

# Compatibilization of poly(ethylene-co-vinyl alcohol) (EVOH) and EVOH/HDPE blends with ionomers. Structure and properties

Costas K. Samios and Nikos K. Kalfoglou\*

Department of Chemistry, University of Patra, 26500 Patra, Greece

(Received 29 April 1997; accepted 2 September 1997)

The compatibility behaviour of melt-mixed blends of poly(ethylene-co-vinyl alcohol) (EVOH)/ionomer was studied in the complete composition range using tensile, dynamic mechanical, thermal, spectroscopic and morphology characterization techniques. The binary blends were mechanically compatible especially when equilibrated to ambient humidity levels. The above techniques were also applied to characterize the ternary HDPE/ionomer/EVOH where the ionomer plays the role of the compatibilizer due to specific interactions (to the EVOH) and athermal mixing with the polyolefin. Morphology examination showed that EVOH is distributed within the PO matrix in laminar form making the polymeric alloy suitable for gas barrier applications. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: EVOH blends; polyolefin blends; structured films)

## INTRODUCTION

It is generally accepted that polymer blending may provide an effective and economical route for polymer properties diversification. Among these, barrier properties are prominent in the packaging industry. Recently, environmental concerns have led to the application of poly(ethylene-co-vinyl alcohol) (EVOH) as a thermoplastic, combining superior gas barrier properties and high oil resistance with excellent transparency and ease of processing<sup>1,2</sup>. Its hydrogen-bonded structure, though beneficial to low permeability, causes moisture absorption which results in the deterioration of the same property. Thus blending with a hydrophobic polymer, e.g. polyolefin, may offset this drawback. Recent relevant work was reported by Kamal and coworkers<sup>3</sup> on the PP/EVOH blend compatibilized with PP modified with maleic anhydride (PP-g-MA). The influence of various processing parameters on morphology, permeability and impact strength were examined for extruded films. In a related work<sup>4</sup>, injection-molded specimens were also examined. Prasad and Jackson<sup>5</sup> reported on the mechanical properties and morphology of melt-blended EVOH in an HDPE matrix using PE-g-MA as a compatibilizer.

Other combinations of EVOH with low permeability thermoplastics, e.g. polyesters and polyamides, were studied by Schultz, Gohil and coworkers<sup>1–6</sup> who characterized blends of poly(ethylene terephthalate) (PET)/EVOH and poly(ethylene-2,6-naphthalate) (PEN)/EVOH. Ahn et al.<sup>2</sup>, Akiyama and Akiba<sup>7</sup> and Cho and coworkers<sup>8</sup> have reported on blends of various aliphatic nylons with EVOH.

In a previous work<sup>9</sup>, the compatibility of poly(vinyl alcohol) (PVOH) with the ionomer Zn<sup>2+</sup> of a modified polyolefin was examined, as well as its application as a compatibilizer for PVOH/HDPE blend.

The present report deals with the characterization of the

compatibility of EVOH/ionomer, Zn<sup>2+</sup> in the complete composition range using dynamic, mechanical, tensile, thermal and optical methods. EVOH has the distinct advantage over PVOH in that it is thermally stable in the melt. The ionomer, Zn<sup>2+</sup> if compatible with EVOH may reduce its hydrophilic nature because of its predominantly olefinic structure. It is of relevance to note that this ionomer was reported to have the lowest hygroscopicity among modified polyolefinic ionomers<sup>10</sup>. Also it may serve as a compatibilizer for the EVOH/HDPE blend “binding” the EVOH into the HDPE matrix. This ternary blend may show low permeability properties provided that EVOH develops into a laminar morphology within the polyolefin matrix. Morphology examination using scanning electron microscopy (SEM) was applied to ternary blends to assess the phase distribution of EVOH.

## EXPERIMENTAL

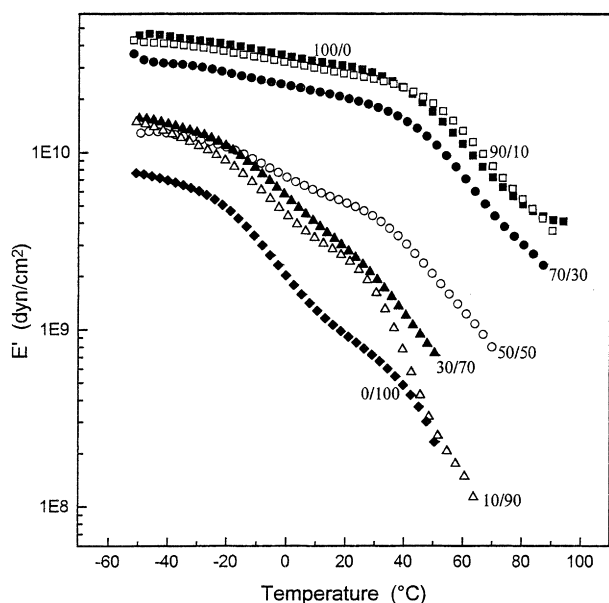
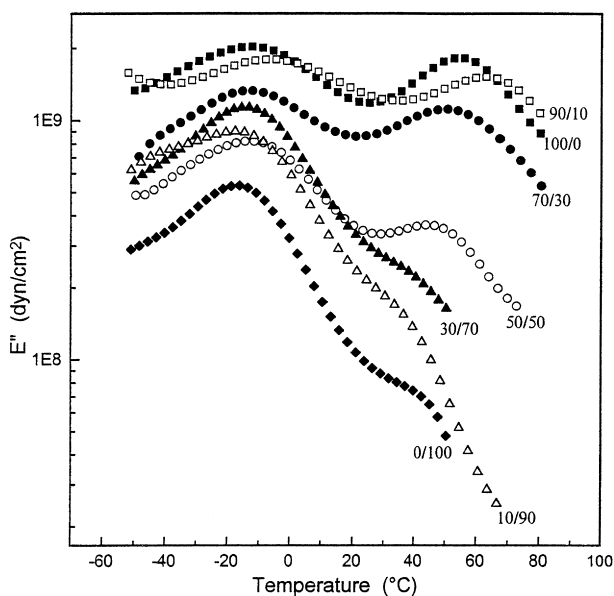
*Materials and preparations.* EVOH (EVAL) from Kuraray Co. Ltd. had a 32 mol% ethylene content, an MFI of 1.3 g/10 min (190°C, 2160 g) and density 1.19 g cm<sup>-3</sup>. The ionomer, Zn<sup>2+</sup> (Surlyn 9020) from Du Pont de Nemours Co. is a random ethylene–methacrylic acid–isobutylacrylate terpolymer with a molar concentration of 78–10–12 respectively and a degree of neutralization of approx. 70%.  $M_n = 25\,000\text{ g mol}^{-1}$ , density = 0.96 g cm<sup>-3</sup> and MFI 1.0g/10 min (190°C, 2160 g).

