Synthesis and evaluation of compatibilizer based on interpenetrating polymer networks (IPN) for PET/LDPE blends

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ABSTRACT: The present work considers the evaluation of recycled polymers, which are generally incompatible and are degraded during recycling with fatal consequences to their thermal and mechanical properties. Regarding this subject, the synthesis of a new compatibilizer in network form was carried out in order to counter such incompatibility. In this sense, low density polyethylene (LDPE) and poly(ethylene terephthalate) (PET) were compatibilized via the implementation of an interpenetrating polymer network (IPN), which was specifically synthesized to possess chemical groups that are akin to both plastics, PET and LDPE. The effects of the relative amount of poly(acrylic acid) (PAA) in the compatibilizer and the amount in the blends of PET/LDPE were evaluated. The results show that mechanical properties and interfacial adhesion of PET/LDPE blends were modified and improved with the addition of the synthesized compatibilizer compared with a commercial compatibilizer (polyethylene grafted with maleic anhydride, PE-g-AA). © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43704.

INTRODUCTION

Nowadays, plastics are the most commonly used polymeric materials. This is basically due to their good mechanical resistance properties, low weight, thermal behavior, and their easy processability. These characteristics have allowed plastics to replace, partly or completely, materials such as steel, glass, wood, and aluminum in many applications. According to Subramanian,[1] the most consumed polymers are low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and poly(ethylene terephthalate) (PET). As consequence of a year-by-year increment in the consumption of these materials, hundreds of tons of plastic waste are generated. For this reason, it is imperative to recycle and reuse them.

The blend of wasted polymers such as PET and polyolefins (polyethylene and polypropylene) may provide an alternative route for the production of recycled materials with satisfactory costs, good yields and high potential for diverse applications.[2–4] One of the drawbacks of PET and polyethylene (PE) blends is their immiscibility, resulting in a material with coarse morphology giving poor thermal and mechanical properties.[5,6] Furthermore, the chemical structure of polyethylene (PE) lacks

functional groups avoiding interactions with most of polymeric materials.[7] Good blends of these polymers can be achieved by appropriate methods of compatibilization and processing technologies by improving interfacial adhesion and dispersion in the blends. Thus, a composite material with better thermal and mechanical properties compared to the starting polymers can be obtained.

According to Aglietto[8] and Schexnaydre,[9] the compatibility of immiscible blends can be improved by any of the following ways:

1. The addition of a third component that has a segment that is able to have a specific interaction and/or chemical reaction with the components of the blend (for example, block or graft copolymers).
2. In the case of PET, mixing it with suitable functionalized polymers capable of carrying out a chemical reaction with the functional group of the polyester.

It has been proven that it is possible to obtain a composite material with improved mechanical characteristics from recycled PET and polyolefins with the use of a compatibilizer based on glycidyl methacrylate.[7] Other compatibilizers based on

copolymers containing functional groups such as maleic anhydride (MA),[10–16] acrylic acid (AA),[17] isocyanate groups,[18] and glycidyl methacrylate (GMA)[7,19] have improved mechanical and thermal properties of polymer blends. However, according to Torres,[19] the synthesis of functionalized polyolefins with GMA is relatively expensive when used for large amounts in products such as blends of HDPE/PET. Moreover, other authors[20] reported that the use of maleic resins does not provide good adhesion between PE and PET. Nevertheless, other authors have shown that better adhesion between the two phases of immiscible blends of PET/PE can be achieved, compared to the reference blend, by using maleic anhydride grafted polyethylene.[7]

Currently, there are different types of commercial compatibilizers including random polymers, block copolymers, grafted polymers, and functionalized polymers. The most used compatibilizers are polyolefins grafted with maleic anhydride (PE-g-MA). In the case of block-type compatibilizers, styrene-ethylene/butylene-styrene (SEBS) and ethylene vinyl acetate (EVA), have been used to compatibilize blends of polyethylene/polycarbonate.[21] Recycled PET was combined with fiberglass along with the addition of SEBS copolymer grafted with maleic anhydride in order to improve its mechanical properties.[16]

Recently, most research on the compatibility of immiscible polymer blends use compatibilizers based on graft or copolymers type. These kinds of compatibilizers usually have a limited number of available functional groups to interact with polymers of the blend. Nishi and Kotaka,[22] show that for improving the compatibility of given polymer pairs, various attempts have been made. One of such attempt was the introduction of cross-links within each component to prepare interpenetrating polymer networks (IPNs) or semi-interpenetrating polymer networks (SIPNs). According to the IUPAC, the Interpenetrating polymer network is an intimate combination of two polymers, both in network form, at least one of which is synthesized and/or cross-linked in the immediate presence of the other. In addition, the Semi-interpenetrating polymer network is a combination of two polymers, one cross-linked and one linear, at least one of which was synthesized and/or cross-linked in the immediate presence of the other.

One thermoplastic elastomer (TPE) with interesting properties is the styrene-ethylene-propylene-styrene triblock copolymer (SEPS). The SEPS has been used as compatibilizer of polymer blends like Polypropylene/Polystyrene (PP/PS).[23] Polypropylene/High Density Polyethylene (PP/HDPE)[24] and Polypropylene/Polycarbonate/Ethylene-octene copolymer (PP/PC/POE).[25] It is important to mention that all these studies consider a compatibilizer quantity of between 1 and 10% by weight. In addition, in some cases, the SEPS has been used to improve the toughness of polymeric materials such as PP.[26] In the case of the poly(acrylic acid) (PAA), Sun[27] showed that the polypropylene/poly(butylene terephthalate) (PP/PBT) blends have been compatibilized using a one-step reactive extrusion process with the addition of monomer of acrylic acid, which are potentially reactive toward the carboxylic and/or hydroxyl groups at the chain ends of the PBT.

For this reason, this work proposes the synthesis of a new compatibilizer based on an interpenetrating polymer network (IPN) since it allows the combination of two or more polymers with different chemical structures, whose synthesis would be difficult by other polymerization methods. This new compatibilizer will have a great number of functional groups presented in the PAA as well as a chemical structure able to interact with the blend components by SEPS, since no grafting reaction takes place. Thus, the new compatibilizer is based on thermoplastic elastomer and poly(acrylic acid) and was added to a blend of recycled PET/LDPE, evaluating the mechanical and thermal properties of the obtained blends.

EXPERIMENTAL

Materials

The PET was obtained from used plastic beverage bottles. The LDPE was obtained from of postconsumer packing materials. The acrylic acid (99% purity) was purchased from Sigma-Aldrich (St. Louis). The thermoplastic elastomer, styrene-ethylene-propylene-styrene triblock copolymer (SEPS) with 30% w/w of styrene, was provided by Dynasol SA de CV (Altamira, Tamaulipas, Mexico). The 4,4′-bis-azoisobutyronitrile (Delaware) with the commercial name of Vazo64 (Dupont), was used as initiator. A phosphate-free detergent dissolved in distilled water (3:7) was used as surfactant and it was provided by HYCEL (Guadalajara, Mexico). Toluene (98% purity) was purchased from Baker (NJ). Distilled water was obtained from reverse osmosis purification system. All the materials were used as they were received.

Compatibilizer Synthesis

The compatibilizer was synthesized in a 500 mL glass reactor. The polymerization of acrylic acid was performed by free radicals in aqueous solution. Distilled water (10 parts for 1 part of monomer) was heated up to 65 °C in the glass reactor, once this temperature was reached the surfactant (1% w/w regarding acrylic acid content) was added followed by the thermoplastic elastomer (which was previously dissolved in toluene with a concentration of 20% w/w) under stirring. Thus, interaction between TPE and acrylic acid is possible in the interface by the surfactant containing TPE within the acrylic acid, generating a TPE embedded into the poly(acrylic acid). Afterwards, once the emulsion was homogenized at 65 °C, the Vazo64 was added (1% w/w in ratio to monomer). Then, the acrylic acid (70 or 90% w/w depending on the desired final product to obtain) was added to the reactive medium. The temperature was increased to 72 °C in order to promote polymerization. The reaction finished 20 min after the peak temperature was reached. Thus, the IPN was obtained, where PAA (70 and 90% w/w) was synthesized in the immediate presence of TPE, 30 and 10% w/w, respectively.

