Toughening of Polypropylene with Styrene/Ethylene-Butylene/Styrene Tri-Block Copolymer: Effects of Reactive and Nonreactive Compatibilization

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ABSTRACT: The effects of compatibilization on the toughening of polypropylene (PP) by melt blending with styrene/ethylene-butylene/styrene tri-block copolymer (SEBS) in a twin-screw extruder were investigated. The compatibilizers used were SEBS functionalized with maleic anhydride (SEBS-g-MA), PP functionalized with acrylic acid (PP-g-AA), and bifunctional compound p-phenylenediamine (PPD). The effects of the compatibilization were evaluated through the mechanical properties as well as through the determination of the phase morphology of the blends by scanning electron microscopy. Reactive compatibilized blends show up to a 30-fold increase in impact strength compared with neat PP; likely the result of the reaction of the bifunctional compound (PPD) with the acid acrylic and maleic anhydride groups, this increase in strength rendered both morphological and mechanical stability to these blends. The addition of PPD to the blends significantly changed their phase morphologies, leading to larger average diameters of the dispersed particles, probably as a result of the morphological stabilization at the initial processing steps during extrusion, with the occurrence of chemical reactions. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3466–3479, 2002

Key words: polypropylene; styrene/ethylene-butylene/styrene tri-block copolymer; toughening; reactive compatibilization

INTRODUCTION

Polypropylene (PP) is a semicrystalline polymer with very interesting mechanical properties (ductility and stiffness), good thermal properties, and excellent chemical and moisture resistance, and it is also easy to process. These characteristics make it a viable candidate for many commercial applications. For applications as an engineering plastic, however, its toughness and, in particular, its notched toughness are not sufficient. Its low impact strength at subambient temperatures may impair its performance, as well. Another limitation of PP is its poor adhesion to the surface of other phases such as rubber or polar materials. This is primarily a result of the nonpolar nature of PP.[1]

The notched impact toughness of the PP matrix can, just as with other polymers, be considerably improved by having a dispersed rubber phase present. In this way, super ductile materials can be obtained.[2]

The deformation and impact behavior of PP–rubber blends has been studied extensively.[3–23] Many researchers have written about blends of PP with ethylene-propylene rubber (PP/EPR), ethylene-propylene-diene monomer (PP/EPDM),[2–6,10,12,23] and with styrene/ethylene-butylene/styrene tri-block copolymers (PP/SEBS).[13–22] The notched fracture behavior of rubber-toughened PP depends on test conditions such as temperature and test speed,[3,4] blend morphology (size, shape, and distribution of the components), and rubber content.[5–7]

Although their molecular structures are similar, PP/rubber blends are considered immiscible.[10,12] Simple blends of immiscible polymers generally have poor mechanical properties because of unfavorable interactions between the molecular segments of the blend components. These physical blends often exhibit a high interfacial tension, and coarse, unstable phase morphologies are obtained during melt processing. In addition, the poor adhesion between the phases in the solid state often leads to premature failure or debonding under an applied stress.

Thus, many attempts have been made to enhance the miscibility and/or the polymer/rubber interfacial interaction to improve the mechanical properties of the blend.[19] The problems with these properties can be mitigated in many cases by the incorporation of a compatibilizer. This material is usually an appropriate block or graft copolymer that preferentially resides at the polymer–polymer interface during melt processing.[7] The compatibilizer can be a previously obtained block or graft copolymer with segments similar to the blend components, but this method is limited by the availability of techniques to form such materials. A generally more useful approach is the *in situ* formation

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Materials	Trade name	Supplier	MFI (dg/min)*	M_n (g/mol)	M_w (g/mol)	Other characteristics
Polypropylene	Prolen KM 6100	Polibrasil	3.5	—	—	Tm = 165°C
SEBS	Kraton G 1652	Shell Chemical	—	50.000	52.000	S/EB ≈ 29/71 wt %[†]
SEBS-g-MA	Kraton FG 1901X	Shell Chemical	—	46.000	57.000	S/EB ≈ 28/72 wt %[†] 2 wt % MA
PP-g-AA	Polybond 1001	Uniroyal Chemical	40	—	—	Tm = 161°C 6 wt % AA
PPD (p-phenilene-diamine)	—	—	—	108.14	—	Tm = 146°C Tb = 267°C

* ASTM 1238 at 2160 gr. and 230°C.
[†] Styrene/Ethylene-Butylene

of an interfacially active species during melt processing through the use of appropriate reactive functionalities. The judicious choice of a compatibilizer can often result in improved mechanical properties of the blend, in many cases with synergistic effects, when the compatibilizer can effectively stitch itself across the interface. This process reduces the interfacial tension between the blend components and minimizes dispersed phase coalescence. Both of these effects promote a stable, fine distribution of the dispersed phase within the matrix phase. In addition, these effects improve the interfacial adhesion between the blend components, which facilitates stress transfer across the interfaces, reducing the possibility of interfacial failure.[7]

SEBS are frequently used as compatibilizers in fragile polymers.[13–22] Many previous investigations have shown that the impact strength of PP is satisfactorily increased in blends with SEBS and that the yield modulus and stress decrease with increasing SEBS content.[13–16,20–22] In PP/nylon blends, a combination of SEBS and SEBS-g-MA through reactive extrusion resulted in a decrease in particle size and improvement in impact strength.[24,25] Investigations on several properties of PP/SEBS blends have shown many advantages in employing SEBS to toughen PP,[13–22] arousing much interest in exploring the behavior of this blend. The *in situ* chemical bonding between maleated PP and maleated EPDM rubber was achieved using a reactive compatibilizer such as polyether amine, which led to better interfacial adhesion between the PP and EPDM phases and improved mechanical properties.[23]

The object of this study was to investigate the effects of the addition of SEBS functionalized with maleic anhydride and of PP functionalized with acrylic acid on the physical and mechanical properties of PP/SEBS blend. A bifunctional compound (p-phenylene-diamine) was also used in this study, and its effects on the compatibility of the PP/PP-g-AA/SEBS-g-MA blends were investigated. The diamine material was expected to chemically bond the rubber SEBS-g-MA and the

PP-g-AA, a method that has been shown to be effective in maleated PP/maleated EPDM blends.[23]

EXPERIMENTAL

Materials

The PP homopolymer used in this work was Prolen KM 6100, in pellets, supplied by Polibrasil S.A.

