

# Compatibilizers Based on Polypropylene Grafted With Itaconic Acid Derivatives. Effect on Polypropylene/Polyethylene Terephthalate Blends

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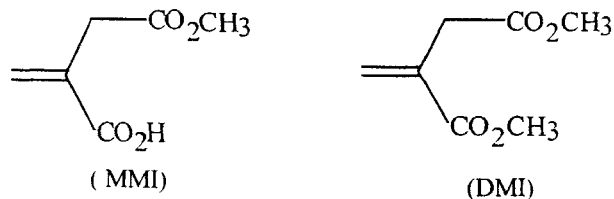
New types of compatibilizers based on functionalized polypropylene (PP) were synthesized by radical melt grafting either with monomethyl itaconate or dimethyl itaconate. The effect of these new modified PP compounds were tested as compatibilizers in PP/polyethylene terephthalate (PET) blends. Blends with compositions 15/85 and 30/70 by weight of PP and PET were prepared in a single-screw extruder. Morphology of the compatibilized blends revealed a very fine and uniform dispersion of the PP phase as compared with that of noncompatibilized blends of the same composition, leading to improved adhesion between the two phases. Whereas dimethyl itaconate derived agent showed less activity, the monomethyl itaconate parent compound showed an increase of the impact resistance of PET in PP/PET blend. This was attributed to the hydrophilic nature of the monomethyl itaconate part of this compatibilizer. The tensile strength of PET in noncompatibilized blends gradually decreases as the PP content increases, while blends containing functionalized PP exhibited higher values.

## INTRODUCTION

Functionalization of polyolefins through grafting of polar monomers has been the subject of intense research during recent years with the aim of introducing functional polar groups into their non-polar olefinic chains (1–9). The resulting compounds have been used as compatibilizers in blends of polyolefins with other polar polymers. Several studies have shown that it is possible to compatibilize polyolefins by blending with a large number of polar polymers in order to improve properties of the final products. Particularly, modified polypropylenes with polar monomers have found wide application as compatibilizers in binary polymer blends in which one component of the mixture is a polar polymer such as polyamides, polyesters, acrylics (10–23), as well as in polymeric composites reinforced with fiber glass, clay, etc. (24–31).

Polypropylene is an important polyolefin because of its versatility and broad range of applications. However, its application in some technologically important fields seems to be limited because of its low impact strength at low temperatures and its lack of polar functional groups that results in its incompatibility with additives, reinforcing agents and other polar polymers. Compatibility of immiscible blends may be improved by adding a third component such as a graft or block copolymer containing functional groups, capable of interacting with the blend constituents and therefore promoting interfacial adhesion between the two phases. Several works deal with functionalization of PP with maleic anhydride, (1, 3, 4, 6, 7, 9). Other polar monomers such as acrylics as well as monomers containing more than one functional group have also been investigated (2, 5, 8). However, the potential use of itaconic

acid, a vinyl monomer containing two carboxylic group, and its derivatives have been recently investigated for this purpose (32–34). The aim of this work was the study of the application of modified PP with itaconic acid derivatives as compatibilizers in blends of PP with PET. The incorporation of large amounts of PET to this type of blends could become an alternative way for PET recycling. The application of itaconic acid and derivatives can be considered interesting because of their carboxylic bifunctionality and because itaconic acid is produced from non-oil based renewable natural resource, i.e. by large scale fermentation of molasses, a by-product from sugar industry.



Recently our group have worked on functionalization of PP, either in solution or in the melt phase, through free radical grafting with itaconic acid and its mono- or dimethyl ester in order to use them as compatibilizing agents in blends of PP with polar polymers (32–34). Blends of PP with polar polymers such as polyamides and polyesters have been reported. Particularly, blends of PP and PET have been studied recently (10–14, 22). The melt flow behavior and dynamic mechanical properties of noncompatibilized PP/PET blends with two compositions, 50% and 30% by weight of PP, were investigated by Rudin *et al.* (10). The blends showed lower melt shear viscosities than those of the parent polymers. Dynamic mechanical analysis showed that the blends were immiscible but can be drawn into oriented monofilaments where the draw ratio was higher than as of PET. Bataille and coworkers (11) have studied PP/PET blends over a wide composition range. They found that the modulus and tensile strength were enhanced slightly by using a commercial polypropylene grafted with acrylic acid as blend compatibilizer. In an attempt to improve the compatibility of PP with PET, an acrylic acid functionalized PP was evaluated as blend compatibilizer by Xanthos *et al.* (12), who showed that the functionalized PP promoted a fine dispersed phase morphology, improved processability and mechanical properties, and modified the crystallinity of the polyester component. Modified and unmodified styrene-ethylene/butylene-styrene (SEBS) block copolymers have been used by Heino *et al.* (13) as compatibilizers in blends of PP/PET. The modified SEBS was either maleic anhydride or glycidyl methacrylate grafted to the midblock. Modified SEBS with glycidyl methacrylate (GMA) was also used as compatibilizer in the PET-rich composition. Addition of the functionalized SEBS resulted in a finer dispersion of the minor phase and improved interfacial adhesion. The compatibilizing effectiveness of different