Materials were dried in dynamic vacuo at 60°C for 24 hr. Blends were prepared by melt-mixing in a home-made stainless steel bob-and-cup type of mixer previously described<sup>9</sup>. The mixing cup was blanketed under an argon atmosphere and a small amount (approx. 1 wt%) of polyolefin stabilizer (“Irgastab”) was added prior to mixing. Based on tensile property optimization, specifically the ultimate elongation  $\epsilon_b$ , the mixing time employed was

\* To whom correspondence should be addressed

**Table 1** Ultimate tensile properties of blends<sup>a</sup>

EVOH/Ion Zn <sup>2+</sup>	Dry films			Films with moisture		
	$\sigma_b$ /MPa	$\epsilon_b$ %	$E_b$ /J cm <sup>-3</sup>	$\sigma_b$ /MPa	$\epsilon_b$ %	$E_b$ /J cm <sup>-3</sup>
100/0	75 ± 1	21 ± 2	11	38 ± 2	217 ± 81	77
90/10	34 ± 5	31 ± 19	11	45 ± 2	462 ± 36	141
70/30	26 ± 2	47 ± 19	11	38 ± 4	389 ± 64	112
70/30 <sup>b</sup>	—	—	—	32 ± 1	127 ± 54	—
50/50	21 ± 2	121 ± 21	23	21 ± 3	237 ± 39	40
30/70	22 ± 1	373 ± 29	59	21 ± 1	409 ± 29	59
10/90	21 ± 3	586 ± 65	78	26 ± 1	693 ± 76	104
0/100	28 ± 2	729 ± 85	109	28 ± 2	729 ± 85	109

<sup>a</sup>Quenched at 0°C.<sup>b</sup>Mixing time 15 min.**Figure 1** Temperature dependence of the storage modulus  $E'$  of EVOH/ion., Zn<sup>2+</sup> blends at the indicated compositions**Figure 2** Temperature dependence of the loss modulus  $E''$  of EVOH/ion., Zn<sup>2+</sup> blends at the indicated compositions

10 min at 240°C;  $\epsilon_b$  was shown in the past<sup>11,12</sup> to be a sensitive mechanical property indicator of the compatibilization of polymeric alloys. For ternary blends, the same criterion established a mixing time of 15 min.

The EVOH/ion., Zn<sup>2+</sup> compositions prepared and

characterized were 90/10, 70/30, 50/50, 30/70, 10/90. Films were obtained by compression-moulding between Teflon sheets at 210°C and 10 MPa for 1.0 min followed by quenching to 0°C.

HDPE (Finathene 58070), a blow-moulding grade, was obtained from Petrofina S. A. MFI = 10 g/10 min,  $d = 0.955 \text{ g cm}^{-3}$ .

**Apparatus and procedures.** Tensile tests were performed at a crosshead speed of  $10 \text{ cm min}^{-1}$  and at 23°C according to ASTM D882 using a J J Tensile Tester type 5001 and rectangular strips measuring  $6.0 \times 0.65 \times 0.25 \text{ cm}^3$ .

DMA data storage modulus  $E'$ , loss modulus  $E''$  and loss angle  $\tan \delta$  were obtained at 10 Hz with the RSA II mechanical spectrometer of Rheometric Scientific Ltd. Specimen dimensions were  $2.3 \times 0.5 \times 0.015 \text{ cm}^3$ .

DSC measurements were carried out using the DSC (SP) equipped with the AutoCool accessory from Rheometric Scientific Ltd. Nominal weight was 10 mg and heating/cooling rate  $10^\circ\text{C min}^{-1}$ . The thermal cycling applied was quenching at  $50^\circ\text{C min}^{-1}$  to  $-50^\circ\text{C}$ , heating to  $200^\circ\text{C}$  (1 min), followed by quenching to  $-50^\circ\text{C}$  and then heating to  $200^\circ\text{C}$ .

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

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

SEM was carried out on a JEOL model JSM-500 instrument. Cryofractured or etched surfaces were examined at a tilt angle of  $30^\circ$ .

## RESULTS

### Binary EVOH/ionomer blends

**Tensile properties.** Data in terms of ultimate strength  $\sigma_b$ , elongation at break  $\epsilon_b$  and energy to tensile failure  $E_b$  are summarized in Table 1 for dry specimens and for films conditioned for 2 days at ambient conditions (23°C, approx. 60% R.H.). Dry samples show an increasingly flexibilizing effect with the addition of the ionomer. The plasticizing action by moisture leading to a dramatic increase of all quantities, especially at high EVOH contents, is also evident. Of interest is the observed maximum at the 90/10 composition. A maximum in EVOH crystallinity (see below) was observed at this composition and this would enhance  $\sigma_b$ . This, combined with the increased ductility, leads to a maximum in toughness  $E_b$  at this composition. Table 1 also indicates that prolonged mixing during blend preparation leads to property deterioration. This cannot be

