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Acrylic-modified polyolefin ionomers as compatibilizers for poly(ethylene-*co*-vinyl alcohol)/aromatic copolyester blends

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Abstract

Polymeric alloys of poly(ethylene-*co*-vinyl alcohol) (EVOH) with an amorphous copolyester (PETG) were prepared using the sodium or the zinc ionomer of acrylic-modified polyolefin ionomers. Composition parameters examined were the main components ratio and at a fixed ratio the compatibilizer content. The techniques applied to assess compatibilization were: tensile testing, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and morphology examination of cryofractured surfaces using scanning electron microscopy (SEM). Both ultimate tensile properties and morphological features indicated that the ionomer, Na^+ is a more efficient compatibilizer, the amount required (ca 5 wt%) being 1/3 to that of the ionomer, Zn^{2+}. A plausible explanation for this finding is proposed. Analysis of DMA moduli data supports the view that films obtained are laminar in structure — a significant result for film barrier applications. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: EVOH polymeric alloys; Aromatic copolyester polymeric alloys; Barrier polymer films

1. Introduction

Polymeric alloys find extensive application in the technology of new polymeric materials. In these blends properties of their components are synergistically combined so that certain homopolymer drawbacks as well as the cost/property ratio are minimized [1,2].

The present study examines the compatibilization of poly(ethylene-*co*-vinyl alcohol) (EVOH) with a copolyester, poly(ethylene-*co*-cyclohexane1,4-dimethanol) (PETG), using acrylic-modified olefinic ionomers as compatibilizers. Both polymers are useful as packaging materials. Dry EVOH combines superior gas properties for O_2 and CO_2 with ease of processing. PETG combines good toughness with film clarity. Its barrier properties are satisfactory and little affected by moisture. Therefore in a suitably structured film it may make EVOH moisture-proof. Two types of ionomers were used as compatibilizers; the sodium ionomer of poly(ethylene-*co*-methacrylic acid) (Ion. Na^+) and the zinc ionomer of poly(ethylene-*co*-methacrylic acid-*co*-isobutylacrylate) (Ion. Zn^{2+}). Both were expected to give mechanically compatible blends with PETG since this was observed in blends with PET [3,4] and the copolyester contains a large proportion of PET units in its structure. Also, Ion. Zn^{2+} was shown to give useful polymeric alloys with PVOH [5] and EVOH [6], either by complexation and/or hydrogen bonding interactions.

Recent work on EVOH blends includes the study of Gopalakrishnan et al. [7] who reported on the rheology and transport properties of EVOH/PET blends with and without a compatibilizer; the latter was a maleic anhydride-modified hydrogenated SBS block copolymer (SEBS-*g*-MA). The same group also reported [8] on the morphology and barrier properties of EVOH/PET and EVOH/poly(ethylene 2,6-naphthalate) blends.

Other combinations of EVOH with low-permeability thermoplastics were non-stratified blends of EVOH with aliphatic nylons studied by Ahn et al. [9] and by Akiba and Akiyama [10] who reported on the miscibility behaviour of EVOH/nylon 6,12 blends. In a related study Ha et al. [11] applied spectroscopic techniques to characterize EVOH/nylon 4,6 blends.

The present report examines the mechanical, thermal and morphological features of PETG/EVOH/ionomer blends. Composition parameters examined were the main components' ratio and at a fixed ratio compatibilizer content. As a preliminary step to ternary compatibilization the EVOH/Ion., Na^+ was also studied. EVOH/Ion., Zn^{2+} blends had been studied before [6]. During the course of this

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Table 1
Ultimate tensile properties of binary EVOH/Ion. Na^+ blends (quenched at 0°C, conditioned for one day at 60% RH)

Blends	Mixing temperature (°C)	Mixing time (min)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%) $\Delta L/L_0$	E_b (J/cm^3)
100/0	–	–	–	38 ± 2	217 ± 81	77 ± 8
85/15	250	15	52 ± 4	51 ± 4	367 ± 47	150 ± 10
75/25	250	15	44 ± 1	31 ± 3	348 ± 52	110 ± 13
50/50	250	15	–	17 ± 1	39 ± 9	5 ± 1
25/75	250	15	–	16 ± 1	199 ± 19	25 ± 3
15/85	250	15	–	20 ± 1	316 ± 13	45 ± 5
0/100	–	–	–	23 ± 1	465 ± 30	63 ± 4

investigation it was discovered that Ion. Na^+ was a more efficient compatibilizer in that a reduced amount was required to compatibilize blends. It is relevant to note that the olefinic ionomers have poor barrier properties to O_2 and CO_2 hence for a successful product the amount used should be kept as low as possible. Also an increased PETG/EVOH ratio is desirable to increase the effectiveness/cost ratio since PETG is much cheaper than EVOH.

2. Experimental

2.1. Materials and specimen preparation

PETG-6763 was obtained from Tennessee Eastman Co., and had $\bar{M}_n = 26,000\ \mathrm{g\ mol^{-1}}$. It was reported [12] to consist of cyclohexane 1,4-dimethanol, ethylene glycol and terephthalic acid in a molar ratio of ca. 1:2:3. EVOH from Kuraray Co. Ltd. (Japan) had a 32 mol% ethylene content, a MFI of 1.3 g/10 min (190°C, 2160 g) and density 1.19 g cm^{-3}. The Ion. Na^+ (Surlyn 8550) has the basic structure of a partially neutralized poly(ethylene-*co*-methacrylic acid), with MFI 3.9 g/10 min (190°C, 2160 g), $d = 0.94\ \mathrm{g\ cm^{-3}}$ and $\bar{M}_n$ ca. 25,000 g mol^{-1}. The Ion. Zn^{2+} (Surlyn 9020) is a random ethylene–methacrylic acid–isobutylacrylate terpolymer with a molar composition of 78–10–12, respectively, a degree of neutralization of ca. 70%, $\bar{M}_n = 25,000$, density 0.96 g cm^{-3} and MFI 1.0 g/10 min (190°C, 2160 g). Both ionomers were donated by Du Pont de Nemours Co.

