounts of the ionomer at melt temperatures (240°C) decrease the viscosity of the mixture facilitating the diffusional process associated with PU crystallization while at higher ionomer contents ( $\geq 70$  wt%), PU crystallinity drops because of dilution and/or ionomer association. The  $T_c$  of PU during cooling could not be obtained because of multiple exotherm peaks obtained. Instead, in *Table 3*, the temperature of the crystallization onset  $T_{\text{ons}}$  is reported. The results again support the proposition that the molten ionomer facilitates the PU crystallization. In this respect

an increase of the nucleating efficiency of the ionomer may alternatively be invoked, in analogy to ionomer, Na<sup>+</sup>/polyester blend<sup>23</sup>. However, no experimental evidence as yet supports such a mechanism for a divalent cation-containing ionomer.

#### Morphology

The results using phase contrast and polarized microscopy on quenched blends are given in *Figures 3* and *4*, respectively. The refractive index of PU<sup>24</sup> 1.55 is higher than that of the ionomer. Hence at positive phase contrast dark areas should correspond to PU. *Figure 3* reveals a progressively finer microdispersion of PU with increasing proportion of the Ion.,Zn<sup>2+</sup>. In *Figure 4* examination with crossed polarizers reveals ill-defined microcrystallites embedded in an amorphous matrix.

### FTi.r. measurements

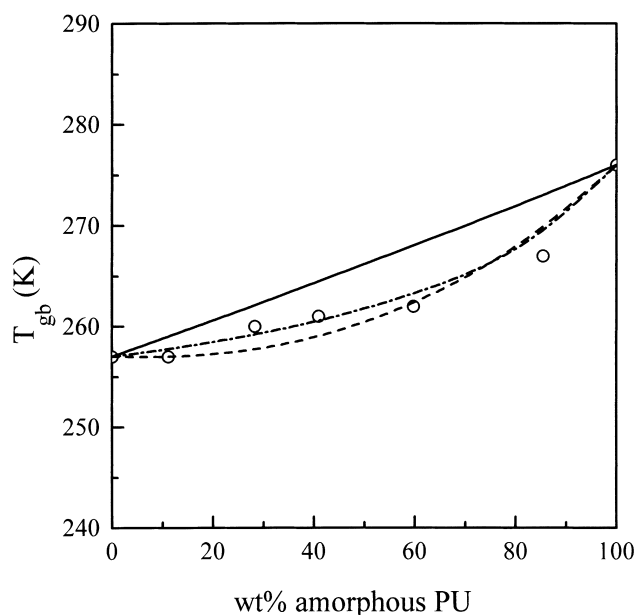
This technique was applied to detect any shift of component characteristic absorptions arising from intermolecular interaction. The method proved useful for blends<sup>25</sup> of PU/polystyrene lightly sulfonated and for the spectroscopic characterization of ion–amide interactions in the ionomer/polyamide system<sup>13,26</sup>. Spectral regions examined were the stretching vibration<sup>25</sup> of N–H at 3334 cm<sup>-1</sup>, the double absorption at 1598 and 1312 cm<sup>-1</sup> due to stretching vibration of the N–C bond and the absorption at 1540 cm<sup>-1</sup> attributed to the bending vibration of N–H and the stretching vibration of the C–N bond. No shift of the above absorptions was observed.

The double peak at 1736 and 1638 cm<sup>-1</sup> which represents the non-hydrogen-bonded carbonyl and the carbonyl stretching vibrations, respectively<sup>22</sup>, was also examined since metal cation complexation with the oxygen of the carbonyl group would shift the absorption to lower frequency due to decrease of the stretching energy of the C–O bond<sup>13</sup>. Our measurements did not indicate any shifts within the resolution capability of the instrument. If the carbonyl groups coordinated with the Zn<sup>2+</sup> ions, i.e. as a Zn<sup>2+</sup>–oxygen ligand, a peak at 1577 cm<sup>-1</sup> would appear<sup>13</sup>, but no such an absorption was detected.

### DISCUSSION

The good tensile properties of the blends, the single  $T_g$  of blends ( $T_{gb}$ ) shifting regularly between the  $T_g$ s of the pure components and the  $T_m$  depression of PU are evidence for blend miscibility. The broad  $T_g$  relaxation reflects the semicrystalline nature of the homopolymers plus interpolymer association in the case of blends<sup>26</sup>. An interpolymer association of the Ion.,Zn<sup>2+</sup> ion pairs as the ionomer content increases is manifested in the 10/90 composition which shows as a shoulder the ion clustering transition of the ionomer, see *Figures 1 and 2*.

