Grafting of Maleic Anhydride onto Polypropylene, in the Presence and Absence of Styrene, for Compatibilization of Poly(ethylene terephthalate)/(ethylene–propylene) Blends

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ABSTRACT: Grafting of polypropylene (PP) by reactive processing in the presence and absence of styrene (ST) was performed to assess the effect of each one of the copolymers obtained in the compatibilization of poly(ethylene terephthalate) and (propylene–ethylene) copolymer blends, PET/EP copolymer (80/20). Grafting reactions of maleic anhydride and ST onto PP were conducted according to an experimental design where the concentrations of maleic anhydride and ST were varied. The amount of reacted maleic anhydride and the extent of degradation in PP were determined by means of Fourier-transformed infrared spectroscopy and melt-flow index, respectively. The PET/EP copolymer blends were obtained in a co-rotating twin-screw extruder. The effect of grafted copolymer type, PP-g-MA (PP grafted with maleic anhydride) or PP-g-MAST (PP grafted with maleic anhydride and styrene) in the compatibilization of PET/EP copolymer blends was assessed through mechanical (tensile test), morphological (scanning electron microscopy), and rheological properties. The presence of ST in the grafting reaction of maleic anhydride onto PP showed to significantly increase the amount of reacted maleic anhydride and reduce PP degradation. However, increasing ST concentration in the reaction mass affected the investigated variables only when maleic anhydride concentration was at its lowest level. Results of the PET/EP blends showed that both graft copolymers improved polymer interface adhesion, however, PP-g-MAST showed improved performance for the same level of compatibilizer used. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polymer modification, manufacture of polymer blends, and composites have been of great interest, because materials can be obtained with specific properties for novel applications with economy in cost and time when compared with the synthesis of new polymers with all the required properties.[1,2]

Reactive processing has been a widely investigated polymer modification technique, because it is a relatively easy process, especially regarding polar monomer grafting onto polyolefins.[2–5] The formed graft copolymers are able to compatibilize incompatible systems, such as blends of polar and nonpolar polymers[6,7] as well as polymer compounds containing natural fibers,[8,9] and among others. One of these graft copolymers obtained by reactive processing is polypropylene (PP) grafted with maleic anhydride (PP-g-MA). In spite of the fact that reactive processing is an easy

operation, low-conversion levels are obtained, because maleic anhydride copolymerizes readily, but is difficult to homopolymerize. This leads to reduced grafting onto PP and pronounced reduction in polymer molecular weight.[10–16] Some authors have investigated the inclusion of an electron-donating comonomer, such as styrene (ST) for instance, which activates the maleic anhydride double bond, making it more reactive toward PP.[15–17]

As mentioned earlier, one of the main uses of PP copolymers grafted with polar monomers is to compatibilize blends consisting of thermodynamically incompatible polar and nonpolar polymers. The graft copolymer acts at the interface between both polymers and promotes adhesion between the two phases which results in stress transfer and reduction in interfacial tension.[6] Studies on PP/poly(ethylene terephthalate (PET) blends have been of great interest as these polymers are extensively

used in the packaging and automobile industry, among others. Moreover, these polymers have very different thermal, mechanical, and physicochemical properties which make blending very interesting from property design point of view. However, blending these two polymers has shown many drawbacks due to their incompatibility. Lower values of mechanical properties have been obtained, particularly impact strength, tensile elongation, and tensile strength than would be expected by simple additivity or by averaging the physical properties of these polymers. The resulting products showed extreme nonuniformity and ugly appearance owing to formation of flow marks, making them unsuitable, for example, for the manufacture of automobile parts or electric and electronic parts.[18]

Compatibilization of PP/PET blends has been proposed by several investigations. Xanthos et al.[19] proposed replacing PP by acrylic acid grafted PP (PP-g-AA) in PP/PET blends and observed that PP-g-AA promoted a more finely dispersed phase morphology than PP. Processing became easier and mechanical properties were improved, which was attributed to reduction in interface tension brought about by the modified PP. Cheng and Chan[20] investigated compatibilization of PP/PET blends by adding PP modified with maleic anhydride (PP-g-MA) and observed an increase in stiffness and strength compared to blends without compatibilizer. However, compatibilizer effect on elongation at break was not significant. Compatibilization efficiency of PP/PET blends was investigated by Papadopoulou and Kalfoglou[21] by adding three types of compatibilizers: PP-g-MA, linear low-density polyethylene grafted with MA, and ST–ethylene/butylene–ST block copolymer grafted with MA (SEBS-MA). The best compatibility results for aged blends were obtained with SEBS-MA and PP-g-MA + thermoplastic elastomer (TPO). According to the authors, TPO improved the effectiveness of PP-g-MA because TPO reduced interface tension and blocked migration of PP-g-MA to the PP phase. Lepers et al.[22,23] investigated the effect of SEBS-MA addition on the compatibilization of unoriented and oriented PP/PET blends and observed a reduction in size of the PP phase dispersed in the PET matrix as well as an increase in compatibility corroborated by improved mechanical properties and scanning electron microscopy (SEM). Heino et al.[24] investigated compatibilization of 20/80 and 80/20 PET/PP blends. Compatibilizers used were SEBS block copolymer, SEBS-MA, and glycidyl methacrylate grafted (SEBS-GMA). Best results in reducing phase morphology and increasing impact resistance were obtained by SEBS-GMA in PET matrix. However, both SEBS-MA and SEBS-GMA showed synergistic impact behavior when added to the blend. Compatibility of PET/PP and PET/PP-g-GMA blends was investigated by Pracella and Chionna.[25] The authors observed that compared to PET/PP blends, PET/PP-g-GMA blends showed improved dispersion and interfacial adhesion. The improved compatibility of the PET/PP-g-GMA blends was attributed to the *in situ* compatibilization reactions between the PP-g-GMA epoxy groups and the PET carbonyl end groups. Pracella et al.[26] developed another through investigation on the effect of several block copolymers [SEBS, styrene-b-(ethylene-*co*-propylene) (SEP), SEPSEP, functionalized or not with glycidyl methacrylate] on the compatibilization of PET/PP blends. They observed that the presence of copolymers functionalized with GMA yielded improved phase dispersion and interfacial adhesion in relation to the nonfunctionalized copolymers. In the blends with PET as matrix, copolymers SEPSEP-GMA and SEBS-GMA showed a more pronounced emulsifying effect, which was attributed to proper mixing of the elastomeric blocks with the PP phase and to the strong interfacial interactions between the GMA groups and the PET end groups. In this investigation, compatibilization effectiveness was also related to copolymer structure, number of grafted groups onto the copolymer, molecular weight, concentration, and localization at the interface.

