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Polyurethane/HDPE blends: 2. Compatibilization with an olefinic ionomer

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Abstract

The compatibility of melt-mixed blends of a partially neutralized poly(ethylene-*co*-methacrylic acid-*co*-isobutyl acrylate) Zn^{2+} ionomer with a polyester-type polyurethane (PU), reported in Part 1 of this work, allowed application of the ionomer as a compatibilizer for incompatible PU/high-density polyethylene (HDPE) blends. The techniques applied were dynamic mechanical analysis (d.m.a.), tensile testing, differential scanning calorimetry and scanning electron microscopy (SEM) of cryofractured surfaces. Once optimization of mixing conditions was established, various composition parameters were examined such as PU/HDPE ratio and compatibilizer content. Blend performance was assessed by means of tensile testing and d.m.a., while morphology was studied mainly by SEM and indirectly by large- and small-deformation behaviour. Although all ternaries studied at ionomer contents of ca. 15 wt% had a satisfactory level of ultimate tensile properties, the PU-rich polymeric alloys performed best. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Ionomer blends; Polyurethane/polyolefin blends; Polymer alloys

1. Introduction

In a previous paper [1], the compatibility of a polyester-type polyurethane (PU) with an acrylic-modified ethylenic Zn^{2+} inomer (Ion.Zn^{2+}) was investigated. It was shown that the binary blend was compatible throughout the composition range and this was attributed to hydrogen bonding between acidic groups of the ionomer and amide groups of PU, plus specific interactions between the Zn^{2+} and the former functionality of PU.

In this work, compatibilization of incompatible PU/high-density polyethylene (HDPE) blends is examined by use of the ionomer as a compatibilizer. This choice was suggested by results reported in Part 1 [1]. In that work, dynamic mechanical analysis (d.m.a.) showed a regular shift in the glass transition temperature of the blend (T_{gb}) with composition between the glass transition temperatures (T'_gs) of the pure components and tensile testing over the complete composition range gave results typical of a compatible system. Analysis of thermal data (depression of the melting point of the semicrystalline PU in the blend, T_{mb}) allowed determination of the polymer–polymer interaction parameter, χ_{12}, which had a near-zero value at the melt temperature (T_m). These are features of a miscible blend. On the other hand, the ionomer gives mechanically compatible blends with the polyolefin because of structure similarity [2,3].

Parameters examined in the ternary were the type and content of compatibilizer, the PU/HDPE ratio and mixing conditions; i.e., temperature, length of mixing time and protocol of mixing. The compatibilization of PU/polyolefin (PO) is of technical importance since it may improve impact strength and extensibility of the highly crystalline PO, and paintability and moisture inertness of the final product.

Related work includes the study of Tang et al. [4], who examined the compatibilization of a thermoplastic PU/polypropylene (PP) blend using as compatibilizer maleated PP (PP–MA) and the same grafted with poly(ethylene oxide) (PEO), (PP–MA)-*g*-PEO. The latter was most effective and compatibilization was attributed to co-crystallization of PP with the PP segments of the compatibilizer, and hydrogen bonding of the etheric oxygen of PEO with the amidic group of PU.

Stutz and co-workers [5] examined the reactive compatibilization of PU/PP with poly(ethylene-*co*-acrylic acid) at various acid levels and poly(styrene-*co*-maleic anhydride). They reported compatibilization with the ethylenic copolymer although no reaction of the carbonyl groups with the –NCO functionality (formed at melt temperatures) was detected. In an extension of this work, Wallheinke et al. [6] examined the morphology evolution of PU/PP blends compatibilized with ethylenic copolymers

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Table 1
Ultimate tensile properties of ternary blends
(a) Effect of composition and mixing time

