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Compatibility study of binary and ternary PVOH/polyolefin blends

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Melt mixed blends of binary poly(vinyl alcohol) (PVOH)/ionomer, Zn^{2+} and PVOH/ionomer, Zn^{2+}/ polyolefin ternary blends were characterized, the former in the complete composition range, using mechanical, thermal, spectroscopic and morphology techniques. Ionomer, Zn^{2+} was a partially neutralized poly(ethylene-*co*-methacrylic acid-*co*-isobutylacrylate) terpolymer and the polyolefins used were high density and linear low density polyethylenes. The binary blends showed good tensile properties at high ionomer contents and this was attributed to complexation reactions at the PVOH/ionomer interphase. Thus, it was possible to use the ionomer as a compatibilizing agent for PVOH/polyolefin blends, which were characterized using most of the above techniques. Morphology studies of the ternaries at increased polyolefin compositions revealed a stratified structure, making its applicability as a barrier structured blend feasible. © 1997 Elsevier Science Ltd.

(Keywords: poly(vinyl alcohol) blends; ionomer blends; poly(vinyl alcohol)/polyolefin blends)

INTRODUCTION

Poly(vinyl alcohol) (PVOH) in addition to numerous other applications may be used as an excellent gas barrier material for oxygen and carbon dioxide[1,2]. Material disadvantages are the difficulty of melt processing because thermal decomposition sets in and poor barrier properties are obtained at increased levels of humidity. These problems may in principle be alleviated when PVOH is properly blended with moisture resistant polymers (e.g. polyolefins) provided that the blend attains a laminar morphology during its processing so that PVOH may retain its effectiveness as the high barrier component. In the context of permeability the parameters determining a useful blend are rheological, to obtain component stratification[3,4] during melt processing, and physicochemical, e.g. interfacial interactions ensuring a satisfactory level of mechanical compatibility. The latter should be moderate enough to ensure useful solid state mechanical properties of the blend without leading to a miscible system so as not to affect adversely morphology, hence the permeability properties of PVOH.

In this report the compatibility behaviour of melt-mixed blends of PVOH with an olefinic ionomer is examined in the complete composition range. It was anticipated that the metal cation (Mg^{2+}) of the ionomer might coordinate with the hydroxyl groups of PVOH, ensuring good adhesion between blend components. Such complexation reactions with a variety of divalent cations have been reported[5]. The olefinic part of the ionomer would reduce the moisture sensitivity of PVOH and could also serve as a compatibilizer for a PVOH/ polyolefin (PO) binary blend, leading also to reduced material cost.

Work of academic interest published lately on PVOH blends resorts to solution casting since melt-blending may lead to degradation. Of interest are the comprehensive compatibility studies of PVOH/poly(3-hydroxybutyrate) blends[6,7] prepared from hexafluoroisopropanol (HFIP) solution. This blend constitutes a fully biodegradable system. The miscibility behaviour of blends of partially hydrolysed PVOH/poly(vinyl acetate) was characterized by Dibbery-Brunelli and Atvars[8] using fluorescence spectroscopy. Of basic and applied interest is the study by Patel and Manley[9] on the transport properties of CO_2 through films of miscible PVOH/cellulose blends cast from N,N-dimethylacetamide containing LiCl.

Available literature on structurized melt-mixed blends containing PVOH as the active barrier component is mostly limited to patents. Among recently published work the reactive blending of PVOH/polyethylene (PE)[10] in the presence of maleic anhydride (MA) and dicumyl peroxide to initiate grafting of MA on to PE is quoted. A related patent[11] describes the reactive extrusion of PVOH/poly(propylene) (PP)–poly(ethylene-*co*-propylene) rubber in the presence of MA and a peroxide to graft the MA on to the PO. Another patent[12] reports good oxygen barrier properties for a co-extruded composite film having the structure LDPE/PVOH/PP, or biaxially stretched poly(ethylene terephthalate) (PET) or nylon replacing PET as the vapour-barrier component. PET— a polymer with good barrier properties—has been combined with PVOH by dissolution in a common solvent (HFIP) to yield transparent films with good mechanical properties and water resistance[13]. In another patent[14], PVOH is mixed with the sodium salt of polyacrylic acid (degree of neutralization 10%) to produce a film, which, after thermal treatment, had excellent oxygen-barrier properties.