As elastomers, a SEBS–Kraton G 1652, and its maleated version, SEBS-g-MA–Kraton FG 1901X, were used (both were supplied by Shell Chemical).

As reactive compatibilizers, a PP functionalized with acrylic acid PP-g-AA–Polybond 1001, supplied by Uniroyal Chemical, and a bifunctional compound p-phenylene-diamine (PPD) were used.

Characteristic properties of those materials used in this study are listed in Table I.

Blend preparation

A Werner and Pfleiderer ZSK-30 intermeshing corotating twin-screw extruder was used (screw diameter $D = 30$ mm; length-to-diameter ratio $L/D = 35$) to prepare the blends. As the SEBS was in the form of flakes, separate feeding was used for each material. For the binary blend (PP/SEBS-g-MA) and ternary blends, all materials were fed together. The materials and the blends were dried at 80°C at least for 4 h in a vacuum oven before compounding; the SEBS-g-MA were dried at 80°C in a vacuum oven for 24 h to remove the humidity because the maleic anhydride link can break and become a diacid in the presence of humidity.

The processing conditions were optimized for the PP/SEBS blends,[22] and all the other blends were processed under the following conditions: the temperature profile from the feed zone to the die was 190°, 200°, 210°, 210°, 210°, and 200°C; the screw speed was 250 rpm; and the feed rate was 10 kg/h.

The elastomer contents were kept constant in 20 wt % (SEBS or SEBS-g-MA). The ternary nonreactive

blends (PP/PP-g-AA/SEBS-g-MA) contained 5 wt %, 10 wt %, 15 wt %, and 20 wt % PP-g-AA. For the ternary reactive blends (PP/PP-g-AA/SEBS-g-MA/PPD), a molar ratio of 1 : 1 of acid groups and anydride was chosen, equivalent to the 5 wt % PP-g-AA, and various levels of p-phenylene-diamine (0.5 molar%, 1 molar%, 1.5 molar%, and 2 molar%) were used. The quaternary blends (PP/PP-g-AA/SEBS-g-MA/SEBS) were also prepared to check the effect of the content of the functionalized components, when SEBS replaces SEBS-g-MA. These blends contained a molar ratio of 1 : 1 of the acid and anhydride groups and 2 molar% PPD.

Morphological and mechanical characterization

The effects of the reactive compatibilization were evaluated through the mechanical properties (yield stress, strain at break, elasticity modulus, and impact strength) and morphology.

Specimens for impact resistance and tensile tests were prepared by injection molding (Arburg Allrounder 270 V). The temperature for injection molding was 190°–215°C at the different heating zones, and the temperature of the mold was 50°C. Before molding, the pelletized resins were dried at 80°C for 4 h.

Tensile tests were performed in an Instron tensile machine with dumbbell-shaped specimens according to ASTM-D 638 at a crosshead speed of 50 mm/min. At least five specimens were tested for each blend.

The Izod impact strength tests were performed according to ASTM D256 in notched samples at room temperature. Ten specimens were tested for each composition.

Before the mechanical tests, all samples were kept at room temperature for at least 48 h. The blend morphology was characterized by means of a scanning electron microscope (SEM). Notched specimens similar to those used in the impact strength tests were kept in liquid nitrogen for 30 min and then cryogenically fractured. The elastomeric particles (SEBS phase) were selectively extracted from the blends by xylene at room temperature for 30 min. All samples were washed in an ultrasonic bath and sputter coated with gold in a Balzers-SCD 050 Sputter Coater. SEM examination was performed with a Leica/Cambridge S440 microscope. A Leica Quantimet image analyzer was used to analyze the micrographs.

Verification of the blends' reactivity

The reactivity of the system was evaluated through Fourier transform infrared (FTIR) spectra analyses and torque curves obtained in a Haake torque rheometer.

The increase in the torque measured with the mixing time is indicative of the occurrence of chemical reactions between the functionalized components, the acid group of the PP-g-AA, the anhydride group of the SEBS-g-MA, and the amine group of the bifunctional compound PPD. All the compositions prepared in the extruder were mixed in a torque rheometer (Haake Rheomix 600). The rotor speed was 50 rpm, the temperature of the mixing chamber was set at 190°C, and the torque value was registered for 10 min of mixing.

FTIR analyses were performed to identify the chemical reaction between the rubber SEBS-g-MA, the PP-g-AA, and the bifunctional compound PPD. The blends prepared by extrusion were hot pressed at 190°C into thin films from which infrared spectra were taken, using a Fourier transform infrared spectrometer (PERKIN-ELMER, Spectrum 1000) at 2 cm^{-1} resolution and 24 scans.

RESULTS AND DISCUSSION

PP/SEBS-g-MA blends

We have previously reported that the impact strength of PP/SEBS blends is superior to that of pure PP for all the conditions studied.[22] Optimum values were reached, and the blend with 20 wt % of SEBS showed an impact strength of 560 J/m, which represents an increase of 25 times as compared with pure PP. These results show the efficiency of the mixture and the great affinity between PP and the rubber block (ethylene-butylene) of SEBS.

In this work, we used functional components to increase the polarity of the system and studied their influence on the mechanical and morphological properties of the blends. The results for blend PP/SEBS-g-MA are discussed first.