**Table 2** Viscoelastic and thermal data of EVOH/Ion Zn<sup>2+</sup> blends<sup>a</sup>

Blends	$T_g$ (°C) (EVOH)	$T_g$ (°C) (Ion Zn <sup>2+</sup> )	$T_{mb}$ (°C) (EVOH)	$T_{mb}$ (°C) (Ion Zn <sup>2+</sup> )	$T_i$ (°C)	$\Delta H_i$ (cal g <sup>-1</sup> )	$T_c$ (°C) (EVOH)	$T_c$ (°C) (Ion Zn <sup>2+</sup> )	$W_{1/2}$ (°C) (EVOH)	$W_{1/2}$ (°C) (Ion Zn <sup>2+</sup> )	$x_c$ (%) (EVOH) <sup>b</sup>	$x_c$ (%) (Ion Zn <sup>2+</sup> ) <sup>c</sup>	$T_{mb}^0$ (°C)
100/0	54.3	—	184.1	—	—	—	162.3	—	4.6	—	71.8	—	187.0
90/10	62.4	-5.4	185.1	87.8	38.9	1.6	161.7	—	7.0	—	80.6	13.6	—
70/30	56.4	-8.6	183.6	87.5	44.3	1.1	161.5	63.6	4.7	—	64.8	13.3	—
50/50	43.2	-14.1	182.6	87.3	41.7	1.1	161.5	62.3	4.7	14.0	59.9	11.1	—
30/70	—	-14.9	182.3	86.9	41.1	1.3	160.7	61.4	6.7	13.2	59.1	15.9	184.4
10/90	—	-16.6	181.2	86.6	40.1	1.4	160.2	62.9	10.2	11.7	52.4	16.0	183.9
0/100	—	-17.1	—	87.9	43.8	2.0	—	59.9	—	7.2	—	16.5	—

<sup>a</sup>Quenched, equilibrated at ambient conditions.<sup>b</sup> $\Delta H_f = 25.6$  cal g<sup>-1</sup>.<sup>c</sup> $\Delta H_f = 66$  cal g<sup>-1</sup>.

attributed to material degradation since materials were stabilized and mixing was carried out in an inert atmosphere. The other alternative suggested by a referee would be unfavorable morphology evolution (coarsening) after prolonged mixing.

**Dynamic mechanical properties.** The DMA spectra obtained under isochronous conditions are given in *Figure 1* and *Figure 2* in terms of the storage modulus  $E'$  and loss modulus  $E''$ , respectively. The main relaxations ( $E''_{max}$ ) of EVOH (at 54°C) and of the ionomer ( $\beta'$  at -17°C) are evident in most compositions though approaching each other. A similar behaviour was observed for the PVOH/ionomer, Zn<sup>2+</sup> blend<sup>9</sup>. Qualitatively, this is explained by a strong association of components due to hydrogen bonding and/or ionic interactions<sup>13</sup> leading to stiffening of the flexible ionomer and the flexibilization of the EVOH; see modulus variation in *Figure 1*. Again the 90/10 composition shows synergy at above ambient temperatures. Its  $T_g$  is also higher than that of pure EVOH. This is characteristic of strong component interactions. Considerable work using the DMA<sup>14–16</sup> and dielectric technique<sup>16,17</sup> has been devoted to the elucidation of the ionomer relaxations. For the particular ionomer, the main relaxation  $\beta'$  is attributed to amorphous short chain segments containing PE branches and non-ionized carboxylate groups. No  $\alpha$  relaxation associated with the crystalline phase was observed. A relaxation due to order–disorder transition<sup>16</sup> in the ionic cluster detected with the DSC is observed in the  $E''$  spectrum as a shoulder at approx. 40°C. This ionic cluster formation may enhance the modulus<sup>18</sup> since it acts as a physical crosslink; see *Figure 1*. The reason why  $E'$  relaxation is less affected is due to the fact that local motion associated with cluster disordering is too small. In the case of DSC where enthalpy changes are measured directly, cluster dissociation involving a finite energy expenditure is readily detected (see below). The EVOH also shows a secondary relaxation at -22°C attributed to short pendant branches originating from the olefinic portion of the modified ethylene copolymer. In general, moduli variation in *Figure 1* leads to the conclusion that blends fall into two classes depending on their composition, the dividing line being the 50/50 blend. Main viscoelastic relaxations maxima ( $E''_{max}$ ) are summarized in *Table 2*.

**Thermal properties.** Melting temperature  $T_{mb}$ , crystallization temperature  $T_c$ , ionic transition  $T_i$  and its associated enthalpy  $\Delta H_i$ , the crystallization exotherm width at half-height  $W_{1/2}$ , and the crystallinity of the blend components  $X_c\%$  are recorded in *Table 2*. The regular  $T_{mb}$  depression of EVOH with composition is noticeable. Crystallinity levels suggest that the presence of the ionomer

hinders crystallization of EVOH and vice-versa. As the  $T_c$  temperatures of the ionomer indicate, the presence of crystalline EVOH facilitates the onset of the ionomer crystallization, possibly by nucleation. As the composition dependence of  $W_{1/2}$  shows, at high ionomer contents crystallite size distribution widens for both components<sup>19</sup>. Among various compositions, the 90/10 blend does not conform to the composition dependence of properties listed in *Table 2*. The higher  $T_{mb}$ ,  $X_c\%$  and  $\Delta H_i$  for this composition are characteristic of increased order and interaction.

The regular  $T_{mb}$  depression of EVOH with dilution may be attributed to morphological and/or thermodynamic miscibility (diluent effect)<sup>20</sup>. The latter is excluded for EVOH compositions higher than 30 wt% since two  $T_g$ 's were observed. The ionomer-rich compositions which showed a single  $T_g$  were treated according to the Hoffman–Weeks procedure<sup>21</sup> to obtain the equilibrium  $T_m^0$  and  $T_{mb}^0$  of EVOH in the pure state and blend, respectively. Annealing was performed in vacuo for 2 hr at various temperatures  $T_c$  in the range 160–140°C for the 100/0, 30/70, 10/90 compositions. Results were analyzed using the equation

$$T_{mb} = T_{mb}^0 \left( 1 - \frac{1}{\gamma} \right) + \frac{T_c}{\gamma} \quad (1)$$

where  $\gamma$  is a lamellar thickening factor and  $T_{mb}$  the experimentally determined  $T_m$  after annealing at  $T_c$ . Extrapolation to the line  $T_m = T_c$  yields the equilibrium  $T_{mb}^0$  recorded in *Table 2*.