Materials were dried in dynamic vacuum at 80°C for 24 h. Blends were prepared by melt-mixing in a home-made stainless steel bob-and-cup type of mixer previously described [5]. The mixing cup was blanketed under an argon atmosphere. Based on tensile property optimization, in particular ultimate elongation ϵ_b%, the mixing time employed was 15 min at 250°C for both binary and ternary blends. Compositions prepared and characterized will be quoted at the appropriate sections.

Films were obtained by compression moulding between Teflon sheets at 250°C and 10 MPa, followed by pressure release and quenching to 0°C. Films were conditioned for one day at ambient conditions (23°C and 60% RH). The effect of ageing and possible additional moisture pick up on tensile properties during storage was also examined for PETG/EVOH/Ion. Na^+.

2.2. Apparatus and procedures

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

Dynamic mechanical analysis (DMA) data, namely storage modulus E', loss modulus E'', and loss angle tan δ were obtained at 10 Hz with the RSA II dynamic mechanical spectrometer of Rheometric Scientific Ltd. Specimen dimensions were $2.3 \times 0.5 \times 0.15\ \mathrm{cm^3}$.

Differential scanning calorimetry (DSC) measurements were carried out using the DSC (SP) equipped with the AutoCool accessory from Rheometric Scientific Ltd. Nominal weight was 8 mg and heating and cooling rate 10°C min^{-1}. The following thermal cycling was applied: quenching at 50°C min^{-1} to −50°C, heating to 250°C, followed by quenching to −50°C and applying a second heat to 250°C.

Scanning electron microscopy (SEM) was carried out with a JEOL JSM 6300 instrument at a tilt angle of 70° and a working distance 16–18 mm on specimens fractured at cryogenic temperature.

3. Results

3.1. Binary EVOH/Ion. Na^+ blends

3.1.1. Tensile properties

The tensile properties are summarized in Table 1, which records yield stress σ_y, strength σ_b, ultimate elongation ϵ_b% and energy to tensile failure E_b obtained from the area under the stress–strain curve. At the 85/15 composition tensile properties are higher than the arithmetic mean of the pure components; such a synergism is characteristic of strong specific forces and has also been observed in the EVOH/Ion. Zn^{2+} blend [6]. Further ionomer increase causes an ϵ_b% drop at the median composition, possibly the result of matrix inversion, followed by an increase of its value approaching the average of the pure component values.

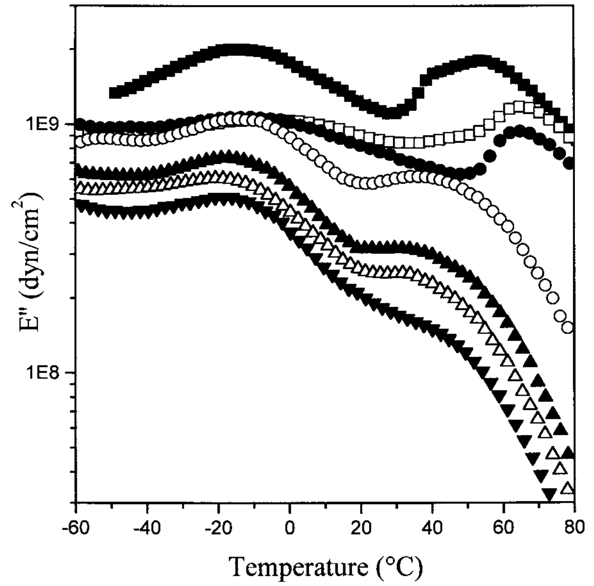


Fig. 1. Temperature dependence of loss modulus of binary EVOH/Ion. Na$^+$ blends: (■) 100/0; (□) 85/15; (●) 67/33; (○) 50/50; (▲) 33/67; (△) 15/85; (▼) 0/100.

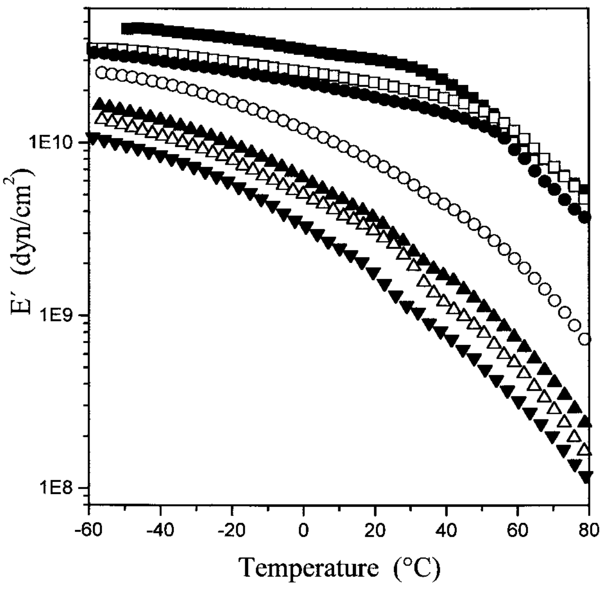


Fig. 2. Temperature dependence of storage modulus of binary EVOH/Ion. Na$^+$ blends: (■) 100/0; (□) 85/15; (●) 67/33; (○) 50/50; (▲) 33/67; (△) 15/85; (▼) 0/100.