Lower-impact strength values were observed for the blend PP/SEBS-g-MA as compared with PP/SEBS with 20 wt % of rubber, as shown in Table II. This fact can be related to the smaller affinity of the blocks (ethylene-butylene) from SEBS functionalized (SEBS-g-MA) with PP. The presence of the functional groups maleic anhydride enhances polarity in the domains of the thermoplastic rubber SEBS-g-MA and consequently hinders interactions between the blocks (ethylene-butylene) of the rubber phase with the matrix of PP, which makes adhesion between phases more difficult. Because adhesion is jeopardized by the polarity of the rubber, the transference of stress from the matrix to the dispersed particles is also being jeopardized, which causes a lesser impact strength in the SEBS-g-MA blend as compared with the PP/SEBS blend. It is probable that the strong repulsion of the polar group (maleic anhydride) of the SEBS-g-MA with the nonpolar PP causes this phenomenon. These results agree with the data obtained for interfacial strength by Setz,[26] who observed less interface resistance for PP/SEBS-g-MA compared with that of PP/SEBS.

TABLE II
Mechanical and Morphological Properties of the PP/SEBS and PP/SEBS-g-MA Blends
with 20 wt % Elastomer

Properties	PP/SEBS	PP/SEBS-g-MA
Izod impact strength (J/m)	561 ± 13	330 ± 12
Tensile modulus (MPa)	1117 ± 12	1166 ± 63
Tensile yield stress (MPa)	25.9 ± 0,1	26.6 ± 0.1
Strain at break (%)	130 ± 17	100 ± 17
Equivalent average diameter (μm)	0.15 ± 0.08	0.15 ± 0.07

As seen in Figure 1, SEBS showed torque values superior to those obtained for SEBS-g-MA, indicating greater resistance to flow, which is related to the viscosity of the material, under those mixture conditions. The average particle size of the dispersed phase is directly related to factors such as viscosity ratio and interfacial tension. The greater the viscosity of the dispersed phase and the interfacial tension, the greater the average size of particles will be. From these observations, one would expect bigger particles for the blend prepared with the rubber SEBS as opposed to that prepared with the rubber SEBS-g-MA. However, the morphologies of both blends showed the same average size of particles, as shown in Figure 2. Therefore, the differences obtained for the impact strength of the blends can be related to the adhesion between the phases, as discussed previously.

The results obtained for the tensile stress tests, seen in Table II, show that the elasticity modulus did not vary for the blends with SEBS or with SEBS-g-MA. However, the yield stress of PP/SEBS is slightly inferior, and consequently, the rate of initiation of toughening mechanisms is faster, making the blend with SEBS supposedly more efficient in this aspect when compared with SEBS-g-MA. As to the deformation as failure, PP/SEBS showed a superior value being, thus, more efficient in controlling propagation and termination of toughening mechanisms.
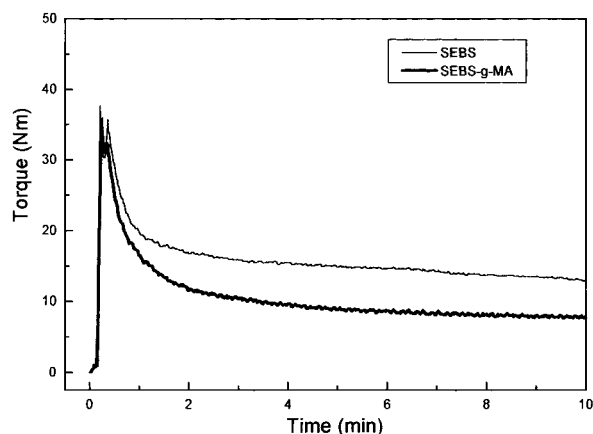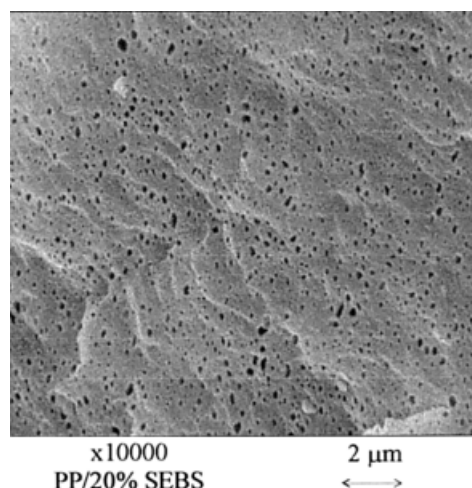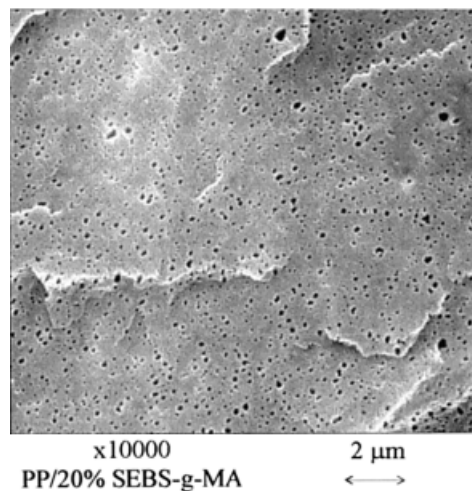

x10000   2 µm
PP/20% SEBS

(a)

x10000   2 µm
PP/20% SEBS-g-MA

(b)

Figure 2 Micrographs of the (a) polypropylene (PP)/20 wt % styrene/ethylene-butylene/styrene tri-block copolymer (SEBS) and (b) PP/20 wt % SEBS functionalized with maleic anhydride (SEBS-g-MA) blends.

Figure 1 Torque versus time curves obtained with a Haake rheometer for the blends polypropylene (PP)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) (80 wt %/20 wt %) and PP/SEBS functionalized with maleic anhydride (SEBS-g-MA) (80 wt %/20 wt %) (at 50 rpm, 190°C, 10 min).