The relevant plot is given in *Figure 3*. Since  $T_{mb}^0 \neq T_m^0$ , it is valid to assume that the  $T_{mb}^0$  depression is caused by the diluent effect.  $T_{mb}^0$  can thus be used to obtain polymer–polymer interaction at elevated temperatures where the ionomer is in the melt state.

**FTi.r. measurements.** *Figure 4* gives the FTi.r. spectra of blends. The broad band between 3450 and 3200 cm<sup>-1</sup> is attributed to the stretching vibration of intermolecularly hydrogen-bonded hydroxyl groups. This absorption is characteristic of polymeric association<sup>22</sup> and its components at 3450, 3300 and 3200 cm<sup>-1</sup> change in strength (reinforcement of the 3450 cm<sup>-1</sup> band) due to dilution effects with ionomer addition.

The bands at 2910–2860 cm<sup>-1</sup> and 1450–1470 cm<sup>-1</sup> are caused by the alkane component of the modified polyolefins. The carbonyl group stretching vibration of the ester, the carboxyl acid and the carboxylate anion gives rise to absorptions at 1735, 1700 and 1586 cm<sup>-1</sup>, respectively. No new peaks related to the above were observed after subtraction of the spectra of the pure blend components. The spectrum of a blend prepared by melt-mixing EVOH with 2 wt% Zn<sup>2+</sup>, (acetate)<sub>2</sub> did not exhibit any new features in the 3450–3200 cm<sup>-1</sup> region.

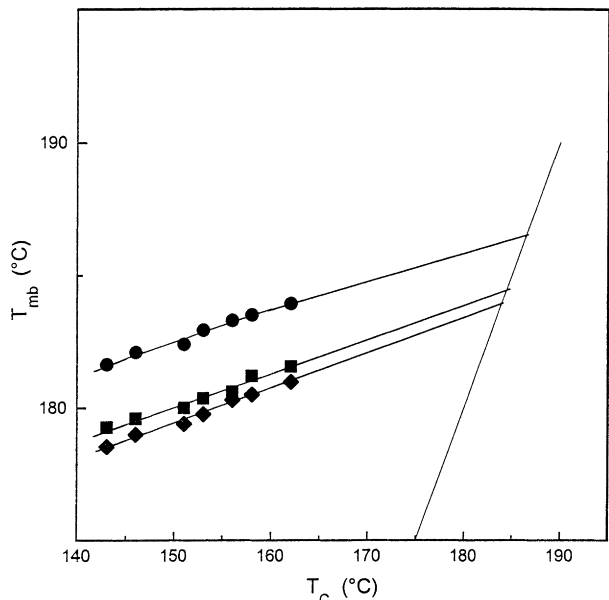


Figure 3 Hoffman-Weeks plots of EVOH/ion., Zn<sup>2+</sup> blends: (●) 100/0; (■) 30/70; (◆) 10/90

*Optical microscopy.* Phase-contrast micrographs in Figure 5a–d show a finely dispersed inhomogeneous blend. The degree of homogeneity increases as a function of ionomer content. The results are similar to those reported

for the PVOH/ionomer blends<sup>9</sup>. Observation with crossed polars shows the dominance of the crystalline superstructure at ionomer contents  $\geq 50$  wt%, see micrographs Figure 5e–h. It is also observed that crystallites are developed at the 90/10 composition where increased crystallinity and higher  $T_m$  were obtained.

*Ternary HDPE/EVOH/ionomer blends*

*Tensile properties.* Table 3 lists the ultimate properties of ternary blends at various compositions.

If ternary blends are to be used as barrier materials, polyolefin (PO) should serve as a moisture-proof matrix wherein EVOH is stratified into thin layers. Thus blends with a high proportion of PO were studied.

Table 3 shows that a 10 wt% ionomer is insufficient to fully compatibilize the 2/1 PO/EVOH composition, as judged by the ultimate tensile elongation  $\epsilon_b$ %. Apparently, the ionomer is diluted by the PO phase because of chemical similarity. Compatibilization is attained at higher ionomer contents and also when the PO/EVOH ratio is reduced to 1/1. Data in Table 3 indicate that a 15 min mixing time is adequate for compatibilization.

*Dynamic mechanical properties.* These are summarized in Figure 6 and Figure 7 for the 1/1 and 2/1 ratio of HDPE/EVOH, at three levels of the ionomer. In Figure 6, increasing the ionomer content flexibilizes the ternary blend at above room temperature and causes limited stiffening at

Table 3 Ultimate tensile properties of ternary blends<sup>a</sup>

HDPE/EVOH/Ion Zn <sup>2+</sup>	$\sigma_y$ (MPa)	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	$E_b$ (J cm <sup>-3</sup> )
66.7/33.3/0	–	22 ± 1	7 ± 0	1
60/30/10	–	17 ± 1	7 ± 2	1
60/30/10 <sup>b</sup>	–	16 ± 1	6 ± 2	1
53.3/26.7/20	20 ± 1	17 ± 1	78 ± 21	13
50/50/0	–	29 ± 3	7 ± 0	1
45/45/10	29 ± 2	24 ± 2	37 ± 13	8
40/40/20	25 ± 3	26 ± 4	346 ± 36	78

<sup>a</sup>Films conditioned at 60% R.H., quenched at 0°C.

<sup>b</sup>Mixing time 20 min.

