Compatibilization of blends of poly(ethylene terephthalate) and linear low density polyethylene with the ionomer of poly(ethylene-*co*-methacrylic acid)

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The effectiveness of the sodium ionomer of poly(ethylene-*co*-methacrylic acid) as a compatibilizer for poly(ethylene terephthalate)/linear low density polyethylene (PET/LLDPE) was investigated at various PET/LLDPE ratios and ionomer contents. The techniques used were optical and electron microscopy, dynamic mechanical spectroscopy, differential scanning calorimetry and tensile tests. The tensile properties were characteristic of mechanical compatibilization since all other techniques indicated a phase-separated system. The PET/LLDPE ratio influenced the degree of compatibilization obtained. Using moderate levels of the compatibilizer (ca. 10 wt%), best properties were obtained at increased PET levels. On the basis of previous findings on the compatibility of PET/ionomer blends it is proposed that compatibilization should be attributed to strong interfacial bonding at the PET/ionomer interphase. An attempt to predict ternary properties from binary blend data using the appropriate theory of mixtures was moderately successful.

(Keywords: ionomer; PET/LLDPE blends; compatibilization)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is an extensively used thermoplastic because of a combination of unique physical, mechanical and permeant properties and processability. As an engineering plastic it offers, among others, excellent high temperature properties, creep resistance and solvent resistance[1,2].

The availability of large amounts of recycled PET largely from the packaging industry[2–4] warrants studies of its blends with other plastics that may also be recyclable. One such important class of commodity plastics is the polyolefins.

Structure considerations (absence of specific interactions) and past experimental findings[5–7] support the view that PET is incompatible with polyolefins. The present work is an offspring of an earlier study[8] examining the compatibility behaviour of PET with the sodium ionomer of poly(ethylene-*co*-methacrylic acid). In that work it was demonstrated that quenched blends prepared by melt mixing are mechanically compatible at high PET contents (>50 wt%), while at high ionomer compositions there is strong evidence of mutual miscibility. Experimental findings presented support the view that mechanical compatibility is caused by the formation of a mixed interphase taking place during melt mixing and ensuring good adhesion between blend partners. These facts plus the reasonable expectation that the ionomer may be compatible with polyethylene led us to investigate the possibility that the ionomer may be used as a compatibilizer for a PET/polyolefin blend.

In this work we report on the compatibilization of PET/linear low density polyethylene (LLDPE) using as a compatibilizer the sodium salt of poly(ethylene-*co*-methacrylic acid). There was no specific reason for choosing LLDPE as the polyolefin other than the fact that this is often combined with PET in soft-drink bottles; hence, it would be unnecessary to separate their blend for recycling if it could be compatibilized to yield a product with acceptable mechanical properties.

Related earlier studies on PET/polyolefin blends include the work of Paul *et al.*[5] who reported an improvement in the adhesion of the incompatible PET/high density polyethylene (HDPE) with the addition of a hydrogenated styrene–butadiene–styrene (SBS) block copolymer as a compatibilizer. More recently, Schreiber *et al.*[6] investigated the mechanical, morphological and permeant properties of PET/polypropylene (PP) blends without and after the addition of acrylic acid grafted PP (PP-*g*-AA) as a compatibilizer. The binary blend was shown to be incompatible and the improvement in adhesion between components after the addition of PP-*g*-AA was found to be marginal. The same system was more thoroughly examined by Xanthos *et al.*[9] using different blending procedures and adding various promoters for interchange esterification reactions. An improved dispersion was obtained when PP-*g*-AA replaced PP in the blend. Tensile strength was also somewhat increased. No results on ultimate elongation, a sensitive indicator of component adhesion, were

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reported. Wilfong *et al.*[7] reported on the crystallization and toughening mechanism of PET to which small amounts (1–10 wt%) of various polyolefins were added. It was shown that the polyolefin particles did not nucleate the crystallization of PET from the melt but depressed its rate of crystallization and the cold crystallization temperature. The latter was attributed to stress-induced crystallization caused by the expansion accompanying the melting of polyolefin particles. Scanning electron microscopy (SEM) demonstrated that in all cases PET/polyolefin blends were incompatible.