PU/Ion.Zn^{2+}/HDPE	Mixing time (min)	σ_b (min)	ϵ_b (%)	E_b (J cm^{-3})
66.67/0/33.33	15	9 ± 1	28 ± 6	2 ± 0.1
56.67/15/28.33	15	14 ± 1	280 ± 6	46 ± 1
	15[a]	13 ± 1[a]	52 ± 16[a]	7 ± 3[a]
	20	14 ± 4	209 ± 41	38 ± 7
50/0/50	15	11 ± 2	9 ± 1	1 ± 0.1
47.5/5/47.5	15	13 ± 2	93 ± 20	7 ± 3
45/10/45	15	14 ± 1	95 ± 30	11 ± 1
42.5/15/42.5	10	14 ± 1	103 ± 20	13 ± 4
	15	14 ± 1	152 ± 30	21 ± 3
	20	12 ± 1	144 ± 30	20 ± 4
33.33/0/66.67	15	9 ± 1	8 ± 2	0.4 ± 0.1
28.33/15/56.67	15	15 ± 1	19 ± 2	3 ± 0
	20	14 ± 2	185 ± 35	23 ± 7
	25	11 ± 1	11 ± 4	2.5 ± 1

(b) Mixing protocol

PU/Ion.Zn^{2+}/HDPE (28.33/15/56.67)	σ_b (MPa)	ϵ_b (%)	E_b (J cm^{-3})
Direct mixing for 20 min	14 ± 2	185 ± 35	23 ± 7
Mixing of PU/Ion. Zn^{2+} for 10 min, adding HDPE and additional mixing for 10 min	15 ± 1	31 ± 16	5 ± 1
Mixing of HDPE/Ion. Zn^{2+} for 10 min, adding PU and additional mixing for 10 min	14 ± 1	91 ± 38	7 ± 3

[a] PU/Ion.Na$^+$/HDPE.

containing varying contents of acrylic acid and butyl acrylate. Since no reaction between PU and the compatibilizer was detected, property improvement in the ternary was attributed to dispersed-phase diminution and morphology stabilization in the presence of compatibilizer.

2. Experimental

2.1. Materials and preparation

Polyurethane (Desmopan 359) was donated by Bayer A.G. It is a polyester-type PU with hard segments formed

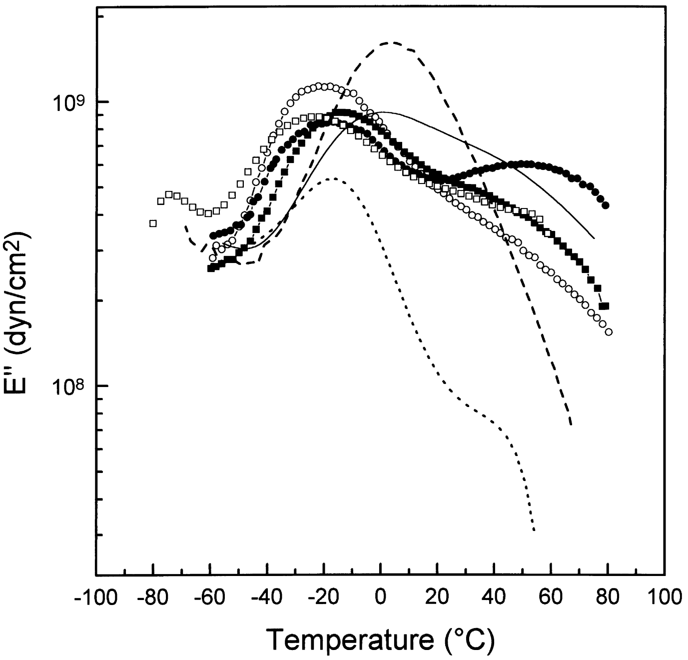

Fig. 1. Temperature dependence of the loss modulus, E'', of PU/Ion.Zn^{2+}/HDPE ternary blends: - - -, Ion.Zn^{2+}; – – –, PU; ——, 50/0/50; ○, 56.67/15/28.33; ■, 42.5/15/42.5; ●, 28.33/15/56.67; □, PU/Ion.Na$^+$/HDPE 56.67/15/28.33.

