

Poly(ethylene-*co*-methacrylic acid)–Lithium Ionomer as a Compatibilizer for Poly(ethylene terephthalate)/Linear Low-Density Polyethylene Blends

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ABSTRACT: Poly(ethylene terephthalate) (PET)/linear low-density polyethylene (LLDPE) blends (75/25), with contents of poly(ethylene-*co*-methacrylic acid) partially neutralized with lithium (PEMA–Li) that were systematically changed from 0 to 45% relative to the LLDPE, were obtained by direct injection molding in an attempt to (1) ameliorate the performance of the binary blend and (2) find the best compatibilizer content. PEMA–Li did not modify the PET or LLDPE amorphous-phase compositions or the crystalline content of PET. However, PEMA–Li did lead to a nucleation effect and to the presence of a second smaller and less perfect crystalline structure. PET induced a fractional crystallization in LLDPE that remained in the presence of PEMA–Li and reduced the crystallinity of LLDPE. The ternary blends showed two similar dispersed LLDPE and PEMA–Li phases with small subparticles, probably PET, inside. The

compatibilizing effect of PEMA–Li was clearly shown by the impressive increase in the break strain, along with only small decreases in the modulus of elasticity and in the tensile strength. With respect to the recycling possibilities of LLDPE, a ternary blend with the addition of 22.5% PEMA–Li, which led to very slight modulus and yield stress decreases with respect to the binary blend and a break strain increase of 480%, appeared to be the most attractive. However, the highest property improvement appeared with the addition of 37.5% PEMA–Li, which led to elasticity modulus and tensile strength decreases of only 9%, along with a very high break strain increase (760%). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1322–1328, 2003

Key words: polyethylene (PE); blends; ionomers; compatibilization

INTRODUCTION

Poly(ethylene terephthalate) (PET) and linear low-density polyethylene (LLDPE), in the forms of beverage bottles, films, molded parts, and so forth, are important contributors to the waste stream. The classification of polymer waste by its chemical nature is difficult.¹ Therefore, the direct use of mixed polymers is one of the most attractive methods of recycling. However, PET/LLDPE blends are almost completely incompatible.^{2–4} As a result, limitations such as unstable morphology, poor interfacial adhesion, and high interfacial tension are present in these blends. Suitable compatibilization can remove these limitations.

The most frequently employed methods to improve compatibility⁵ are the addition of a third component, which must react or interact with at least one component of the blend, and the generation of copolymers *in situ* during the preparation of blends with functionalized

polymers. The major types of compatibilizers used for polyester/polyolefin blends are styrenic block copolymers^{6–13} and polyolefin copolymers.^{1,6,10,12–17}

The compatibilization of the PET/LLDPE system was attempted by means of diethylmaleate-grafted polyethylene, as reported in the open literature;³ this led to dispersed particle size reduction, but the mechanical properties of the blends were not measured. Recently, sodium, zinc, and other metal ionomers have been used as compatibilizers with good results,^{2,11,18–29} the compatibilizing effect changing with the nature of the cation. For instance, the sodium ionomer of poly(ethylene-*co*-methacrylic acid) (PEMA–Na) added at three levels was an effective compatibilizer² for PET/LLDPE blends. This was seen by the adhesion at the PET/ionomer interface, which led to notable break strain improvements at high compatibilizer contents. For PET/high-density polyethylene (HDPE) blends, when a PEMA–Zn ionomer was used as a compatibilizer,¹¹ the fine morphology seemed to stem from the strong affinity between HDPE and the ionomer and the ion–dipole interaction between the acid in the ionomer and the dipoles in the carbonyl group of PET. A salt of poly(ethylene-*co*-methacrylic acid) partially neutralized with lithium (PEMA–Li) has recently been used in PET/HDPE blends with positive effects,¹⁸ but not to our knowledge in blends of PET with LLDPE,

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which has properties and applications different than those of HDPE.

In this work, a 75/25 PET/LLDPE blend was modified with amounts of PEMA-Li that were systematically changed from 0 to 45% of the LLDPE content with the aim of measuring the compatibilizing ability of PEMA-Li and determining the optimum compatibilizer content. Blending was performed through direct injection mixing, the solid-state characteristics of the blends were studied with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMTA), and the morphology was examined with scanning electron microscopy (SEM). The mechanical properties were determined with tensile and impact tests.