Other studies where use was made of the acid-modified polyolefin as a compatibilizer for PET/HDPE and polyamide/HDPE have been reported by Subramanian and Mehra[10]. Emphasis was given to morphology examination (laminar stratification of polyamide or polyester was induced) with the object of exploiting the barrier properties of these blends. No information was published on the compatibility behaviour of these ternary blends. Subramanian[11,12] has also reported on the toughness, morphology, crystallinity and permeability of PET/ionomer binary blends using a variety of ionomers at a single composition. Most recently, Akkapeddi *et al.*[13] reported on the application of ethylene/glycidyl methacrylate copolymer as a reactive compatibilizer for PET/polyolefin blends. Good tensile properties were reported for LDPE and ethylene/propylene copolymer and moderate properties for HDPE at increased levels of PET and moderate levels of the reactive compatibilizer (up to 20 wt%).

A related work dealing with blends of poly(butylene terephthalate) (PBT) and HDPE compatibilized with the sodium ionomer of poly(ethylene-*co*-methacrylic acid) has been reported by Joshi *et al.*[14,15]. This work covered the morphological, mechanical and thermal behaviour of these ternary blends. The authors reported an improvement of tensile and flexural strength with the addition of the ionomer. However, ultimate elongation dropped compared to the binary PBT/HDPE, thus casting doubt on whether compatibilization was achieved.

In the present work the techniques used were optical and electron microscopy (SEM), tensile tests, differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.). Compositional parameters investigated were the effects of varying the PET/LLDPE ratio at a constant level of compatibilizer (ionomer) and varying the content of the latter at a constant PET/LLDPE ratio.

EXPERIMENTAL

PET was extrusion grade obtained from Akzo (Arnite DO2 300). It was reported to have terminal hydroxy groups, an $\bar{M}_n$ of 23 500 g mol^{-1}, a T_m of 252°C and an amorphous product density of 1.34 g cm^{-3}. The ionomer (film grade) was obtained from DuPont (Surlyn 1605) with a melt flow index of 0.28 g min^{-1}. LLDPE was donated by Dow Hellas (Dowlex 2045). PET was dried for 12 h at 150°C *in vacuo*, the ionomer for 4 h at 60°C *in vacuo*. Blends were prepared by melt mixing at ca. 280°C using a CSI mixing extruder model CS-194AV at 45 rev min^{-1}. Ternary blends were prepared at a constant ionomer content with varying PET/LLDPE ratio (3:1, 1:1, 1:3) and at a constant PET/LLDPE ratio (1:1) with varying ionomer content. Films were prepared by compression moulding between Teflon sheets at ca. 285°C and 5 MPa with quenching at 0°C.

Optical micrographs were obtained with an Olympus BH-2 microscope. Specimens were prepared by melt pressing between a cover glass and microscope slide and quenching to 25°C. Some specimens were examined after annealing at 80°C for 2 h. A JEOL model JSM-5200 was used for SEM. Cryofractured surfaces under impact were examined at a tilt angle of 30°.

D.m.a. data for complex modulus $|E^*|$ and tan δ were determined at 110 Hz using a Rheovibron model DDVII-C.

D.s.c. measurements were performed with a DuPont 910 calorimeter coupled with a 990 programmer/recorder. The nominal sample weight was 10 mg and the heating rates were 10°C min^{-1} for T_g and 20°C min^{-1} for crystallinity determination.

Tensile tests were performed according to ASTM D882 at 23°C using a J.J. tensile tester type T5001 and film strips measuring $4.00 \times 0.65 \times 0.005$ cm^3.