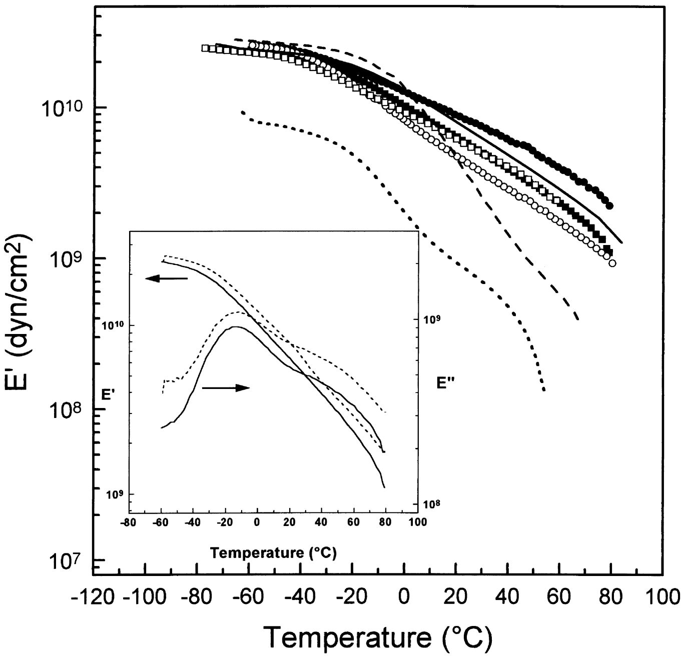

Fig. 2. Temperature dependence of storage modulus, E', of PU/Ion.Zn^{2+}/HDPE ternary blends: - - -, Ion.Zn^{2+}; – – –, PU; ——, 50/0/50; ○, 56.67/15/28.33; ■, 42.5/15/42.5; ●, 28.33/15/56.67; □, PU/Ion.Na^{+}/HDPE 56.67/15/28.33. Inset — effect of moisture on the thermomechanical spectra of ternary blend 42.5/15/42.5: - - -, saturated with moisture; ——, dry specimen.

by the addition of butanediol to diphenyl methane-4-4′-diisocyanate (MDI). The soft segment, with number-average molecular weight ($\bar{M}_n$) of ca. 2000 g mol^{-1}, consists of polyester chains formed by polycondensation of adipic acid and butanediol-1,4. Density was 1.23 g cm^{-3}. The zinc ionomer (Surlyn 9020) was donated by DuPont de Nemours Co. It is a random terpolymer of ethylene–methacrylic acid–isobutyl acrylate with a molar composition of 78/10/12, respectively, and a degree of neutralization of 70%. Its properties are $\bar{M}_n = 25\,000$ g mol^{-1}, density = 0.74 g cm^{-3} and melt-flow index (MFI) of 1.0 g/10 min. The sodium ionomer (Surlyn 8550), obtained from DuPont de Nemours International S.A., is a copolymer of ethylene and methacrylic acid with an MFI of 3.9 g/10 min. HDPE (Finathene 58070), a blow-moulding grade, was obtained from Petrofina S.A., Belgium with MFI = 10 g/min and density = 0.955 g cm^{-3}.

The ionomers and the polyolefin were 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 consisting of a cylindrical rotor rotating into a thermostatted cylindrical cup at about 100 rev mim^{-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 (argon) and the maximum amount

Table 2
Thermal and viscoelastic data of ternary blends[a]

Ternary blends (PU/Ion.Zn^{2+}/HDPE)	E_1"(max) low temp. (°C)	E_2"(max) high temp. (°C)	[T_m (°C)]		[X_c (%)]	
			PU	HDPE	PU	HDPE
100/0/0	3 α					
0/100/0	−16 β					
0/0/100		53 α				
56.67/15/28.33	−20	—[c]				
56.67/15/28.33[b]	−24	—[c]				
50/0/50	1	—[c]	198	131	39	65
47.5/5/47.5	—	—	192	131	50	63
45/10/45	—	—	201	132	59	57
42.5/15/42.5	−16	—[c]	197	132	55	64
28.33/15/56.67	−16	53				

[a] Quenched to 0°C.
[b] PU/Ion.Na^{+}/HDPE.
[c] Shoulder.