EXPERIMENTAL

PET with an intrinsic viscosity of 0.82 dL/g was supplied by Brilen (Barbastro, Huesca, Spain). LLDPE (Dowlex), supplied by Dow Chemical (Schwalbach, Germany), had a melt-flow index of 10.74 g/10 min (ASTM D 1238) with a 2.16-kg load at 190°C. The ionomer used as the compatibilizer was an ethylene/methacrylic acid copolymer with 15 wt % methacrylic acid in which the methacrylic acid was partially neutralized with Li (PEMA-Li). It was supplied by Aldrich Chemical Co., Inc. (Milwaukee, WI), and its melt-flow index, determined at 190°C with a 2.16-kg load, was 2.6 g/10 min.

The PET and compatibilizer were dried before processing for 14 h at 120°C in an air circulation oven and for 8 h at 60°C in a vacuum oven, respectively. The 75/25 PET/LLDPE binary blend was obtained as a reference. The ternary blends were prepared at a constant PET/LLDPE ratio (3/1) with ionomer contents of 7.5, 15, 22.5, 30, 37.5, and 45% with respect to the LLDPE. Therefore, the 30% PEMA-Li blend, for example, had a percentage composition of 69.75/23.25/7. All the blends were prepared by direct melt mixing with a Battenfeld BA 230E (Kottingbrunn, Austria) reciprocating-screw injection-molding machine (screw diameter = 18 mm, length/diameter ratio = 17.8). A barrel and nozzle temperature of 280°C, a mold temperature of 18–19°C, an injection speed of 4 cm³/s, and an injection pressure of 1050 bar were used. Previous mixing by extrusion gave worse results because the ionomer degraded. The PEMA-Li specimens for DMTA testing were prepared by compression molding at 120°C and 450 bar for 10 min.

The thermal behavior of the blends was studied by DSC with a Perkin-Elmer (Norwalk, CT) DSC-7 calorimeter. The samples first were heated at 20°C/min from 30 to 280°C, then were cooled at the same rate, and finally were reheated again. The crystallization temperatures (T_c 's) and melting temperatures (T_m 's) and the crystallization and melting heats were deter-

mined at the maximum and from the areas of the corresponding peaks, respectively. The phase structure was not clear by DSC, and so it was studied by DMTA with a Polymer Laboratories DMTA instrument (Shropshire, UK). A heating rate of 4°C/min and a frequency of 1 Hz were used.

The interfacial tension was calculated by the two-liquid harmonic method.³⁰ The contact-angle measurements were carried out on a CAM 100 goniometer (KSV, Tokyo, Japan) on injection-molded tensile bars with water and ethylene glycol. The mean standard deviation of the measurements was 2–3°, which led to an error of approximately 20%. Fourier transform infrared (FTIR) spectra were obtained with a Nicolet Magna 560 spectrophotometer (Madison, WI). An attenuated total reflectance objective attached to a Spectra Tech microscope (Shelton, CT) and a mercury-cadmium-telluride detector were used.

The tensile tests were carried out with an Instron 4301 (Canton, MA) at a crosshead speed of 10 mm/min and at 23 ± 2°C on ASTM D 638 type IV (1.8-mm-thick) specimens. The mechanical properties (Young's modulus, yield stress, and break strain) were determined from the load-elongation curves. Impact tests (ASTM D 256) were carried out with a Ceast pendulum (Torino, Italy) on injection-molded specimens with a cross section of 12.7 mm × 3 mm. Notched (depth = 2.54 mm, radius = 0.25 mm) and unnotched specimens were tested. The notches were machined after molding. At least eight specimens were tested for each reported value in both the tensile and impact tests.

SEM was performed on the surfaces of cryogenically fractured specimens after gold coating. A Hitachi S-2700 electron microscope (Tokyo, Japan) was used at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Solid-state behavior

The glass-transition temperature (T_g) value of PET, the order-disorder-transition temperature of the ionic clusters, and the T_m range of LLDPE and PEMA-Li crystals were similar. Additionally, the T_g value of HDPE had a only slight intensity that diminished in the blends containing PET. As a result, the miscibility level of the components in ternary blends could not be inferred; therefore, it was studied in binary blends. The full immiscibility of the PET/LLDPE²⁻⁴ and PET/PEMA-Li¹⁸ blends is well known. The miscibility level of the binary LLDPE/PEMA-Li blend is discussed next.