RESULTS

Morphology

The results on morphology are given in *Figures 1* and *2* from optical microscopy and SEM, respectively. In *Figure 1*, given the refractive indices of PET ($n_D^{23} = 1.64$) and LLDPE ($n_D^{23} = 1.51$) at positive phase contrast, the dark areas should correspond to PET. Decreasing the PET/LLDPE ratio (*Figures 1a–c*) causes a coarsening of the PE phase and some stratification (*Figure 1c*). Increasing the ionomer content (from 5 to 15 wt%) at constant PET/LLDPE ratio (1:1) (*Figures 1d, 1b* and *1e*) seems to cause some improvement in dispersion at an ca. 10 wt% ionomer content (*Figure 1b*). However, at this level of ionomer the most uniform dispersion is obtained at the 3:1 PET/LLDPE ratio. *Figure 1f* shows the degree of dispersion after a second mixing of the blend; no improvement is evident (compare with *Figure 1d*). Examination with crossed polarizers for quenched (*Figure 1g*) and annealed (*Figure 1h*) samples indicates a less uniform crystalline superstructure for the latter specimen resulting from the cold crystallization of the PET component. This is expected to affect the mechanical properties of the blends (see below).

The results of SEM examination of cryofractured surfaces are shown in *Figure 2*. At low magnification, samples with varying PET/LLDPE ratio (*Figures 2a–c*) show a mixed brittle/ductile surface. A finer dispersion of the PE phase is obtained with a 3:1 PET/LLDPE ratio in the blend, in agreement with phase contrast microscopy. This particular composition, which showed improved mechanical properties, was examined in more detail (*Figures 2d* and *2e*). The PE phase is dispersed as deformed globules (*Figure 2d*) in a matrix of PET/ionomer (*Figure 2e*). In earlier work[8], SEM gave evidence of good bonding of these components in the binary blends (limited cavity formation). An examination was also made of extrudates of these blends obtained from the mixing extruder. No new features were obtained except at a 1:3 PET/LLDPE ratio where the PE phase (more deformable than PET) forms a cell-like interpenetrating network (see *Figure 2f*). This may explain the satisfactory ductility of these compositions (see *Figure 4*), although much of this structure is destroyed when films are prepared for tensile testing.