The obtained product of reaction (IPN) was thoroughly washed with distilled water in order to remove residual monomer. Finally, the IPN was dried in an oven for 48 h at 80 °C and then passed through a ball mill (Retsch, Germany) to obtain powder. The IPN synthesis yield was about 96%.

Blend Preparation

PET and LDPE blends were obtained considering the following factors: PET/LDPE ratio, compatibilizer formulation regarding

Table I. Composition of Polymer Blends According to Design of Experiments (DOE)

Blend	Identification	PET (% w/w)	LDPE (% w/w)	Compatibilizer type	PAA/TPE ratio (% w/w)	Compatibilizer concentration (% w/w)
1	1-75C90/1	74.25	24.75	IPN	90/10	1
2	2-25C90/1	24.75	74.25	IPN	90/10	1
3	3-75C70/1	74.25	24.75	IPN	70/30	1
4	4-25C70/1	24.75	74.25	IPN	70/30	1
5	5-75C90/5	71.25	23.75	IPN	90/10	5
6	6-25C90/5	23.75	71.25	IPN	90/10	5
7	7-75C70/5	71.25	23.75	IPN	70/30	5
8	8-25C70/5	23.75	71.25	IPN	70/30	5
9	75/25	75.00	25.00	None	-	-
10	25/75	25.00	75.00	None	-	-
11	MC1	74.25	24.75	PE-g-MA	-	1
12	MC2	71.25	23.75	PE-g-MA	-	5
13	MC3	24.75	74.25	PE-g-MA	-	1
14	MC4	23.75	71.25	PE-g-MA	-	5

PAA/TPE ratio (90/10 and 70/30) and concentration of compatibilizer (1 and 5% w/w) in the blends. Also, control blends (with no compatibilizer) and reference blends (with commercial compatibilizer, PE-g-MA) were obtained to contrast and compare the obtained results of samples containing the new compatibilizer. The total number of samples and percentages of PET and LDPE are summarized in Table I.

Blends of PET/LDPE were obtained using a Twin-Screw 20 mm model (Theysohn, Germany) with eight heating zones. For all the blends, with PET and LDPE matrix, the established temperature profile was: 170, 190, 220, 250, 250, 270, 270, and 270 °C. The obtained material was cut into small pieces in a pelletizer. Once the pellets of the blends were obtained, they were injected using an injection molding machine model 400 (Battenfeld, Austria) at a temperature range of 240–260 °C, in molds for mechanical testing under standardized conditions according to ASTM D638.

Characterization
The samples obtained were characterized according to the following techniques under the described conditions.

Fourier Transformed Infrared Spectroscopy (FTIR). The infrared spectroscopy analysis of the synthesized samples, with and without the compatibilizer in different proportions, were characterized by ATR-IR (Attenuated Total Reflectance-Infrared) using a Nicolet FTIR-1700 spectrometer (Thermo, USA), in the wavelength range 4000–550 cm^{-1}, with 64 scans per sample.

Mechanical Analysis. The stress-elongation tests of the obtained samples were performed using a universal machine model 33R4467 (INSTRON, USA), according to ASTM D638 (speed of 50 mm/min at 23 °C and relative humidity of 54%).

Flexural Test. The flexure tests were carried out in the INSTRON-LNMA01 equipment according to ASTM D790 (speed of 1.3 mm/min, with 50 mm of space, at 21 °C and relative humidity of 45%).

Izod Impact Test. This test was carried out in the equipment TMI-MONITOR X according to ASTM LBPN08 with a pendulum capacity of 2 FTLB. All the test specimens have a groove type "V" in the center.

Differential Scanning Calorimetry (DSC). The calorimetric analysis was performed using DSC Q200 equipment (TA instruments, USA). It was carried out with an initial heating sweep from −80 °C to 300 °C, with a ramp of 10 °C/min, followed by cooling to 30 °C with the same ramp and followed by a second cycle under the same conditions. The reported values correspond to those obtained during the second cycle, since the first cycle was used to erase the thermal history of the sample.

Proton Nuclear Magnetic Resonance (^{1}HNMR). Characterization by proton NMR was performed on a Varian Inova 400 Mhz NMR spectrophotometer (USA) in CDCl$_3$ at room temperature, using TMS as internal standard.

Scanning Electron Microscopy (SEM). The morphological analysis of the samples was carried out by SEM using a FEI Environmental Scanning Microscope, QUANTA 200 (FEI Company, USA). Prior to analysis, the samples were submerged in liquid nitrogen and then fractured. The fractured samples were fixed on an aluminum pin and covered with gold nanoparticles.

RESULTS AND DISCUSSION

Infrared Spectroscopy and H^{1}RMN Analysis
Figure 1 shows the spectra corresponding to the synthesized compatibilizer at two different PAA/SEPS ratios: 70/30 and 90/10% w/w. Regarding the IPN components, the thermoplastic elastomer exhibits the characteristic bands of C—C single bonds near to 571 cm^{-1} and aromatic ring at 733 cm^{-1}. Symmetric torque vibrations related to C—H occur at 1376 cm^{-1} and
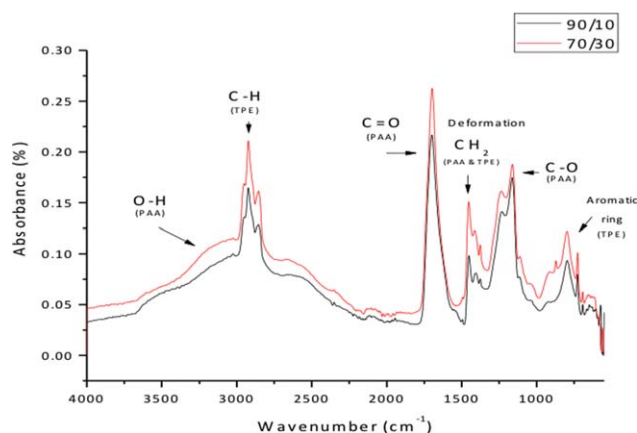
Figure 1. IR spectra of synthesized compatibilizer with different PAA/TPE ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

deformation vibrations for $>CH_2$ are shown at 1459 cm^{-1}. Finally, two bands, one at 2853 cm^{-1} and 2921 cm^{-1} for vibrations stretching of C—H appear. On the other hand, PAA exhibits the following band: at 603 cm^{-1} which is characteristic for single bonds (C—C), another at 1163 cm^{-1} corresponding to the stretching vibrations of C—O bonds, another band is observed at 1696 cm^{-1} for the carbonyl (C═O) of saturated carboxylic acids, the band at 2360 cm^{-1} from the stretching vibration (C—H) and finally a band at 2957 cm^{-1} corresponding to stretching vibrations (O—H).

