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Characterization of PET/LLDPE blends compatibilized with DEM-grafted-polyethylene

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Summary

Polyethylene terephtalate (PET)/linear low density polyethylene (LLDPE) blends compatibilized with diethylmaleate grafted polyethylene (DEM-g-LLDPE) were characterized by FTIR spectroscopy, thermogravimetrical analysis (TGA) and scanning electron microscopy (SEM). FTIR and TGA results indicate that there are interactions between the components of the blends, which produced variations in the infrared bands associated with the conformational changes (from gauche to trans) within the glycolic sequences of the polyester and a sinergistic effect on the thermal-oxidative stability of the compatibilized blends. Morphological analysis showed a dispersed particle size reduction and a better adhesion between the matrix and the disperse phase.

Introduction

When incompatible thermoplastic polymers such as polyolefins and polyesters are mixed, the interfacial adhesion is weak resulting in lower mechanical properties and poor dispersion of the components (1). In many cases, a third component has been added to improve the compatibility (2), i.e. to achieve satisfactory interfacial adhesion and interfacial stress transfer between the phases. One alternative uses a chemically modified material as the third component: Xantos *et.al* (3) and P. Bataille *et.al* (4) had employed acrylic acid-functionalized-PP as a compatibilizer for PP/PET blends; Carté and Moet (5) blended PET and HDPE with maleic anhidride-grafted-SEBS; Dagli and Kamdar (6) also blended PET/HDPE with an ethylene-diglycilmethacrilate copolymer and Jabarin *et.al* (7) studied blends of PET/HDPE compatibilized with components containing maleate groups.

Blends of polyolefin with polyesters are a versatile alternative to the development of materials that combine the intrinsic properties of each component. Specifically, PET has high module, high melting point, good chemical resistance and high impact strength. LLDPE has high break elongation, good processability and low moisture absorption.

Our study focuses on intermolecular interactions between PET/LLDPE with diethylmaleate-grafted-LLDPE (DEM-g-LLDPE) as a compatibilizer through FTIR spectroscopy, thermogravimetric analysis and scanning electron microscopy.

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Experimental

Blends based on PET (Kodapak 7352 from Eastman Chemical), and LLDPE (Sclair 11D1 from Dupont) -see Table 1- using two DEM-g-LLDPEs with different grafting degrees as a compatibilizer were prepared.

Compatibilizers were obtained by the functionalization of LLDPE with DEM (diethylmaleate), in solution under two different conditions (see Table 2), as previously described by Rojas *et al* (8).

Table 1. Characteristics of the pure polymers.

Polymer	Mn (g/mol)	Mw (g/mol)	Tm (°C)	MFI (g/10min)
LLDPE	29000	135000	116	0.6
PET	23000	46000	243	-

Table 2. Functionalization conditions of the LLDPE.

Condition	T(°C)	t(min)	DEM(%)[(a)]	(I)[(b)]
C1	140	45	20	0.5
C2	160	45	20	2.0

[(a)] With respect to LLDPE [(b)] ml/100g LLDPE

The obtained grafting degrees were 0.03 (C1) and 0.3 (C2) molar percentage of polar groups per ethylene unit measured through an FTIR-^{1}HNMR calibration curve. The melt flow was difficult to measure because the grafted polymer degraded during the test. Based on previous work (9), it was assumed that the average molecular weight and the polydispersity do not change after functionalization.

The polyester and DEM-g-LLDPEs were dried in a vacuum oven. The components were mixed in a Haake Rheometer at 260°C and 60 rpm. The polyethylene phase in each blend was constituted by a 12% of the compatibilizer and 88% of pure LLDPE. Blends without the compatibilizer were also prepared.

The samples for the IR analysis were prepared by the conventional method of pressing into a KBr matrix. Spectra were recorded using a Nicolet Magna 550 FTIR spectrometer with a KBr beamsplitter and a DTGS KBr detector. For each spectrum, a resolution of 4 cm^{-1} was used and 32 scans were signal averaged. The carbonyl absorption region, the methylene rocking region (900-1000 cm^{-1}) and the methylene bending region (1300-1550 cm^{-1}) were analyzed in order to determine the conformational changes in the glycolic segments of the polyester which could be produced by intermolecular interaction between the components.

TGA curves were obtained using a Polymer Labs STA 625 Simultaneous Thermal Analyzer. Samples were scanned at 10°C/min, at a temperature range between 50 and 600°C, under non-controlled atmosphere. The temperature required by each sample to lose 10% of its initial weight ($T_{10\%}$) was obtained from TGA curves. Theoretical curves were constructed in order to compare them with the experimental curves.