compatibilizers for PP/PET blends was studied by Papadopoulou *et al.* (14). One of these compatibilizers was PP grafted with maleic anhydride. The use of hydrogenated SBS block copolymer grafted with maleic anhydride as a compatibilizer reduced migration of the grafted PP with maleic anhydride into the PP phase. Finally, Bae *et al.* (22) evaluated the compatibilization effect of PP grafted with 2-hydroxyethyl methacrylate-isophorone diisocyanate on reactive blending of PP with PET. They found that the presence of modified PP reduced the particle size of the dispersed phase by the reduced interfacial tension between the PP and PET phases, indicating that PP was grafted to PET during melt blending. Moreover the water resistance of PET was improved.

In this work we present results from the use of functionalized PP with itaconic acid derivatives, namely monomethyl itaconate (MMI) and dimethyl itaconate (DMI), as compatibilizers in blends of PP/PET.

## EXPERIMENTAL

A commercial sample of PP (PTK-1100, MFI = 7.5 g/10 min.; 230°C; 2.16 Kg) in powder form, from Petroquímica Cuyo, Mendoza, Argentina, was used as received. Itaconic acid was from Aldrich. Monomethyl itaconate (MMI) and dimethyl itaconate (DMI) were synthesized by esterification of itaconic acid (Aldrich) with methanol. 2,5-Dimethyl-2,5-bis(*tert*-butylperoxy)hexane (Lupersol 101) from Akzo was used as radical initiator. Functionalized PP samples used in this study were obtained by melt grafting either with MMI or DMI onto PP by using the mixing head of a Brabender-Plasticorder under a nitrogen stream at 190°C for 6 min. and with a mixing speed of 75 rpm. Evidence of grafting as well as its extent, expressed as weight percent of grafting, was obtained by FTIR spectroscopy. Details on the melt functionalization of PP, through grafting with MMI or DMI, and the characterization of the functionalized PP samples are already reported in our previous work (34). The percentage of grafting of PP samples, either with MMI or with DMI, used here, as compatibilizers was 0.7% and their MFI values were 43 for PP functionalized with DMI and 39 for PP functionalized with MMI. The PET sample used was cut into pieces from used soft drink bottle. Pieces without any graphic impression were selected and washed with dilute alkali solution at room temperature, rinsed thoroughly with distilled water and dried at 60°C/14 h in a vacuum oven. Blends of PP/PET with compositions 15/85 and 30/70 wt% were prepared in a Haake single-screw extruder by using PP grafted with either MMI (PP-g-MMI) or DMI (PP-g-DMI) as compatibilizers. Blends of PP/PET of the same composition without use of compatibilizers were also prepared under the same conditions as those with functionalized PP as compatibilizer. The extruder barrel had five temperature zones from 160°C to 270°C and the blending time was 10 min. The rotor speed was set at 80 rpm. Immediately after completion of

mixing, the materials were pelletized and then injection molded at 270°C to obtain specimens for testing.

The blend morphologies were characterized by scanning electron microscopy (SEM) by using a Tesla BS 343 A, scanning electron microscope. Micrographs were obtained after extraction of the PP phase from the surface of cryogenically fractured samples by using hot xylene. The mechanical properties of these blends, as well as those of PP and PET, were determined by tensile strength at 20°C on an Instron dynamometer, model 4301, according to ASTM D 638M. Tests were carried out at a cross-head speed of 5 mm/min. Impact resistance measurements were carried out according to ASTM D-256 (v-notched) at 20°C, in an Charpy pendulum Ceast model Resil 25, with an impact speed of 3.48 ms<sup>-1</sup> recording the maximum force and the energy to fracture. The notches were prepared in a Ceast electrical notching apparatus at a 20% of the thickness and the angle of the "V" side grooves was 45°. Results of mechanical properties were taken as the average of at least seven measurements.