In the current work, reactions of MA grafting onto PP have been performed in the presence and absence of an electron-donating monomer, that is, ST, according to an experimental design. The effect of initial maleic anhydride and ST concentrations on the amounts of reacted anhydride and ST onto PP and on melt-flow index (MFI) was analyzed. Reactions were performed in the melt and in the presence of peroxides. To assess the effect of compatibilizer type on PET/ethylene–propylene (EP) blend compatibilization, the copolymers prepared by reactive processing [PP-g-MA and polypropylene grafted with both maleic anhydride and styrene (PP-g-MAST)] were added to the blend and mechanical and morphological properties were assessed.

Like PET, EP copolymer represents a large volume of recyclables in Brazil, since it is extensively used in battery housings. It was, therefore, decided to use EP copolymer instead of PP homopolymer, since, despite the fact that the current investigation used virgin polymers, the intention is to develop investigations on these blends with recycled material.

EXPERIMENTAL

Materials

PP was supplied by Braskem (Mauá, São Paulo, Brazil) under code JE-6100, with MFI of 2 g/10 min (230°C, 2.16 kg). Maleic anhydride used was from Riedel-de Haen, with 99% purity and the ST monomer was supplied by Central Polímeros da Bahia (Camaçari, Bahia, Brazil). The peroxide selected for our investigation was a 46.5% concentrate of 2.5-dimethyl-2.5-di(t-butyl-peroxy) hexane in $CaCO_3$, supplied by Archema (Rio Calro, São Paulo, Brazil), (Luperox 101 XL).

PET pellets were supplied by RHODIA-STER, currently M&G—Gruppo Mossi & Ghisolfi (Poços de Caldas, Minas Gerais, Brazil), as RHOPET® S80, with intrinsic viscosity of 0.8 dL/g.

The EP copolymer, was supplied by Quattor, currently Braskem (Mauá, São Paulo, Brazil), under code EP 200K, with MFI of 3.0 g/10 min (230°C, 2.16 kg). This EP copolymer is a heterophase copolymer containing 12% ethylene.

PP-g-MA, used as compatibilizer in the PET/EP blends, was obtained by reactive extrusion, in a Werner & Pfleiderer ZSK-25 twin-screw extruder.[11] The degree of maleic anhydride grafted onto PP was 0.56 wt % and MFI measured at 190°C and 2.16 kg was 63.5 g/10 min. Molecular weights, from gel permeation chromatography were $\bar{M}_w = 12{,}4045$, $\bar{M}_n = 4{,}7872$, and $\bar{M}_w/\bar{M}_n = 2.59$.

PP grafted with both maleic anhydride and ST (PP-g-MAST) was also obtained by reactive processing, as will be described

Table I. Formulations Prepared in the Haake Torque Rheometer

Formulations	Cper (phr)	Cma (phr)	Cst (phr)
H1	–	–	–
H2	0.1	–	–
H3	0.1	5.0	–
H4	0.1	–	5.0
H5	0.1	2.5	2.5
H6	0.1	5.0	2.5
H7	0.1	2.5	5.0
H8	0.1	5.0	5.0

Cper, peroxide concentration; Cma, maleic anhydride concentration; Cst, styrene concentration.

next. The sample used for compatibilization was H6, because of the high degree of grafting obtained. For confection of the blends, 20 reactive processing runs were performed to produce the necessary amount for extrusion.

Methods

Maleic Anhydride and ST Grafting onto PP. Maleic anhydride grafting reactions onto PP, in the presence of ST, were conducted in a Haake torque rheometer (Karlsruhe, Germany), equipped with a Rheomix 600p mixing chamber. Reactive processing was performed according to 2^2 Experimental Design (H5–H8), where maleic anhydride (Cma) and ST (Cst) concentrations were varied for an exploratory analysis. Reactive processing with just one type of monomer and peroxide (H3 and H4), with just peroxide (H2), and pure PP (H1) was also performed for control. The investigated formulations are shown in Table I. The following process conditions were used: reaction temperature 180°C, rotor frequency 55 rpm, reaction time 10 min, and $N_{2(g)}$ atmosphere.

PP was placed in the torque rheometer and left to melt for 1.5 min. Subsequently, a PP bag containing peroxide and previously in-liquid-nitrogen-cooled monomers (maleic anhydride and/or ST) was added. Cooling was performed to lower monomer temperature up to incorporation into the reaction mass and to minimize monomer evaporation.

After processing in the rheometer, samples were pressed to thin sheets at 180°C to facilitate cutting into small pellets.

The samples processed at this stage were submitted to MFI measurements for verification of the extent of degradation, and to Fourier-transformed infrared spectroscopy (FTIR) measurements for analysis of reacted maleic anhydride and ST.

Purification Method. To assess the level of reacted maleic anhydride by FTIR, purification of the modified PP was performed by removing unreacted maleic anhydride, ST, polystyrene, maleic anhydride oligomers, and ST–maleic anhydride copolymers in the polymer mass. Only nongrafted and grafted PP precipitate in acetone, that is, PP, PP-g-MA, PP-g-ST, and PP-g-MAST, whereas monomers, oligomers, homopolymers, and copolymers of MA and ST are soluble in acetone. Hence, after purification, the level of reacted maleic anhydride can be assessed.

The purification method: 4 g PP-g-MAST were dissolved in 400 mL xylene under reflux at 130°C for 1 h. The temperature was lowered and acetone was added. The precipitate was vacuum filtered and washed several times with acetone. The sample was then left in a vacuum oven for solvent removal.

Next, the purified samples were pressed into films in a Luxor press at 190°C and 100 kgf/cm^2, and then submitted to heat treatment in a vacuum oven at 125°C for 24 h, to convert succinic acid groups into anhydride groups.

FTIR Spectroscopy. Transmittance analyses were performed in a Nicolet Magna IR 750 Spectrophotometer (Madison, WI), with resolution of 2 cm^{-1} and 128 scans per spectrum. All analyses were triplicated.