The single  $T_{gb}$  criterion for miscibility may be validly correlated with composition if the amorphous phase compositions are used. These are obtained from the



**Figure 5** Composition dependence of  $T_{gb}$  of quenched blends: (O) experimental points; (—) FOX equation; (---) Gordon–Taylor equation; (- · -) Kwei equation. See text for details

known crystallinity of blend components, see *Table 3*. *Figure 5* gives the  $T_{gb}$  variation with composition. To correlate data the following equations were used.

The simple Fox relationship<sup>27</sup>

$$\frac{1}{T_{gb}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

the Gordon–Taylor equation<sup>28</sup>

$$T_{gb} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (2)$$

and the Kwei equation<sup>29</sup>

$$T_{gb} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \quad (3)$$

In the above equations  $w_i$  and  $T_{gi}$  are the weight fractions of component  $i$  and its  $T_g$ , respectively, and  $k$  is the ratio between the volume expansion coefficient difference in the viscoelastic and glassy state of the homopolymers and it is generally used as an empirical fitting parameter. Parameter  $q$  is also determined as an empirical fitting parameter and gives a measure of the specific interactions in the blend. However, it is not very discriminating since it cannot distinguish between interactions among homopolymer monomers and those between blend partners.

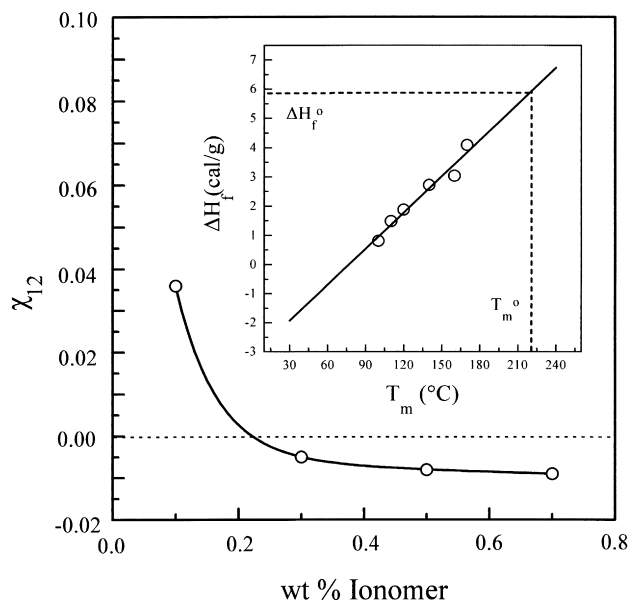
Inspection of *Figure 5* reveals that the best prediction of  $T_{gb}$  is obtained using the Gordon–Taylor equation with  $k = 3.01$  and the Kwei equation with  $k = 0.6$  and  $q = -35.12$ . The negative value of  $q$  is usually taken to mean that the interaction is weak; however, this is not necessarily so as a systematic study by Pennacchia *et al.*<sup>30</sup> on hydrogen-bonded miscible blends indicated. In that work, involving *para*-substituted polymeric blends with poly(methyl methacrylate), the acidic strength and the size of the substituent was shown to affect directly the hydrogen-bonding strength leading to miscibility. However, as the  $T_{gb}$  variation showed, only the absolute value of  $q$  (not its sign) is of significance in quantifying hydrogen bonding interactions, since both positive and negative  $T_{gb}$  variations were observed for these strongly interacting blends. It was also proposed that a decreased deviation from the weight average line is characteristic of a non-uniform distribution of hydrogen bonds. These findings support the view that the present binary blend in the solid state exhibits specific interactions; hydrogen bonding and dipole–dipole.

The  $T_m$  depression of PU caused by the ionomer at elevated temperatures may be caused by the free energy change (diluent effect) and/or morphological factors. If the latter are eliminated, and assuming a mean field approach for these interactions, the polymer–polymer interaction parameter  $\chi_{12}$  may be obtained using the simplified equation of Nishi and Wang<sup>21</sup>, valid for high-molecular-weight components, i.e.

$$\left( \frac{1}{T_{mb}^o} - \frac{1}{T_m^o} \right) \frac{1}{\phi} = - \frac{R \bar{V}_{1u}}{\Delta H_f^o \bar{V}_{2u}} \chi_{12} \phi_2 \quad (4)$$

where  $\bar{V}_{iu}$  and  $\phi_i$  are the molar volume and volume fraction of polymer  $i$ . Indices 1 and 2 refer to the crystalline and amorphous polymer, respectively, and  $\Delta H_f^o$  is the enthalpy of fusion of the pure crystalline component at equilibrium conditions.  $T_{mb}^o$  and  $T_m^o$  are the melting points of the crystalline component at equilibrium in the blend and in the pure state, respectively.