Of relevance to PVOH/PO blends is the work of Kamal *et al.*[3] who investigated processing conditions to achieve

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laminar morphology in the related poly(ethylene-*co*-vinyl alcohol) (EVOH)/PP system. EVOH, also a high oxygen-barrier material, has the distinct advantage over PVOH in that it is thermally more stable hence easier to process; however, it is more expensive.

In the present work the compatibility behaviour of blends was characterized with tensile testing, dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.), Fourier transform infra-red (*FT*i.r.), wide-angle X-ray spectroscopy (WAXS) and morphology, using optical microscopy and scanning electron microscopy (SEM). Large deformation behaviour would indicate interphase adhesion, d.m.a. and *FT*i.r. would characterize the degree of mixing and possible group interactions, while morphology using SEM on etched specimens would be aimed at revealing possible component stratification. Our findings on PVOH/ionomer/PO ternary blends are also reported, using most of these techniques.

EXPERIMENTAL

Materials and preparations

PVOH (Mowiol 8-88) was supplied by Hoechst AG. Its $\overline{DP}_n$ was given as 1400, $\bar{M}_n = 67\,000\,\text{g}\,\text{mol}^{-1}$ and the degree of hydrolysis (saponification) 88 mol%. The zinc ionomer (Surlyn 9020) was donated by DuPont de Nemours Co. It is a random ethylene–methacrylic acid–isobutyl acrylate terpolymer with a molar composition of 78/10/12, respectively, and a degree of neutralization of 70%; $\bar{M}_n = 25\,000\,\text{g}\,\text{mol}^{-1}$, density $(d) = 0.96\,\text{g}\,\text{cm}^{-3}$ and MFI $= 1.0\,\text{g}/10\,\text{min}$. Linear low density PE (LLDPE–Dowlex 2045) was donated by Dow Hellas Ltd; MFI $= 1.0\,\text{g}/10\,\text{min}$ ($190°\text{C}/2.16\,\text{kg}$), $d = 0.92\,\text{g}\,\text{cm}^{-3}$. HDPE (Finathene 58070), a blow moulding grade, was obtained from Petrofina SA; MFI $= 10\,\text{g}/10\,\text{min}$ and $d = 0.955\,\text{g}\,\text{cm}^{-3}$.

Materials were dried *in vacuo* at 60°C for 24 h. Blends were prepared by melt-mixing in a stainless steel home-made batch mixer consisting of a cylindrical rotor rotating into a thermostated cylindrical cup at about $100\,\text{rev}\,\text{min}^{-1}$. The base of the rotor was tapered into a flat cone (*ca* 2°). Clearance between the rotor and cup at the circumference was 1 mm. To improve mixing, the rotor was also given intermittently a vertical movement to 'fold' the molten material over itself. Mixing was carried out under a blanket of inert gas (Ar) and the maximum amount produced per batch was *ca* 10 g.

Based on tensile property optimization, mixing time employed was 20 min at 220°C. PVOH/ionomer compositions prepared were 90/10, 70/30, 50/50, 40/60, 30/70 and 10/90. Films were obtained by compression moulding between Teflon sheets at 220°C and 10 MPa, followed by quenching to 0°C.

Apparatus and procedures

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

The d.m.a. data complex modulus $|E^*|$ and tan δ were determined at 110 Hz using a Rheovibron Model DDVII-C (Toyo-Baldwin). Specimen dimensions were $3.0 \times 0.2 \times 0.02\,\text{cm}^3$.

The d.s.c. measurements were performed with a Du Pont 910 calorimeter coupled with a 990 programmer recorder. The nominal weight was 10 mg and the heating

rate was $20°\text{C}\,\text{min}^{-1}$. The heating cycle applied was $25 \rightarrow 200°\text{C}$ (1 min) $\rightarrow -80 \rightarrow 200°\text{C}$. Thermal data were determined during the last heat scan.

Optical micrographs with phase-constant and crossed polars arrangement were obtained with an Olympus BH-2 microscope; SEM was a Jeol model JSM-5200. Surfaces after etching were examined at a tilt angle of 30°.

The *FT*i.r. spectra were obtained using a Perkin-Elmer 1600 spectrometer. Films were prepared by casting a water solution in a petri dish. Drying was carried out at 40°C for several days in a vacuum oven.

WAXS diffractograms were obtained using Ni-filtered Cu K_α radiation and a Philips 1840/30 diffractometer. Flat specimens were $1\,\text{cm}^2$.