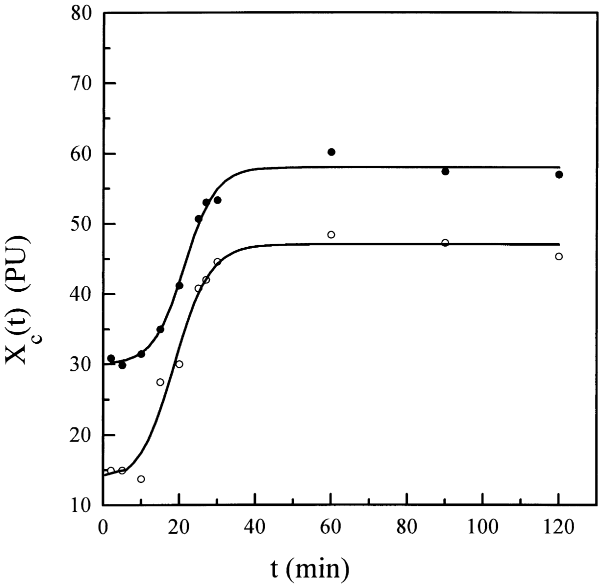

Fig. 3. Evolution of crystallinity, $X_c(t)$, of PU in blends: ●, 42.5/15/42.5; ○, 50/0/50. Crystallization temperature: 160°C.

produced per batch was ca. 10 g. On the basis of tensile property optimization, in particular the ultimate elongation at break (ϵ_b), the mixing time employed was 10 min at 240°C.

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

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. A J.J. Tensile Tester type 5001 and rectangular film strips measuring 6.0 cm × 0.65 cm × 0.25 cm were used.

D.m.a. data were obtained at 10 Hz with an RSA II mechanical spectrometer from Rheometric Scientific Ltd. Specimen dimensions were 2.3 cm × 0.5 cm × 0.015 cm.

Differential scanning calorimetry (d.s.c.) measurements were carried out on an SP+ calorimeter equipped with the Autocool accessory from Rheometric Scientific Ltd. The thermal cycling applied was 25 to 250°C with 20°C min^{-1} heating rate, quenching to −50°C at a controlled cooling rate of 50°C min^{-1} and heating to 250°C at 10°C min^{-1} heating rate.

Scanning electron microscopy (SEM) was performed with a JEOL model JSM-5200 instrument. Micrographs were obtained at a tilt angle of 30°.

3. Results and discussion

3.1. Tensile properties

Large-deformation behaviour (as well as morphology evaluation by means of SEM) was used to assess mechanical performance and optimize mixing conditions. It has been established [7,8] that elongation at failure (ϵ_b) and at