3.1.2. Dynamic mechanical properties

The DMA spectra at the isochronous condition are given in Figs. 1 and 2, in terms of loss E'' and storage E' moduli, respectively. The main relaxations of EVOH (at 54°C) and of the ionomer (β' at −19°C) though shifted with composition are evident in all blends; see Fig. 1 and Table 2. At the 85/15 and 75/25 compositions there is a considerable shift upwards in temperature of the $T_{g,\mathrm{EVOH}}$ with a concomitant stiffening of modulus, see Fig. 2 and σ_b enhancement, see Table 1. Similar trends were reported [6] in the case of EVOH/Ion. Zn^{2+} blends. Further ionomer increase reverses the $T_{g,\mathrm{EVOH}}$ shift. These changes may be attributed to a strong association of components due to hydrogen bonding and/or ionic interactions [14]. Low temperature transitions are broad because certain relaxations superimpose. Thus, a secondary relaxation of EVOH (at −22°C) attributed to short olefinic branches is close to that of the ionomer (β') originating from similar groups of the modified polyolefin. Storage moduli variation in Fig. 2 reflects the matrix inversion the stiff EVOH-rich compositions changing to flexible ionomer-rich blends. Main viscoelastic transitions ($E''_{\max}$) are summarized in Table 2 together with thermal properties.

3.1.3. Thermal properties

In addition to T_g, the other thermal properties recorded in Table 2 are: T_m, crystallization temperature T_c, and bulk crystallinity of components in the blend X_c% and T_i an endotherm observed with DSC and associated with the ionomer cluster dissociation during the heat scan of aged blends. The T_m depression of EVOH suggests a reduction of crystal perfection with the ionomer addition. To a smaller extent this is also the case for the ionomer. The presence of ionomer impedes EVOH crystallization (T_c is depressed) and this is the result of partial component miscibility, the mixed interphasial material reducing the rate of crystallization [13]. Crystallization of the ionomer is facilitated due to

Table 2
Thermal and viscoelastic properties of binary EVOH/Ion. Na$^+$ blends

Blends	T_g (EVOH) (°C)	T_g (Ion. Na$^+$) (°C)	T_m (EVOH) (°C)	T_m (Ion. Na$^+$) (°C)	T_i (Ion. Na$^+$) (°C)	T_c (EVOH) (°C)	T_c (Ion. Na$^+$) (°C)	X_c^{a} (EVOH) (%)	X_c^{b} (Ion. Na$^+$) (%)
100/0	54.3	–	184.1	–	–	162.3	–	71.8	–
85/15	65.1	−3.5	181.5	90.7	–	159.5	76.2	44.4	4.5
75/25	64.6	−7.7	181.3	93.9	41.1	158.4	77.2	46.9	8.8
50/50	35.7	−12.6	181.3	95.5	38.1	158.3	76.1	36.6	18.0
25/75	29.6	−14.7	177.4	95.8	36.0	155.5	77.6	31.1	11.2
15/85	29.5	−20.9	179.1	96.1	33.1	154.4	75.9	22.1	9.5
0/100	–	−19.0	–	95.6	37.3	–	67.6	–	13.5

[a] $\Delta H_f = 25.6$ cal g^{-1}.
[b] $\Delta H_f = 66$ cal g^{-1}.

Table 3
Ultimate tensile properties of ternary PETG/EVOH/Ion. Zn^{2+} blends (quenched at 0°C, conditioned for one day at 60% RH)

Blends	Mixing temperature (°C)	Mixing time (min)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%) $\Delta L/L_0$	E_b (J/cm^3)
50/50/0	250	15	–	48 ± 2	7 ± 2	2 ± 1
45/45/10	250	15	–	28 ± 4	5 ± 2	1 ± 0
42.5/42.5/15	250	15	–	33 ± 2	7 ± 2	1 ± 0
40/40/20	250	15	27 ± 3	23 ± 3	20 ± 10	4 ± 1
37.5/37.5/25	250	15	25 ± 2	23 ± 2	21 ± 8	5 ± 1
35/35/30	250	15	20 ± 0	18 ± 1	19 ± 5	3 ± 1
67/33/0	250	15	–	34 ± 4	7 ± 2	1 ± 0
60/30/10	250	15	–	23 ± 1	7 ± 0	1 ± 0
56.7/28.3/15	250	15	22 ± 1	21 ± 2	65 ± 37	12 ± 6
53.3/26.7/20	250	15	23 ± 1	21 ± 1	133 ± 25	26 ± 3
46.7/23.3/30	250	15	18 ± 1	19 ± 1	117 ± 24	21 ± 4
75/25/0	250	15	–	35 ± 1	10 ± 3	2 ± 1
67.5/22.5/10	250	15	–	25 ± 1	8 ± 2	1 ± 0
63.7/21.3/15	250	15	27 ± 1	26 ± 2	233 ± 47	52 ± 8
60/20/20	250	15	26 ± 2	28 ± 2	265 ± 25	59 ± 2

the nucleating effect of the EVOH crystals formed during the cooling scan. Bulk crystallinity levels of EVOH is reduced with the addition of the ionomer — again the result of component interaction. The maximum of the $X_{c,\text{ionomer}}$ is attributed to the net effect of two opposing factors; the increased rate of crystallization due to nucleation caused by the EVOH and the component interaction reducing it, with the addition of EVOH.

The increase of the T_i with the addition of EVOH suggests an enhanced level of the ionomer organization their initial disorientation followed by a tighter structurization due to the olefinic components increase in the blend leading to an environment of a higher dielectric constant.