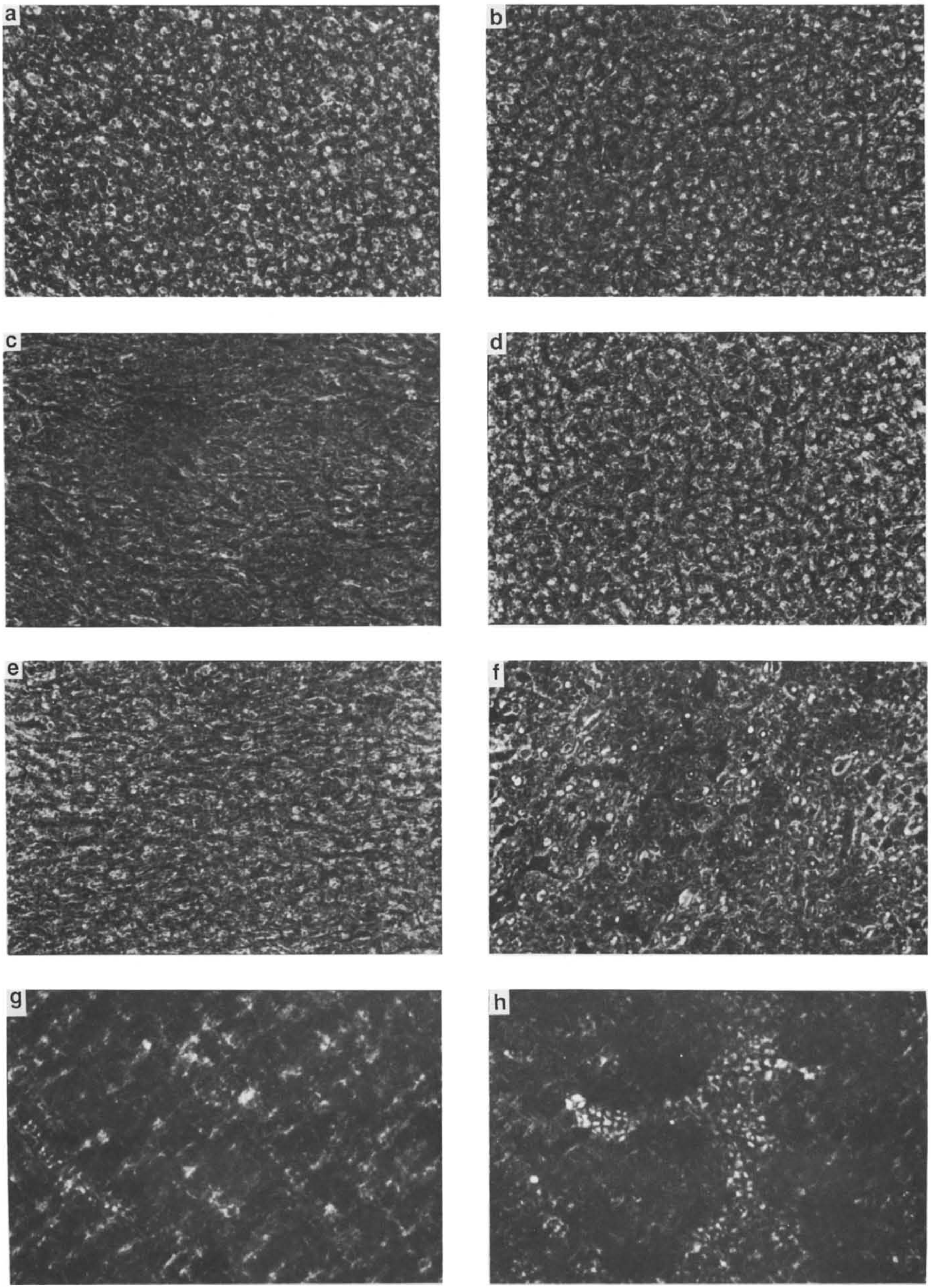

Figure 1 Optical micrographs of quenched PET/LLDPE/ionomer blends (a–f, phase contrast; g and h, crossed polarizers): (a) 68.2:22.7:9.1; (b) 45.5:45.5:9; (c) 22.7:68.2:9.1; (d) 47.5:47.5:5; (e) 42.5:42.5:15; (f) 22.7:68.2:9.1 mixed twice; (g) 68.2:22.7:9.1; (h) 68.2:22.7:9.1 annealed