When analysis of grafted maleic anhydride onto PP was performed in the PPs functionalized with maleic anhydride only, carbonyl absorbance was measured at 1789.6 cm^{-1}, and when ST was present, carbonyl absorbance was measured at 1780.9 cm^{-1}. Previous work indicates a shift of the carbonyl band absorption due to reaction of ST with maleic anhydride to form a branch on PP.[17] The behavior will be discussed in "Results and Discussion" Section

Analyses of these bands allowed calculating the carbonyl index (CI):

$$CI_{MA} = \frac{A_{1789.6}}{A_{1167}} \quad (1)$$

$$CI_{MA-ST} = \frac{A_{1780.9}}{A_{1167}} \quad (2)$$

where A_{1167} is the characteristic absorbance of CH_3 groups and used as an internal reference band, proportional to the amount of PP.

The relative amount of ST present in the sample was also obtained from the infrared spectra and is given by the ratio

$$\text{Index of ST} = \frac{A_{704}}{A_{1167}} \quad (3)$$

where the 704 cm^{-1} band may be attributed to the aromatic C—C bonds in ST–maleic anhydride copolymer.

The calibration curves for maleic anhydride grafting, in the absence and presence of ST, have been constructed for the investigated systems and can be found in previous works[10–12,17] and the obtained equations are presented

$$y_1 = 0.1790 \times x \quad (4)$$

$$y_2 = 0.50315 \times x \quad (5)$$

where $y_1 = A_{1789.6}/A_{1167}$, that is, CI CI_{MA} $y_2 = A_{1780.9}/A_{1167}$, that is, CI CI_{MAST} and $x = \%$ succinic anhydride present.

The calibration curve for quantifying ST by FTIR was constructed in previous work.[17] A fit of the data allowed obtaining equation:

$$y_3 = 0.12537 \times x_2 \quad (6)$$

where $y_3 = A_{704}/A_{1167}$ and $x_2 = \text{wt }\% \text{ ST}$.

Table II. Composition of EP/PET Blends with Compatibilizer PP-g-MA or PP-g-MAST

Blends	EP (wt %)	PET (wt %)	PP-g-MA or PP-g-MAST (phr)
01	20	80	0
02	20	80	2
03	20	80	5
04	20	80	10
05	20	80	15
06	20	80	20

MFI. MFI (230°C and 2.16 kg) was performed in a Davenport plastometer (Harts, England), according to ASTM D-1238, to verify the extent of PP degradation. Analyses were triplicated.

Extrusion Blending. Blends were prepared in a B & P Process Equipment and Systems (Saginaw, MI) co-rotating twin-screw extruder, model MP-19TC, with diameter of 19 mm, L/D 25, at the following extrusion conditions: temperature profiles 200, 250, 250, 240, and 230°C and screw rotation 100 rpm. All blend components were dried in a vacuum oven at 120°C for 8 h.

PET/EP blends, containing compatibilizer PP-g-MA, were prepared to compare properties of this blend with those of PET/EP blends compatibilized with PP-g-MAST.

PET/EP blend compositions, compatibilized either with PP-g-MA or PP-g-MAST are shown in Table II.

Injection Molding. Type I tensile test specimens were injection molded in an Arburg Allrounder 270 V injection molding machine (Lossburg, Germany), with clamping force of 30 tons and screw diameter of 25 mm, at the following conditions: screw rotation, 125 rpm; mold temperature, 65°C; temperature profiles, 220, 250, 250, 260, and 265°C; injection pressure, 600 bar.

Tensile Tests. Tensile tests of the injection molded specimens were performed in a DL 2000 EMIC Universal Testing Machine (São José dos Pinhais, PR, Brazil), according to ASTM D638. The Type I specimens were tested at a rate of 5 mm/min.

SEM. SEM measurements were performed for morphological analysis of the blends using scanning microscope (SEM Philips XL30 FEG, The Netherlands) on molded bars. The samples were fractured at liquid nitrogen temperature. The PP phase was extracted by hot xylene for 1 h.

The fractured surfaces of both samples, with EP and without EP (extracted), were analyzed in an electron microscope after sputter coating with gold (2 nm layer).

Rheological Measurements. Rheological tests were performed to get insight into the rheological properties of the extruded blends. All samples were dried in a vacuum oven at 80°C for 8 h, to prevent PET hydrolysis during rheometer testing.

To assess the tendency of phase segregation, capillary rheology of neat polymers was performed at 270°C in an Instron 3211 capillary rheometer, using different shear rates. All tests were done in triplicate.

Complex viscosity, loss, and storage modulus measurements were conducted in oscillatory parallel plate rheometer (ARES AGR 2 Rheometer). Shear rate ranged from 0.01 to 700 s^{-1}, to assess compatibilization between phases in the presence and absence of compatibilizer.

RESULTS AND DISCUSSIONS

Reactive Processing

FTIR spectra of samples H3 (PP-g-MA only) and H8 (PP-g-MAST) are shown in Figure 1. The 1789.6 cm^{-1} carbonyl absorption band (sample H3) is seen to shift to 1780.9 cm^{-1} (sample H8), indicating a change in maleic anhydride neighboring groups, in this case, the bond with ST. Another feature is the appearance of the 704 cm^{-1} absorption band, characteristic of aromatic C—C bonds in ST–maleic anhydride copolymer, for sample H8. Because of the variation of carbonyl groups absorption, in the presence and absence of ST, we used different calibration curves for determining the content of reacted maleic anhydride.

Table III shows average results of FTIR analysis, amount reacted maleic anhydride and ST, and MFI of the samples submitted to reactive processing.

Comparison of the sample containing maleic anhydride as single monomer (H3) with samples having the same initial maleic anhydride concentration, but reacted in the presence of ST (H6 and H8), shows a significant increase in the amount of reacted maleic anhydride and a decrease in MFI for the samples of which the reactions were conducted in the presence of ST (H6 and H8). This behavior has also been observed by Hu et al.[15] According to these authors, incorporation of an electron-donating monomer in the reaction mixture (in this case, ST) activates the maleic anhydride double bond by forming a charge transfer complex, which increases reactivity toward PP.

Furthermore, the increase in percentage-reacted maleic anhydride in PP indicates that the reactivity of maleic anhydride in relation to PP is not the only event that might occur. The increase in % MAr may also arise from a higher amount of anhydride as comonomer of a maleic anhydride–ST copolymer branch.