3.2. Ternary PETG/EVOH/Ion. Zn^{2+} blends

3.2.1. Tensile properties

Table 3 summarizes the data on these properties screening useful compositions. It is evident that at increased PETG/EVOH ratio (2/1, 3/1) the amount of compatibilizer required should be ≥15 wt%. Considering the poor barrier properties of the ionomer (VA), the particular ionomer is unsuitable for the intended applications of these blends. Though other properties (DMA and thermal) were determined and are reported elsewhere [15] these do not differ qualitatively from the ternary with the Ion. Na^+ examined next.

3.3. Ternary PETG/EVOH/Ion. Na^+

3.3.1. Tensile properties

Pertinent data at the 2/1 PETG/EVOH ratio and increasing contents of the ionomer are recorded in Table 4. A 5 wt% of Ion. Na^+ is adequate for the compatibilization of the incompatible PETG/EVOH blend and this composition 63.3/31.7/5 offers the best combination of strength, ductility and impact strength (E_b) in this blend series. Further ionomer increase does not lead to improvement; in fact ultimate properties are reduced. This finding may be attributed to ionomer agglomeration [16]. A longer conditioning at ambient conditions does not differentiate properties. Thus no moisture pick-up that may influence tensile and

Table 4
Ultimate tensile properties of ternary PETG/EVOH/Ion. Na^+ blends (quenched at 0°C, conditioned for one day at 60% RH)

Blends	Mixing temperature (°C)	Mixing time (min)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%) $\Delta L/L_0$	E_b (J/cm^3)
67/33/0	250	15	–	34 ± 4	7 ± 2	1 ± 0
63.3/31.7/5	250	15	37 ± 3	36 ± 3	305 ± 60	89 ± 7
60/30/10	250	15	28 ± 1	32 ± 3	324 ± 45	78 ± 9
56.7/28.3/15	250	15	34 ± 4	33 ± 3	205 ± 45	59 ± 5
53.3/26.7/20	250	15	27 ± 1	30 ± 2	265 ± 21	62 ± 4
67/33/0[a]	250	15	–	35 ± 3	8 ± 2	2 ± 1
63.3/31.7/5[a]	250	15	34 ± 2	33 ± 3	311 ± 39	75 ± 12
60/30/10[a]	250	15	32 ± 1	31 ± 4	331 ± 39	80 ± 11
56.7/28.3/15[a]	250	15	27 ± 1	26 ± 4	287 ± 38	59 ± 10
53.3/26.7/20[a]	250	15	26 ± 2	25 ± 4	289 ± 58	62 ± 11

[a] After 15 days physical ageing.

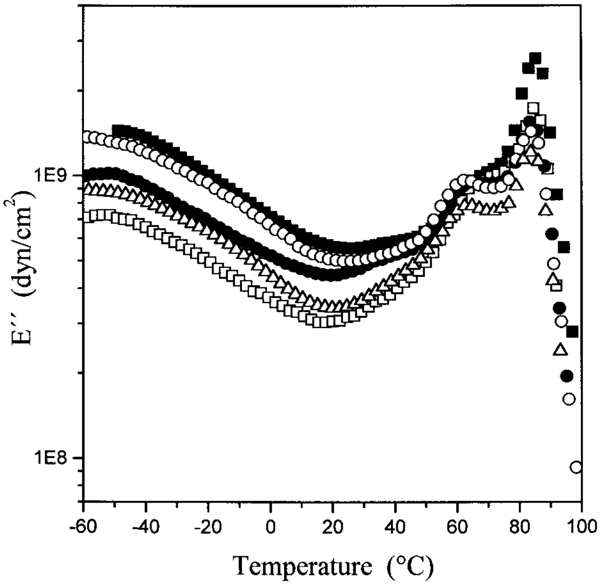


Fig. 3. Temperature dependence of loss modulus of ternary PETG/EVOH/Ion. Na^+ blends: (■) 67/33/0; (□) 63.3/31.7/5; (●) 60/30/10; (○) 56.7/28.3/15; (△) 53.3/26.7/20.

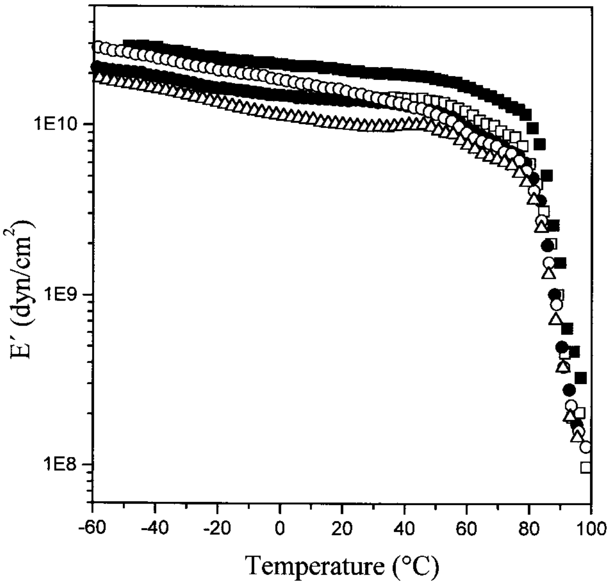


Fig. 4. Temperature dependence of storage modulus of ternary PETG/EVOH/Ion. Na^+ blends: (■) 67/33/0; (□) 63.3/31.7/5; (●) 60/30/10; (○) 56.7/28.3/15; (△) 53.3/26.7/20.

barrier properties are anticipated beyond one day of film preparation.

3.3.2. Dynamic mechanical properties

Figs. 3 and 4 show the E'' and E' spectra at isochronous conditions and Table 5 records the E''_{max} of the main components. Only the high temperature relaxations of PETG (at 85°C) and EVOH (at 67°C) can be identified since the ionomer relaxations are close to the primary and secondary relaxations of EVOH; see Fig. 1. It is of interest to note the upward $T_{g,EVOH}$ shift in the absence of the compatibilizer; see Table 5. Addition of the Ion. Na^+ causes limited flexibilization (T_g reduction) for both components without T_g convergence.