The overlapping of bands corresponds to the different components of IPN that have the same wavenumber. It is important to mention that no new band in the spectrum appears, which
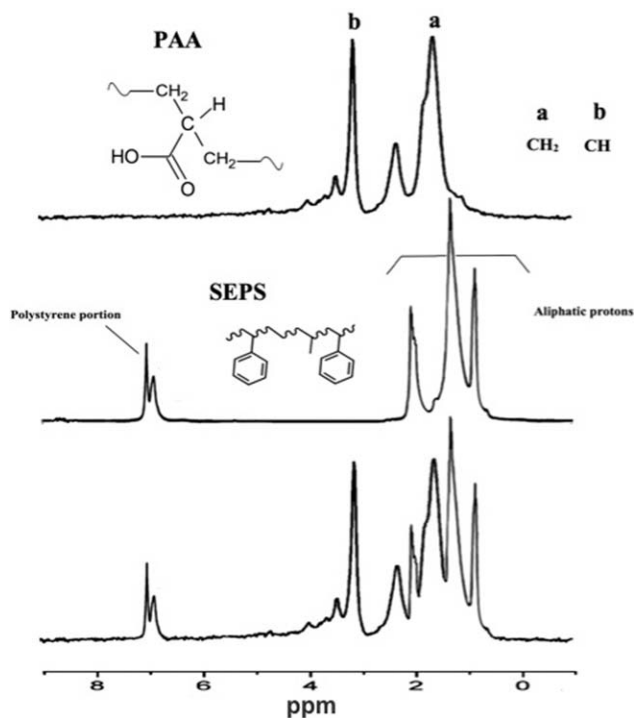
indicates that such components (PAA and SEPS) do not react chemically between them; they just interact physically. Thus, the functional groups of each component in the compatibilizer remain free and are able to interact with the functional groups of the polymer blend (LDPE and PET).

Regarding the ^{1}HRMN analysis, Figure 2 shows the spectra of PAA, SEPS, and IPN.

From Figure 2, the characteristic chemical shift of the PAA's protons assigned to —CH$_2$ and —CH— entities on the backbone at 1.1–2.1 and 2.9–3.3 ppm, respectively, can be observed. The signal of the proton in carboxyl groups cannot be detected because of chemical exchange.

The aliphatic proton signals at 0.8 and 1.2 ppm are attributed to the saturated groups (—CH$_3$ and —CH$_2$).

The ^{1}HNMR spectrum of SEPS consists of two main apex groups that appeared at (7.50–6.8) and (2.5–0.6) ppm, which correspond to the phenyl and saturated aliphatic groups, respectively.

The spectrum of IPN shows the signals corresponding to each component, PAA and SEPS, and no new signal is detected, which confirms the infrared spectroscopy results, i.e., there are no chemical reactions between such components.

In the case of PET, its FTIR spectrum shown in Figure 3 exhibits its bands at 724 and 872 cm^{-1} corresponding to the C—H bonds of the aromatic rings, at 1015 and 1092 cm^{-1} corresponding to the symmetric stretching vibrations of C—O ester bonds (—COO—), the bands at 1239 and 1341 cm^{-1} are associated with the asymmetric stretching vibration of C—O bonds. The —CH$_2$— groups appear at 1453 cm^{-1}. The bands at 1504 and 1577cm^{-1} are related to the C—C bonds of the aromatic ring. At 1714 cm^{-1} the band corresponds to the carbonyl groups ($>$C═O) of aliphatic ester symmetric vibration and at 2917 cm^{-1} to the symmetric vibration of the CH$_2$ group. Regarding LDPE, the typical bands appear between 2960 and 2850 cm^{-1} corresponding to the stretching vibrations of C—H bonds. Figure 3 also shows the FTIR spectra of the blends with

Figure 2. ^{1}H NMR spectra of PAA, SEPS, and IPN.
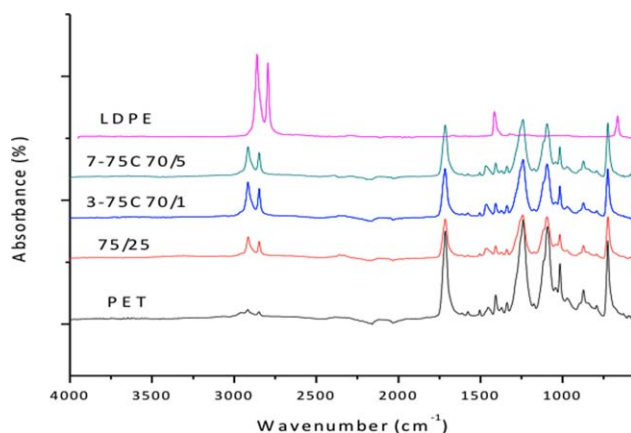
Figure 3. IR spectra of blends 3-75C70/1 (with 1% w/w compatibilizer), 7-75C70/5 (with 5% w/w compatibilizer) 75/25 (without compatibilizer), PET and LDPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
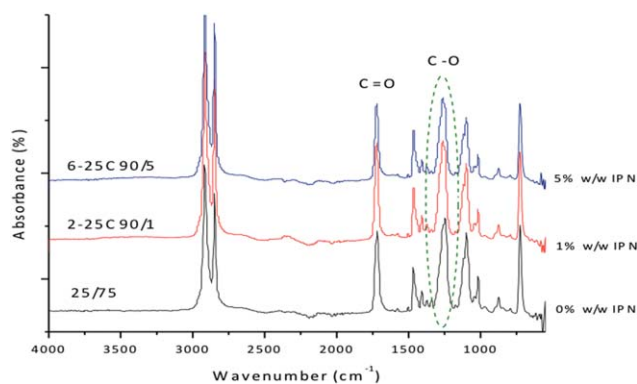
Figure 4. IR spectra of blends PET/LDPE ratio of 25/75, with compatibilizer at 1% w/w (2-25C90/1) and with compatibilizer at 5% w/w (6-25C90/5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a 75/25% w/w ratio of PET/LDPE, containing IPN with a PAA/SEPS ratio of 70/30% w/w, at two different concentrations (1 and 5% w/w) and without a compatibilizer.

As can be seen in Figure 3, the spectra show the characteristic bands for each compound of the polymer blends, with and without the compatibilizer. The lack of new bands can be observed because there is no chemical reaction between the polymers and the compatibilizer. However, secondary interactions could occur by means of hydrogen bonds, where the carbonyl functional group (C=O) and hydroxyl end groups of PET interact with the carboxylic group (—COOH) of PAA, since the carbonyl signal at 1714 cm^{-1} is slightly broader, especially with 5% w/w of compatibilizer, which is indicative of secondary interaction such as hydrogen bonding.[28] The blends having a LDPE matrix (4-25C70/1 and 8-25C70/5) using the same compatibilizer, exhibited a similar behavior in the infrared spectra.

The FTIR spectra for blends with a PET/LDPE ratio of 25/75% w/w are shown in Figure 4. The band corresponding to C—O bond, located at 1245 cm^{-1} in the noncompatibilized blend, had a shift to a higher wavenumber (1262 cm^{-1}) when the compatibilizer was added, especially for that with 5% w/w. This displacement, in accordance with Cesteros,[29] is due to the effect of the association of hydrogen bonds, which confirms secondary interactions between the compatibilizer and PET. Furthermore, the band corresponding to C=O (associated to the carboxylic and steric group of PET) at 1720 cm^{-1} and the band of C—O bonds show a slight decrease in the intensity of absorbance bands when the concentration of the compatibilizer increases; therefore, it may be due to interactions with the polymer blend and the compatibilizer.

However, this shift is only present for blends with compatibilizer that contains 90% w/w of PAA, which suggests that higher concentrations of PAA promote this type of interaction due to a higher quantity of carboxylic groups. In addition, it is worth noting that a decrease in the C=O and C—O bands' intensity could be due to trans-esterification or hydroxyl functional group substitution (O—H) present in the PAA compatibilizer and the alkoxy group (RO) ester as has been previously

reported by Lei.[10] It is important to mention that the compatibilizer is considered to act as an emulsifier in the interface,[19] thereby improving the interaction between the blend components.

Figure 5 shows possible interactions between components, LDPE, PET, and the compatibilizer. These interactions correspond to the formation of domains between the LDPE and the ethylene group of TPE while the carbonyl group of PET forms hydrogen bonds with the hydroxyl group of carboxylic group from PAA.

The interaction between the olefinic groups, —CH$_2$—, from SEPS and LDPE are of the dispersion type, even with the backbone or with the branch of LDPE. In the case of the SEPS, it must be pointed out that the saturated portion is constituted by polyethylene and polypropylene structures, since the parent elastomer portion was polyisoprene. Thus, Van der Waals interactions can take place between such saturated portion and the LDPE.