RESULTS

Tensile properties

Large deformation behaviour is a practical screening test for the blend utility of a material, giving an assessment of its mechanical integrity and of the degree of component adhesion at the interface, in the case of a phase separated system. Ultimate elongation ϵ_b is particularly useful in this respect[15]. The results are summarized in *Table 1* where ultimate elongation ϵ_b, ultimate strength σ_b and yield strength σ_y, are recorded. Blends have good strength and satisfactory ultimate elongation at ionomer contents $\geq 60\,\text{wt}\%$. The non-linear dependence of these properties on composition suggests a non-miscible blend. This is corroborated by the d.m.a. results.

Dynamic mechanical properties

These are summarized in *Figures 1* and *2* in terms of the temperature dependence of storage E' and loss modulus E'', respectively. The main viscoelastic relaxation (E''_{max}) of the ionomer is located at 0°C and of PVOH at *ca* 73°C. The latter depends on its degree of hydrolysis, moisture content and crystallinity[16]. A thorough analysis of the viscoelastic behaviour is available[16] and taking into account the frequency effect, our data are in essential agreement with previous d.m.a. results on
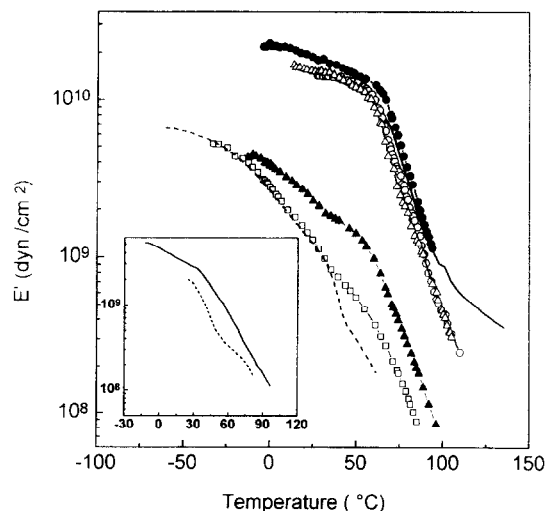

Figure 1 Composition dependence of storage modulus of PVOH/ion. Zn^{2+} blends: (- -) 100/0; (○) 90/10; (●) 70/30; (△) 50/50; (▲) 30/70; (□) 10/90; (- - -) 0/100. Inset, 40/60 blend: (—) dry; (- - -) with moisture

Table 1 Mixing conditions and tensile properties of blends

PVOH/ionomer, Zn^{2+} (%)	Mixing temperature (°C)	Mixing time (min)	σ_b (MPa)	σ_Y (MPa)	ϵ_b (%)
0/100	220	20	31 ± 3	—	562 ± 48
10/90	220	20	20 ± 2	8 ± 1	641 ± 153
30/70	220	20	14 ± 2	10 ± 1	340 ± 60
40/60^a	220	20	8 ± 1	8 ± 1	45 ± 35
40/60	220	20	8 ± 1	9 ± 1	28 ± 11
50/50	220	20	29 ± 6	35 ± 7	20 ± 4
70/30^a	220	20	29 ± 6	36 ± 8	41 ± 8
70/30	220	20	35 ± 7	—	6 ± 2
90/10	220	20	37 ± 3	60 ± 4	36 ± 13
100/0	220	20	79 ± 13	—	10 + 3

^{a} With moisture

Table 2 Thermal and viscoelastic transitions of blends

PVOH/ionomer, Zn^{2+} (%)	T_g (°C) (d.s.c.)		T_m (°C)		T_g (°C) (d.m.a.)	
	Ion., Zn^{2+}	PVOH	Ion., Zn^{2+}	PVOH	Ion., Zn^{2+}	PVOH
100/0	—	65	—	180	—	72.7
90/10	−4	65	85	175	—^{b}	69.2
70/30	−5	—^{a}	87	165	3.0	65.4
50/50	−5	48	87	165	—^{b}	64.3
40/60	−8	46	87	185	1.6	56/36.1^c
30/70	−10	41	90	165	0.0	56.3
10/90	−10	40	90	185	0.0	54.5
0/100	−15	—	90	—	0.0	—