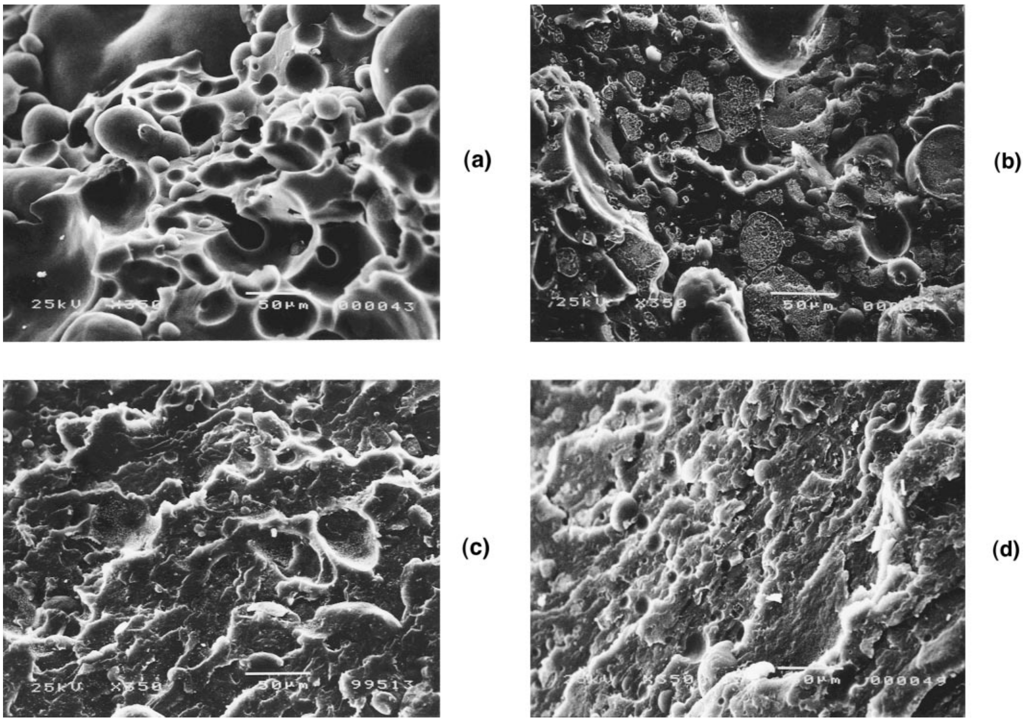

Fig. 4. SEM micrographs of cryofractured PU/HDPE blends at 1/1 ratio with increasing amounts of compatibilizer: (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, (d) 15 wt%. Mixing time: 15 min.

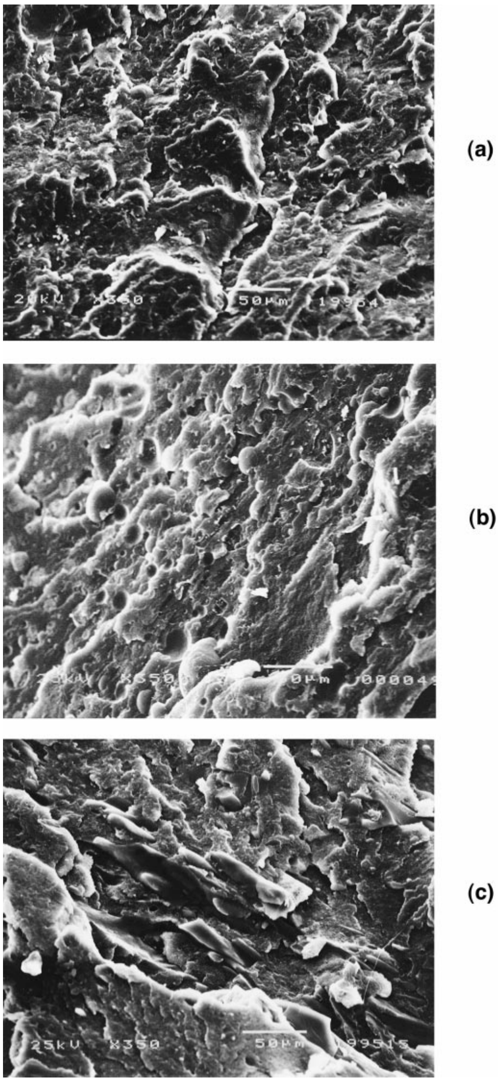

Fig. 5. SEM micrographs of cryofractured PU/Ion.Zn^{2+}/HDPE ternary blends at various PU/HDPE ratios: (a) 56.37/15/28.33, (b) 42.5/15/42.5, (c) 28.33/15/56.67. Mixing time: 15 min.