The interactions between the compatibilizer and PET occur through hydrogen bonds, as was mentioned. In this case, it is highly probable that such interactions will take place since every repetitive unit of PAA contains one carboxylic acid able to interact with the carbonyl from the ester group of the PET molecule due to the hydrogen of the pendant hydroxyl group. In addition, it could be considered that the interaction between polystyrene molecules located at both ends of SEPS and the aromatic groups of PET could take place, and it is probable to occur through dispersion interactions. Thus, the designed and synthesized compatibilizer is able to establish interactions with both plastics, PET, and polyolefin.

Mechanical Properties: Tensile-Elongation

The mechanical properties of compatibilized and noncompatibilized blends were evaluated according to ASTM D638 tests. Figure 6 shows the results of tensile for blends with a continuous phase of PET (75% w/w). The blend without compatibilizer has a greater elongation at break compared to that for pure PET. This means that at low LDPE concentrations (25% w/w) in a
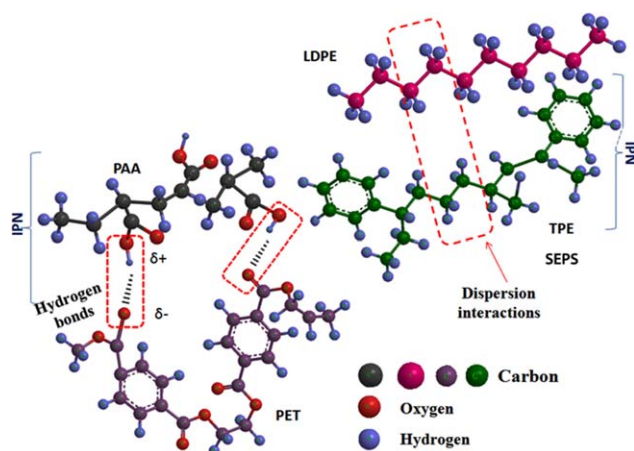
Figure 5. Interactions between the components, LDPE and PET, and compatibilizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
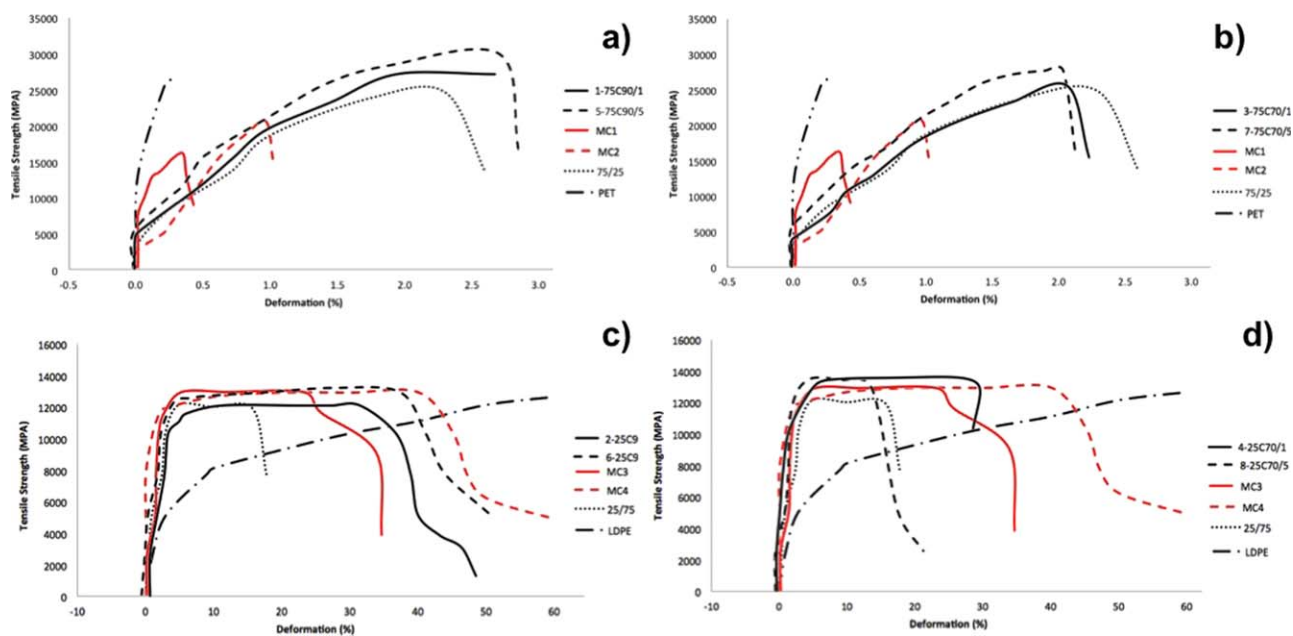
Figure 6. Tensile strength behavior of: (a) blends with PET matrix (75% w/w) and compatibilizer (with 90% w/w PAA) compared with: noncompatibilized blend, compatibilized with commercial material and pure PET, (b) blends with PET matrix (75% w/w) and compatibilizer (with 70% w/w PAA) compared with: non- compatibilized blend, compatibilized with commercial material and pure PET, (c) blends with LDPE matrix (75% w/w) and compatibilizer (with 90% w/w PAA) compared with: non-compatibilized blend, compatibilized with commercial material and pure LDPE, and (d) blends with LDPE matrix (75% w/w) and compatibilizer (with 70% w/w PAA) compared with: non-compatibilized blend, compatibilized with commercial material and pure LDPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PET matrix, an increase in the plasticity of the material takes place probably due to a plasticization effect by LDPE. However, the components in the blend will tend to separate over time, due to their incompatibility.

In the case of the compatibilized blends, 1-75C90/1 and 5-75C90/5, these showed higher elongation and tensile strength than non-compatibilized blends and blends with a commercial compatibilizer (MC1 and MC2). The highest elongation was obtained with the blend 5-75C90/5, which exhibited an elongation 24% greater than the blend without the compatibilizer due to the high concentration of PAA inside the IPN. In this blend, the IPN may act as a plasticizer and give more flexibility to the material, allowing a better interaction with PET. Thus, the tensile strength was improved. In addition, the toughness of the compatibilized blends with the synthesized IPN was higher than all the other samples, which is indicative of the better interaction between LDPE and PET, since better dispersion all along the PET matrix was achieved, as will be shown later by electronic microscopy.

From Figure 6(a), it can be seen that samples containing compatibilizer with 90% w/w of PAA exhibit a significant increase in tensile strength, between 8.7 and 12.0% higher than the non-compatibilized sample. Furthermore, it was observed that increasing the concentration of the compatibilizer in the blend gives better results due to the increase of the PAA concentration in the blend, which generates more secondary interactions with PET, achieving better interfacial adhesion.

In Figure 6(b), the compatibilized blends with IPN (70% w/w PAA content) 3-75C70/1 and 7-75C70/5 exhibited a lower elongation at break than blends 1-75C90/1 and 5-75C90/5 (with

90% w/w PAA in IPN) shown in Figure 6(a), due to an increased stiffness of the material generated by the formation of domains between LDPE with SEPS, because they are chemically akin, forming more dispersion-like interactions between the compatibilizer and the blend but also the number of interaction between PAA and PET, by their functional groups was reduced, then the plasticizer effect was slighter. The blend 3-75C70/1 (1% w/w IPN with 70% w/w PAA) had an increment of 5.9 times the Young's modulus in comparison to pure PET and 7.9 times higher than the blend without the compatibilizer. This is associated to the dispersion type interactions between SEPS with LDPE, and additionally to the affinity between the aromatic groups of PET, and those of SEPS. It is worth noting that this behavior is attributed to the interaction between the functional groups of PET and PAA, in addition to the presence of PAA, which is a rigid plastic.