TABLE III
Izod Impact Strength of the PP/PP-g-AA/SEBS-g-MA Blend, Tested 48 h and 30 days After Injection of the Samples

	Izod Impact Strength (J/m)	
Wt % PP-g-AA	48 h	30 days
0	330 ± 12	330 ± 12
5	400 ± 14	79 ± 10
10	267 ± 33	78 ± 8
20	162 ± 50	50 ± 4
30	210 ± 89	64 ± 1

PP/PP-g-AA/SEBS-g-MA blends

Using PP-g-AA as the compatibilizing agent of PP/SEBS-g-MA, a slight tendency toward the increase of the impact strength was verified for the content of 5 wt %, and immediately after this content, the value dropped, as shown in Table III and Figure 3. Most of the compositions showed moderate dispersion, which can be related to the nonhomogeneity of the mixtures, lack of interaction between the reactive groups, instability in the possible chemical interactions, and so forth.

These results also showed considerable decrease of the values for impact strength throughout a period of 30 days, as shown in Table 3 and Figure 3. The necessity of further study of the possible interaction between the chemical groups in the mixture and the mixture's stability as a function of time was justified. The instabilities can be related to the reversibility of chemical interactions between the functional groups.

The use of torque rheometry is common in the study of reactive polymeric blends. The torque curves allow for the evaluation of the behavior of materials under flow conditions, and they can also indicate the occurrence of chemical reactions in reactive systems through the increase of torque as a function of time for the mixture of components.

With this objective, tests were carried out in a Haake torque rheometer to check for the behavior of the PP/PP-g-AA/SEBS-g-MA. The compositions were the same that were used for the mechanical tests.

The torque curves, presented in Figure 4, do not indicate the occurrence of chemical reactions between the acid group of the PP and the anhydride group of the SEBS, as they show no increase in the values of torque. There was a slight reduction in torque values with increasing quantities of PP-g-AA, probably because of the smaller viscosity of this material compared with PP.

This study reveals that it is necessary to use a more appropriate material to interact and/or react simultaneously with the acid groups of PP and the anhydride groups of SEBS.

PP/PP-g-AA/SEBS-g-MA/PPD blends

The addition of a bifuncional compound (PPD) capable of reacting simultaneously with both functional groups (maleic anhydride and acrylic acid) is a possible way to improve interface adhesion[27] and at the same time stabilize the properties for PP/PP-g-AA/SEBS-g-MA.

The bifuncional compound that was chosen was PPD, as it possesses two amine groups that could react simultaneously with PP functionalized with acrylic acid and with SEBS functionalized with maleic anhydride. Amine, an important class of modifiers, pre-
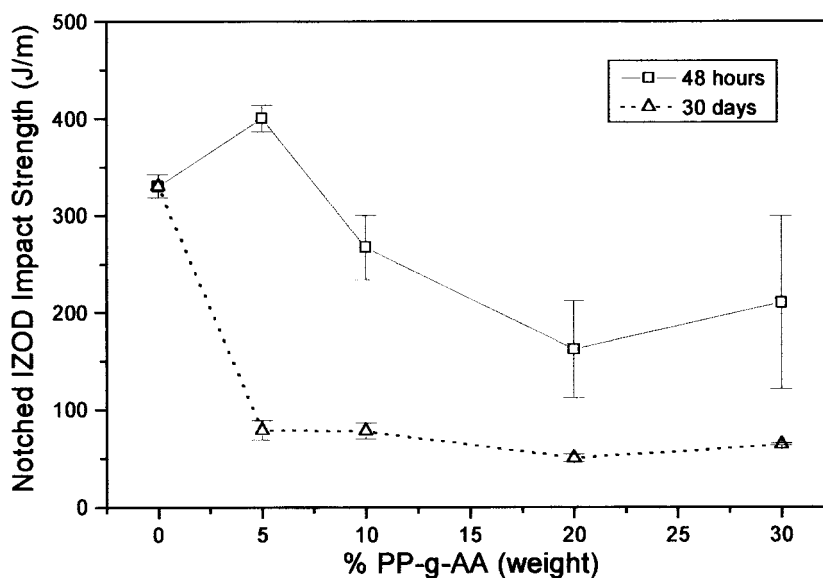

Figure 3 Izod impact strength as a function of the percentage of polypropylene functionalized with acrylic acid tested 48 h e 30 days after injection.
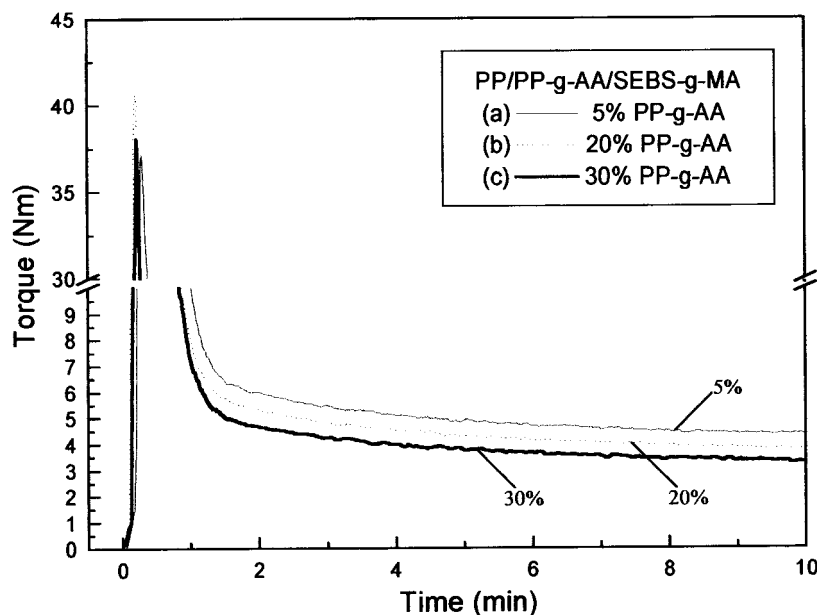
Figure 4 Torque versus time curves obtained for the blends polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA) (a) 5 wt %, (b) 20 wt %, and (c) 30 wt % PP-g-AA (at 50 rpm, 190°C, 10 min).

sents a high reactivity with polymers that contain carboxylic acids or maleic anhydride.