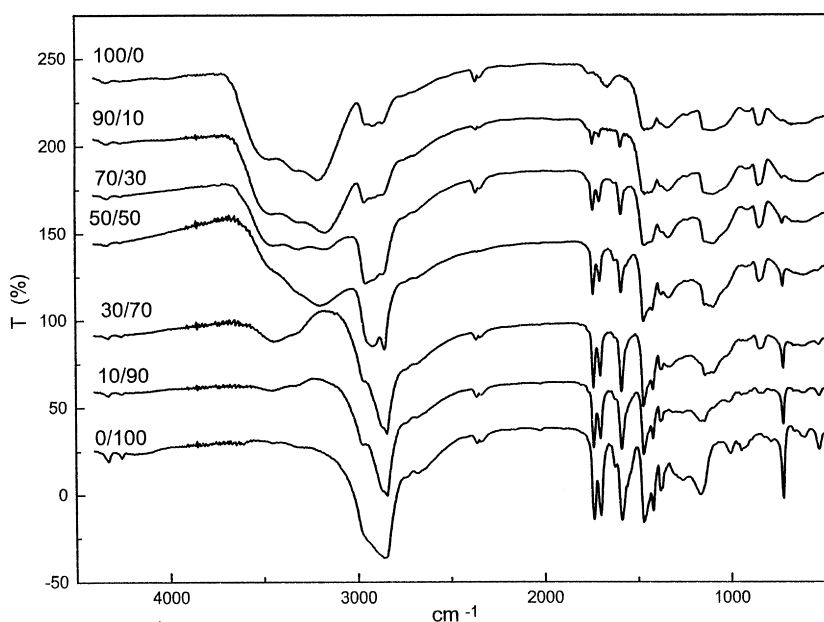
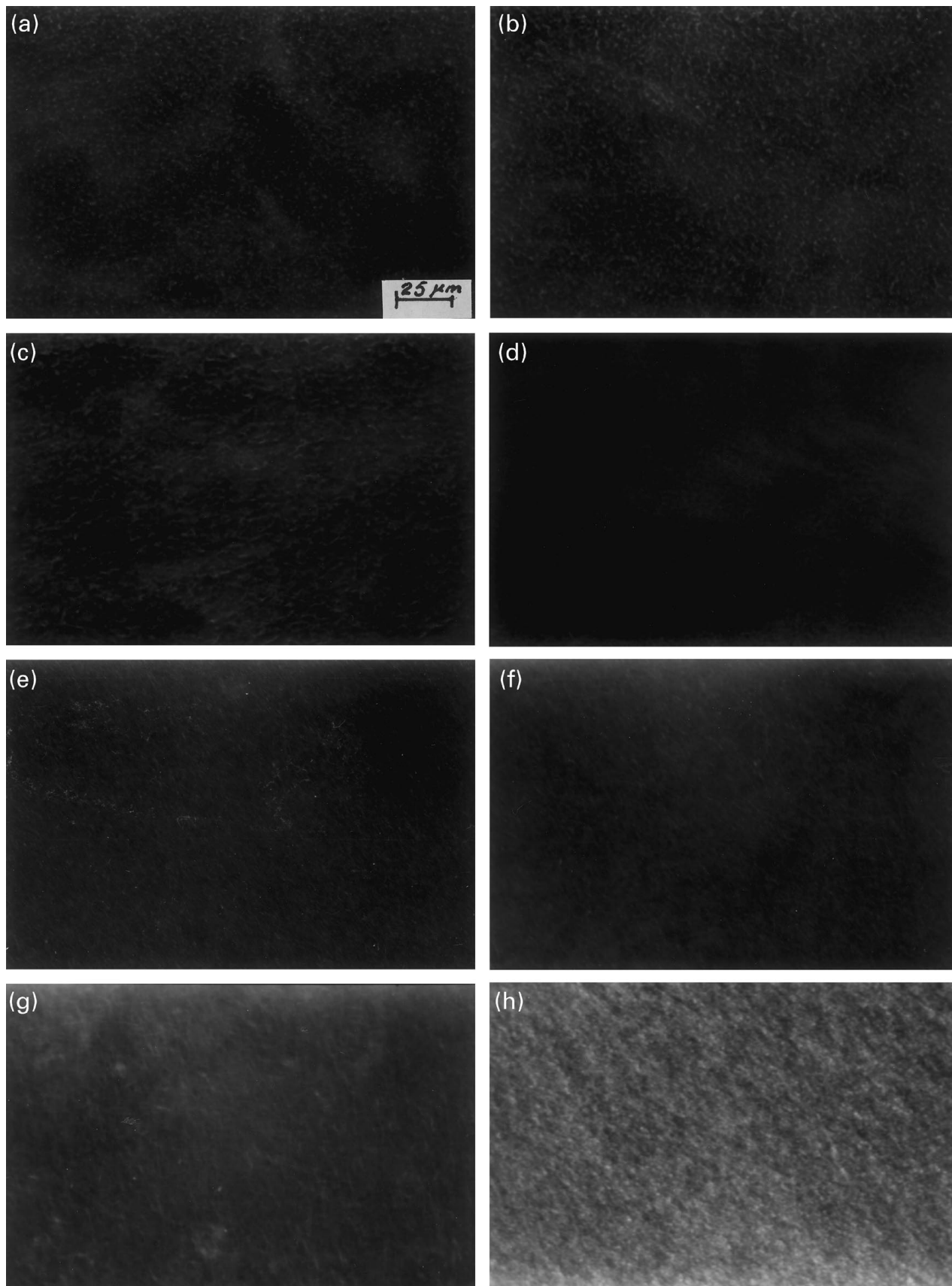


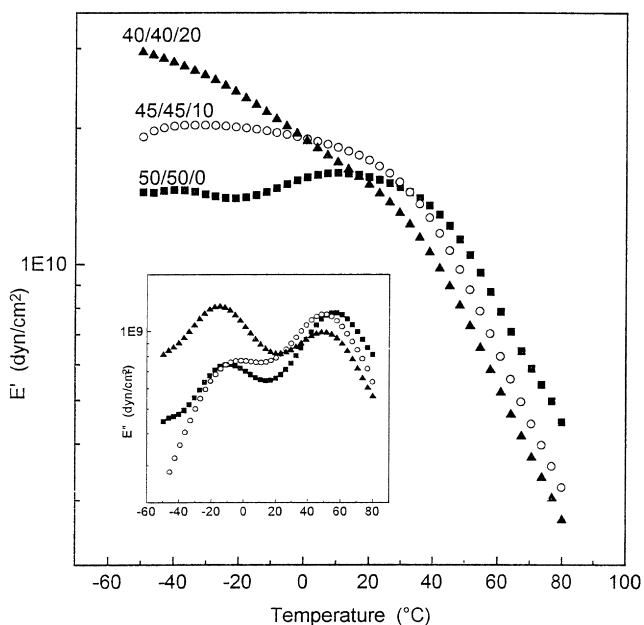
Figure 4 FTi.r. spectra of EVOH/ion., Zn<sup>2+</sup> blends at the indicated compositions