3.3.3. Thermal properties

Relevant data are reported in Table 5. The T_m of both crystalline components are depressed compared to what was observed in the binary EVOH/Ion. Na^+ (VA), and the effect is more pronounced in the case of EVOH. This T_m depression should be attributed to morphological factors since viscoelastic and tensile properties showed that the ternary is a polymeric alloy. The T_m of the ionomer is shifted upwards. A significant $T_{c,EVOH}$ depression is also observed as the ionomer content is increased, i.e. crystallization of EVOH is impeded. As in the case of the EVOH/Ion. Na^+ these effects are smaller for the ionomer. Addition of small amounts of the ionomer (5–10 wt%) seems to enhance EVOH crystallinity and this also was observed for the related binary; see Table 1.

3.3.4. Morphology

Cryofractured blends are shown in Fig. 5. In the incompatible PETG/EVOH blend, Fig. 5a, EVOH is dispersed as globules in the PETG matrix. Where EVOH is pulled out smooth craters are left — a characteristic of poor interfacial adhesion. Addition of 5 wt% Ion. Na^+, Fig. 5b, drastically reduces the dimensions of the minor phase leading to improved dispersion of EVOH; cavities becomes more uniform and interfacial bonding stronger as indicated by

Table 5
Thermal and viscoelastic properties of ternary PETG/EVOH/Ion. Na^+ blends

Blends	T_g (PETG) (°C)	T_g (EVOH) (°C)	T_m (EVOH) (°C)	T_m (Ion. Na^+) (°C)	T_c (EVOH) (°C)	T_c (Ion. Na^+) (°C)	X_c[a] (EVOH) (%)	X_c[b] (Ion. Na^+) (%)
67/33/0	85.0	67.2	179.6	–	159.1	–	35.4	–
63.3/31.7/5	84.4	64.3	176.2	91.8	152.1	79.6	41.4	18.2
60/30/10	83.6	65.0	172.0	93.7	143.3	82.0	37.2	18.0
56.7/28.3/15	83.5	62.1	168.7	93.8	138.9	80.0	32.2	21.0
53.3/26.7/20	83.4	64.9	167.0	93.9	132.8	78.4	32.5	14.7

[a] $\Delta H_f = 25.6$ cal g^{-1}.
[b] $\Delta H_f = 66$ cal g^{-1}.