Blends with commercial a compatibilizer (MC1 and MC2 samples) with a continuous PET matrix (75% w/w) have a lower performance compared to compatibilized blends with designed and synthesized IPN. This is due to the greater number of functional groups in the PAA that can interact with PET compared with the small amount of MA (1% w/w) present in the commercial compatibilizer. Thus, the quantity of functional groups present in the compatibilizer is important to improve the interfacial adhesion between the plastics to be blended. Also, it is important to have specific functional groups akin to the plastics to be blended, which was achieved with the new compatibilizer.

Figure 6(c) shows the results of mechanical testing for the continuous LDPE matrix (75% w/w) of blends with and without
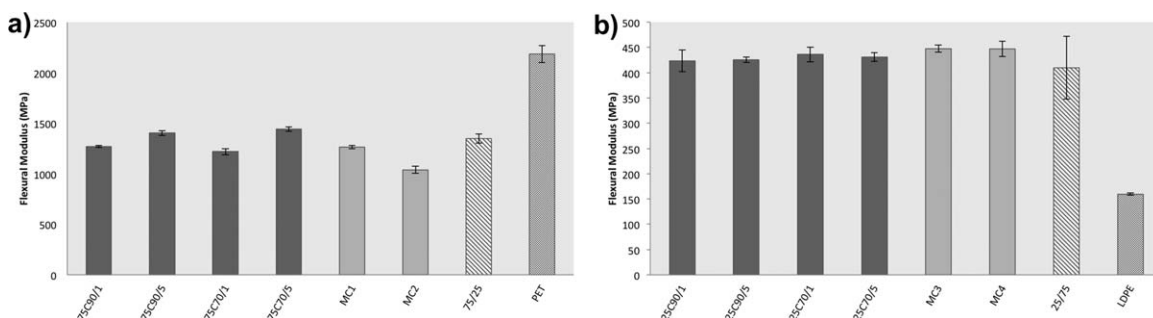
Figure 7. Flexural modulus of: (a) blends 75/25 (PET/LDPE) with and without compatibilizer and PET, and (b) blends 25/75 (PET/LDPE) with and without compatibilizer and LDPE.

the compatibilizer, blends with the commercial compatibilizer and pure LDPE. In this Figure, it can be observed that all compatibilized blends exhibit higher elongation at break than the blend without compatibilizer. Also, all the compatibilized blends exhibited higher tensile strength and higher Young's Modulus than pure LDPE. The blends with the commercial compatibilizer, MC3 and MC4, showed good performance due the higher content of polyethylene (PE) in the commercial compatibilizer (at least, 99% w/w of PE) which has a natural chemical affinity for the continuous phase of LDPE in the blend, and the grafted maleic anhydride in the commercial compatibilizer was able to interact with the PET. Thus, the elongation in the samples with commercial compatibilizer was increased when its concentration was augmented.

The blend containing the new synthesized compatibilizer, 6-25C90/5, showed the highest elongation at break (3.3 times higher than the blend without compatibilizer). This is due to a good interaction between the components, particularly between the PAA and PET. The increase of the IPN compatibilizer concentration to 5% w/w generated more interactions between the components producing an increment in the elongation at break of this blend (with 5% w/w of IPN) compared to the blend with 1% w/w. Note that all blends had less elongation compared to pure LDPE sample, due to the presence of rigid material like PET in the blend. Furthermore, the LDPE has the ability to reorient polymer chains during tensile stress, but in the case of blends with PET this characteristic is limited.

The mechanical behavior for compatibilized blends, with 70% w/w of PAA in IPN, is shown in Figure 6(d). The addition of 25% w/w PET to LDPE matrix leads to an increased stiffness, which is reflected by an increment of the Young's modulus. The IPN-compatibilized blends have higher elastic modulus regarding to the blend without compatibilizer. However, the blends with commercial compatibilizer showed higher elongation at break that the blends with IPN (70% w/w PAA). Thus, it is assumed that reduction of PAA concentration reduces the interaction with PET and its dispersion into the LDPE matrix was deficient.

In this case, and even when the SEPS concentration in the IPN-based compatibilizer was higher and, therefore, a better interaction with the LDPE was expected, blends with such compatibilizer showed lower elongation at break than the blends with commercial compatibilizer.

Such results confirm how important it is not only to consider the interaction between functional groups of polymers, but also the quantity of each component in the compatibilization of plastics.

**Mechanical Properties: Flexion**
Figure 7(a) shows the flexion test results for the different obtained blends. It can be seen that compatibilized blends with 5% w/w of IPN exhibit a higher flexural modulus (10 and 14% for 90% and 70% PAA, respectively) regarding the blend without compatibilizer. Thus, the compatibilizer gives better interaction between the plastics, LDPE and PET. All the blends had lower flexural modulus than PET due to presence of LDPE. In the case of the blends obtained with the commercial compatibilizer, they showed a lower modulus in contrast with the blends containing the IPN, especially for those containing 5% w/w. This is because the quantity of SEPS in the IPN has an elastomeric portion, which can give enough flexibility to blends and disperse the flexural stress.

In the case of blends with 75% w/w of LDPE, the compatibilized blends show an increment of 17.7 to 30 MPa compared to blends without IPN and pure LDPE, respectively [Figure 7(b)]. This is because the dispersed phase of PET in the blend and the effect of IPN provide greater stiffness to final material, and therefore more energy is required to bend the sample. In the case of blends with commercial compatibilizers, these showed a slight higher flexural modulus regarding to the samples containing IPN. This behavior is due to the polymeric matrix of commercial compatibilizer is more akin to the LDPE continuous phase.

Mechanical Properties: Izod Impact
The impact test results are shown in Figure 8. It can be seen in Figure 8(a) that the resistance of compatibilized blends with the PET continuous phase is better than that of blends without compatibilizer, and also better than that of blends with commercial compatibilizer.

The blends with 90% of PAA, in the IPN, have better impact resistance than blends without compatibilizer due to the interaction of the functional groups between PET and PAA. Furthermore, the compatibilizer (90/10) acts as a plasticizer giving the blend greater ability to dissipate energy, hence the blend has a toughening effect improving impact resistance. In the case of the blend with 70% w/w of PAA into the IPN (third bar) a
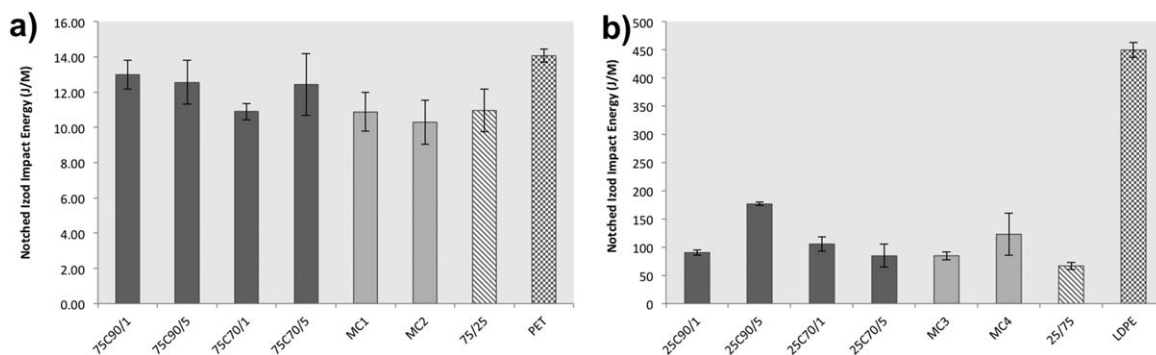
Figure 8. Impact resistance of: (a) blends 75/25 (PET/LDPE) with and without compatibilizer and PET, and (b) blends 25/75 (PET/LDPE) with and without compatibilizer and LDPE.

decrement in the impact resistance can be seen since it has only 1% of IPN and such quantity could be insufficient to provide enough toughness to material. However, when compatibilizer content was increased from 1 to 5% (fourth bar) the blend shows an improvement in impact resistance. Blends with the commercial compatibilizer show lower impact resistance regarding the sample without compatibilizer, which indicates and confirms that the interaction of its chemical structure with that of PET is not good enough.