In order to perform morphological analysis, each sample was fractured under liquid nitrogen and gold-sputtered before viewing in a Scanning Electron Microscope (Phillips 505).

Results and Discussion

Analysis of the FTIR spectra shows two important changes in the carbonyl absorption band and in the absorption bands related to the glycolic residue. The FTIR spectra of pure PET and two PET-rich blends (with C2) between 1800-800 cm^{-1} are shown in Fig.1. The carbonyl band at 1740 cm^{-1} associated with the stretching of the carbonyl within the ester group in the functionalized polymer disappeared in the presence of the polyester. In addition, the width of the carbonyl band at 1720 cm^{-1} increased with the presence and content of the compatibilizer. As previously reported by Benedetti *et al* (2), mixing of DEM functionalized polyolefins with polar polymers could give rise to a shift of the carbonyl band of the ester groups towards lower frequencies with a simultaneous broadening of the band itself.

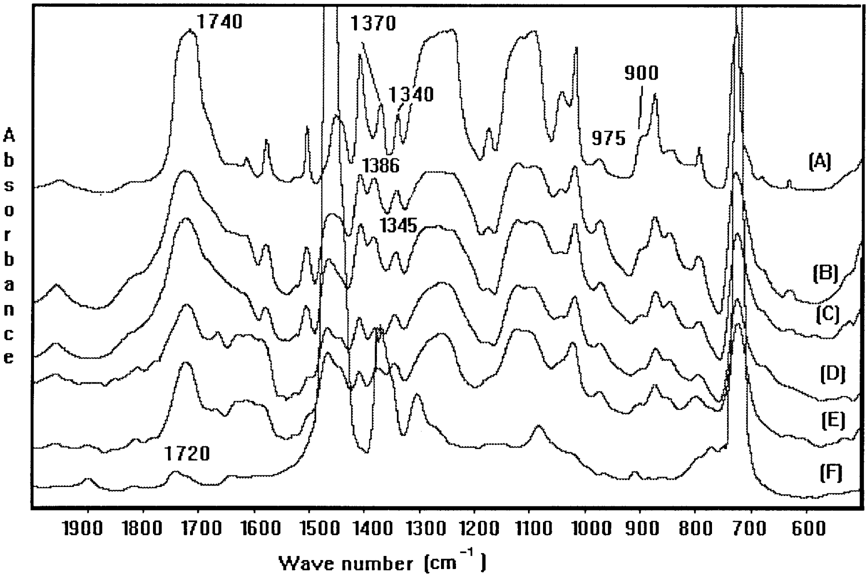

Figure 1. FTIR spectra between 1800-700 cm^{-1} for: (A) 100/0/0; (B) 90/8.8/1.2; (C) 60/35.2/4.8; (D) 40/52.8/7.2; (E) 10/79.2/10.8 y (F) 0/100/0 PET/LLDPE/DEM-g-LLDPE blends.

On the other hand, the spectral bands related to conformations of the glycolic sequences within the polyester chains, at 1340 and 975 cm^{-1} (attributed to the vibration of the trans conformations), and at 1370 and 900 cm^{-1} (associated with the gauche ethylene glycol conformations), showed some variations in intensity. The intensity ratio of the 1370 cm^{-1} band to 1340 cm^{-1} band decreased from 1.22 for PET to 1.15 for 90/8.8/1.2 composition. In the same way, the relative intensity of the 900 cm^{-1} band to the 975 cm^{-1} band decreased with the compatibilizer content. According to these results, the gauche conformations are changing to trans conformations. This behaviour could be attributed to the interaction between the polyester and the functionalized polyethylene. Figure 2 shows a model of the trans and gauche conformations for the PET/LLDPE/DEM-g-LLDPE system; we can see that the steric hindrance in the gauche conformation forces the molecule to adopt the trans conformation when the interaction occurs.

Additionally, for PET-based blends, there were slight band displacements from 1370 cm^{-1} towards 1386 cm^{-1} and from 1340 cm^{-1} to 1345 cm^{-1}, possibly caused by the presence of the grafted polyolefin. These results could indicate that changes in the carbonyl bands might be attributed to interchange reactions between the ester groups from DEM and -OH, -COOH or ester groups in the polyester main chain. Similar results were reported by Porter and Wang (10) on a review of compatibilization through transesterification reactions. It was found that the occurrence of these reactions produced band broadening and shifted to lower frequencies of the carbonyl band at about 1740 cm^{-1}. Therefore, this could account for the changes in conformation due to these reactions.