As grafting reactions compete with degradation reactions, a result of the higher reactivity of maleic anhydride is a decrease in PP degradation, as chain scission in PP decreases. Moreover, since ST is more reactive toward PP than maleic anhydride, data indicate that ST might be reacting with tertiary PP macroradicals before β scission occurs and therefore reduce degradation. After ST has bonded to PP, maleic anhydride likely reacts with ST to form a ST–maleic anhydride copolymer branch of PP (evidenced by the carbonyl absorption; Figure 1).

The presence of anhydride carbonyl at 1780.9 cm^{-1} is a strong indication of alternating copolymerization of maleic anhydride and ST. These assumptions could only be made because the materials obtained during reactive processing of PP, MA, ST, and peroxide were purified. During solubilization in xylene and precipitation in acetone, residual monomers, unreacted maleic anhydride oligomers, and unreacted ST–maleic anhydride
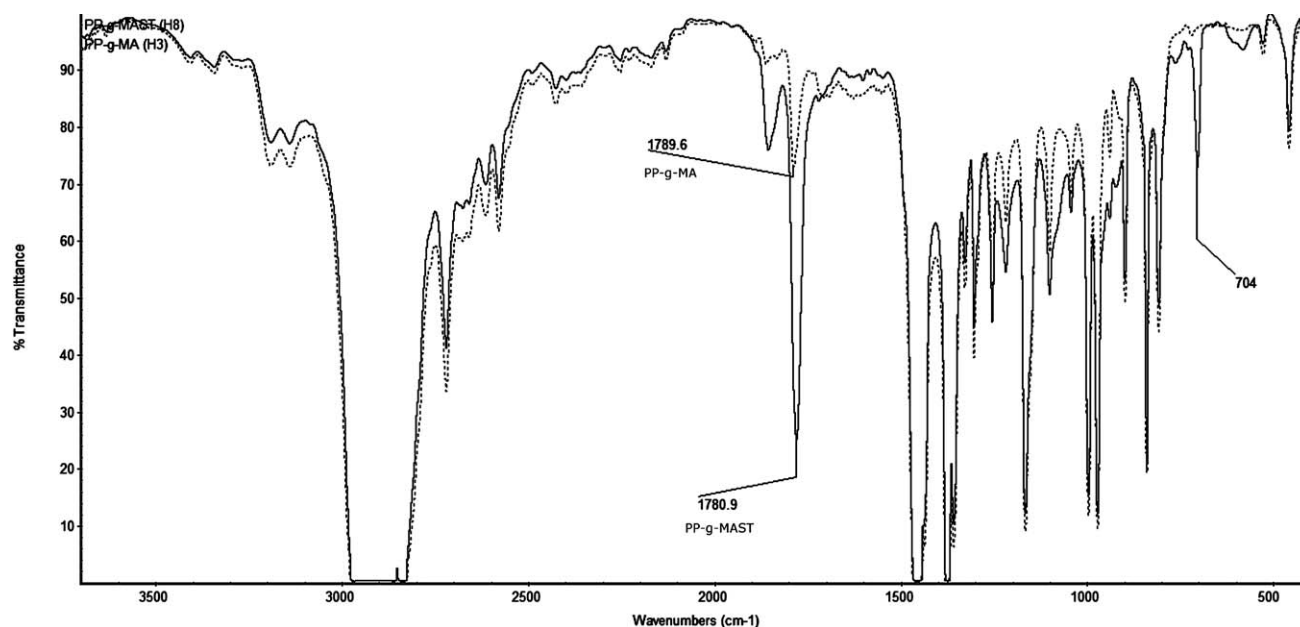
Figure 1. FTIR spectra of samples H3 (PP-g-MA) and H8 (PP-g-MAST).

copolymers dissolve in acetone, whereas PP-g-MA, PP-g-MAST, PP-g-ST, and PP precipitate in acetone. Therefore, the ST–maleic anhydride copolymer in the precipitate is likely bonded to PP and not just mixed in the reaction mass.[17]

The next stage of this study consisted in checking whether variation in initial maleic anhydride and ST concentrations would affect the dependent variables (relative amounts of reacted maleic anhydride and ST and MFI).

Analysis of Table III shows that initial maleic anhydride concentration is the independent variable with the greatest effect on the responses % MAr and MFI, which are related to the relative amount of reacted maleic anhydride and PP degradation, respectively.

The increase in initial maleic anhydride concentration leads to an increase in both reacted maleic anhydride content and MFI. With increasing initial maleic anhydride concentration, the

probability that MA molecules come into contact with the polymer macroradicals increases and therefore the possibility that they react with each other. In spite of the fact that ST causes a decrease in MFI, increase in initial C_{MA} of 2.5–5 phr leads to increase in MFI. This behavior might be explained by the fact that the termination reactions of the monomers involved tend to occur by chain transfer, which lead to chain scission.[10,12]

It should also be mentioned that in spite of the fact that the presence of ST leads to a considerable increase in the amount of reacted maleic anhydride and reduction in MFI, increase in initial ST concentration from 2.5 to 5.0 phr causes an increase in amount reacted maleic anhydride and ST and reduction in MFI only when initial MA concentration is at its lowest level (2.5 phr). When initial MA concentration is 5.0 phr, variation in initial ST concentration does not cause significant variations in these variables. This behavior shows that the investigated level of the variable affects the response, and may indicate that