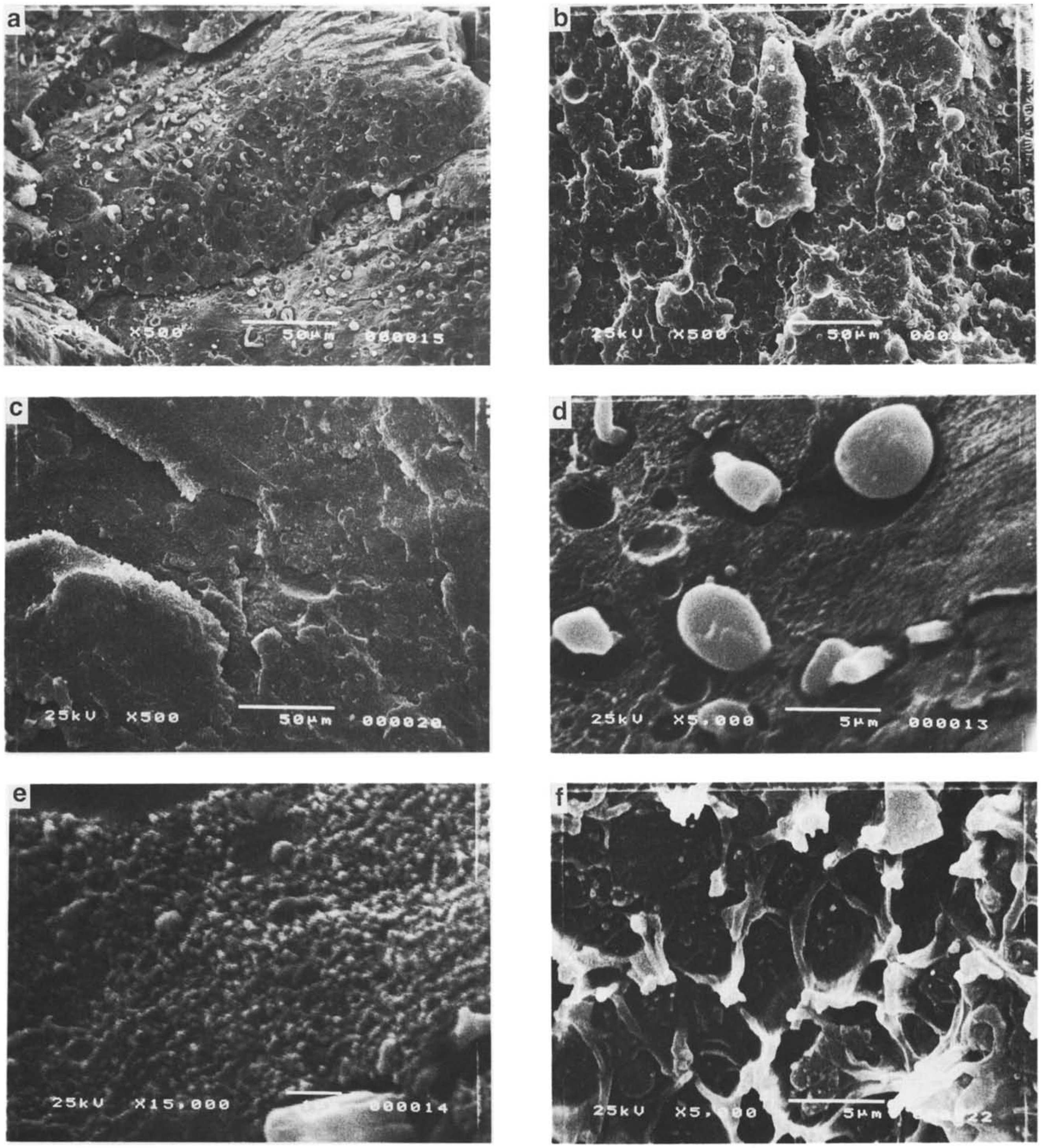

Figure 2 SEM micrographs of quenched PET/LLDPE/ionomer blends: (a) 68.2:22.7:9.1; (b) 45.5:45.5:9; (c) 22.7:68.2:9.1; (d) 68.2:22.7:9.1 (× 5000); (e) 68.2:22.7:9.1 (× 15 000); (f) 22.7:68.2:9.1 with fracture surface of extrudate perpendicular to its axis

Tensile properties

Figure 3 gives the stress/strain properties of the three possible binary blends obtained from PET, ionomer and LLDPE in a 50:50 ratio, studied in order to obtain a frame of reference to judge the effect of adding the ionomer. It is evident that both PET/ionomer and LLDPE/ionomer are mechanically compatible; they show good strength and especially good ultimate elongation, in contrast to the obvious incompatibility of the PET/LLDPE blend (inset).

The effect of adding ionomer to this blend is shown in *Figure 4* (inset), where increased ductility is caused by increased amounts of the ionomer. No yielding is observed, in contrast to the pure PET component (see *Figure 3*). More interesting results are obtained by changing the PET/LLDPE ratio at constant ionomer content (9 wt%). These findings are also reported in *Figure 4* and indicate excellent tensile properties when the PET/LLDPE ratio is 3:1. Thus, the tensile properties support the view that the ionomer may be used as an effective compatibilizer for the PET/LLDPE blend.

The observation[16] that increased levels of crystallinity in PET lead to a reduction in the ultimate elongation ($\varepsilon_b \approx 10\%$ for 33% crystallinity) led us to examine the