**Figure 5** Phase-contrast micrographs of EVOH/ion., Zn<sup>2+</sup> blends: (a) 90/10; (b) 70/30; (c) 50/50; (d) 10/90. With crossed polars: (e) 90/10; (f) 70/30; (g) 50/50; (h) 30/70

low temperatures. A more regular trend is observed at the 2/1 composition, see *Figure 7*. Relaxation spectra in *Figure 6* (inset) indicate that main component relaxations are conserved, the HDPE spectrum being flat<sup>9</sup> merging with those

of the ionomer and EVOH. At the 2/1 composition, *Figure 7*, a considerable amount of the ionomer has mixed with the PO phase and an increasing proportion of it is also interacting with EVOH; see mutual shift of  $E''_{\max}$  of components in



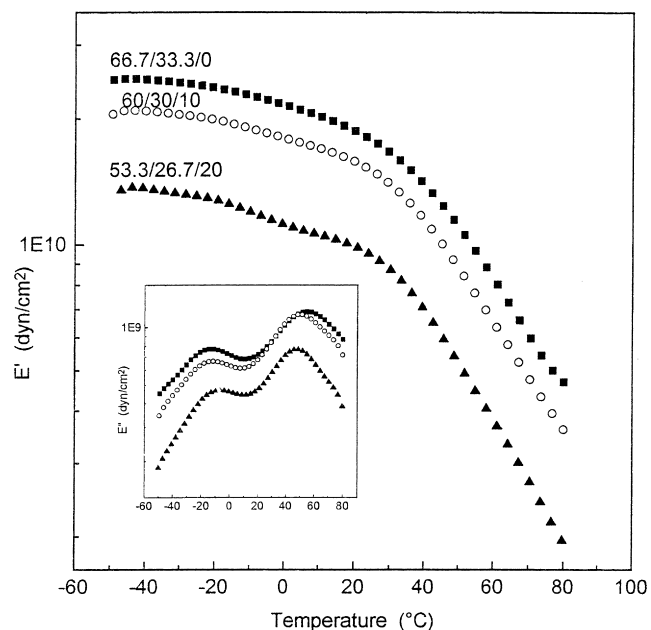
**Figure 6** Temperature dependence of storage modulus  $E'$  of ternary HDPE/EVOH/ion.,  $Zn^{2+}$  blends at the indicated compositions. Inset: Loss modulus  $E''$  at corresponding compositions

Figure 7 (inset). The above explain the decrease in the ionomer relaxation strength, notwithstanding its increased proportion in the ternary blend.

**Morphology.** SEM of cryofractured surfaces of compositions 50/50/0 and 45/45/10 are shown in Figure 8a,b. Figure 8a reveals that EVOH is coarsely distributed as globules in the HDPE matrix. When 10 wt% ionomer is added, the resulting material exhibits a fracture surface of a compatibilized blend, see Figure 8b, i.e. distinct phase boundaries disappear and features of ductile fracture characterizing strong component adhesion are evident. The phase distribution of EVOH is of practical significance for gas barrier applications as mentioned before. This was examined after leaching out EVOH from the smooth cross-section cut out of films using a surgical blade. Use was made of 1,1,1,3,3,3-hexafluoro-2-propanol as a selective solvent (1 hr at room temperature). The results obtained from these etched surfaces are shown in Figure 8c,d for compositions 45/45/10 and 60/30/10, respectively. EVOH is stratified within the polyolefin matrix, making these ternary blends suitable for packaging applications. Additional work is needed, however, to optimize blend composition and film processing conditions along the lines suggested in related work<sup>1,3,4</sup>.

## DISCUSSION AND CONCLUSIONS

Large deformation mechanical behaviour, shifts of viscoelastic relaxations, and thermal data support the existence of interpolymer interactions in the binary EVOH/ionomer blends. These are predominantly of the hydrogen bonding type involving the acrylic acid moiety of the ionomer and the proton-accepting oxygen of EVOH<sup>23</sup>. Moisture enhances this type of interaction. As evidenced by tensile properties, the water molecules might provide "bridges" for the two interacting components as the results on tensile testing show. An additional possibility would be the



**Figure 7** Temperature dependence of the storage modulus  $E'$  of ternary HDPE/EVOH/ion.,  $Zn^{2+}$  blends at the indicated compositions. Inset: loss modulus  $E''$  at corresponding compositions

polymethacrylic acid interacting as proton donor with the vinyl acetate residues of EVOH as the proton acceptor<sup>24</sup>. In principle,  $Zn^{2+}$  may also complex with the electronegative oxygen of EVOH during melt-mixing. However, no FTIR spectral evidence for this was found.

At high ionomer contents, the existence of a single  $T_g$  led us to apply the Nishi-Wang<sup>25</sup> equation to extract a polymer-polymer interaction parameter  $\chi_{12}$ , using  $T_m$  equilibrium data obtained before. The working equation is

$$\frac{1}{T_{mb}^0} - \frac{1}{T_m^0} = - \left( \frac{\chi_{12} R \bar{V}_{u2}}{\bar{V}_{u1} \Delta H_{u2}} \right) \varphi_1^2 \quad (2)$$

where indices 1 and 2 refer to the amorphous and the crystalline component, respectively. The variables  $\varphi$ ,  $\bar{V}_u$  and  $\Delta H_u$  are the normalized volume fraction, molar volume and molar enthalpy of fusion of the component indicated. In this case,  $\bar{V}_{u1} = 69.8 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\bar{V}_{u2} = 33.3 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta H_{u2} = 1029.6 \text{ cal mol}^{-1}$ . A plot of the left hand side of equation (2) versus  $\varphi_1^2$  should give  $\chi_{12}$ . For the two compositions used, this treatment gave a value of  $\chi_{12} = -0.02$  at 187°C for both compositions. This is characteristic of weak intermolecular forces since strong ionic or hydrogen bonding interactions are typically larger by an order of magnitude<sup>7</sup>. In view of the excellent tensile properties of the blends in Table 2, the low  $\chi_{12}$  value is surprising. This apparent contradiction may be explained if the role of moisture is considered. Thermal data (hence  $\chi_{12}$ ) are determined under essentially moisture-free condition. In these conditions the degree of blend compatibility, see Table 1, is considerably reduced. The interacting groups of the proton donor/acceptor types are available but are shielded to some extent by the inert polyethylene portion of the macromolecular chains. When moisture is present, water molecules readily establish and extend the hydrogen bonding network, thus increasing the availability of the interacting groups.