## RESULTS AND DISCUSSION

Noncompatibilized as well as compatibilized blends of PP/PET with either 15% or 30% by weight of PP were prepared. Functionalized PP, either with MMI or DMI, used as compatibilizer in this work, had a grafting percentage of 0.7%. Functionalized PP with either MMI or DMI was used as compatibilizer in a 5% by weight of the blend and forming part of the total amount of PP used in the mixture. SEM micrographs of the PP/PET (15/85) are shown in Fig. 1. The hollow dark areas in all SEM micrographs correspond to the PP phase removed by solvent extraction. As shown in Fig. 1 the noncompatibilized blend (Fig. 1a) exhibited a clear two-phase morphology as indicated by existence of large voids corresponding to the PP phase. However, when 5% of functionalized PP with DMI was used as compatibilizer there was a much finer dispersion of PP domains in the continuous PET phase (Fig. 1b). The PP phase is distributed as spherical particles in the continuous PET phase. The use of PP grafted with MMI as compatibilizer resulted in even a better dispersion of PP as the minor phase increasing the components interface and thereafter to an improvement of the adhesion between the two phases (Fig. 1c).

The morphology of blends with 30% by weight of PP is shown in Fig. 2. The noncompatibilized blend in this case also showed an even more pronounced two-phase behavior as compared with those blends with lower PP content (Fig. 2a). Here, again the addition of functionalized PP with DMI, as blend compatibilizer, improved the morphology of the blend (Fig. 2b), particularly when PP grafted with MMI was used (Fig. 2c). Although both functionalized PP used in this study clearly reduced the average particle size of PP domains, the reduction in PP particle size was more pronounced when functionalized PP with MMI was used as compatibilizer of the blends.

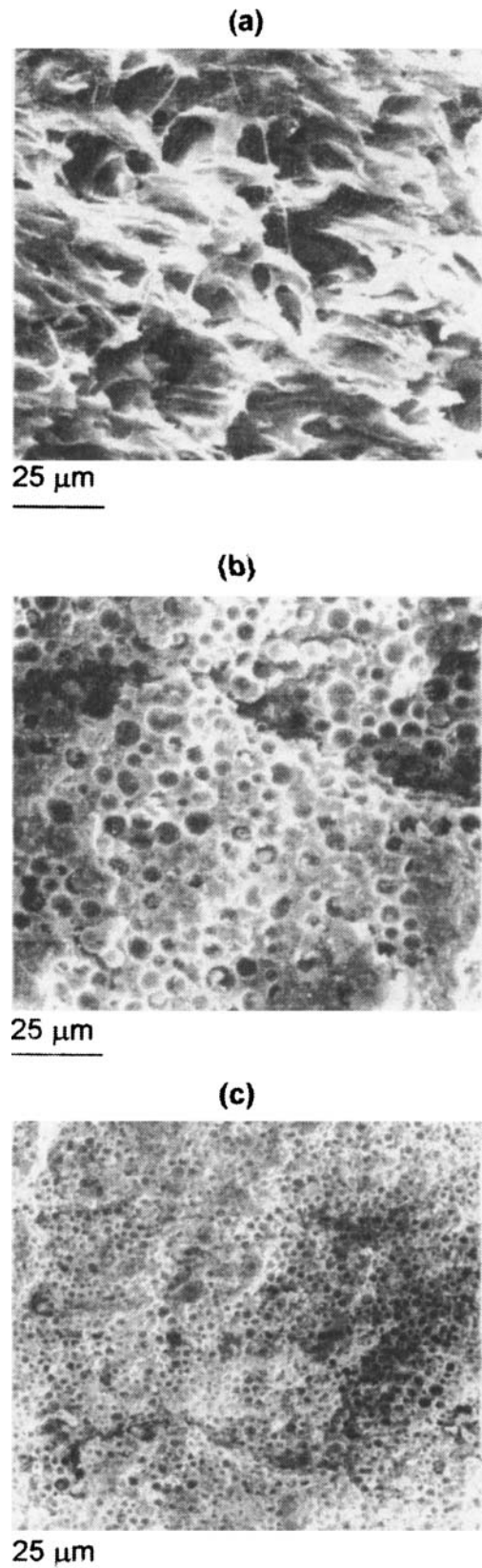


Fig. 1. Scanning electron micrographs of PP/PET (15/85 Wt.) blends: a) noncompatibilized, b) compatibilized with 5% by weight PP grafted with DMI and c) compatibilized with 5% by weight PP grafted with MMI.