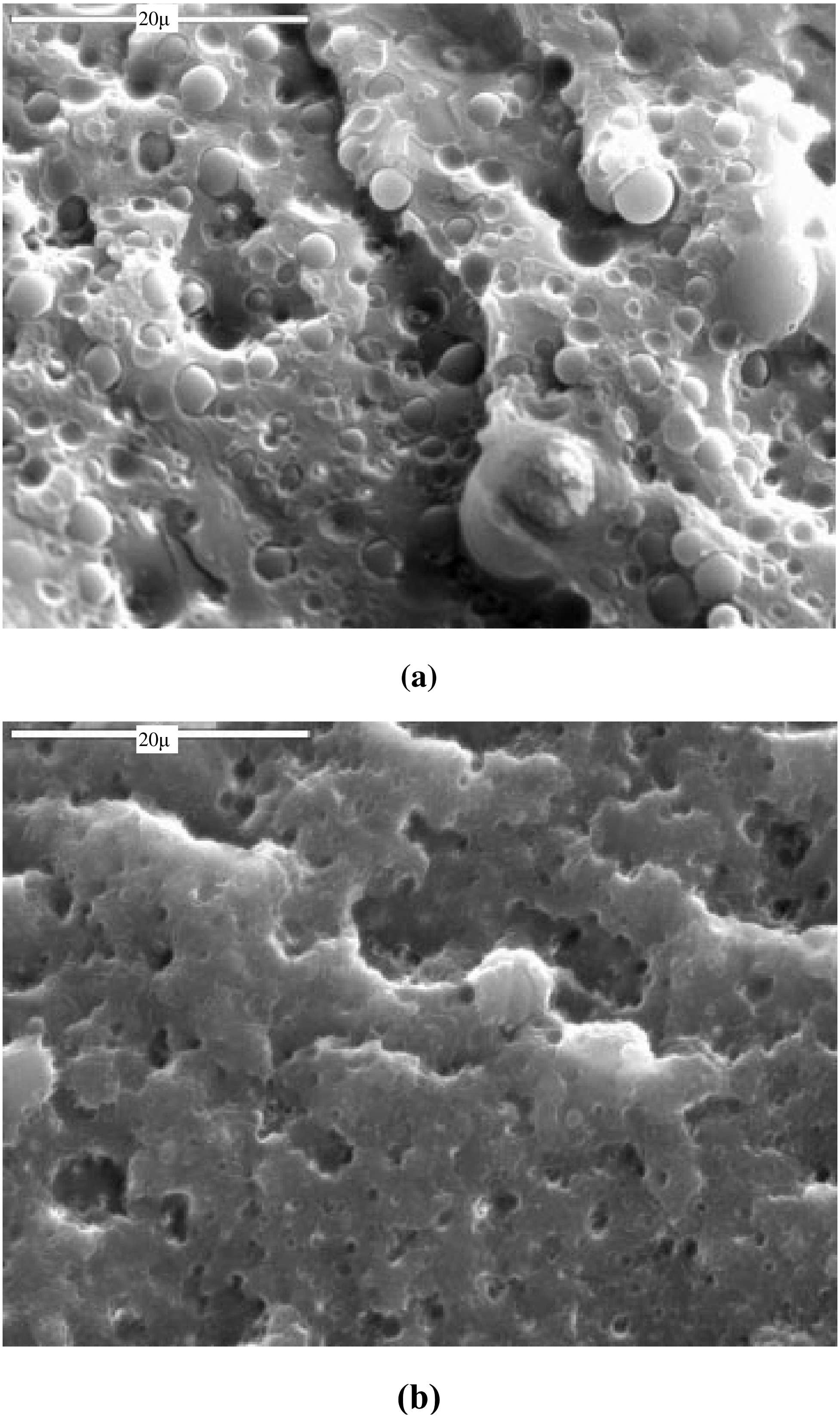
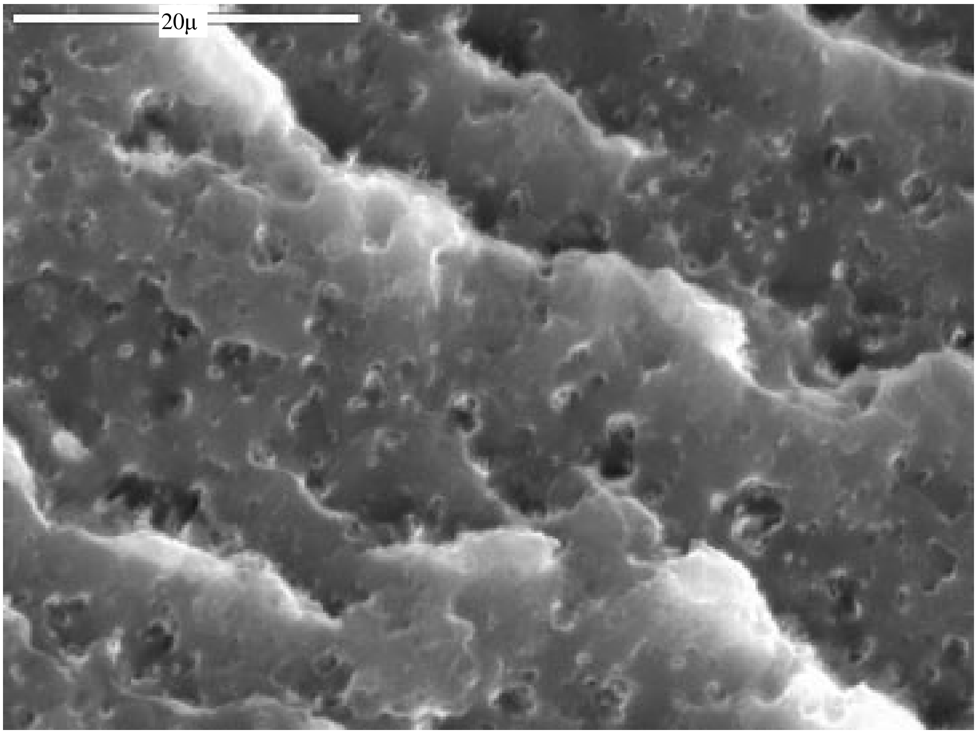
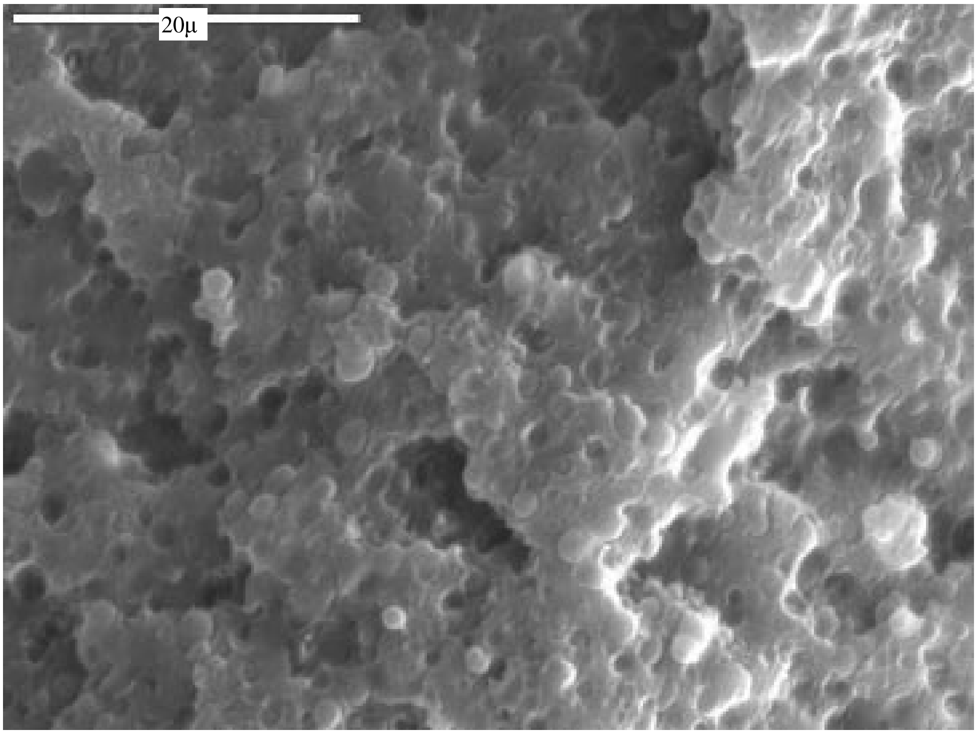


Fig. 5. SEM micrographs of cryofractured ternary PETG/EVOH/ionomer blends: (a) PETG/EVOH 67/33; (b) PETG/EVOH/Ion. Na^+ 63.3/31.7/5; (c) PETG/EVOH/Ion. Na^+ 56.7/28.3/15; (d) PETG/EVOH/Ion. Zn^{2+} 56.7/28.3/15.