The stratified structure obtained in the ternary blends is of practical importance since the EVOH having a low permeability property may be utilized. This morphology evidenced by SEM was further confirmed by the application

**Table 4** Ternary blend modulus prediction for various phase connectivities<sup>a</sup>

HDPE/EVOH/Ion Zn <sup>2+</sup>	$ E^* _{obs}$ (dyn/cm <sup>2</sup> )		$ E^* _{obs}/ E^* _{calc}$ at 30°C					
	(1)	(2)	(3)	(4)	(5)	(6)	(6)	
66.7/33.3/0	1.676E10	1.073	—	—	—	—	1.292	
60/30/10	1.408E10	1.005	1.444	1.234	1.550	1.649	2.569	
53.3/26.7/20	8.802E9	0.861	1.121	0.959	1.067	1.198	2.512	
1/1/0	1.482E10	0.730	0.959	—	—	—	0.929	
1/1/10	1.503E10	0.815	—	0.848	1.205	2.013	2.291	
1/1/20	1.289E10	0.776	1.624	0.864	1.086	1.952	3.148	

Key: 1, HDPE; 2, EVOH; 3, Ion Zn<sup>2+</sup>.  
<sup>a</sup>Force applied parallel to film surface.

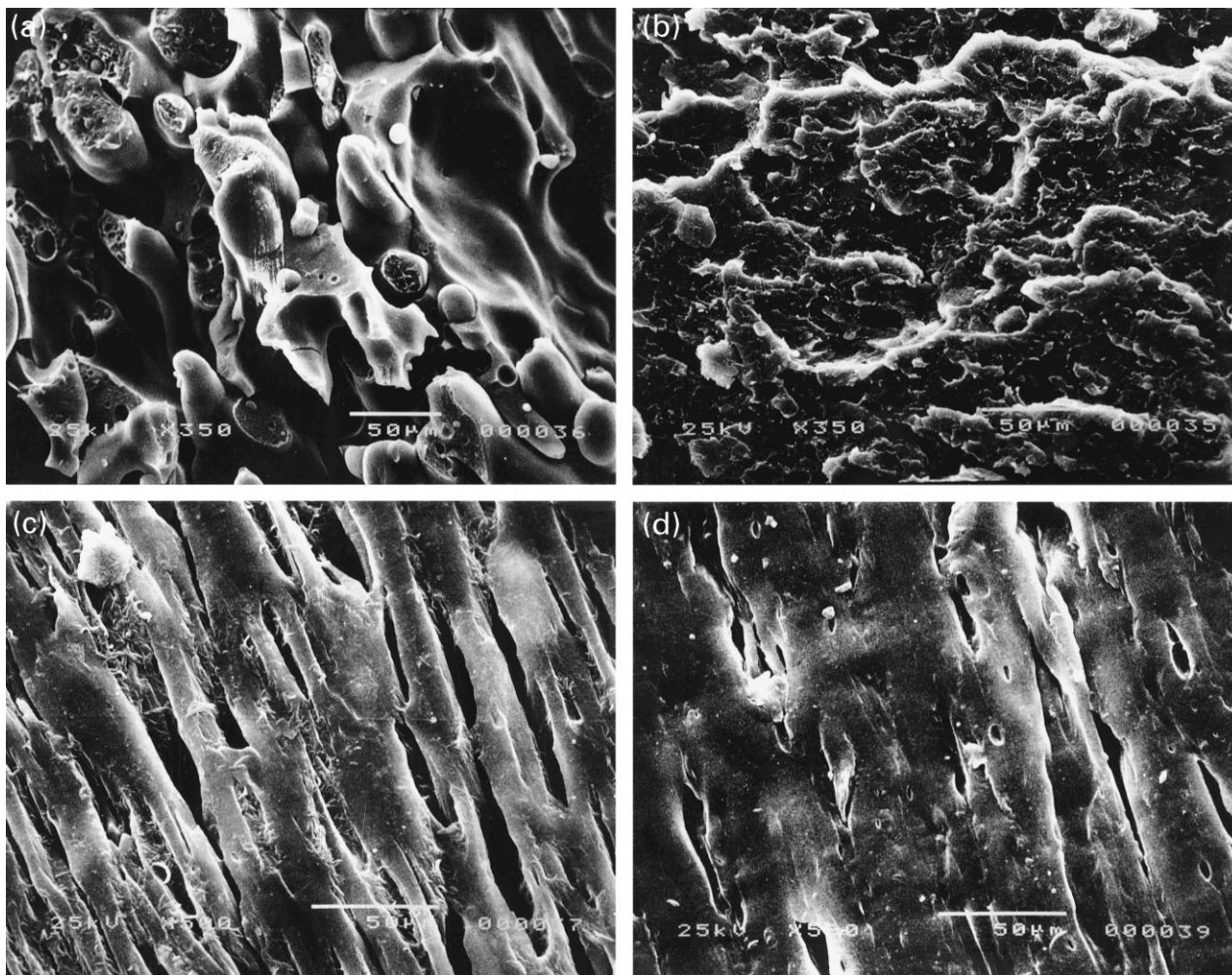
of mechanics models using the moduli data of pure components and ternary blends. It is relevant to note that modulus is a conductance property; hence mechanics models may give insight into the permeability properties of blends. Table 4 gives various types of phase connectivities combining the parallel and series models as limiting cases. Use was made of the basic equations<sup>26,27</sup> and the known component volume fraction in the ternary. Thus, for example, for connectivity (3) the blend modulus is calculated by

$$|E^*_{calc}| = \varphi_{EVOH}|E^*_{EVOH}| + (1 - \varphi_{EVOH}) \left( \frac{\varphi_{ion}}{|E^*_{ion}|} + \frac{\varphi_{HDPE}}{|E^*_{HDPE}|} \right)^{-1} \quad (3)$$