^{a} Non-resolvable
^{b} Not measured
^{c} With moisture
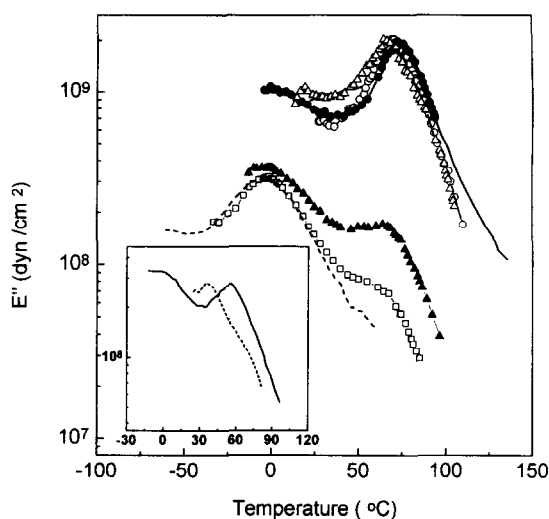
Figure 2 Composition dependence of loss modulus of PVOH/ion., Zn^{2+} blends: (—) 100/0; (O) 90/10; (●) 70/30; (△) 50/50; (▲) 30/70; (□) 10/90; (---) 0/100. Inset, 40/60 blend: (—) dry; (---) with moisture

Figure 3 Composition dependence of the average interchain distance $\langle R \rangle$ of PVOH/ion., Zn^{2+} blends. Inset: composition dependence of the half-width of the maximum scattering

PVOH. In one case a blend (40/60) gave a lower T_g by 20°C when equilibrated to ambient humidity levels (RH *ca* 60%). The E'' spectra in *Figure 2* show that both transitions, though shifted to each other, are maintained. Increased ionomer contents lower the PVOH relaxation and vice versa. Thus, the system is phase separated and the individual components retain their identity. The T_g shifts are caused possibly by complexation reactions at

the components' interface, ensuring good adhesion. The composition dependence of storage modulus in *Figure 1* shows the dominance of PVOH down to 50 wt% while further decrease indicates the flexibilizing influence of the ionomer due to its lower T_g. The above are corroborated by the tensile testing findings. Main transitions are summarized in *Table 2* where results from d.s.c. are also

included. Both viscoelastic and thermal T_g data characterize a non-miscible blend.

Thermal properties

These are summarized in *Table 2*. The T_m of the ionomer and of PVOH are depressed at high PVOH contents by *ca* 5°C. This is attributed to morphological effects. At high ionomer contents the T_{m_2} of PVOH is increased due to increased amounts of Zn^{2+}, leading to stiffening caused by higher levels of complexation. Such a T_m increase has been reported for PVOH/lead salt complexes[5]. In the case of T_g, however, this stiffening is offset by the flexibilizing action of the polyolefinic component of the ionomer attached to PVOH.

FTi.r. characterization

Complexation of PVOH with Zn^{2+} was demonstrated to take place using this spectroscopic technique. *FT*i.r. spectra obtained from dry films cast from a PVOH/ $ZnCl_2$ aqueous solution indicate that the hydroxyl transmittance shifts from 3346 to 3356 cm^{-1}. This is to be expected if Zn^{2+} interacts with the H–O bond. In a recent report on the *FT*i.r. spectroscopic investigation of the specific interactions of MA grafted PP/sulfonated EPDM, Zn^{2+}, ionomer blends, Ha *et al.*[17] reported a systematic shift to higher wavenumbers of the sulfonate group transmittance with the ionomer content. In our case the O^- of PVOH plays the role of the SO_3^- group in PVOH/Zn^{2+}, ionomer blends. In the latter, transmittance data obtained at various compositions were, respectively: 3346 cm^{-1} at 100/0, 3349 cm^{-1} at 70/30, 3349 cm^{-1} at 40/60 and 3356 cm^{-1} at 30/70.

WAXS characterization

This technique when applied to blends gives information[18] on the average distance $\langle R \rangle$ between polymer chains and the degree of disorder or the change of the supermolecular structure in blends. In non-miscible blends, $\langle R \rangle$ is the weight average of its pure components. This quantity, expressed in Å, is calculated using the equation:

$$\langle R \rangle = \frac{5}{8} \left(\frac{\lambda}{\sin \theta} \right) \quad (1)$$

where λ is the wavelength (1.54 Å) of the monochromatic light used and θ is the angle at the scattering maximum.

Figure 3 gives $\langle R \rangle$ as a function of composition. The results show an increase of the average interchain spacing in the blends, hence an increase in the free volume usually associated with T_g depression. However, data obtained by d.m.a. exclude the possibility of blends being miscible. In the same figure (inset), the deviation of the half-width of the maximum scattering from the weighted average indicates that the new packing order in blends is less efficient than that of either of the pure components[18].