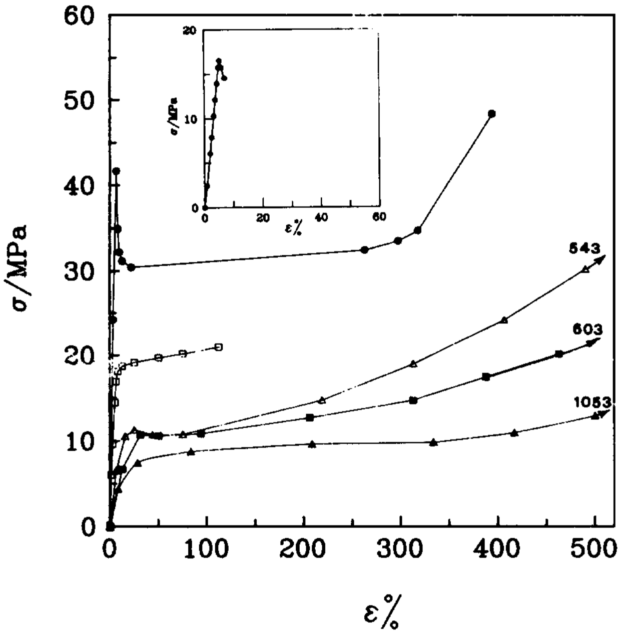

Figure 3 Stress/strain properties of quenched binary blends at the 50:50 composition: (□) PET/ionomer; (■) LLDPE/ionomer. The inset shows the properties of PET/LLDPE. Also shown are plots for the pure components: (●) PET; (△) ionomer; (▲) LLDPE

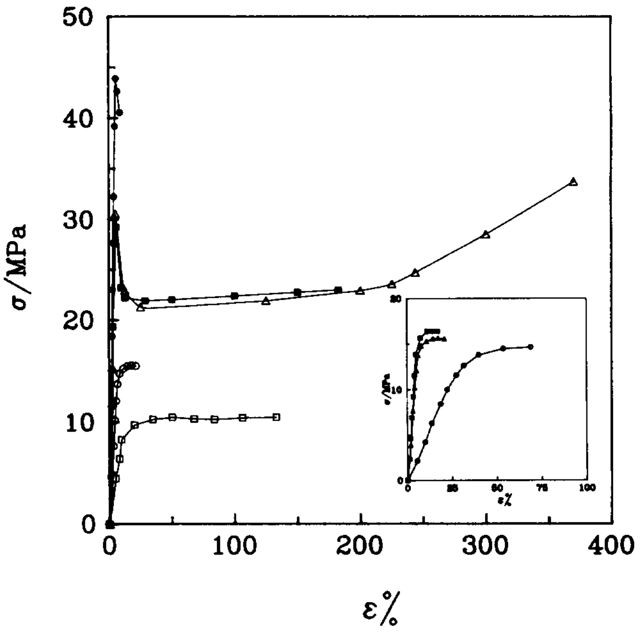

Figure 4 Stress/strain properties of quenched PET/LLDPE/ionomer blends: (△) 68.2:22.7:9.1; (○) 45.5:45.5:9; (□) 22.7:68.2:9.1. Plots are also shown for the annealed samples: (●) PET; (■) 68.2:22.7:9.1 blend. The inset shows the effect of compatibilizer content for the following blends: (□) 47.5:47.5:5; (△) 45.5:45.5:9; (○) 42.5:42.5:15

effect of annealing at a moderate temperature (2 h at 80°C) on the PET/LLDPE blend. This (80°C) is approximately the temperature where the cold crystallization of PET sets in. The results indicate (see *Figure 4*) a significant reduction in ε_b for PET and the ternary blend. Thus, mechanical compatibilization is obtained with PET in the amorphous state. It is possible that failure to obtain quenched blends may have led to the poor mechanical properties reported in earlier related work[6,9].

To facilitate the optimization procedure an attempt was made to predict the ultimate tensile properties of the ternary blends using data on pure components and all their possible binary blends at the 50:50 composition. Binary properties were fitted to a polynomial in composition and the results obtained using the relevant theory of mixtures[17] are given in *Figure 5* for the ultimate tensile strength σ_b. The predicted value for the ternary with a 3:1 PET/LLDPE ratio at the 9 wt% ionomer level was 22 MPa, whereas the experimental value was 34 ± 2 MPa. The discrepancy is attributed to the limited data used for the binary blends involved (only the 50:50 blends and the corresponding pure components). Nevertheless, this ternary diagram correlating compositions and properties is useful in predicting from limited data (three binary blends and three components) whether an optimum composition exists that maximizes any given property of the ternary. In this particular case no such optimum composition is predicted, but the desired property (i.e. σ_b) increases in the direction of increasing amount of PET in the ternary. Obviously, other constraints should be superimposed, e.g. cost, degree of effective mixing, etc., to arrive at a realistic composition. It also gives in the form of 'isobars' those ternary compositions giving a constant property value (e.g. σ_b).