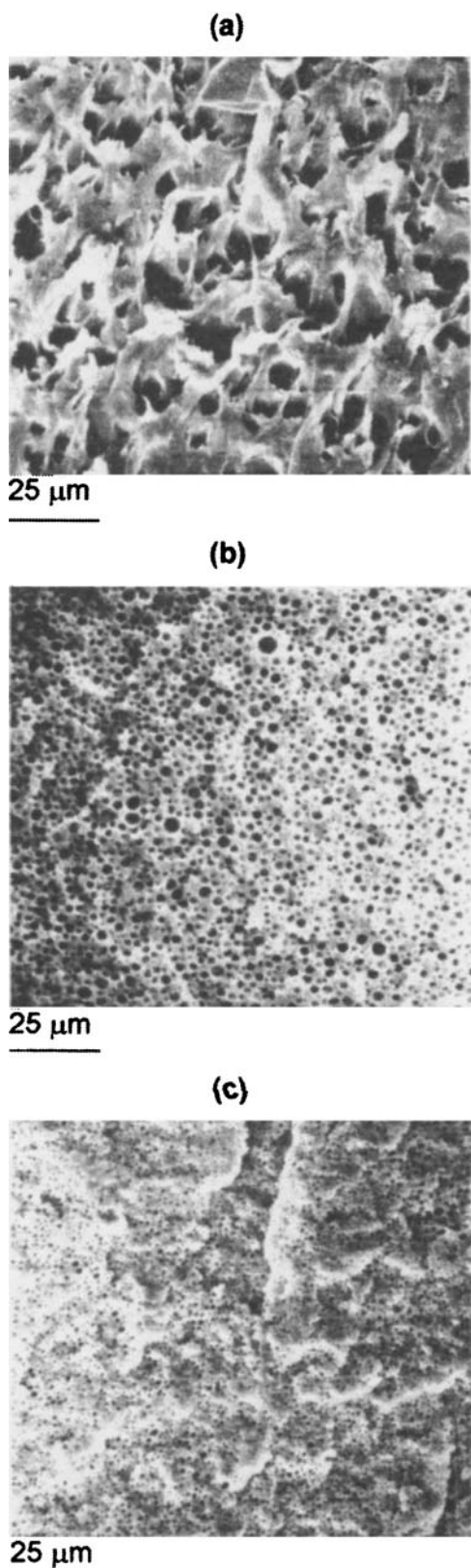


Fig. 2. Scanning electron micrographs of PP/PET (30/70 Wt.) blends: a) noncompatibilized, b) compatibilized with 5% by weight PP grafted with DMI and c) compatibilized with 5% by weight PP grafted with MMI.

Mechanical properties of blends were determined by tensile strength and impact resistance measurements. The results from impact resistance measurements are shown in *Table 1*. The impact strength measurements showed that incorporation of PP in the PET matrix hardly affected the impact resistance of PET in noncompatibilized blends. However, when functionalized PP with either MMI or DMI was used as blend compatibilizers, there was an increase of the impact resistance of PET, specially when MMI grafted PP is used as compatibilizer of the blends. This probably is due to specific interactions and/or chemical reaction (e.g. transesterification) between the functional groups of the compatibilizer with the blend constituents resulting in a finer dispersion of the minor phase leading to improved interfacial adhesion.

The results from tensile strength measurement are shown in *Table 2*. The tensile strength of PET in noncompatibilized blends gradually decreases as the PP content increases, especially for PP/PET blends of 30/70 composition by weight but blends containing functionalized PP exhibited higher values in relation to those noncompatibilized blends with the same composition. It is important to note that mechanical properties of PET were not diminished by blending with PP, but rather are improved. It can be concluded that monomers based on itaconic acid could replace maleic anhydride and acrylic based monomers for obtaining efficient compatibilizers. This could be an advantageous approach to the use of products from natural origin.

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Table 1. Charpy Impact Resistance of PP, PET, Noncompatibilized and Compatibilized PP/PET Blends.

PP/PET	Noncompatibilized (J/m)	Compatibilized with 5% (PP-g-DMI) (J/m)	Compatibilized with 5% (PP-g-MMI) (J/m)
0/100	25 ± 2.8	—	—
15/85	25 ± 3.2	26 ± 4.1	34 ± 4.2
30/70	27 ± 3.4	26 ± 3.7	32 ± 4.5
100/0	35 ± 3.5	—	—

Table 2. a) Tensile Strength and b) Elongation at Break of PP, PET, Noncompatibilized and Compatibilized PP/PET Blends.

PP/PET	Noncompatibilized (MPa)	Compatibilized with 5% (PP-g-DMI) (MPa)	Compatibilized with 5% (PP-g-MMI) (MPa)
0/100	(a) 46.5 ± 1.53 (b) 253 ± 22	—	—
15/85	(a) 40.1 ± 1.42 (b) 22 ± 2.7	(a) 42.7 ± 0.75 (b) 32 ± 4.1	(a) 39.4 ± 0.60 (b) 84 ± 8.5
30/70	(a) 23.8 ± 0.82 (b) 10 ± 1.5	(a) 27.8 ± 0.46 (b) 21 ± 2.8	(a) 29.9 ± 0.52 (b) 60 ± 5.8
100/0	(a) 29.4 ± 0.58 (b) 370 ± 28	—	—

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