yield (ϵ_y) characterizes interphase adhesion in polymer alloys. The results are summarized in Table 1 in terms of the following ultimate properties: elongation at failure (ϵ_b), failure strength (σ_b) and energy to tensile failure (E_b). In part (a) of Table 1 it is seen that the optimum mixing time is 15–20 min depending on blend composition. It is possible that a more efficient industrial mixer might attain better results at the lower mixing time. Further increase of mixing time (beyond 15 min for PU-rich or 20 min for PO-rich ternaries) led to property deterioration, possibly due to ionomer agglomeration [9]. The best improvement in properties was attained by mixing all three components simultaneously, see part (b) of Table 1. Significant deterioration in ϵ_b is detected during batch-wise component addition, in particular when adding PO to premixed PU/Ion.Zn^{2+}. This is attributed to a strong coupling of these two components, making difficult their subsequent uniform dispersion in the non-polar PO phase. Better results are obtained by first diluting the Ion.Zn^{2+} in the HDPE component. These results are in agreement with ternaries involving polar components [9]. Examination of the effect of blend composition, Table 1 part (a), shows that PU/HDPE is incompatible, as expected. Of the three ratios examined, the blend with higher PU content has better properties. The effect of compatibilizer content was examined at the PU/HDPE 1/1 ratio. At just 5 wt% compatibilizer content ϵ_b is significantly improved and compatibilization is attained with ca. 15 wt% compatibilizer. At this compatibilizer level and for a mixing time of 15 min, the mechanical properties of the ternaries rank in the order 2PU/1HDPE $>$ 1PU/1HDPE $>$ 1PU/2HDPE. In the latter case it is reasonable to assume that a portion of the compatibilizer has migrated into the PO phase and is not readily available for compatibilization. This is alleviated by increasing the mixing time (20 min), since this allows new interphases to come into contact so that additional ionomer becomes available for interaction.

Substitution of Ion.Zn^{2+} with Ion.Na^{+} leads to a deterioration of properties. A less efficient compatibilization has been reported [10] for the alkali ionomer and was attributed to the higher ionic character of this ionomer leading to a decreased degree of dispersion.

3.2. Dynamic mechanical properties

The results are summarized in Figs 1 and 2 in terms of the temperature dependence of the loss and storage moduli, E'' and E', respectively. The E'' thermomechanical spectra confirm the phase-separated nature of the blends since the primary relaxations of the ionomer, PU and HDPE are obtained at ca. -16°C, 3°C and 53°C, respectively, although shifted and modified in strength considerably. Noteworthy is the masking of the PU relaxation by that of the ionomer as a result of their association. Even at high PU contents the viscoelastic response of PU in terms of E'' is dominated by that of the ionomer. Increased amounts of HDPE give rise to its broad α relaxation at ca. 53°C. In general, the broad relaxations observed suggest the composition heterogeneity expected in these polymeric alloys. In Fig. 2 the modulus variation shows the stiffening effect of compatibilizing PU with HDPE at temperatures greater than ambient. In these ternaries modulus is unaffected by moisture as was the case for PU/Ion.Zn^{2+} with high ionomer contents [1]. This is shown in the inset of Fig. 2, where results are given for a dry sample and a specimen where moisture was condensed during the run. This is the result of the hydrophobic nature of PO, which moisture-proofs the PU phase.

3.3. Thermal properties

These properties are reported in Table 2, where the viscoelastic maxima of Fig. 1 are also included. Compatibilization may decrease crystal size and this is observed for the T_m of PU which interacts with the ionomer. At high ionomer contents heterogeneous nucleation effects due to the presence of the polyolefins may contribute to crystal growth, leading to an elevation in T_m. An increased level of ionomer content increases the PU crystallinity. We suggest that this may be caused by the nucleating effect of the ionomer in analogy to the sodium ionomer/polyester [11] blends, although this has not been reported for divalent cations. The crystallinity of HDPE is little affected — not only because it is an inert diluent, but also because its crystallization is taking place within an adhering environment of crystallized PU which constrains unimpeded crystal growth of the polyolefin.