Table IV shows the values of mechanical properties and the average size of particles for the blends with PPD. As shown in Figure 5, the proportions of 0.5 wt % and 1 wt % of PPD in the blends lead to a decrease in the values of impact strength in relation to the blend without PPD. However, with bigger proportions such as 1.5 wt % and 2 wt %, the impact strength improved remarkably. With small amounts of PPD (proportions of 0.5 wt % and 1 wt %), the mating of reactive groups on the surface could become more difficult, and consequently, there could be a smaller incidence of chemical reactions taking place. This small number of bonds is likely to be also caused by the presence of some nonreactive functional groups that might be hampering the performance of the blend, reducing the impact strength.

Impact strength is a mechanical property that is directly related to the absorption of energy through the action of toughening mechanisms. How efficiently these mechanisms will act on multiphase systems depends strongly on the dispersed particles' size and on

the adhesion between phases in the system. For each type of material there is an optimum particle size for toughening. Adhesion can be improved by chemical reactions, as the reactions can reduce interfacial tension and the size of the dispersed particles during the preparation of the mixtures.

Blends with PPD did not show reduced particle size; adversely, the particles showed larger average sizes both in the ternary blends without PPD and in the binary blends PP/SEBS and PP/SEBS-g-MA. The morphologies and average diameters of the particles are presented in Figures 6 and 7, respectively.

Hu[28] observed that reactive blends have their phase morphology developed in the initial steps of the mixing process soon after the melting zone, which prevents any changes occurring because of the action of the final segments of the extrusion screw. The chemical reactions that take place are able to stabilize the morphology for the blend at the beginning of the extrusion process, whereas this fact was not observed for the mechanical blend without chemical reaction. In conventional nonreactive mechanical blends, rubber particles only reach their final morphology when leav-

TABLE IV
Mechanical and Morphologic Properties of the PP/PP-g-AA/SEBS-g-MA/PPD Ternary Blends Used in This Study

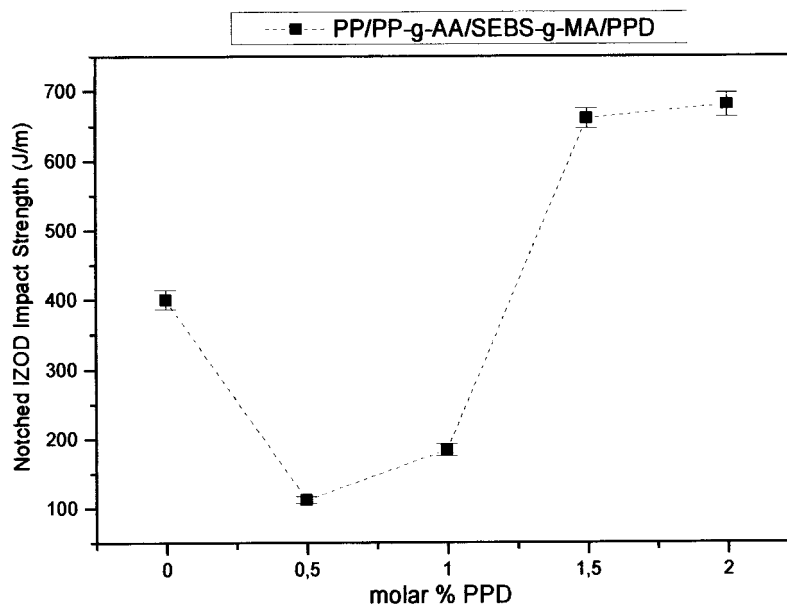| Properties	A110	A1105	A111	A1115	A112
Izod impact strength (J/m)	400 ± 14	112 ± 5	184 ± 9	660 ± 14	680 ± 17
Tensile modulus (MPa)	1092 ± 0	1087 ± 41	1046 ± 23	1070 ± 30	1039 ± 71
Tensile yield stress (MPa)	26.1 ± 0.1	25.9 ± 0.1	25.1 ± 0.2	24.3 ± 0.3	24.1 ± 0.1
Strain at break (%)	177 ± 9	77 ± 15	67 ± 2	168 ± 6	189 ± 5
Equivalent average diameter (μm)	0.23 ± 0.15	0.33 ± 0.18	0.39 ± 0.18	0.44 ± 0.21	0.47 ± 0.20

Figure 5 Izod impact strength in relation to the proportions of p-phenylenediamines (PPD) (% molar) added to the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block co-polymer) functionalized with maleic anhydride (SEBS-g-MA)/PPD blends.

ing the extruder; that is, their morphology is developed throughout the process within the extruder.

In this study, it was verified that for the reactive system, there is no such strong reduction in the size of particles compared with the nonreactive blends. The final morphology of the blends with PPD shows rubber particles with average sizes superior to the blends without PPD. This phenomenon can be related to the observations made by Hu,[28] who suggests that at the beginning of the process, soon after the melting zone, the rubber particles could have a larger average diameter as they would not yet have passed the shearing zone of the extruder. Subsequently, with the occurrence of chemical reactions, this morphology could have stabilized with larger average diameters and thus, passed through the other shearing zones without changing diameter. After the morphology of the reactive blends is established, they do not change throughout the mixture, as the dispersed particles are stabilized by the formation *in situ* of reactions between functional groups.

The results of the tensile tests are presented in Table IV. As to the elasticity modulus, the blends showed almost the same values for the different contents of PPD. With the addition of PPD, there was a slight decrease in yield strength; however, the maximum deformation at failure was smaller for PP/PP-g-AA/ SEBS-g-MA/PPD (1 : 1 : 0.5) and (1 : 1 : 1). Therefore, this indicates that the sizes of the dispersed particles were not appropriate to generate a large number of shearing bands and/or crazes of small size throughout the specimen, which caused small absorption of the energy used to deform the specimen and, conse-

quently, a decrease of maximum deformation at failure and impact resistance. The PP/PP-g-AA/SEBS-g-MA/PPD blends (1 : 1 : 1.5 and 1 : 1 : 2) showed increased deformation at failure, with average particle sizes that were capable of initiating and terminating toughening mechanisms, leading to excellent mechanical properties.