Evidences of molecular interactions can be also observed by thermogravimetric analysis. TGA curves in Figures 3, 4 and 5 show the thermal-oxidative stability of the neat polymers and their blends, and the $T_{10\%}$ for each polymer that is a qualitative measurement of the initiation of the degradation process.

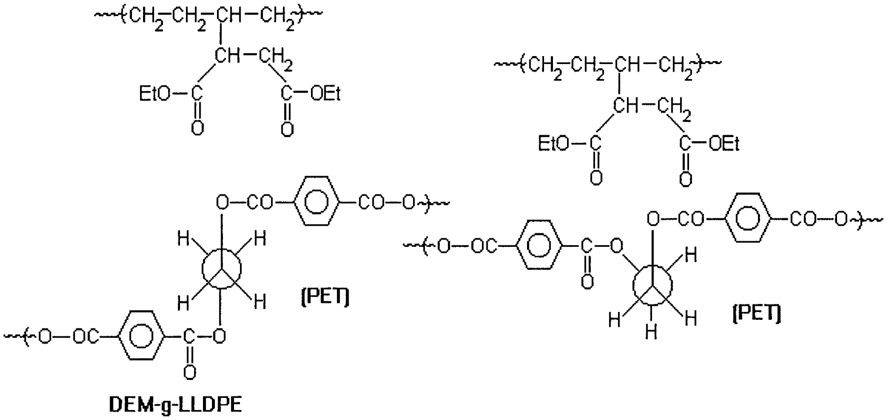

Figure 2. Model of the trans and gauche conformation of the ethylene glycol segments within the polyester chains.

Fig. 3 shows that PET has more thermal stability than LLDPE, and as expected, the chemical modificacion, i.e. the grafting of functional groups into LLDPE, produced significant effects on the thermal stability of the neat polyolefin. Increase in the grafting degree induces a decrease in the thermal stability in the presence of oxygen. From the TGA curve for the higher grafted polymer, it is observed that there is a small weight loss (<10%) at 121-200°C. The observed weight loss can probably be related to the elimination of inserted units as diethyl succinate with the formation of double bonds on the main chain.

The degradations of LLDPE and the modified polyolefin are not a single decomposition process but seem to follow a more complex degradation pattern. According to Hinsken *et al* (11) degradation of PE generally leads to the formation of crosslinking and branched chains that compete with the backbone cleavage reactions. The introduction of functional groups in the PE backbone increases the amount of tertiary carbons that could induce chain scission instead of crosslinking. When the grafting degree increased, it was more difficult to differentiate more than one stage in the TGA curves. This might be due to the generation of a higher amount of intermediate degradation products which follow their degradative propagation as the temperature is increased.

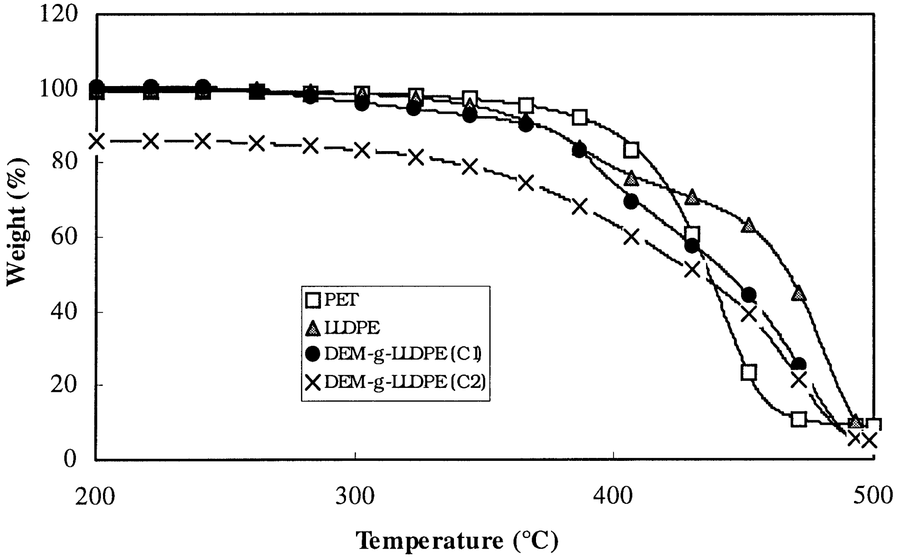

Figure 3. TGA curves at 10°C/min for the neat polymers and the compatibilizers. The $T_{10\%}$ for PET was 394°C, for LLDPE, 373°C, and for C1 and C2, 365 and 354°C respectively.