Fig. 3 gives the crystallinity evolution of PU in blends annealed at 160°C for various lengths of time. The thermal history of these blends differs from that of the quenched specimens reported in Table 2. In annealed blends two regions of PU development are observed; see Fig. 3. In the presence of ionomer the bulk crystallinity is higher than in the uncompatibilized PU/HDPE 50/50 blend, as expected. The rate of crystallization beyond 10 min is significantly increased, more so for the ternary blend. In general, data cannot be analysed in a meaningful way since secondary crystallization may set in, as was shown by Hwang et al. [12] for the simpler case of a binary crystalline/amorphous blend [12]. Finally, beyond a crystallization time of 30 min, the rate of crystallization levels off possibly as a result of exhaustion of the nucleating agent.

3.4. SEM

Morphology examination of cryofractured surfaces gave additional direct evidence for the effects of various composition and mixing parameters in determining compatibilization. Fig. 4 shows morphology changes as the amount of compatibilizer added is increased at the 1/1 PU/HDPE ratio. In the absence of compatibilizer, Fig. 4(a), the PU globules are dispersed randomly in the PO matrix and, when detached, smooth craters are formed in the matrix — a feature characterizing the absence of adhesion. Addition of 5 wt% Ion.Zn^{2+}, Fig. 4(b), gives a morphology with some of the previous features and evidence of microfibrillation caused by the separation of strongly adhering ductile phases. Further ionomer increase, Fig. 4(c), shows microfibrillation as a common feature. At the highest Ion.Zn^{2+} level studied, Fig. 4(d), very few globules are observed and the material breaks in a ductile manner — a feature typical of a compatibilized alloy. Analogous morphological features have been reported [8] for compatibilized polymer alloys of t-butylaminoethyl-methacrylate-grafted PE with methylacrylate–methacrylic acid copolymer and for polymeric alloys of Nylon 6 with ethylene–methacrylic acid copolymers [13].

Fig. 5 shows the morphology evolution of the ternary due to variation of the PU/HDPE ratio at constant compatibilizer level (15 wt%). In all cases there is evidence of ductile fracture. However, when the ratio changes from 2/1 [Fig. 5(a)] to 1/2 [Fig. 5(c)], the texture of the fractured surface is less uniform. This observation is in line with tensile properties reported in Table 1. Fig. 6 shows the morphology changes when mixing time is increased. At 20 min and at the 2/1 [Fig. 6(a)] and 1/1 [Fig. 6(b)] component