$T_m$  equilibrium data were obtained using the Hoffman–Weeks procedure<sup>31</sup>. *Table 2* gives these equilibrium data as



**Figure 6** Interaction parameter  $\chi_{12}$  for PU/Ion.,Zn<sup>2+</sup> blends at various compositions calculated using equation (4). Inset: experimental determination of  $\Delta H_f^\circ$  of PU

well as the slope  $\eta$  of the Hoffman–Weeks equation, a parameter which gives a measure of the PU crystal stability.

$$T_{mb} = \eta T_c + (1 - \eta) T_m^o \quad (5)$$

According to this procedure a plot of  $T_{mb}$  versus the crystallization temperature  $T_c$  yields a straight line given by equation (5). The intersection of this line with  $T_m = T_c$  gives the  $T_{mb}^o$  and  $T_m^o$  of the perfect crystal in the blend and the pure state, respectively. Blends and pure PU were annealed for 1 h in the range of 130 to 170°C. Since  $\chi_{12}$  may be composition dependent<sup>26</sup>, equation (4) was used to obtain the interaction parameter at each composition. The results are reported in Table 2 and depicted in Figure 6. The near zero  $\chi_{12}$  values predict miscibility of the amorphous components of the blend at the compositions studied. The trend in  $\chi_{12}$  data shows reduced interaction at high PU contents and this is expected since at this composition range the concentration of the active groups of the ionomer (H<sup>+</sup>, Zn<sup>2+</sup>) leading to miscibility, decreases. It is relevant to note that good solid state mechanical properties as well as  $T_{gb}$  data at ambient temperatures may not reflect the  $\chi_{12}$  magnitudes determined.  $\chi_{12}$  is determined at elevated temperatures (220°C) and in these polar systems  $\chi_{12}$  decreases with rising temperature<sup>32</sup>. Free volume theory also predicts  $\chi$  to be a decreasing function of temperature (see for example ref. <sup>33</sup>). The  $\chi_{12}$ -composition dependence shows an opposite trend to that reported by Lu and Weiss<sup>26</sup> in that in the present system  $\chi_{12}$  decreases (i.e. miscibility is favoured) at increased amounts of the ionomer. This is attributed to the fact that in the analogous system<sup>26</sup> involving a polyamide-6 and a polystyrene functionalized with about 10 mol% manganese sulfonate groups, the ionomer involved had a higher content of active polar groups. This is also shown by the much higher  $\chi_{12}$  values reported.

Phase contrast micrographs in Figure 3 are typical of a micro-phase separated blend; however, it is possible that the white areas belong to the crystalline domains of the ionomer which is not miscible with PU at room temperature.

The fact that FTi.r. failed to reveal the nature of the specific forces involved may be accounted for by the small

concentration of the interactive groups involved plus the low resolution capability ( $\pm 2 \text{ cm}^{-1}$ ) of the spectrometer employed.

Data used in the above calculations are as follows: molar volumes,  $\bar{V}_{PU} = 2100 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\bar{V}_{\text{Ion.,Zn}^{2+}} = 63 \text{ cm}^3 \text{ g mol}^{-1}$ .  $d(\text{PU}) = 1.23 \text{ g cm}^{-3}$ ,  $d(\text{Ion.,Zn}^{2+}) = 0.74 \text{ g cm}^{-3}$  at 25°C. The quantity  $\Delta H_f^\circ$  used in equation (4) was not available in the literature. This was obtained by plotting experimental values of  $\Delta H_f^\circ$  versus  $T_m$  of PU and extrapolating to  $T_m^o$  to obtain  $\Delta H_f^\circ$  (see Figure 6 inset). The value thus obtained was  $\Delta H_f^\circ(\text{PU}) = 5.825 \text{ cal g}^{-1}$ .

## CONCLUSIONS

- (1) Melt-mixed PU/Ion.,Zn<sup>2+</sup> blends are compatible throughout their composition range.
- (2) D.m.a. and d.s.c. results support the view that the amorphous components of the blend are miscible at ambient and at elevated temperatures. Miscibility seems to be less favoured at rich PU compositions.
- (3) Miscibility may be mostly attributed to dipole–dipole and hydrogen bonding interactions.

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