The tan δ /temperature plots of the 75/25 LLDPE/PEMA-Li blend and the pure components are shown in Figure 1. For clarity, the curves are shifted 0.2 tan δ units from one another. The transition of the blend at

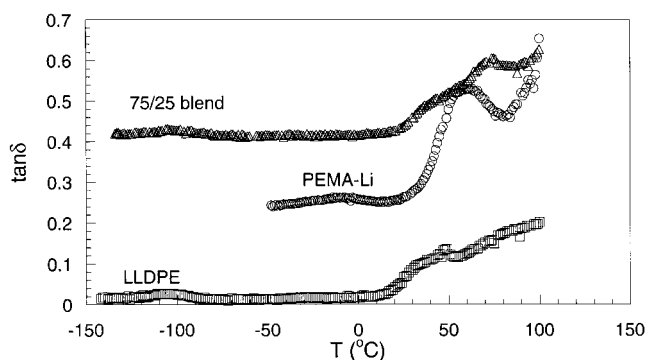


Figure 1 DMTA plots of $\tan \delta$ versus the temperature for the LLDPE, PEMA-Li, and 75/25 LLDPE/PEMA-Li blend.

approximately -105°C appeared at almost the same temperature as that in pure LLDPE. Another transition of the blend appeared at a temperature (70°C) higher than that in pure PEMA-Li (60°C). This could not be due to the presence of amorphous LLDPE and was influenced by the surrounding presence of the crystalline LLDPE. This indicated the presence of two almost pure phases and the immiscibility of the blend. As a result of the immiscibility of all the binary blends, the ternary PET/LLDPE/PEMA-Li blends were fully immiscible from a practical point of view.

The crystallization of PET during cooling in ternary blends took place at higher temperatures (190 – 200°C) than those for pure PET and the binary blend (170°C), indicating the nucleation effect of PEMA-Li on the crystallization of PET. This agreed with observations of PET/ionomer blends³¹ and previous patents.^{32–34} The nucleating activity of several sodium salts on the PET crystallization has also been reported.³⁵ The melting enthalpy (ΔH_m) value in the second heating scan and, therefore, the crystallinity level did not change. Finally, a second T_m of PET at 242°C , in addition to the usual one at 250°C , was seen for PEMA-Li contents higher than 22.5%. This indicated that PEMA-Li induced the presence of a second less perfect crystalline structure with thinner lamellae. LLDPE did not influence the crystalline characteristics of PET.

With respect to the crystalline phase of LLDPE, the T_m value of the binary blends in the second heating scan was smaller (132°C) than that of pure LLDPE (137°C). This indicates that, in the presence of PET, the crystalline phase was less perfect and that the crystallization of LLDPE was slightly more difficult. However, as for the PEMA-Na compatibilizer,² T_m did not change in the presence of PEMA-Li. Besides the usual T_c during the cooling of LLDPE at 110°C , PET induced another T_c of lower intensity at a lower temperature (104°C), indicating a fractional crystallization of LLDPE. This unusual crystallization behavior may be explained by the fact that the crystallized matrix restricted the movement of the flexible dispersed phase

upon cooling.³⁶ The PEMA-Li presence reduced the low T_c , which indicated that it also hindered the formation of the less stable crystalline LLDPE structure. Finally, the crystallinity of LLDPE (84%) in the pure state and in the binary blend decreased to roughly 60% in the ternary blends.

Morphology

The morphologies of the broken surfaces of the 0, 7.5, 15, and 37.5% PEMA-Li blends are shown in Figure 2(a–d), respectively. The morphology of the 22.5% PEMA-Li blend was similar to that of Figure 2(c), and the morphology of the 45% PEMA-Li blend was similar to that of Figure 2(d). The morphology of the 30% PEMA-Li blend was between those of Figure 2(c,d). The morphology hardly changed from the binary blend of Figure 2(a) to the ternary blend of Figure 2(b). At higher PEMA-Li contents, however, the morphology clearly changed because almost all the particles were broken and the fracture surface was continuous, without holes or protuberant particles. Some large dispersed phases, with small subparticles inside, also appeared. When the PEMA-Li contents increased, as shown in Figure 2(b–d), the PEMA-Li dispersed phase had to appear. However, the LLDPE and PEMA-Li dispersed phases were not clearly distinguished from each other. For this reason, the morphology of the typical fracture surface of both binary 75/25 PET/LLDPE and 75/25 PET/PEMA-Li blends is shown in Figure 3(a,b). Both LLDPE and PEMA-Li dispersed phases showed the presence of small (0.2 – $1\text{-}\mu\text{m}$) subparticles, probably of PET. The particle size was similar in both blends, and the only apparent notable difference was a clearer slight debonding surrounding most of the particles of the PET/LLDPE blend of Figure 3(a). This kind of morphology should appear in most of the particles of Figure 2(c) and should be less common at the higher PEMA-Li contents of Figure 2(d). However, the slightly debonded particles do not appear in Figure 2(c,d). This indicates that the slight debonding characteristic of the LLDPE particles hardly took place in the presence of PEMA-Li contents equal to or greater than 15%. This should have a definite influence on the fracture properties of the blends.