Ternary PVOH/ionomer/PO blends

Tensile properties. These are summarized in *Table 3* for various compositions and mixing conditions. As expected, good tensile properties are obtained at increased ionomer contents. This reflects the improved tensile properties of the PVOH/ionomer blends at increased levels of the ionomer (*Table 3*). Substitution of LLDPE with HDPE leads to some property enhancement (ϵ_b% increase). The protocol of mixing, i.e. direct mixing or mixing in two stages (see *Table 3*) does not seem to affect results.
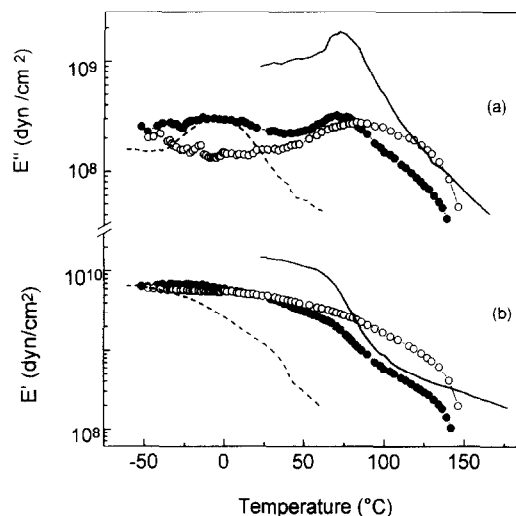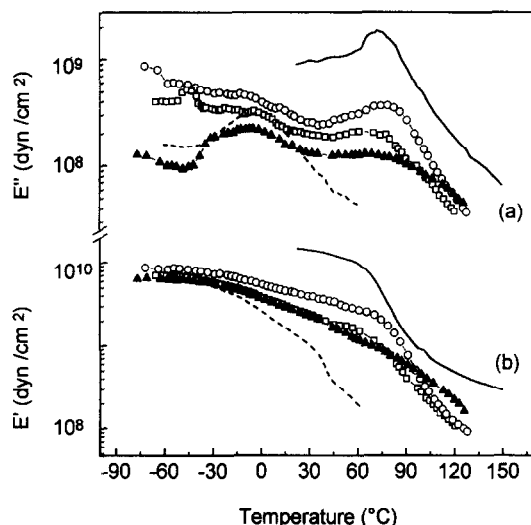

Figure 4 Thermomechanical spectra of a ternary PVOH/ion., Zn^{2+}/ HDPE blend: (a) loss modulus; (b) storage modulus: (—) PVOH; (O) HDPE; (---) ion./Zn^{2+}; (●) blend 25/25/50

Table 3 Mixing conditions and tensile properties of PVOH/ionomer/Zn^{2+}/PO blends

PVOH/ion., Zn^{2+}/LLDPE[a]	Mixing temperature (°C)	Mixing time (min)	σ_b (MPa)	σ_y (MPa)	ϵ_b (%)
52.5/22.5/25	215	10	11 ± 3	—	5 ± 1
52.5/22.5/25%[b]	215	10	10 ± 4		7 ± 3
37.5/37.5/5.25	215	10	8 ± 2	11 ± 2	22 ± 13
25/25/50	215	10	6 ± 1	9 ± 2	30 ± 21
35/15/50	215	10	10 ± 2	—	12 ± 3
PVOH/ion., Zn^{2+}/HDPE					
25/25/50	215	10	15 ± 1	16 ± 2	22 ± 9
25/25/50[c]	215	10	14 ± 1	15 ± 4	43 ± 12
15/35/50	215	10	13 ± 1	14 ± 1	111 ± 59

[a] PO added to premixed PVOH/ion., Zn^{2+} blends
[b] Direct mixing of the polymers
[c] With moisture

Dynamic mechanical properties. The d.m.a. spectra (E' versus temperature) of pure components and ternaries are given in *Figures 4a* and *5a*. For both systems the spectra are characteristic of a phase separated blend. The ionomer fuses with the PO in the region of β relaxation at *ca* $-5°$C, while the α relaxation at *ca* $85°$C (for

HDPE) in the ternary merges with the PVOH relaxation at *ca* $75°$C (*Figure 4a*). Modulus variation in *Figure 5b* for the PVOH/ionomer/LLDPE shows the stiffening effect of PVOH on the composite film.