As discussed previously, PP/PP-g-AA/SEBS-g-MA showed a decrease in impact strength with time. Consequently, a bifuncional compound, which was able to interact simultaneously with both the acid and anhydride groups of the PP and SEBS, was used to stabilize both the morphology and impact strength of the blends. A very interesting result was found for the reactive system. Both the impact strength and the morphology did not change with time. From Figure 8, it is possible to verify that the impact strength of the PP/PP-g-AA/SEBS-g-MA/PPD blends (1 : 1 : 2) remained around 680 J/m for different intervals of time between the preparation of specimens and the test. These systems did not show any decrease of this property, as observed previously without the bifuncional compound. No changes were observed on the morphology of the blends, either, as seen in Figure 9. The chemical reactions, which occurred between the components, probably led to the morphological and mechanical stabilization that was observed.

Diamine reactions with polymers containing acid and anhydride groups should lead to the formation of primary chemical bonds, which would cause higher molecular weight and viscosity in the system. It is for that reason that we expected higher torque during the processing in the melt state. The torque values versus
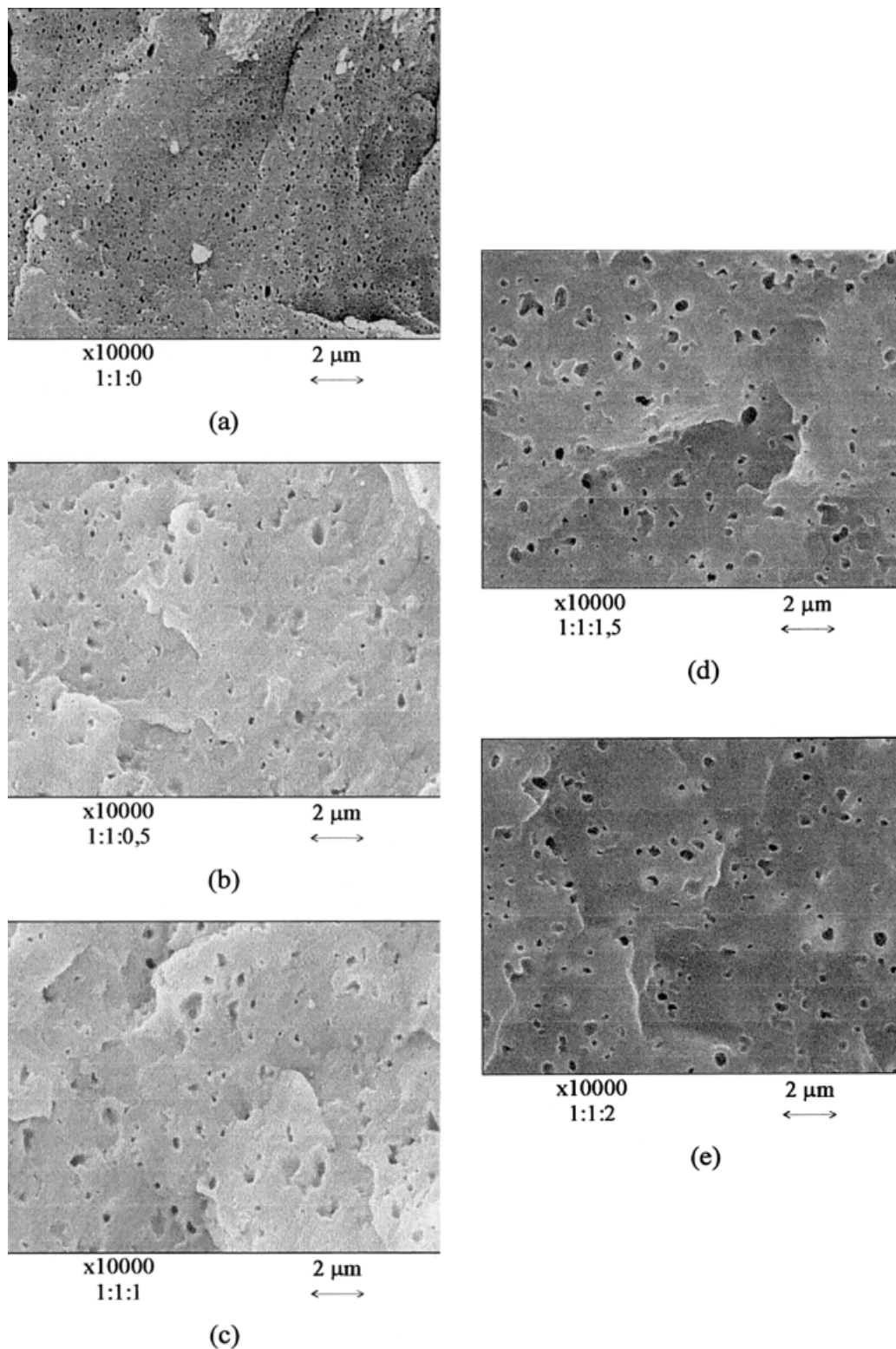
Figure 6 Micrographs of the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/p-phenylenediamines blends with proportions (a) 1 : 1 : 0, (b) 1 : 1 : 0.5, (c) 1 : 1 : 1, (d) 1 : 1 : 1.5, and (e) 1 : 1 : 2.

time are presented in Figure 10, where it is possible to verify an increase in torque for the blend with PPD after melting.