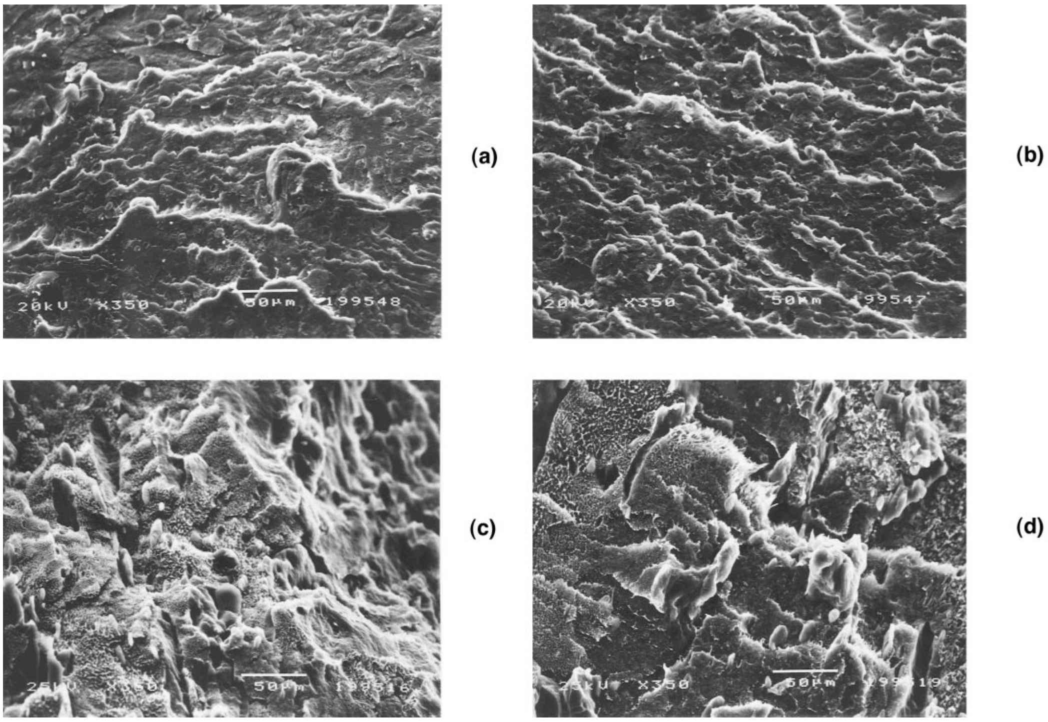

Fig. 6. SEM micrographs of cryofractured PU/Ion.Zn^{2+}/HDPE ternary blends after 20 min mixing time: (a) 56.67/15/28.33, (b) 42.5/15/42.5, (c) 28.33/15/56.67 and (d) 28.33/15/56.67 after 25 min mixing time.

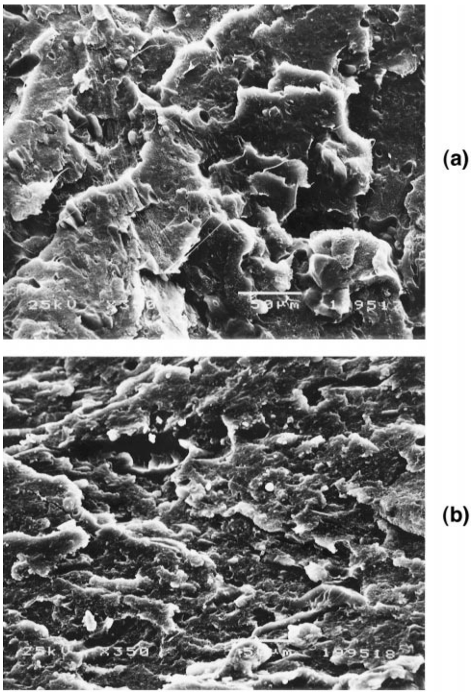

Fig. 7. Effect of mixing protocol on morphology, at 20 min total mixing time: (a) dilution of the ionomer in PU followed by the addition of PO; (b) dilution of the ionomer in PO followed by the addition of PU.

ratios, the ductile morphology observed is more uniform; compare with Fig. 5(a) and (b). At the 1/2 PU/HDPE ratio microfibrillation is also apparent; however, a coarser fracture surface is obtained [Fig. 6(c)]. No improvement is attained at still higher mixing times [25 min, Fig. 6(d)]. In this case a drop in tensile properties was observed; see Table 1 and Section 3.1.

Fig. 7 shows the morphologies obtained when using different mixing protocols. As indirectly supported by the tensile data reported in Table 1 and considering also the micrographs in Fig. 6, the most effective adhesion is obtained when all three blend components are mixed simultaneously (see Fig. 6(c)). Second best is dilution of the ionomer by PO followed by the addition of PU; see Fig. 7(b). Morphology and tensile properties are least satisfactory when the two interacting components are first combined; Fig. 7(a). This is also discussed further in Section 1.

4. Conclusions

1. The Zn^{2+} ionomer added at moderate concentrations (10–15 wt%) is an effective compatibilizer for melt-mixed and quenched PU/HDPE blends.
2. As the thermomechanical spectra indicate, the ionomer strongly ‘solvates’ the PU component.
3. Compatibilization is caused by the strong adhesion of the PU/ionomer component due to specific forces [1] and the ‘mechanical’ compatibility of the ionomer–polyolefin components.

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