These morphological observations were comparable to those for the PET/HDPE/PEMA-Li blends¹⁸ and indicated the compatibilizing effect of PEMA-Li. The compatibilizing effect was tested by a comparison of the interfacial tension of the binary blends and that of the 30% PEMA-Li blends, both calculated from measurements of the contact angle. Although the results were not definitive because of the hydrophilic nature of the ionomer, which should reduce the surface tension between the water and LLDPE/ionomer blend, the interfacial tension decrease from 3 mN/m between

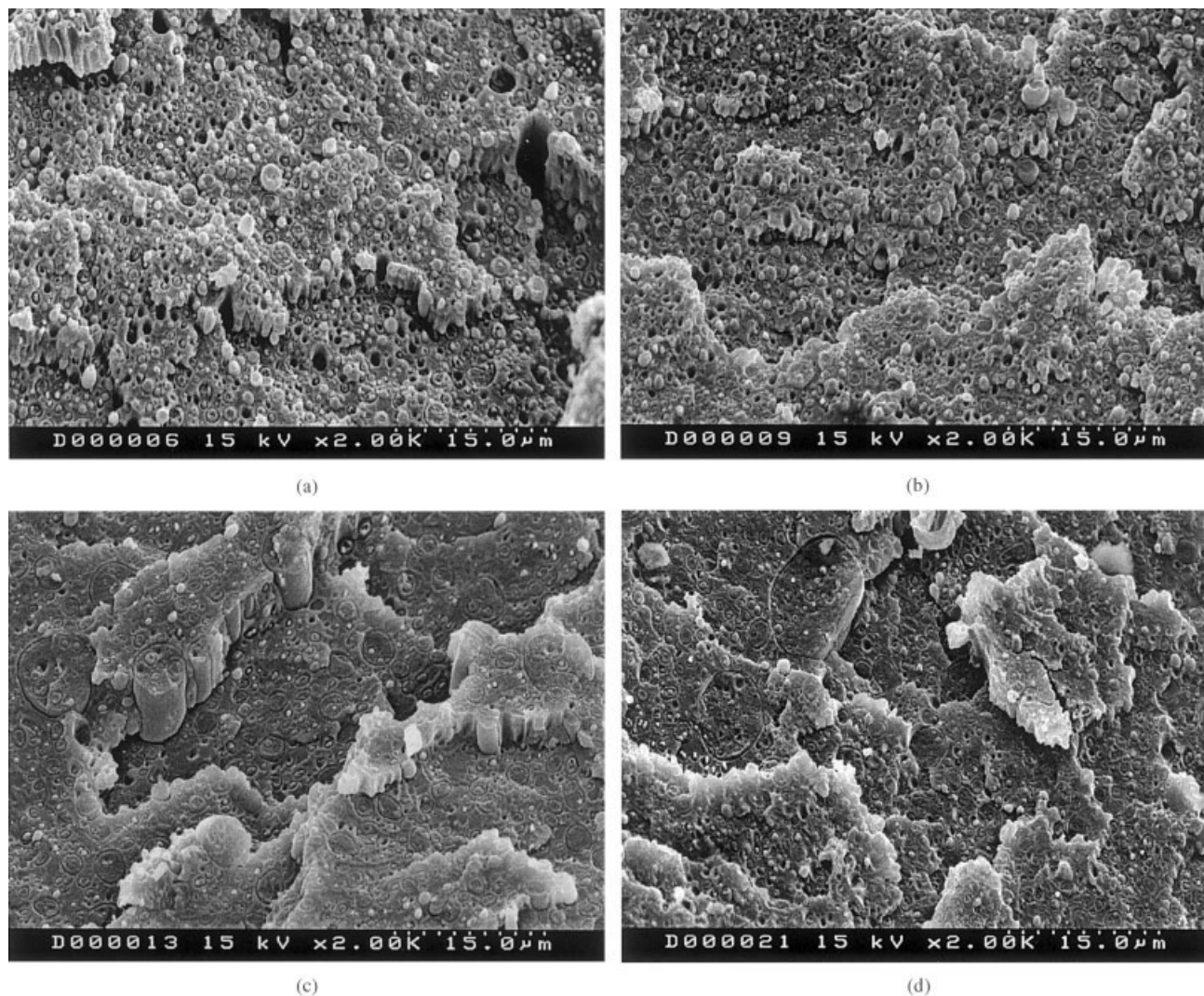
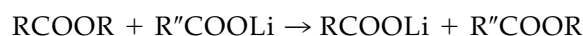
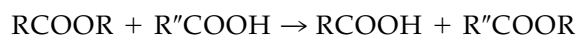