The characterization of the possible chemical reactions between the acid and anhydride groups with PPD was carried out through FTIR of the films ob-
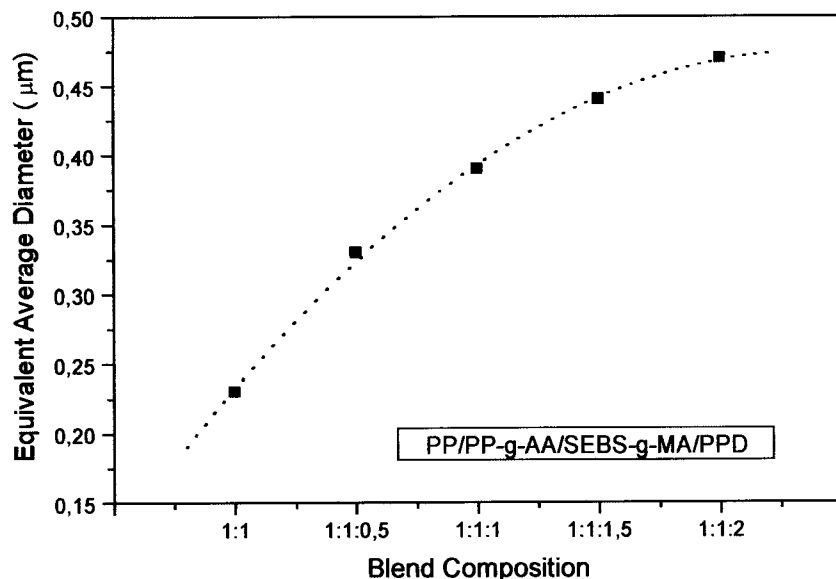
Figure 7 Equivalent average diameter of the dispersed phase as a function of the proportion of p-phenylenediamines (PPD) added to the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/PPD blends.

tained from the blends prepared in a twin-screw extruder. The evaluation of the most likely chemical reactions was done through the observation of the behavior of peaks corresponding to the absorption of the functional groups of each component and verifying the development, or lack thereof, of new peaks as a result of the chemical reactions that occurred.

The identification of the characteristic peaks of the functional groups and the analysis of the infrared absorption spectra were hindered by the low concentrations of the functionalized components in the

blends and also by the superposition of some of the characteristic peaks. Figures 11 and 12 show the spectra obtained for PP/PP-g-AA/SEBS-g-MA with different contents of PPD.

The analysis of the spectra show that with the addition of PPD, there was a decrease in the intensity of the peaks of absorption situated around the regions of 1782 and 1865cm^{-1} that corresponds to the stretching of the carbonyl of maleic anhydride in SEBS. There was also an increase in the intensity of the peak of absorption at 1710 cm^{-1} that corresponds to the vibra-
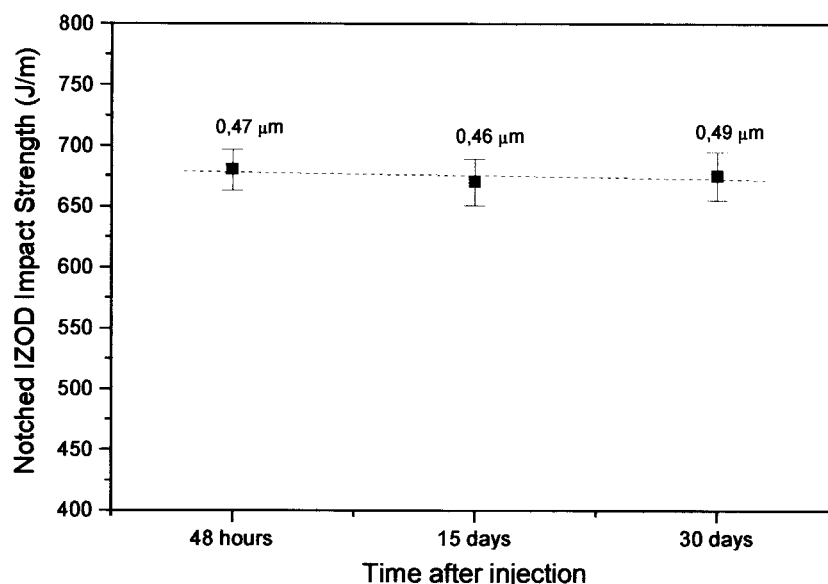

Figure 8 Izod impact strength for the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/p-phenylenediamines blend (1 : 1 : 2) as a function of time and its equivalent average diameter of the dispersed phase.
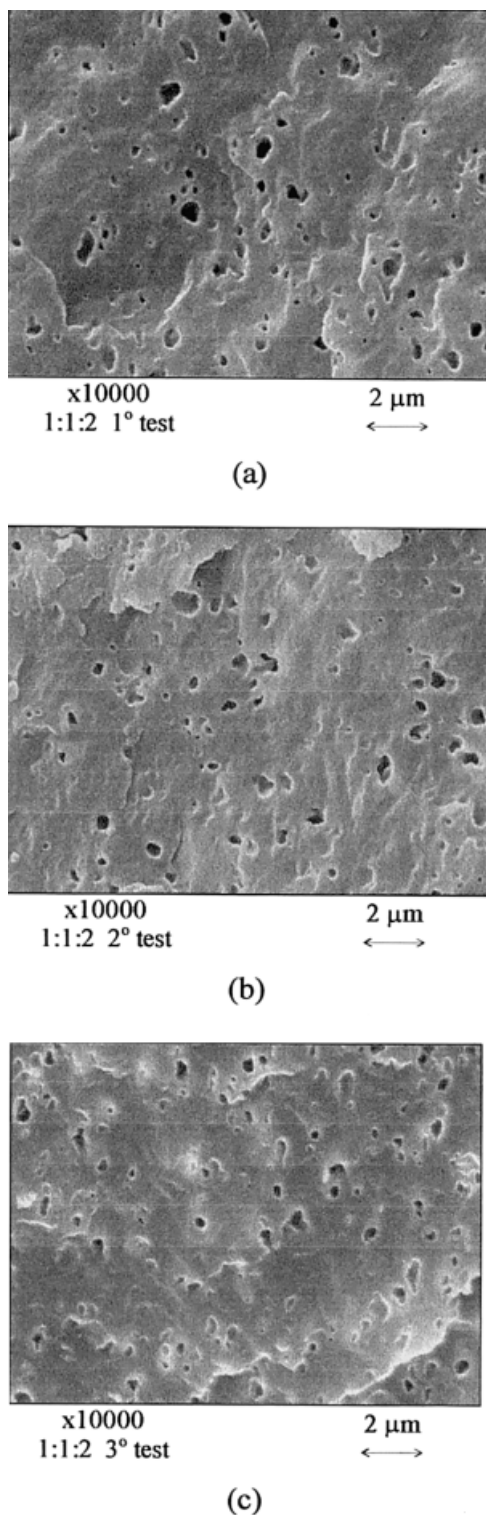
Figure 9 Micrographs of the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/p-phenylenediamines blend (1 : 1 : 2) used to verify the stability with time (a) 48 h, (b) 15 days, and (c) 30 days after injection.