For the blends with an LDPE continuous phase, the Izod impact results are shown in Figure 8(b).

All blends compatibilized with IPN show higher impact resistance compared with the blend without compatibilizer (25/75), especially blend 25C90/5, which had a 133% increment. For the samples containing the commercial compatibilizer, these have higher impact resistance than samples without compatibilizer, especially those with 5% compatibilizer, although it has lower impact resistance than the corresponding sample with the same quantity of the synthesized compatibilizer (25C90/5). Such results confirm that mechanical behavior of the samples depends on the quantity of compatibilizer and also on its chemical structure and relative amount of its components.

Differential Scanning Calorimetry (DSC)
The interpenetrated polymer network (IPN) with two PAA/TPE ratios (70/30 and 90/10% w/w) was evaluated by thermal analysis. Figure 9 shows that the glass transition temperature (T_g) for the SEPS remains at same value ($-58 \pm 1\,^{\circ}$C) in both types of

compatibilizer, which corresponds to the T_g of the elastomeric portion, and the T_g corresponding to the plastic portion (polystyrene) was not detected due to its relatively low concentration. However, for the case of PAA, there is a shift in T_g for both types of IPN (70/30 and 90/10% w/w PAA/SEPS) of approximately 32 $^{\circ}$C above the corresponding value of pure polymer, which is indicative of the intimal interaction between both polymers.

Considering the Free-Volume Theory established by Eyring,[30] where the molecular motion in the bulk state depends on the presence of holes, or places, where there are vacancies or voids, the PAA has fewer empty spaces due to the presence of TPE, and the movement of the PAA polymer segments is restricted and thus its T_g increases. The change of T_g is reflected only in the PAA due to the molecular weight difference (M_n) between both polymers, while the molecular weight of PAA is about 20,000 g/mol and the molecular weight of SEPS is about 150,000 g/mol. Therefore, the PAA mobility in the IPN is limited due to the presence of the SEPS which is much more voluminous and have longer polymeric chains.

The percentage of crystallinity (χ_c) for LDPE and PET was calculated according to eq. (1) shown as follows[19]:

$$\chi_C(\text{wt } \%)=100\times\frac{\Delta H_m}{\Delta H_m^{\circ}} \qquad (1)$$

where ΔH_m° for crystalline PET is 119.8 J/g and ΔH_m° for LDPE is 293.0 J/g.[13]
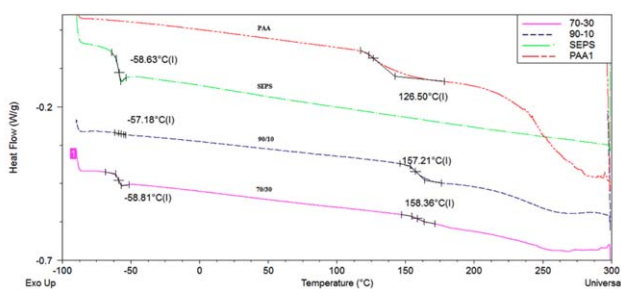
Figure 9. DSC analysis of the IPN at two proportions (70/30 and 90/10 wt %) and their components (PAA and SEPS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
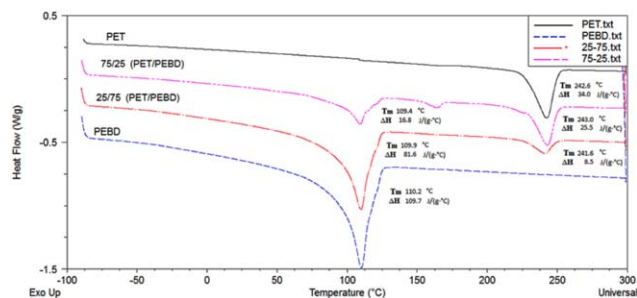
Figure 10. Calorimetric analysis of blends without compatibilizer, PET, and LDPE alone. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermal Properties of the Blends PET/LDPE (75/25% w/w), with and without Compatibilizer

	LDPE			PET		
Blends	T_m °C	ΔH_m J/(g·°C)	% crystallinity	T_m °C	ΔH_m J/(g·°C)	% crystallinity
PET	–	–	–	242.6	34.0	28.4
LDPE	110.2	109.7	37.4	–	–	–
75/25	109.4	16.8	5.7	243.0	25.5	21.3
1-75C90/1	108.9	55.1	18.8	243.8	40.3	33.7
5-75C90/5	108.4	30.6	10.4	242.4	24.9	20.8
3-75C70/1	109.1	48.6	16.6	243.2	32.6	27.2
7-75C70/5	108.4	25.8	8.8	242.7	25.6	21.4

At a heating rate of 10 °C/min, the PET exhibited a melting temperature (T_m) of 242.6 °C and for LDPE the melting temperature was detected at 110.2 °C (Figure 10).

The melting temperatures for noncompatibilized blends 75/25 and 25/75% w/w (PET/LDPE) were very close to the T_m of pure components, i.e., no significant changes occurred due to the incompatibility of components and then the thermal behavior of such blends corresponds to that of the pure components. Table II shows the values of the melting temperatures (T_m), the melting enthalpy (ΔH_m) and the percentage of crystallinity (χ_c) of blends with continuous phase of PET, with and without compatibilizer, as well as for the components blends.

The blend 3-75C70/1 has two T_m due to its two components, LDPE and PET [Figure 11(a)]. The T_m of LDPE decreased 1 °C by the addition of compatibilizer and exhibits another melting transition at 118.6 °C which may represent a change in the regular structure of the blend due to compatibilizer presence, which could be acting as a nucleation agent and thus the crystallinity % of such blend for the polyolefins portion is higher than the noncompatibilized blend, even when the concentration of the compatibilizer was increased to 5% w/w. Such behavior was also observed for the PET portion, which had higher crystallinity % regarding the noncompatibilized blend (see rows 4 and 3, respectively). Nevertheless, the T_m of PET in the blend did not change considerably. Furthermore, the blend 7 (75/25% w/w PET/LDPE) with 5% w/w of compatibilizer (70/10% w/w PAA/TPE) have a slight decrement of T_m and melting enthalpy (ΔH_m) of the LDPE, as consequence of interactions between the PET and LDPE.[18]

The crystallinity of the LDPE phase was increased with the addition of 1% w/w of compatibilizer for both types. However, in the case of higher compatibilizer content (5% w/w) a reduction of the crystallinity of LDPE takes place. These results are similar to those obtained by Pracella[7] for blends 75/25% w/w (PET/HDPE) using E-GMA, E-AA, and HDPE-g-MA as compatibilizers. Both behaviors for the continuous phase of PET, which may be affected by the presence of the compatibilizer and the content of functional groups resulting in reduced mobility of the chains, are similar. The interaction between functional groups reduces the flexibility of the chain, and stereoregularity destroys symmetry and decreases the crystallinity of PET. Additionally, there was a decrement of the size of the dispersed particles of LDPE (shown later in the microscopy section), and the compatibilizing effect in the crystallization of PET becomes more pronounced. The ΔH_m in all compatibilized blends was modified, in contrast to the non-compatibilized blends, by the presence of the compatibilizer due to suitable interaction with the two polymers in the blend.