Morphology. Given the refractive indices of PEs and PVOH ($n_{PE}^D = 1.510$; $n_{PVOH}^D = 1.530$) at positive phase contrast, white areas should correspond to the polyolefinic phase. In *Figures 6a* and *b* the results on ternary blends show a stratified structure. With crossed polars (*Figures 6c* and *d*) a finer microcrystalline texture is observed when HDPE is the PO component. Observation of the specimens' cross-section with SEM, after leaching out PVOH with warm water, was more revealing of the PVOH distribution. In binary PVOH/ionomer blends, increased amounts of PVOH, see *Figure 7a*, yields an insoluble PO network with extensive void formation—formerly the PVOH phase domains. At high ionomer compositions (*Figure 7b*), swollen PVOH particles, mostly in the submicrometre range, are attached on to the ionomer matrix through complexation. This prohibits PVOH dissolution during etching. In the case of ternary PVOH/ionomer/HDPE blends, extraction of the PVOH phase reveals its stratification within the polyolefinic component—a morphological feature desirable for PVOH to retain its full barrier properties (see *Figures 8a* and *b*). It is recognized, however, that further work is necessary to optimize film processing conditions[3] to obtain an improved PVOH stratification.

Figure 5 Thermomechanical spectra of ternary PVOH/ion., Zn^{2+}/ LLDPE blends: (a) loss modulus; (b) storage modulus: (—) PVOH; (O) 37.5/37.5/25; (□) 25/25/50; (▲) LLDPE; (---) ion., Zn^{2+}
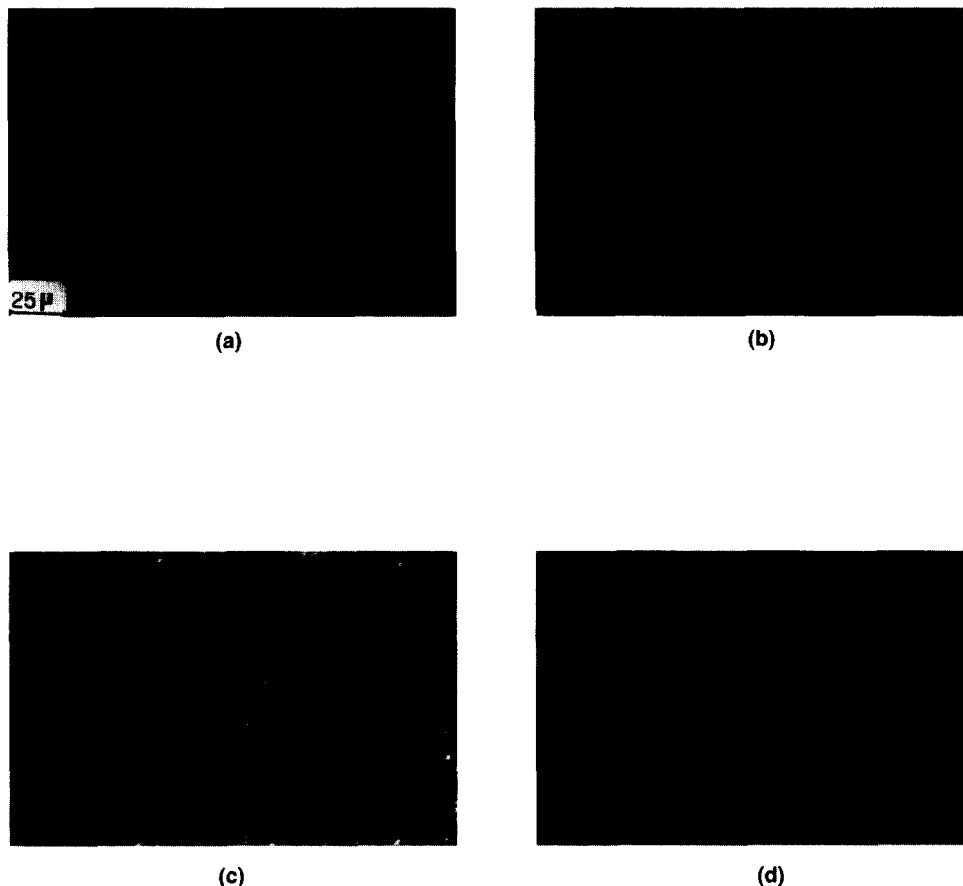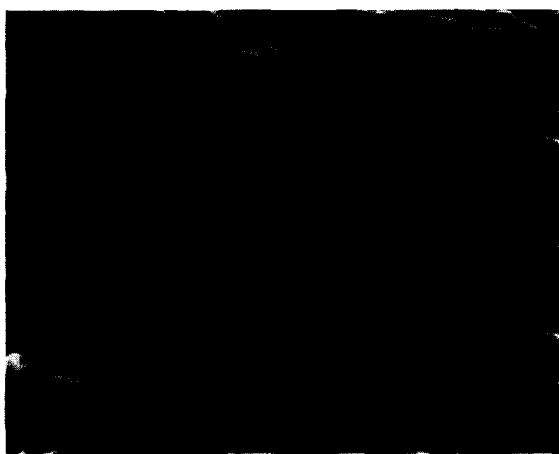