(c)



(d)

Fig. 5. (*continued*)

the irregularity of cavities. Further addition of compatibilizer (Fig. 5c) does not alter these features. Overall, the fracture surface is of the ductile type. In Fig. 5d the PETG/EVOH/Ion. Zn^{2+} ternary at the same ionomer level shows a different morphology; compare with Fig. 5c. EVOH globules still persist though smaller in size compared to those in Fig. 5a, cavities are circular and have a smooth surface. This is in line with the decreased compatibilizer efficiency observed for the Ion. Zn^{2+} on the basis of the tensile properties at similar compatibilizer levels; see Tables 3 and 4.

4. Discussion

The present system has properties similar to the HDPE/EVOH/ionomer blends studied before [6]. Both small and large deformation mechanical behaviour support the view that the binary and ternary blends are phase-separated polymeric alloys with strong interpolymer interactions involving the EVOH/ionomer and possibly the PETG/ionomer blends; the latter because of structure similarity should not differ from PET/Ion. Na^+ blends [3]. Strong interpolymer interactions as evidenced by converging viscoelastic transitions lead to good ultimate tensile properties. However, the fact that individual T_gs persist is an indication of immiscibility at the segmental level. These results are supported by thermal analysis and SEM findings. The latter technique, as well as tensile testing, also indicates an improved compatibilizing efficiency of the sodium versus the zinc ionomer, in the ternary blend. For this one could invoke the reduced ionic character of the Ion. Zn^{2+} [17] and the proposition that the aggregation of anion–Na^+ pairs may be favoured entropically since there is little orientation restriction in adding a new ion pair to existing aggregates in contrast to the anion–Zn^{2+} [17,18]. Moreover, the mechanism of compatibilization reaction for the PETG/ionomer may differ for the two types of ionomers. For the Ion. Na^+ it is suggested that this involves an acidolysis reaction demonstrated for PET/Ion. Na^+ blend [19], i.e.

$$2\mathrm{PETG} + \mathrm{RCOONa} \rightarrow \mathrm{PETGCOONa} + \mathrm{PETG{-}R} \qquad (1)$$

The sodium salt of PETG, in addition to nucleation effects, may subsequently interact with EVOH by dipole–dipole interaction, hydrogen bonding involving the acrylic acid moiety of the ionomer and the proton-accepting oxygen of EVOH and/or complexation. In the case of the Ion. Zn^{2+} reaction (1) has not been verified. Other interchange reactions involving terminal ester groups of PETG and ionomer carboxyl groups may also be involved according to

$$\mathrm{PETG{-}COOR'} + \mathrm{R''COOH} \rightarrow \mathrm{PETG{-}COOH} + \mathrm{R''CO{-}OR'} \qquad (2)$$

Physical interactions and/or interchange reactions explain the good tensile properties for the PET/Ion. Na^+ [3] and the PET/Ion. Zn^{2+} [4] blends. Interchange reactions leading to transesterification and/or graft-copolymer formation would concentrate the products at the interface and reduce the interfacial tension and/or bind components together leading to enhancement of the tensile behaviour observed. However, the fact that in the past in both cases thermal embrittlement during annealing led to property deterioration lends higher credibility for the physicochemical interpretation of compatibilization in these blends.

As mentioned in the Introduction, the morphology of these blends when applied as films may be of considerable importance since EVOH is usefully utilized as a barrier polymer if layered parallel to a film surface.

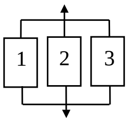
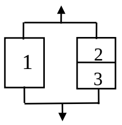
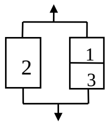
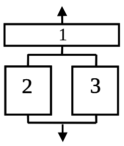
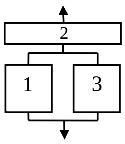
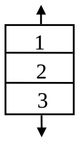
A direct method involving selective extraction of EVOH followed by SEM examination, previously proved successful [6], could not be applied since no selective solvent could be found. PETG has a radically different solubility behaviour compared to PET. Thus solvents dissolving the ionomer also dissolved the polyester. Moreover, the theoretical approach of predicting morphology at equilibrium using surface tension data of ternary blends [20] or surface data tension plus rheological data during processing [21], could not be applied since these data were not available. Hence an attempt was made to assess morphology indirectly by applying mechanics models and the moduli data of pure components to predict the modulus of blends. Table 6 gives various types of phase connectivities combining the parallel and series models as limiting cases. Use was made of the basic equations [22,23] and the known component volume fraction in the ternary. This approach is of relevance to permeability studies since modulus is a conductance property. For a certain composition the criterion for the validity of certain connectivity is that $|E^*|_{obs}/|E^*|_{calc} \cong 1$.

Inspection of data in Table 6 indicates that in general, a purely parallel phase connectivity (1) reproduces the best moduli data for both types of ternary blends. These data also show that the presence of the compatibilizer promotes film structurization. In the case of the PETG/EVOH/Ion. Na^+ blend, some deviation is observed; e.g. for compositions 63.3/31.7/5 and 60/30/10 connectivities (2) and (3), respectively, are in better agreement with the experimental results. This implies a mixed EVOH/Ion. Na^+ layer in parallel with PETG for type (2) configuration. However, experimental errors involved in determining $|E^*|$ may also cause such small deviations.