Dynamic mechanical properties

The results are summarized in *Figures 6* and *7* in terms of the temperature dependence of the storage modulus E' and loss modulus E'' at the one composition that showed increased compatibilization. Some temperature reduction (ca. 2°C) of the main PET relaxation at 93.5°C and a shift of the PET β relaxation at -36°C to higher temperatures (ca. -23°C), intermediate between those of PET and LLDPE, are evident. These features are characteristic of a mixed interphase formation in an incompatible blend and were also observed in the PET/ionomer system[8].

Thermal properties

D.s.c. measurements are complicated by the presence of two crystalline components giving two endotherms at 125°C (LLDPE) and 252°C (PET) and a cold crystalliza-

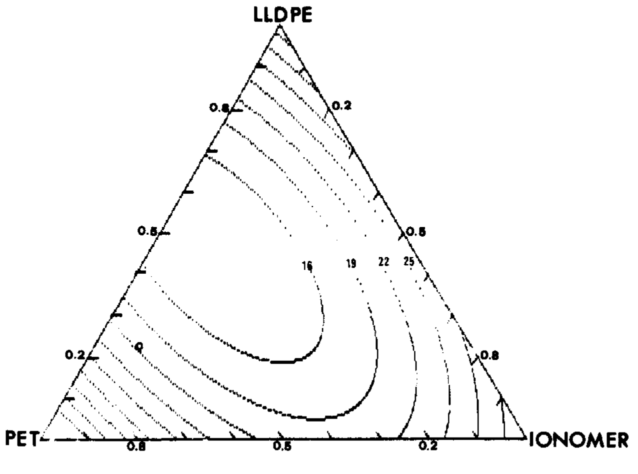

Figure 5 Prediction of tensile strength (σ_b in MPa) as a function of composition with a triangular diagram. Numbers on curves indicate a constant σ_b value along the curve. Numbers on axes are weight fractions. The open circle (○) denotes the predicted value for the ternary 68.2:22.7:9.1 PET/LLDPE/ionomer blend

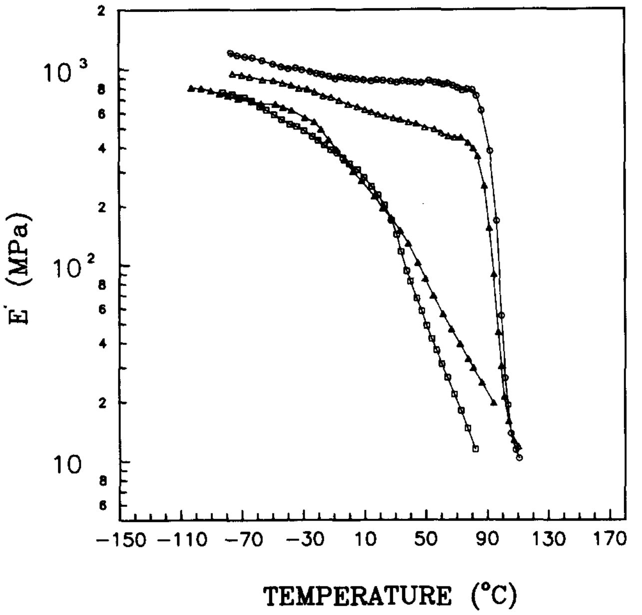

Figure 6 Temperature dependence of the storage modulus for the ternary 68.2:22.7:9.1 PET/LLDPE/ionomer blend and its pure components: (△) blend; (○) PET; (□) ionomer; (▲) LLDPE