Table III. Results of FTIR Analyses and MFI of the Samples Submitted to Reactive Processing in the Haake Torque Rheometer

| Test | Variables | | | | | Responses | | | |
	Cma (phr)	Cst (phr)	$\frac{A_{1789.6}}{A_{1167}}$	$\frac{A_{1780.9}}{A_{1167}}$	% Mar (wt %)	$\frac{A_{700}}{A_{1167}}$	$\frac{A_{704}}{A_{1167}}$	% STr (wt %)	MFI (g/10 min)
JE 6100	–	–	–	–	–	–	–	–	2.3
H1	–	–	–	–	–	–	–	–	2.8
H2	–	–	–	–	–	–	–	–	76.5
H3	5.0	–	0.11710	–	0.65	–	–	–	74.1
H4	–	5.0	–	–	–	0.11114	–	a	15.2
H5	2.5	2.5	–	0.45388	0.90	–	0.10862	0.87	26.9
H6	5.0	2.5	–	0.84010	1.67	–	0.16706	1.33	46.2
H7	2.5	5.0	–	0.56741	1.13	–	0.16527	1.32	15.0
H8	5.0	5.0	–	0.74864	1.49	–	0.15978	1.27	46.6

a Quantification of % reacted styrene was not possible, as no calibration curve was constructed for absorption at 700 cm^{-1}.
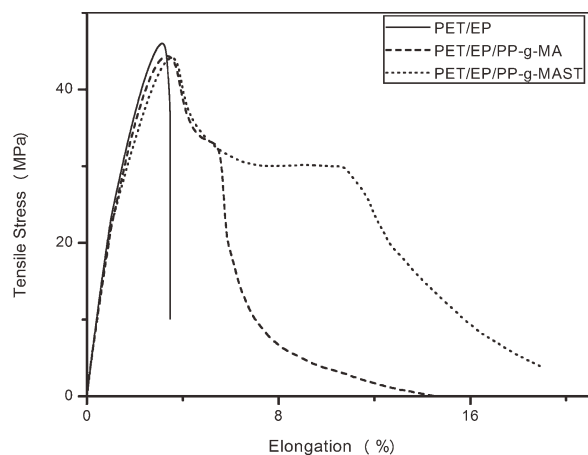
Figure 2. Stress strain curves of noncompatibilized PET/EP blends and compatibilized with PP-g-MA and PP-g-MAST.

Figure 3. Effect of compatibilizer type on % elongation at break.

ST is present in equimolar amounts or in excess to activate the maleic anhydride double band.[17,27]

There is an indication that when ST reacts with the tertiary PP macroradicals, maleic anhydride subsequently bonds to ST and so forth. The fact that ST reacts with the tertiary PP macroradicals minimizes the degradation that would occur as a consequence of β scission. When maleic anhydride concentration was 5 phr, increase in ST concentration did not cause increase in the amount of reacted ST and, consequently, did not add maleic anhydride to ST nor avoided degradation by chain scission.
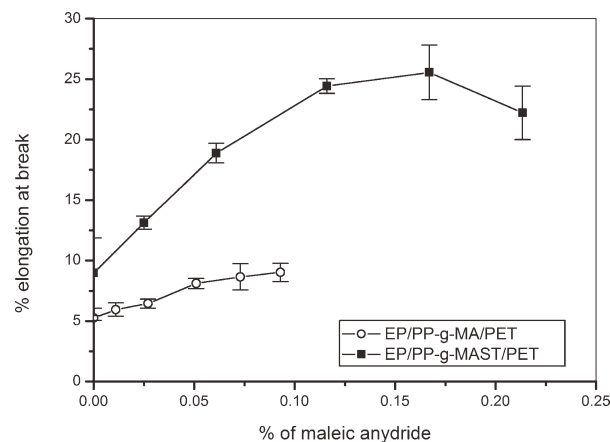
PET/EP Blends

The main objective of this stage was to compare the effect of the two modified PPs obtained by reactive processing, PP-g-MA and PP-g-MAST, on the compatibilization of PET/EP blends. A compatibilizer might provide for the necessary interactions for stress transfer between the polymers, resulting in blends with a desirable balance of properties.

The PP-g-MAST chosen for this stage was that from sample H6, because the amount reacted maleic anhydride was the highest (1.67 wt %) of all the investigated formulations. However, during reactive processing to produce the compatibilizer, peroxide showed reduced reactivity. Hence, 20 reactive processing runs were necessary to produce the required sample amount and an average of 1.28 wt % reacted MA was obtained.

Table IV. Calculation of % Maleic Anhydride in the EP/PET Blends, Compatibilized with PP-g-MA or PP-g-MAST

Compatibilizer concentration (phr)	Wt % maleic anhydride in the blend (PET/EP)	
	PP-g-MA	PP-g-MAST
0	0	0
2	0.011	0.025
5	0.027	0.061
10	0.051	0.116
15	0.073	0.167
20	0.093	0.213

Figure 2 shows typical stress–strain curves of noncompatibilized PET/EP blends, and those compatibilized with PP-g-MA and PP-g-MAST. It can be seen that the property most sensitive to changes at the interface is elongation at break. The addition of compatibilizer resulted in an increase in elongation at break. This increase was greater for PP-g-MAST. This behavior can be explained by the fact that defects are generated by adding a second incompatible component, thereby reducing the elongation at break. When the compatibilizer is added, the defects at the interface are reduced due to the adhesion between the components (PET or PE), increasing elongation at break. To assess the influence of structure of each compatibilizer on the PET/EP blend, the amount of maleic anhydride in the blends was calculated from the amount of maleic anhydride grafted onto PP-g-MA and PP-g-MAST, which were 0.56 and 1.28 wt %, respectively. Table IV shows the amount of maleic anhydride in the processed blends.

Figure 3 shows a graph of the amount of maleic anhydride in the blend versus elongation at break, for the two compatibilizers. In spite of identical processing conditions, values of the reference blends (PET/EP without compatibilizer) presented slightly different values, since different EP and PET lots were used.