Similar behavior is observed for the case of the PET continuous phase where mainly ΔH_m decreased when concentration of compatibilizer was increased, which is due to the effect of the compatibilizer that is miscible with LDPE phase and exhibits chemical interactions with the functional groups of the PET chain.[18]
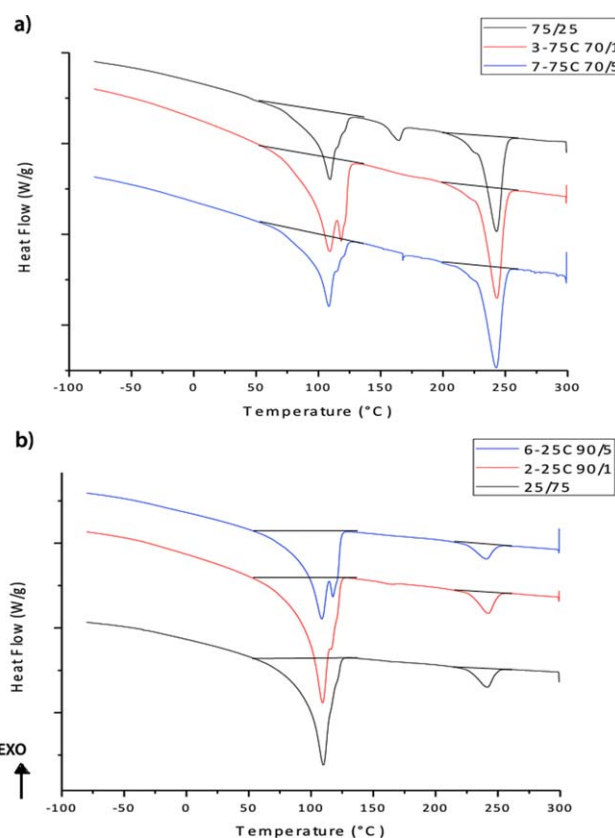
Figure 11. Thermograms of (a) the compatibilized blends PET/LDPE, 75/25% w/w, and blend without compatibilizer and (b) the compatibilized blends PET/LDPE, 25/75% w/w, and blend without compatibilizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Properties of PET/LDPE Blends (25/75% w/w) With and Without Compatibilizer

| Blends	LDPE			PET		
	T_m °C	ΔH_m J/g	% Crystallinity	T_m °C	ΔH_m J/g	% Crystallinity
PET				242.6	34.0	28.4
LDPE	110.2	109.7	37.4			
25/75	109.9	81.6	27.9	241.6	8.5	7.1
2-25C90/1	109.4	109.4	37.3	242.3	10.5	8.8
6-25C90/5	108.8	84.2	28.7	240.8	7.2	6.1
4-25C70/1	110.4	118.5	40.4	243.2	12.1	10.1
8-25C70/5	108.6	80.0	27.3	240.4	9.0	7.5

For blends with LDPE continuous phase, the observed T_m for the two components that form the polymer blend, are presented in Table III.

The melting enthalpy (ΔH_m) and the percentage of crystallinity (χ_c) for the LDPE decreased when PET is added to the blend without compatibilizer, but with the addition of 1% w/w of compatibilizer, either with 70 or 90% w/w PAA, the crystallinity was increased up to and higher than the percentage of the pure LDPE. The crystallinity of LDPE increased because the compatibilizer may be acting as a nucleating agent facilitating and promoting the crystallization of LDPE.[18]
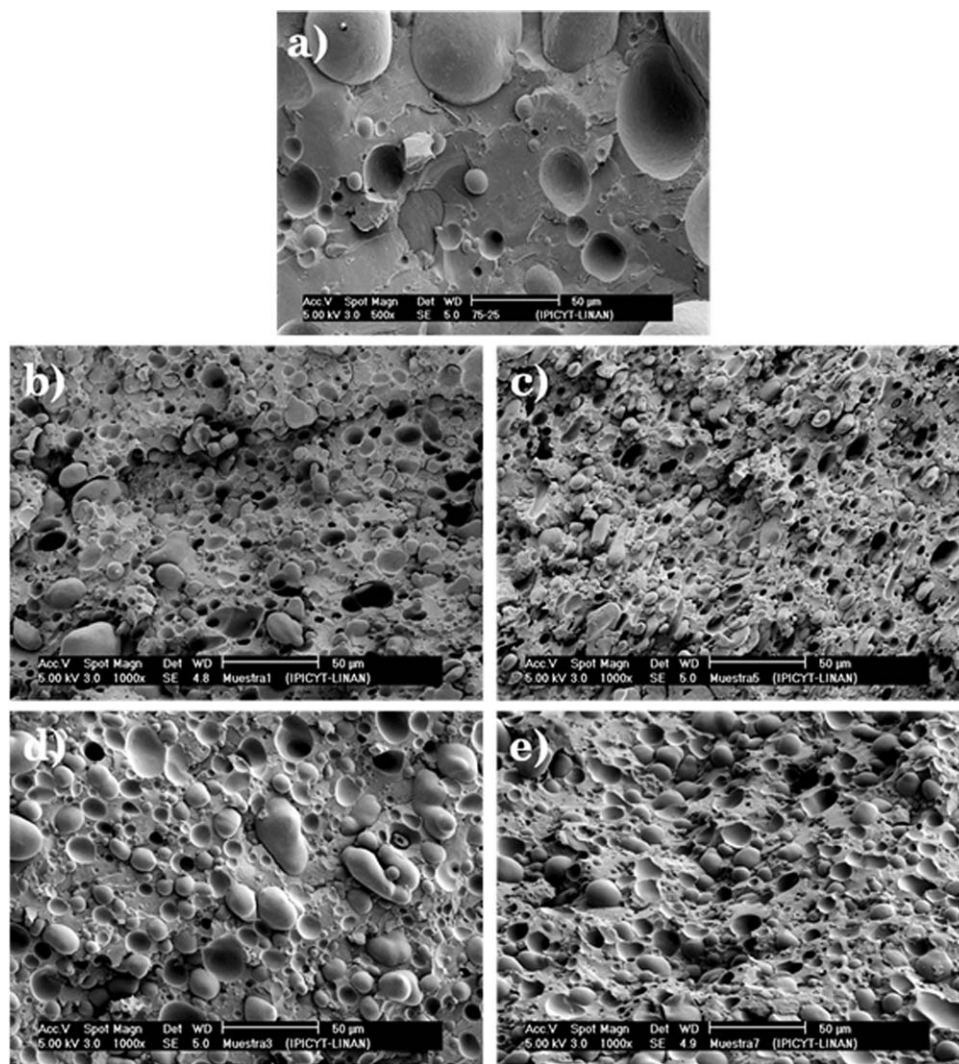
Figure 12. Micrographs at 1000× magnification: (a) Blend 75/25 (PET/LDPE) without compatibilizer, (b) compatibilized blend: 1-75C90/1, (c) compatibilized blend: 5-75C90/5, (d) compatibilized blend: 3-75C70/1, (e) compatibilized blend: 7-75C70/5.
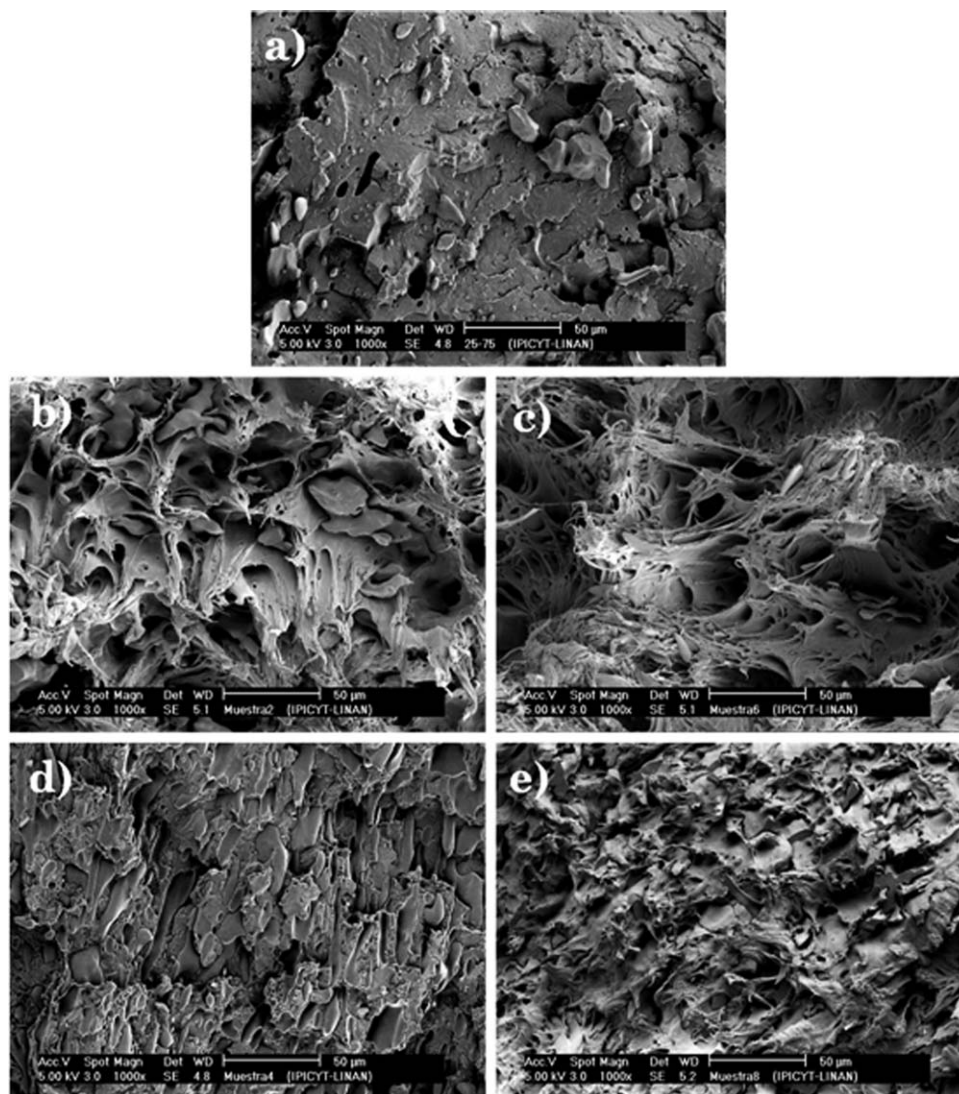
Figure 13. SEM images at 1000× magnification: (a) Blend 25/75 (PET/LDPE) without compatibilizer, b) Compatibilized blend: 2-25C90/1, (c) Compatibilized blend: 6-25C90/5, (d) Compatibilized blend: 4-25C70/1 and (e) Compatibilized blend: 8-25C70/5.