Figure 4 and 5 show the thermal behaviour of blends. The presence of the compatibilizer (DEM-g-LLDPE) seems to increase the blend stability independently of the grafting degree (as seen in Fig.4). This could indicate the presence of interactions within the system that can reduce the amount of sites prone to the initiation of the thermal-oxidative degradation.

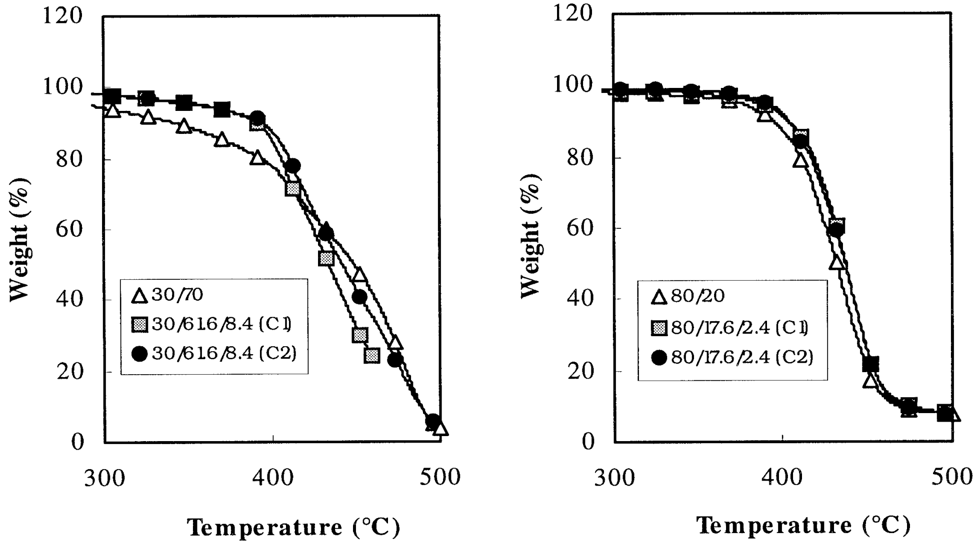

Figure 4. TGA curves at 10°C/min for PET/LLDPE/DEM-g-LLDPE blends. The $T_{10\%}$ values obtained from TGA curves were: 394°C (80/20) and 403°C (80/17.6/2.4, with C1 and C2); 342°C (30/70) and 392°C (30/61.6/8.4, with C1 and C2).

Figure 5 shows that the experimental curves for PET-rich and PET-non rich blends (with C2) are above the theoretical curves. This synergistic effect could be attributed to the interaction between the components. Effects of phase interaction on the thermal stability of blends have also been reported by Müller *et al* (12) on Nylon 6 with functional polymers and by McNeill *et al* (13), on blends of ethylene-ethyl-acrylate copolymer with polydimethylsiloxane. In general, blends were more thermally stable than both pure polymers.

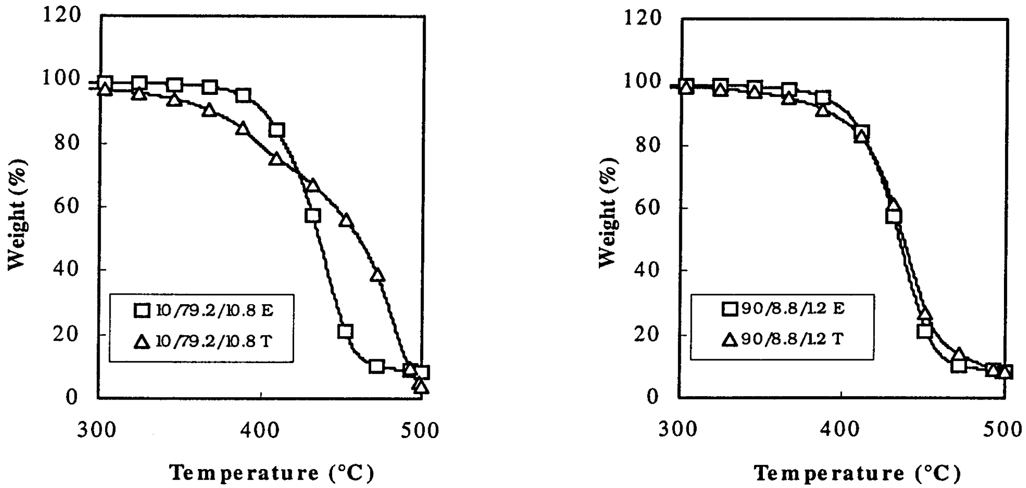

Figure 5. TGA experimental (E) and theoretical (T) curves at 10°C/min for PET/LLDPE/DEM-g-LLDPE blends (with C2).