Increase in either PP-g-MA or PP-g-MAST concentration in the blend resulted in increase in elongation at break. This property is very sensitive to morphology variations and blend adhesion. Our results indicate that incorporation of either PP-g-MA or PP-g-MAST in the blends resulted in reduced interfacial tension between the polymers, improving adhesion, corroborated by the increase in elongation at break. PET is a polymer that exhibits brittle fracture and low elongation at break below T_g. In contrast to PET, EP has very high elongation, around 450%. The blends in our work were prepared at a PET : EP ratio of 80 : 20, that is, a PET matrix and a dispersed EP phase. Hence, elongation at break is expected to be low. Yet, if there is some compatibilization between the two polymers, an increase should result, which occurred in our experiments. The curve shown did not reveal a maximum, indicating that higher concentrations of PP-g-MA could be incorporated and perhaps improve compatibilization. The values of elongation at break of the PP-g-MA
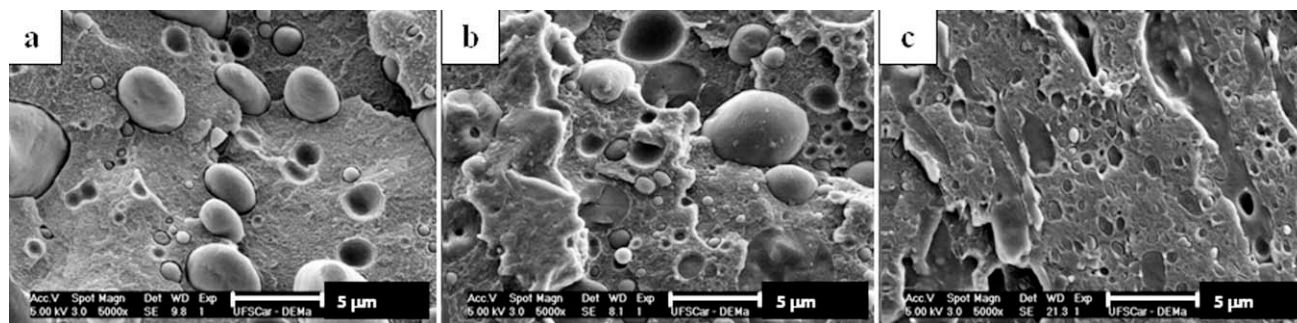
Figure 4. SEM micrographs of the fractured surfaces in the liquid nitrogen temperature of the blends PET/EP (80/20) (a) without compatibilizing agent; (b) with PP-g-MA; (c) with PP-g-MAST.

compatibilized and noncompatibilized blends are similar to those encountered by Cheng and Chan.[20] Vainio et al.[28] also encountered the same behavior of elongation at break in incompatible polybutylene terephthalate (PP/PBT) blends containing compatibilizer PP grafted with oxazoline.

Analysis of Figure 3 shows that incorporation of PP-g-MAST, with the same maleic anhydride concentrations as in PP-g-MA, resulted in higher values of elongation at break. Increase in maleic anhydride content in PP-g-MAST also shows a more pronounced increase. It should be mentioned that when we refer to the amount of maleic anhydride in the blends, for example, 0.025 wt % maleic anhydride, we refer to addition of 2 phr of PP-g-MAST and 5 phr of PP-g-MA (Table IV). Even addition of a smaller amount of PP-g-MAST will result in the same concentration of anhydride in the blend and superior properties. Thus, addition of a lower amount of PP-g-MAST will yield superior

properties compared with those of PP-g-MA at equal added maleic anhydride content.

To assess this behavior, morphological analysis was performed and SEM images for noncompatibilized and compatibilized blends, with PP-g-MA and PP-g-MAST, are shown in Figures 4 and 5. The samples in Figure 4 were fractured in liquid nitrogen and in Figure 5, the same samples were submitted to solvent extraction of the dispersed EP phase.

From these figures, one can clearly observe the adhesion promoted by the compatibilizers, with smaller particle size of the dispersed phase in the matrix. Moreover, the dispersed phase in the blends compatibilized with PP-g-MAST is smaller than those compatibilized with PP-g-MA. When the dispersed phase was not removed by solvent extraction (Figure 4), a large amount of this phase (EP) was removed from the matrix during fracture in liquid nitrogen due to poor adhesion to the matrix
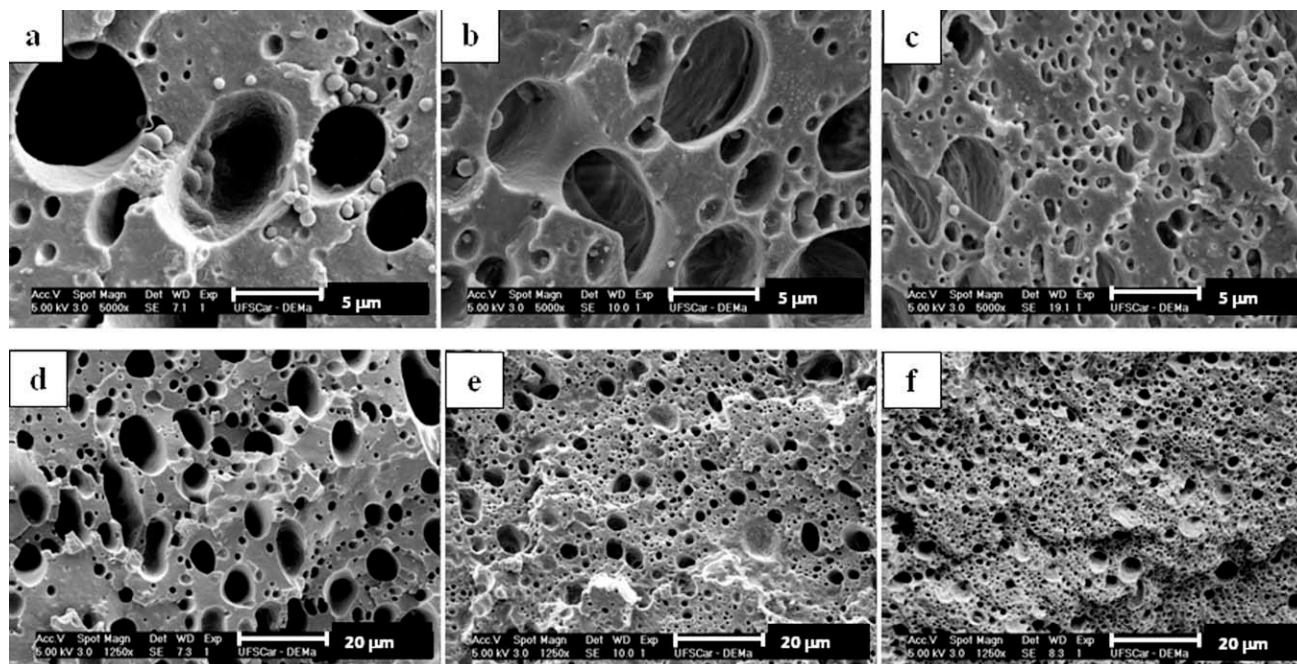
Figure 5. SEM micrographs of the fractured surfaces in the liquid nitrogen temperature of the PET/EP (80/20) blends, whose dispersed EP phase was extracted with hot xylene solvent (a) and (d) without compatibilizing agent; (b) and (e) with PP-g-MA; (c) and (f) with PP-g-MAST. Magnification: 5000× (a–c) and 1200× (d–f).
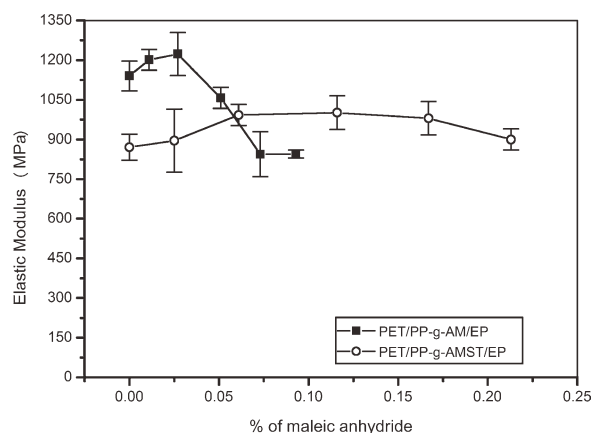
**Figure 6.** Effect of compatibilizer type on elastic modulus.