On the other hand, when the concentration of compatibilizer was increased up to 5% w/w there was a decrement in the percentage of crystallinity of LDPE matrix [Figure 11(b)]. This is because there was a greater amount of compatibilizer that interacts at the interface of the blend, which decreases the degree of perfection of the crystals of LDPE.

Another indication of the compatibility of the polymer blend by action of the compatibilizer is the presence of double melting peaks (thermograms not shown), which are the same that with those reported by Mbarek.[31] When the mass of the crystallizable polymer is dispersed into small particles by the action of the compatibilizer in an immiscible matrix, a fractional crystallization phenomenon is generated.

Scanning Electron Microscopy (SEM)

The obtained blends were analyzed by scanning electron microscopy (SEM) to observe its morphology. In order to determine the particle diameter of the dispersed phase, between 50 and 100 particles were considered. The number average (D_n) and

weight average diameters (D_w) and polydispersity index (PDI) were determined using the following equations[25]:

$$Dn = \frac{\sum N_i D_i}{\sum N_i} \tag{2}$$

$$Dw = \frac{\sum N_i D_{i^2}}{\sum N_i D_i} \tag{3}$$

$$PDI = \frac{D_w}{D_n} \tag{4}$$

Figure 12 shows the representative micrographs for the blends with the continuous phase of PET and dispersed phase of LDPE, with and without compatibilizer.

As it can be seen in the image corresponding to the specimen without compatibilizer [Figure 12(a)] the interaction of the matrix with the dispersed phase is minimal, there is a kind of space around the PET particle. The average particle size is 29 μm, and has low interfacial adhesion. The large particle size and lack of adhesion between the matrix and the dispersed phase

confirms the incompatibility of the components.[19] Figure 12(b) corresponding to the blend with 1% w/w of compatibilizer with a PAA/TPE ratio of 90/10% w/w, shows a clear particle size decrement (from 29 to 7 μm) of the dispersed phase in the matrix of PET, which is due to a better interaction between the blend components. Thus, a small amount of compatibilizer is enough to obtain a substantial decrease in average particle size and improve the interfacial adhesion. Figure 12(c) corresponding to the compatibilized blend with 5% w/w of compatibilizer clearly shows the LDPE particles dispersed inside the matrix of PET, which has an improved interfacial adhesion and interfacial interaction in contrast to the non-compatibilized blend. However, the average size of the domain of LDPE was 12 μm, a size which is greater than that observed in the blend with 1% w/w compatibilizer, which, according to mechanical and thermal tests shows to be an adequate amount to improve continuity of the blend. For the images of Figures 12(d) and (e), with 1 and 5% w/w of IPN-based compatibilizer (PAA/TPE ratio of 70/30% w/w), the average particle size was 10 and 8 μm, respectively, which means that particle size decreases as higher amount of compatibilizer is added. However, the average diameter is greater than that obtained with the IPN-based compatibilizer having a PAA/SEPS ratio of 90/10, with only 1% w/w of this present in the blend, which shows and confirms that for the blends with the PET matrix, interactions are greater when there is more PAA in the IPN.

Furthermore, Figure 13 shows the micrographs of the blends with LDPE continuous phase with and without compatibilizer. In image 13-a, corresponding to the blend without compatibilizer, a clear vitreous break occurs due to low interfacial interaction between the polymers of the blend, confirming poor compatibility of the dispersed phase of PET in the matrix of LDPE. In contrast, the compatibilized blends with 1 and 5% w/w of compatibilizer (PAA/SEPS ratio of 90/10% w/w) are shown in images 13-b and 13-c, respectively. These figures exhibit a marked change in the morphology, which is more homogeneous and nonspherical and fibrous type morphology is obtained. This can be related with mechanical behavior, in fact, for these blends higher tensile strength are obtained due to plastic behavior by the addition of the compatibilizer.

Comparing the images of the compatibilized blends with the compatibilizer, with 90 and 70% w/w of PAA, it is confirmed that a higher amount of PAA in the compatibilizer gives a plasticization effect and fibrous-like morphology. In addition, the concentration increment of compatibilizer in the blend gives a higher interaction between dispersed and continuous phases. Moreover, the images of Figure 13(d) and (e), corresponding to compatibilizer with 70% w/w of PAA, showed a more rigid structure. In fact, when concentration of the compatibilizer was increased it showed a great improvement on the morphology of the phases as well as a marked reduction in interfacial tension, in comparison with the noncompatibilized blend, containing only 1% w/w of compatibilizer [Figure 13(d)] confirming its favorable effect on the blend. The PET exhibits good dispersion in the phase LDPE matrix, since the particle sizes are smaller. The reduction in particle size dispersed in the presence of com-

patibilizer is related to the decrease of interfacial tension and coalescence suppression, which depends on the amount of compatibilizer in the blend, as it has been previously mentioned by others researchers.[7]

CONCLUSIONS

A new compatibilizer based on interpenetrated polymer network (IPN) was synthesized and it improves the thermal and mechanical behavior of recycled PET/LDPE blends.

In addition, the new synthesized compatibilizer can act as a plasticizer in the blend of PET and LDPE and also improves the interfacial adhesion between them, modifying the morphology of blends.

This new synthesized compatibilizer is quite different to those reported in the literature, and opens the possibility of improving the compatibilization of waste plastics to provide materials which are able to be used again by reducing their degradation. Such compatibilized recycled plastics showed good mechanical properties, as a consequence of the new compatibilizer presence, being materials that offer higher tensile strength, higher elongation at break, higher flexural modulus and better impact resistance, that could be used for different purposes.

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