Another approach for the analysis of moduli data was to examine the applicability of Kerner's model for a ternary blend [24]. In this model randomly distributed spherical inclusions of type i are well adhering and suspended in a matrix (PETG). The equation has the following form:

$$G_b = G_1 \frac{\displaystyle\sum_i \frac{G_i \varphi_i}{(7-5\nu_1)G_1 + (8-10\nu_1)G_i} + \frac{\varphi_1}{15(1-\nu_1)}}{\displaystyle\sum_i \frac{G_1 \varphi_i}{(7-5\nu_1)G_1 + (8-10\nu_1)G_i} + \frac{\varphi_1}{15(1-\nu_1)}}$$

Table 6
Ternary blend modulus prediction for various phase connectivities (force applied parallel to the film surface) (keys: 1, PETG; 2, EVOH; 3, ionomer)

PETG/EVOH/ionomer	$\lvert E^*\rvert_{obs}/\lvert E^*\rvert_{calc}$ at 30°C					
	(1)	(2)	(3)	(4)	(5)	(6)
						
66.7/33.3/0	1.249	–	–	–	–	1.534
63.3/31.7/5[a]	0.934	0.976	0.888	1.461	1.674	1.510
60/30/10[a]	0.950	1.118	0.982	1.442	1.714	1.846
56.7/28.3/15[a]	1.075	1.598	1.172	1.592	1.949	2.376
56.7/28.3/15[b]	0.995	1.746	1.260	1.471	1.829	3.540
53.3/26.7/20[b]	0.944	1.711	1.237	1.368	1.755	3.843
75/25/0	1.257	–	–	–	–	1.551
67.5/21.3/15[b]	0.996	1.509	1.373	1.513	1.601	3.296
60/20/20[b]	1.070	1.662	1.541	1.613	1.729	4.032

[a] Ion. Na^+.
[b] Ion. Zn^{2+}.

where subscripts b, 1 and $i = 2, 3$ refer to the blend, the matrix and the dispersed components, respectively, and G, φ and ν refer to the elastic shear modulus, volume fraction and Poisson ratio, respectively. The above equation is also valid for the case where elastic shear moduli G are replaced by the dynamic shear moduli G^* [25]. The latter may further be converted to the dynamic Young's moduli using the standard expression $E^* = 2G^*(1 + \nu^*) \cong 2G^*(1 + \nu)$ where the viscoelastic Poisson ratio ν^* was assumed to be a real constant, i.e. $\nu^* \cong \nu' \cong \gamma$.

The results of these calculations are given for a wide temperature range in Fig. 6. The large discrepancies between observed and calculated E^* invalidate the basic assumption of a blend morphology with randomly distributed inclusions in the PETG matrix and supports our previous findings; i.e. a laminar film morphology. Obviously further development work is needed in the area of film processing to optimize this type of morphology along the lines suggested by the work of Kamal [26].

Data used in the above calculations: densities of PETG (d_{PETG}), EVOH (d_{EVOH}), Ion. Na^+ ($d_{Ion.\ Na^+}$) and Ion. Zn^{2+} ($d_{Ion.\ Zn^{2+}}$) are 1.285, 1.19, 0.94 and 0.96 g ml^{-1}, respectively. The corresponding Poisson ratios are $\nu_{PETG} = 0.38$, $\nu_{EVOH} = 0.38$, $\nu_{Ion.\ Na^+} = \nu_{Ion.\ Zn^{2+}} = 0.45$.

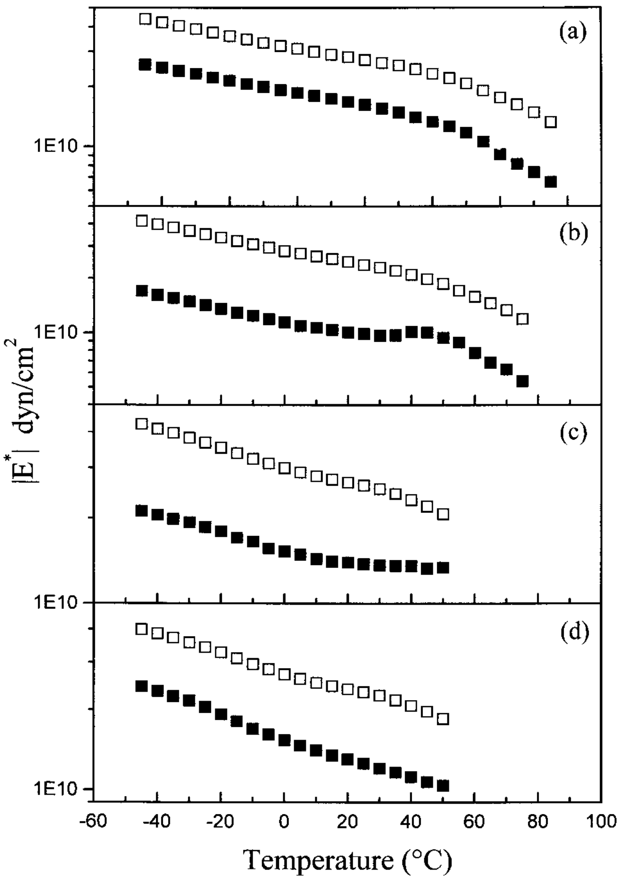


Fig. 6. Observed (■) and calculated (□) dynamic modulus of ternary blends using Kerner's model; see text. PETG/EVOH/Ion. Na^+: (a) 56.7/28.3/15; (b) 53.3/26.7/20. PETG/EVOH/Ion. Zn^{2+}: (c) 56.7/28.3/15; (d) 53.3/26.7/20.

5. Conclusions

1. Melt-mixed blends of PETG/EVOH may be compatibilized using the ethylene-acrylic ionomers of sodium or zinc.

2. Of the two ionomers the Ion. Na^+ is more efficient.
3. There is evidence that films of these ternary polymeric alloys may be obtained in laminar arranged component layers, making them suitable for barrier film applications.

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