For a certain composition, the criterion for the existing connectivity is that the ratio

$$|E^*_{obs}|/|E^*_{calc}| \cong 1.0$$

Inspection of data in Table 4 indicate that, in general, a parallel phase connectivity best represents moduli data. For example, at the 60/30/10 composition, connectivity (1) is valid. It is interesting to note that increasing the compatibilizer (ionomer), hence miscibility, invalidates the purely parallel model. In this case, models (3) and (4), for composition 53.3/26.7/20, provide for the mixing of EVOH/ionomer or HDPE/ionomer, respectively. These alternative connectivities have a physical basis, since ionomer may interact with EVOH and, in the other case, HDPE may be



**Figure 8** SEM micrographs of cryofractured HDPE/EVOH/ion., Zn<sup>2+</sup> blends: (a) 50/50/0; (b) 45/45/10. Etched blends: (c) 45/45/10; (d) 60/30/10

miscible with the ionomer because of structure similarity. This finding is in line with the observation of other workers<sup>4</sup> who reported that enhanced compatibilization is detrimental to component stratification. Table 4 indicates that when the EVOH/HDPE ratio is 1 the applicability of parallel connectivity is less successful. In this case, for composition 40/40/20 model (4) is most suitable, i.e. HDPE is mixing with both the EVOH and the ionomer components which are layered in parallel to the applied force.

To conclude: (i) Melt-mixed binary EVOH/ion., Zn<sup>2+</sup> blends give strong, tough films when conditioned at ambient humidity levels. (ii) In dry conditions, increased amounts of ionomer are required to obtain compatible blends. (iii) In ternary HDPE/EVOH/ion., Zn<sup>2+</sup> melt-mixed alloys, at moderate ionomer levels, good mechanical properties are obtained. The ionomer probably plays a role in attaching EVOH into the PO matrix. (iv) Both morphology examination and mechanics models indicate that, depending on ternary composition, EVOH may stratify in the PO matrix.

#### ACKNOWLEDGEMENTS

This work was supported in part with a grant of the General Secretariat of Research and Technology (IIENEΔ-95, code N° 96), administered by the University of Patra. Thanks are also due to Prof. P. Koutsoukos for the use of the SEM facility and Dr. J. Kallitsis for useful discussions related to FTi.r. results.

#### REFERENCES

1. Kit, K. M., Schultz, J. M. and Gohil, R. M., *Polym. Eng. Sci.*, 1995, **35**, 923.
2. Ahn, T. O., Kim, C. K., Kim, B. K., Jeong, H. M. and Huh, J. D., *Polym. Eng. Sci.*, 1990, **35**, 42.
3. Kamal, M. R., Garmabi, H., Hozhabr, S. and Arghyris, L., *Polym. Eng. Sci.*, 1995, **35**, 42.
4. Walling, N. and Kamal, M. R., *Adv. Polym. Technol.*, 1995, **5**, 269.
5. Prasad, A. and Jackson, P., *Polym. Mater. Sci. Eng.*, 1996, **75**, 281.
6. Gopalakrishnan, R., Schultz, J. M. and Gohil, R. M., *J. Appl. Polym. Sci.*, 1995, **56**, 1749.
7. Akiba, I. and Akiyama, S., *Polym. J.*, 1994, **26**, 873.
8. Ha, C.-S., Ko, M.-G. and Cho, W.-J., *Polymer*, 1997, **38**, 1243.
9. Papadopoulou, C. P. and Kalfoglou, N. K., *Polymer*, 1997, **38**, 4207.
10. Yano, S., Tadano, K., Nagao, N., Kutsumizu, S., Tachino, H. and Hirasawa, E., *Macromolecules*, 1992, **16**, 175.
11. Gravalos, K. G., Kallitsis, J. K. and Kalfoglou, N. K., *Polymer*, 1995, **36**, 1393.
12. Koulouri, E. G., Gravalos, K. G. and Kallitsis, J. K., *Polymer*, 1996, **37**, 2555.
13. Natansohn, A., Murali, R. and Eisenberg, A., *Macromol. Chem. Macromol. Symp.*, 1988, **16**, 175.
14. MacKnight, W. J., McKenna, L. W. and Read, B. E., *J. Appl. Phys.*, 1967, **38**, 4208.
15. Tachino, H., Hara, H., Hirasawa, E., Kutsumizu, S., Tadano, K. and Yano, S., *Macromolecules*, 1993, **26**, 752.
16. Tadano, K., Hirasawa, E., Yamamoto, H. and Yano, S., *Macromolecules*, 1989, **22**, 226.
17. Yano, S., Nagao, N., Hattori, M., Hirasawa, E. and Tadano, K., *Macromolecules*, 1992, **25**, 368.
18. Hirasawa, E., Yamamoto, Y., Tadano, K. and Yano, S., *Macromolecules*, 1989, **22**, 2776.
19. Nadkarni, V. M. and Jog, J. P., in *Two-Phase Polymer Systems*, L. A. Utracki, ed. Hanser Publ., Munich, 1991, ch. 8.
20. Scott, R. H., *J. Chem. Phys.*, 1949, **17**, 279.
21. Hoffman, J. D. and Weeks, J. J., *J. Res. Natl Bur. Stands.*, 1962, **66A**, 13.
22. Dyer, J. R., *Applications of Absorption Spectroscopy of Organic Compounds*. Prentice-Hall, Inc., NJ, 1965.
23. Olabisi, O., Robeson, L. M. and Shaw, M. T., *Polymer-Polymer Miscibility*. Academic Press, New York, 1979, ch. 4.
24. Hughes, L. J. and Britt, G. E., *J. Appl. Polym. Sci.*, 1961, **5**, 337.
25. Nishi, T. and Wang, T. T., *Macromolecules*, 1975, **8**, 909.
26. Takayanagi, M., Harima, M. and Iwatu, Y., *Mem. Fac. Eng., Kyushu Univ.*, 1963, **23**, 1.
27. Nielsen, L. E., *Mechanical Properties of Polymers and Composites*. Marcel Dekker, New York 1974, Vol.2, ch.7.