Figure 2 Cryogenically broken surfaces of (a) the 75/25 PET/LLDPE blend, (b) the 75/25/7.5 PET/LLDPE/PEMA-Li blend, (c) the 75/25/15 PET/LLDPE/PEMA-Li blend, and (d) the 75/25/37.5 PET/LLDPE/PEMA-Li blend. The photographs were obtained by SEM at an angle of 30° from the perpendicular to the surface.

PET and LLDPE to 0.5 mN/m between PET and a 100/30 LLDPE/PEMA-Li blend suggested a compatibilizing effect of PEMA-Li on the PET/LLDPE blend.

The compatibilizing effect could be due to athermal mixing between LLDPE and the ethylene units of the ionomer and due to ion-dipole interactions between the acid in the ionomer and the carbonyl groups of PET.¹¹ However, it could be influenced by interchange reactions. To test the possibility of chemical reactions during processing,² we obtained PET/PEMA-Li (3/1) blends in the melt state and compared their FTIR spectrum with that obtained from the weighted addition of the spectra of the pure PET and PEMA-Li. These two spectra are shown in Figure 4. As can be seen in Figure 4, in the experimental spectrum, there is a displacement of the carbonyl of the blend with respect to the calculated one. This proves that, besides a probable interaction at the interface, reactions also

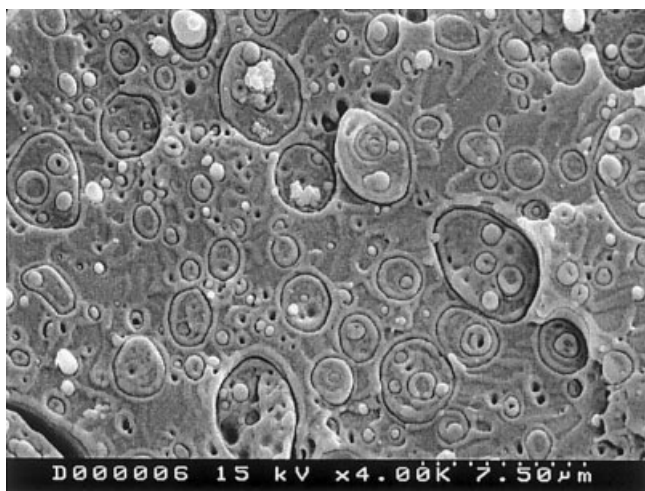
took place. Because the lithium-neutralized methacrylic acid (MA-Li) units were involved, the reaction was probably an intermolecular acidolysis between PET and PEMA-Li:²



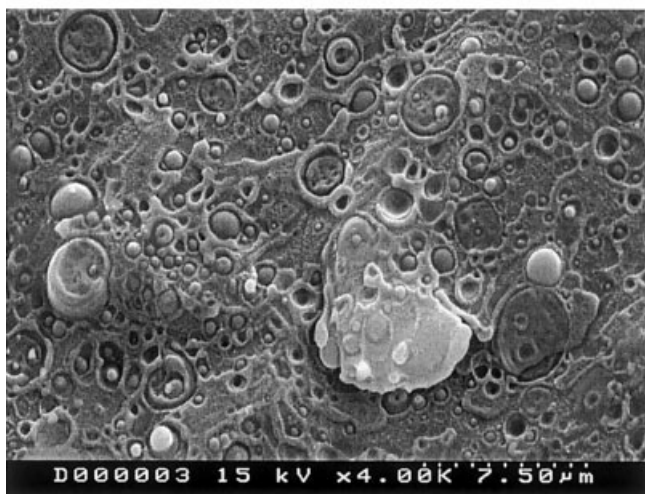
where RCOOR represents the PET structure and R''COOH and RCOOLi represent the free acid and the lithium ionomer, respectively.