(PET). These results can be explained by the greater chemical similarity of the PP-g-MAST with the PET matrix due to presence of the aromatic ring in its branches. This chemical similarity likely leads to improved adhesion of the compatibilizer with PET, yielding improved adhesion at the EP–PET interface.

Figure 6 shows maleic anhydride content in the blends versus elastic modulus (% increase or decrease in relation to the blend without compatibilizer). The elastic moduli were measured in linear elastic regime in deformation between 0.1 and 0.5%.

Variation in PP-g-MA concentration in the blend resulted in a slight increase in elastic modulus, followed by a reduction at concentrations above 5 phr (wt % maleic anhydride in the blend: 0.027%, when compatibilizer was PP-g-MA). The increase in elastic modulus up to 5 phr might be an indication of compatibilization brought about by the introduction of the compatibilizers. A possible explanation for the reduction in this property above 5 phr is that PP-g-MA might be acting as plasticizers in the blend and reduce elastic modulus. PP-g-MA has low-molecular weight ($M_n = 47{,}872$ g/mol) when compared to the original PP ($M_n = 329{,}848$ g/mol) and may therefore act as a plasticizer.[12] Moreover, this graft copolymer has residual
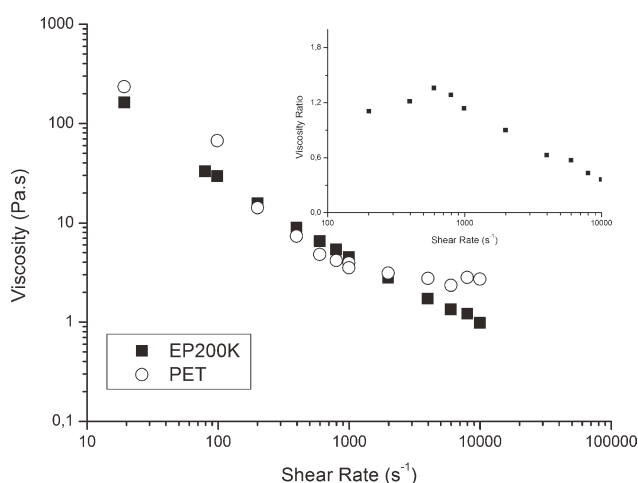
Figure 7. Viscosity and viscosity ratios ($p = \eta_d/\eta_m$) as a function of the shear rate of EP and PET.
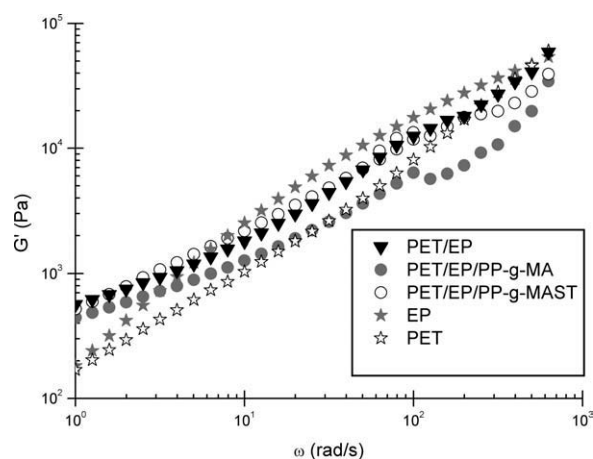
Figure 8. Curves of G' versus oscillation frequency obtained by oscillatory rheometry for pure components, noncompatibilized, and compatibilized blends.

amounts of maleic anhydride (not reacted but only incorporated into the polymer mass), which may also act as a plasticizer and decrease modulus.

Analysis of Figure 6 shows that the elastic modulus tends to increase with increasing maleic anhydride content in the blend for PP-g-MAST up to approximately 0.061–0.116 wt % after which this property decreases. In addition, modulus values for blends compatibilized with PP-g-MAST are superior to those of blends compatibilized with PP-g-MA (at MA content exceeding 0.061 wt %). In addition, when MA concentration increases, ST concentration also increases. ST has aromatic rings, which reduce molecular mobility. The lower mobility and hence greater rigidity increases elastic modulus.

Moreover, the PP-g-MAST sample has a higher molecular weight than PP-g-MA, evidenced by the lower MFI values (Table III). Hence, the blends containing PP-g-MAST present improved mechanical properties, especially when large amounts of compatibilizer are added to the blends.

These results confirm those presented by the elongation at break, and PP-g-MAST is seen to be more suitable than PP-g-MA for compatibilizing 80/20 PET/EP blends.