Figure 6 Optical micrographs of ternary blends: PVOH/ion., Zn^{2+}/LLDPE (25/25/50) (a) phase contrast; (c) with crossed polars. PVOH/ion., Zn^{2+}/ HDPE (25/25/50) (b) phase contrast; (d) with crossed polars

(a)

(b)

Figure 7 SEM micrographs of etched PVOH/ion., Zn^{2+} blends: (a) 70/30; (b) 30/70

(a)

(b)

Figure 8 SEM micrographs of etched ternary PVOH/ion./Zn^{2+}/HDPE blends: (a) 15/35/50; (b) 25/25/50

DISCUSSION AND CONCLUSIONS

Small deformation mechanical behaviour indicates limited mixing at the components' interphase. This is further corroborated by the tensile testing results for the PVOH/ionomer, Zn^{2+} blends—characteristic of strong adhesive forces. Based on the FT i.r. findings these may arise from the complexation reactions of the Zn^{2+} of the ionomer with the electronegative oxygen of the pendant hydroxyl groups of PVOH. In the case of the ternary blends, mechanical integrity is secured by the mechanical compatibility of the PO (LLDPE or HDPE) with the ionomer—essentially a modified PO. Though immiscible on a molecular scale[19], these two components were reported to give blends with good tensile properties[19,20]. Morphological findings on binaries and ternaries show evidence for PVOH stratification.

Some evidence of phase connectivity is further obtained by the analysis of d.m.a. results using complex modulus $|E^*|$ data. In the case of binary PVOH/ionomer, Zn^{2+} blends the matrix inversion at the 50/50 composition is evidenced by the modulus prediction mechanics models[21]. In *Figure 9* the relative complex modulus $|E_b^*|/|E_{ion.,Zn^2}^*|$ is plotted *versus* binary blend composition. At high PVOH contents the parallel connectivity represents data well characteristic
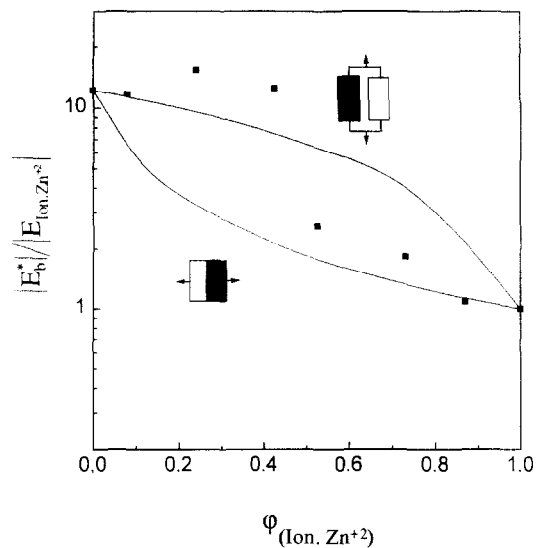

Figure 9 Phase connectivity prediction at 25°C using mechanics models

of stratified film structure. At $\varphi_{ion.,Zn^2} \geq 0.50$ interphase formation through complexation is extensive and this is reflected by the applicability of the series model[22].

To conclude, (i) melt mixed blends of PVOH/ionomer, Zn^{2+} have good mechanical properties at increased

ionomer levels due to complexation reactions at their interphase; (ii) in blends with POs, mechanical property levels are reduced at low ionomer contents. These ternary blends give structured films and there is experimental evidence that PVOH is stratified into layers parallel to the film surface.

It is relevant to note that modulus is a property analogous to permeability[23]; however, no data are available to test film internal structure using this property.

ACKNOWLEDGEMENTS

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