Mechanical properties

The modulus of elasticity of the PET/LLDPE blends versus the PEMA-Li content is shown in Figure 5, and



(a)



(b)

Figure 3 Amplification of the cryogenically broken surfaces of (a) the 75/25 PET/LLDPE blend and (b) the 75/25 PET/PEMA-Li blend. The photographs were obtained by SEM at an angle of 30° from the perpendicular to the surface.

the yield stress versus the PEMA-Li content is shown in Figure 6. Up to 22.5% PEMA-Li, the modulus of elasticity did not vary with the PEMA-Li content.

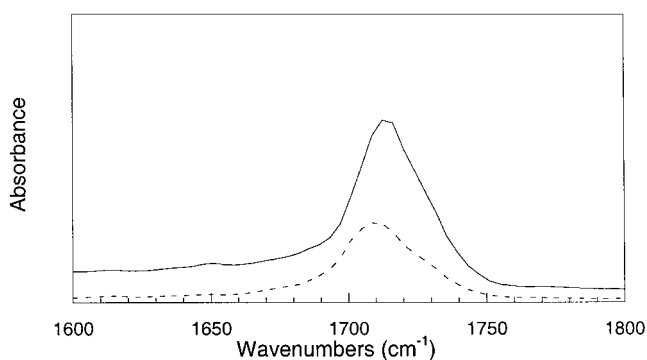


Figure 4 (—) Experimental FTIR spectrum and (---) weighted addition spectrum of the 3/1 PET/PEMA-Li blend.

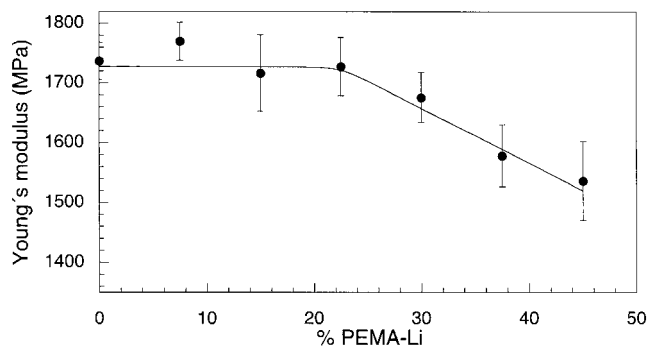


Figure 5 Young's modulus values of the uncompatibilized and compatibilized blends versus the PEMA-Li content.

When PEMA-Na² was used, the behavior was similar, although the modulus decrease was 10% in the blend with 20% PEMA-Na (based on the LLDPE content). A similar slight decrease (roughly 5–6% for the 22.5% PEMA-Li blend) was also seen¹⁸ in PET/HDPE/PEMA-Li blends. The behavior of the yield stress was similar to that of the modulus, although its value remained constant up to higher (30%) PEMA-Li contents. At greater PEMA-Li contents, both small strain properties decreased with the PEMA-Li content, up to the maximum PEMA-Li content studied. These small strain property changes do not appear to be related to a morphology change because the morphologies of the 15 and 37.5% PEMA-Li blends of Figure 2(c,d) were rather similar and because the main change in the morphology took place between 7.5 and 15% PEMA-Li. The fracture properties were probably sensitive to such a morphology change.

The break strain values are shown in Figure 7 against the PEMA-Li content. The break strain values of the ternary blends with a PEMA-Li content higher than 7.5% were very high, indicating that adhesion had improved at the interface and that compatibilization had taken place. This was evident in the morphology because almost all the dispersed particles were broken during cryogenic fracture. Moreover, the break strain increase took place between 7.5 and 15%

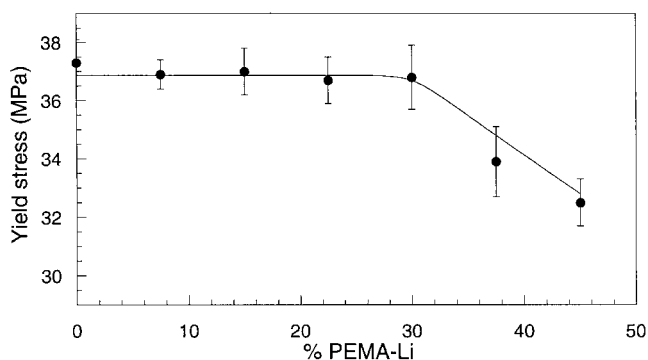


Figure 6 Yield stress values of the uncompatibilized and compatibilized blends versus the PEMA-Li content.