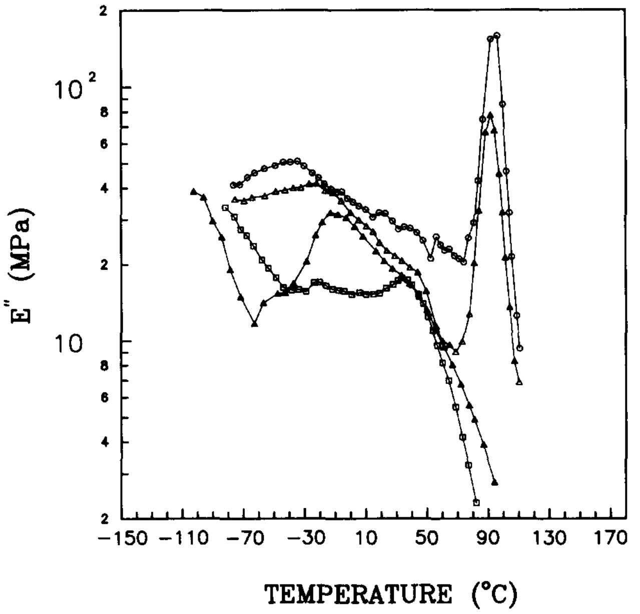

Figure 7 Temperature dependence of the loss modulus for the ternary 68.2:22.7:9.1 PET/LLDPE/ionomer blend and its pure components: (△) blend; (○) PET; (□) ionomer; (▲) LLDPE

tion exotherm of PET commencing at 95°C, making difficult any quantitative measurement of the polyolefin crystallinity. In addition, two baseline shifts caused by the T_g values of the components are discernible. The data were used to detect any T_m shift of the ternary with increasing amounts of the ionomer up to 15 wt% (at a constant PET/LLDPE ratio). No such systematic shift was observed – a feature of an incompatible crystalline blend.

The compatibilizing effectiveness of the ionomer can be traced to its strong adhesion to PET – the result of intermolecular chemical reactions (transesterification by acidolysis) occurring at their interface when blending at high temperatures, i.e.

$$RCOOR + R''COOH \rightarrow RCOOH + R''COOR$$

$$RCOOR + R''COONa \rightarrow RCOONa + R''COOR$$

where R″COOH and R″COONa stand for the free acid and its sodium ionomer, respectively.

The subject of compatibilization covering other reactions that take place when components are mixed at elevated temperatures has been discussed recently[18]. Once the strong interfacial bond between PET and the ionomer is obtained it is reasonable to expect a compatibilizing action in the ternary since the PE component should be (at least) mechanically compatible with the olefinic portion of the ionomer because of structural similarity. This is indeed the case (see the relevant data in *Figure 3*).

As to the effect of the specific PET/LLDPE ratio that was observed to optimize compatibilization, this should be attributed to the increased dispersability of the ionomer at increased PET levels, i.e. morphological factors. The minimum in tensile properties at the 50:50 composition is to be expected in an incompatible blend. On the other hand, increasing the amount of LLDPE may increase ductility; however, the decreased amount of PET may lead to an incomplete 'coupling' of the ionomer which must also be attached to the polyester to act as an effective compatibilizer. The level of the compatibilizer is moderate (ca. 10 wt%) and varying it does not seem to alter the properties drastically. Thus, compatibilization in this case should be regarded partly as a chemical rather than a physical phenomenon (interfacial tension minimization). The picture is complicated, however, since two apparently non-reacting components the ionomer and LLDPE are also involved.

With respect to the specificity of the type of ionomer involved, preliminary results[19] indicate that the Zn^{2+} ionomer is less effective at similar PET/LLDPE ratios. As to the type of polyolefin that may be combined with PET, that is a topic for future investigation.

CONCLUSIONS

1. The sodium ionomer of poly(ethylene-*co*-methacrylic acid) is an effective compatibilizer for melt-mixed and quenched PET/LLDPE blends.
2. Compatibilization is caused by the strong adhesion at the PET/ionomer interface and the athermal mixing and/or entanglement at the ionomer/polyolefin interface. It is optimized at increased levels of PET and at moderate levels of the ionomer.

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