To assess the effect of polymer viscosity on the dispersion of the PET/EP blends, polymer viscosity was measured in a capillary rheometer under conditions similar to those encountered during extrusion. Figure 7 shows the viscosity versus shear rate and the viscosity ratios ($p = \eta_d/\eta_m$) of EP and PET versus shear rate. It appears that the viscosity ratios are close to 1, but usually greater than this value at shear rates normally used during extrusion. This measurement may indicate the tendency of the dispersed phase droplets to break. The particle size of the dispersed phase is directly proportional to the interfacial tension and smallest particles are obtained when $P = 1$.[29] However, interfacial tension can be varied more readily over a wide range than the viscosity using dispersants or compatibilizers. SEM analysis of fractured surfaces shows that the size of the dispersed phase decreases when either PP-g-MA or PP-g-MAST are added; however, PP-g-MAST seems to be more effective, suggesting a reduction in interfacial tension,

and consequently, increased adhesion between the blend components, for both compatibilizers. In addition to reducing the interfacial tension in the presence of compatibilizers, coalescence of the dispersed phase droplets is minimized, thereby stabilizing them. Figure 8 shows the curves of G' versus oscillation frequency obtained by oscillatory rheometry for pure components, noncompatibilized, and compatibilized blends. It can be seen from the curves that there are no significant differences between the G' values of compatibilized and noncompatibilized blends, in the investigated shear rate range. A higher G' was expected for the compatibilized blends at low frequencies. However, compatibilizers have very different structures, both in terms of molar mass and type of branching. Therefore, there are other variables that may affect this analysis. Interestingly, although the curves of the blends show an increase in the value of G', this increase is not large enough to state that, even in the presence of compatibilizers, there are chemical interactions between the blend components, because when there is chemical interaction between components, G' tends to increase by nearly 10 times the G' of the pure component.[30]

CONCLUSION

The presence of the ST monomer during the grafting reaction of maleic anhydride on PP significantly increased the amount of reacted maleic anhydride and reduced PP degradation. However, increase in ST concentration in the reaction mass affected the investigated variables only when maleic anhydride concentration was at its lowest level (2.5 phr).

Initial maleic anhydride concentration showed to be the variable that affected most the responses: amount of reacted maleic anhydride and MFI.

The investigated compatibilizers likely increased interaction between the PET/EP blend phases resulting in increase in elongation and in elastic modulus of the blends. Comparing the two compatibilizers PP-g-MA and PP-g-MAST in the PET/EP blends, by means of mechanical and morphological properties, PP-g-MAST showed improved performance over PP-g-MA. This enhanced effect was attributed to the presence of ST in PP-g-MAST branches, which rendered the grafted copolymer chemically more similar to PET than the PP modified only with maleic anhydride. Moreover, o PP-g-MAST has higher molar mass than PP-g-MA.

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REFERENCES

1. Utracki, L. A. Polymer Blends Handbook; Kluwer Academic Publishers: The Netherlands, **2002**, p 1442.

2. Xanthos, M. Reactive Extrusion: Principles and Practice; Oxford University Press: New York, **1992**; p 75.

3. Hu, G.-H.; Li, H.; Feng, L.-F.; Pessan, L. A. *J. App. Polym. Sci.* **2003,** *88*, 1799.

4. Shi, D.; Yang, J.; Yao, Z.; Wang, Y.; Huang, H.; Jing, W.; Yin, J.; Costa, G. *Polymer* **2001,** *42*, 5549.

5. Güldogan, Y.; Egri, S.; Rzaev, Z. M. O.; Piskin, E. *J. Appl. Polym. Sci.* **2004,** *92*, 3675.

6. Dagli, S. S.; Xanthos, M.; Biesenberger, J. A. *SPE ANTEC* **1990,** *1924.*

7. LaMantia, E. P. *Adv. Polym. Technol.* **1993,** *12*, 47.

8. Bettini, S. H. P.; Bicudo, A. B. L. C.; Augusto, I. S.; Antunes, L. A.; Morassi, P. L.; Condotta, R.; Bonse, B. C. *J. Appl. Polym. Sci.* **2010,** *118*, 2841.

9. Bettini, S. H. P.; Antunes, M. C.; Magnabosco, R. *Polym. Eng. Sci.* **2011,** *51*, 2184.

10. Bettini, S. H. P.; Agnelli, J. A. M. *J. Appl. Polym. Sci.* **1999,** *74*, 247.

11. Bettini, S. H. P.; Agnelli, J. A. M. *J. Appl. Polym. Sci.* **1999,** *74*, 256.

12. Bettini, S. H. P.; Agnelli, J. A. M. *J. Appl. Polym. Sci.* **2002,** *85*, 2706.

13. Machado, V.; Covas, J. A. *Adv. Polym. Technol.* **2004,** *23*, 196.

14. Cha, J.; White, J. L. *Polym. Eng. Sci.* **2001,** *41*, 1227.

15. Hu, G.-H.; Flat J. J.; Lambla, M. *Makromol. Chem. Macromol. Symp.* **1993,** *75*, 137.

16. Hu, G. H.; Flat, J. J.; Lambla, M., *SPE ANTEC 1994, San Francisco, California,* **1994,** *2775.*

17. Bettini, S. H. P.; Ruvolo Filho, A. C. *J. Appl. Polym. Sci.* **2008,***107*, 1430.

18. Tekkanat, B.; Mckynney, B. L.; Faust, H. *U.S. Pat. 5,280,*066, **1994.**

19. Xanthos, M.; Young, M. W.; Biesenberger, J. A. *Polym. Eng. Sci.* **1990,** *30*, 335.

20. Cheng, M. K.; Chan, D. *Polym. Int.* **1997,** *43*, 281.

21. Papadopoulou, C. P.; Kalfoglou, N. K. *Polymer* **2000,** *41*, 2543.

22. Lepers, J.-C.; Favis, B. D.; Tabar, R. J. *J. Polym. Sci. Part B Polym. Phys.* **1997,** *35*, 2271.

23. Lepers, J.-C.; Favis, B. D.; Kent, S. L. *Polymer* **2000,** *41*, 1937.

24. Heino, M.; Kirjava, J.; Hietaoja, P., Seppälä, J. *J. Appl. Polym. Sci.* **1997,** *65*, 241.

25. Pracella, M.; Chionna, D. *Macromol. Symp.* **2003,** *198*, 161.

26. Pracella, M; Chionna, D.; Pawlak, A.; Galeski, A. *J. Appl. Polym. Sci.* **2005,** *98*, 2201.

27. Odian, G. Principles of Polymerization; John Wiley and Sons: Hoboken, New Jersey, **2004,** p 812.

28. Vainio, T.; Hu, G.-H.; Lambla, M.; Seppälä, J. *J. Appl. Polym. Sci.* **1997,** *63*, 883.

29. Wu, S. *Polym. Eng. Sci.* **1987,** *27*, 335.

30. Baker, W. E.; Scott, C.; Hu, G.-H. Reactive Polymer Blending; Carl Hanser Verlag: Cincinnati, Ohio, **2001**, p 289.