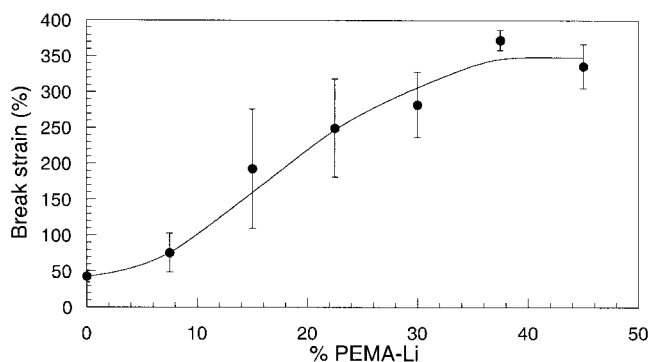


Figure 7 Ductility values of the uncompatibilized and compatibilized blends versus the PEMA-Li content.

PEMA-Li, in which range a clear morphology change also took place. For PET/HDPE blends compatibilized with PEMA-Li at low (20%) PEMA-Li contents, the lack of an abrupt morphology change led to a continuous and less important (184%) break strain increase. This is experimental evidence of the morphology-property relationship in these blends. The overall increase in break strain as the PEMA-Li presence increased should be due, in part, to the rubbery nature of the PEMA-Li, but the impressive, roughly eightfold break strain values were much larger than those expected with a PEMA-Li content of roughly 10% of the full blend (45% of the LLDPE content). The relevancy of these break strain values is seen by the fact that they can be compared with those of the pure components, both of them recognized ductile polymers.

This confirms the previously observed^{2,28} influence of the nature of the cation of the ionomer on the compatibilization level. Significant break strain values (roughly 375%) were obtained in another 75/25 PET/LLDPE blend upon the addition of 9% PEMA-Na² (40% with respect to LLDPE).

The presence of PEMA-Li did not increase the low (25 J/m) notched impact strength of the binary blends, whatever the PEMA-Li content was. Similar behavior was found¹⁸ for PET/HDPE blends. This dissimilarity between the break strain and the notched impact strength behaviors was not unusual and was due to the high notch sensitivity of the PET matrix. The notch sensitivity of PET was seen in the unnotched impact tests because the impact strength reached a value twice that of the binary blend (400 J/m) with the minimum PEMA-Li content and because the specimens did not break at higher PEMA-Li contents.

CONCLUSIONS

The 75/25 PET/LLDPE blends were fully immiscible even in the presence of PEMA-Li. PEMA-Li did not change the crystallinity level of PET but nucleated it and induced another less perfect crystalline structure

with thinner lamellae in blends at high PEMA-Li contents. The crystallinity content of LLDPE (81%) was maintained in the binary blend but decreased in the presence of PEMA-Li. The fractional crystallization of LLDPE took place in both the binary and ternary blends.

Very small (0.1–1- μm) PET subparticles appeared occluded inside both the LLDPE and PEMA-Li dispersed phases. The slight debonding of the dispersed LLDPE phase in the binary PET/LLDPE blend disappeared in the compatibilized blends.

The Young's modulus and yield stress remained constant up to roughly 25% PEMA-Li and then slightly decreased (12% at 45% PEMA-Li). There was an abrupt break strain increase between 7.5 and 15% PEMA-Li, in which range the morphology also changed from mostly debonded particles to clear and cohesive fractures. The notched impact strength did not increase in the ternary blends because of the high notch sensitivity of PET, which was evidenced by the high unnotched impact strength improvements upon compatibilization. The ternary blend with a PEMA-Li content of 22.5% (5.3% in the whole blend) appeared the most interesting from a recycling point of view. This was because break strain increases of 480% with respect to that of the binary blend were obtained with a return of only 0.5 and roughly 2% modulus and yield stress decreases. The impressive 760% break strain increase of the blend with 37.5% PEMA-Li (8.6% in the whole blend), which was accompanied by only 9% modulus and yield stress decreases, indicated that this was the most interesting composition from the point of view of mechanical performance.

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