Morphological evidences of compatibilization in similar systems have been reported in the literature (5,14,15); SEM micrographs (see Fig.6) show that there was a particle size reduction within the disperse phase of the blends and a better adhesion between dispersed particles and the matrix with the presence of the compatibilizer.

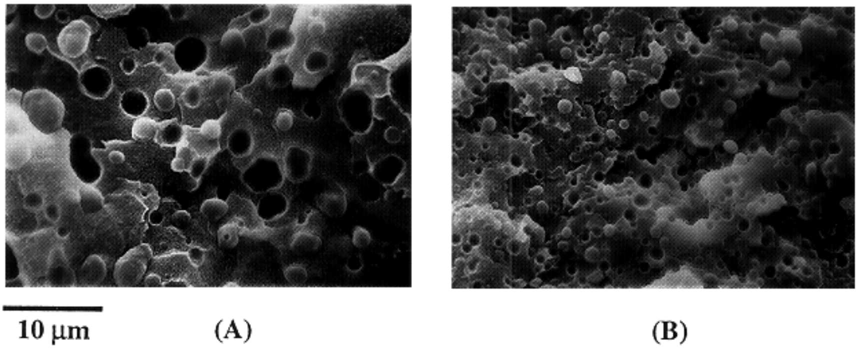

Figure 6. SEM micrographs of blends containing 70 % of PET in LLDPE without (A) and with compatibilizer (B).

Figure 7 shows the micrographs of 50/50 blends with and without the compatibilizer where a continuous structure can be observed. The non-reactive blend shows some macrodomains and the reactive blend shows a more homogeneous morphology. To verify the adhesion between phases, a non-cryogenically fractured sample of the 50/44/6 blend (with C2) was observed (see Fig. 8). It revealed a distinguished morphology of the deformed olefinic phase and the adherence between the two polymers phases.

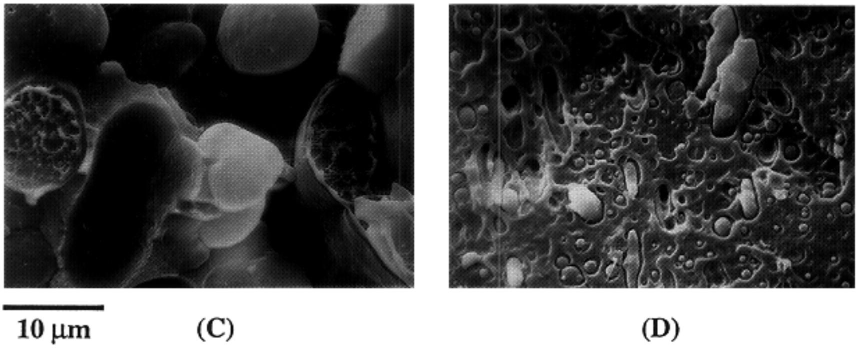

Figure 7. SEM micrographs of blends containing 50 % of PET in LLDPE without (C) and with compatibilizer (D).

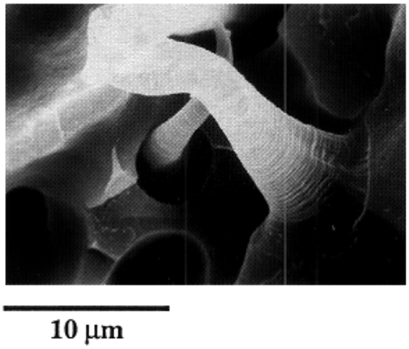

Figure 8. SEM micrographs of blends containing 50 % of PET in LLDPE with compatibilizer C2 non-cryogenically fractured sample.

Conclusions

The compatibilizer promotes interactions between homopolymers; these interactions depend on the grafting degree of the compatibilizers. FTIR results showed that there have been interactions between PET's ester groups and DEM's ester groups grafted to LLDPE. The thermo-oxidative results indicate there is a synergistic effect on the thermo-oxidative stability of PEL/LLDPE blends compatibilized with DEM-g-LLDPE, which might be due to the intermolecular interactions within the system; this effect can be obtained by the addition of the compatibilizer with the lower grafting degree. SEM results pointed out that the compatibilizer agent is a modifier of the interfacial activity; interactions cause a finer and more homogeneous morphology and a reduction in the particle size of the disperse phase. The adherence between phases is good and directly related to the amount of compatibilizer in blends.

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