tion of carbonyl of carboxylic acid in the PP. The fact that the peaks of absorption at 1865 and 1782 cm^{-1} are totally absent for PP/PP-g-AA/SEBS-g-MA/PPD (1 :

1 : 2) indicates a considerable extension of the reaction. The intensification of the absorption around 1710 cm^{-1} indicates the conversion of anhydride into carboxylic acid groups and amide. Figure 13 illustrates the possible reactions that are taking place in these systems.

The vibration of carbonyl from an amide group usually occurs around 1620 cm^{-1}, and as observed in Figure 11, it was not possible to identify any absorption in this region for PP/PP-g-AA/SEBS-g-MA/PPD (1 : 1 : 0.5). However, there is a peak of absorption in the spectra of PP/PP-g-AA/SEBS-g-MA/PPD (1 : 1 : 2) at 1620 cm^{-1}. Amide groups can also show infrared absorption peaks between 3360 and 3445 cm^{-1}, corresponding to the vibration of the group N–H of the secondary amide. Figure 12 shows spectra where it is possible to observe the presence of two new peaks of absorption at 3365 and 3445 cm^{-1} for PP/PP-g-AA/ SEBS-g-MA/PPD (1 : 1 : 2), whereas for PP/PP-g-AA/ SEBS-g-MA, these peaks were not present. These observations support the suggestion of the formation of amide groups through the reaction that was proposed. The increase in absorption around 1515 cm^{-1} for the blends with PPD is related to the vibrations of angular deformation of groups N–H of the secondary amides.

It is believed that the possibility of existence of nonreacted maleic anhydride is minimal because of the total disappearance of absorption at 1865 and 1782 cm^{-1} for PP/PP-g-AA/SEBS-g-MA/PPD (1 : 1 : 2). However, it is difficult to make any statement about acrylic acid because, with the opening of anhydride for the reactions, an acid group also formed, causing the superposition of peaks, which hindered the identification of nonreactive acid. Either PP/PP-g-AA/ SEBS-g-MA/PPD (1 : 1 : 0.5) and (1 : 1 : 1) did not show any traits of the formation of amide groups because of the nonexistence of absorption peaks at 1620 cm^{-1} or the level of reaction was not high enough to be detected by the FTIR spectra. This can be related to the decrease of impact strength for these blends. It is likely that the nonreactive groups or the low level of reaction spoilt this property.

As a result of the study of infrared spectroscopy, it is possible to assume that the reactions between the acid groups of PP and maleic anhydride of SEBS with PPD occurred through the formation of amide groups, according to the reactions proposed in Figure 13.

PP/PP-g-AA/SEBS-g-MA/SEBS blends

For economic reasons and also because of the possibility of diluting the concentration of maleic anhydride, the blends were prepared with both elastomers (SEBS and SEBS-g-MA), where the functionalized elastomer was replaced in the concentration by the elastomer without functionalization. Blends both with PPD and without PPD were prepared. The proportion
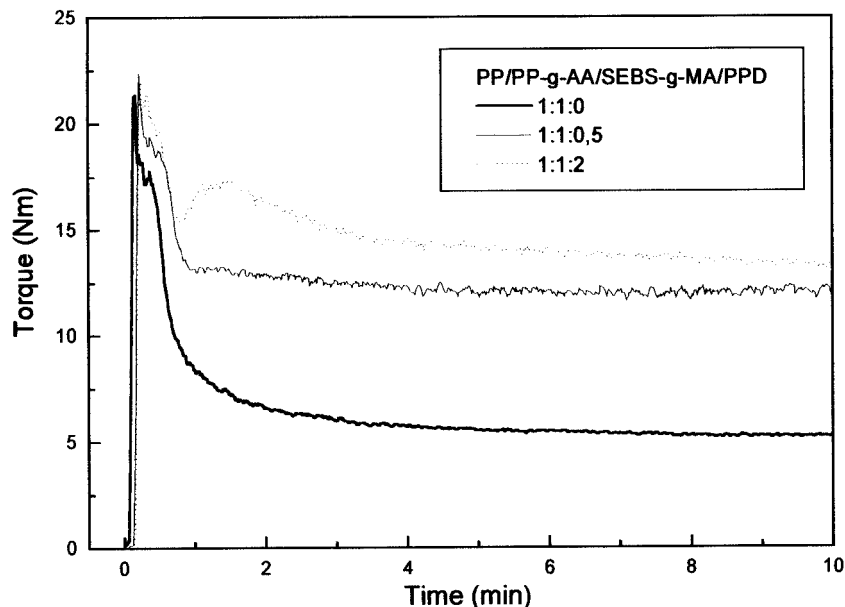
Figure 10 Torque versus time curve obtained by torque rheometer for polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/p-phenylenediamines (1 : 1 : 0, 1 : 1 : 0.5, and 1 : 1 : 2).

of acid to anhydride was kept at 1 : 1, and the proportion of PPD was 2. These proportions were established taking our previous work into consideration. Mechanical and morphological properties are shown in Table V.

Figure 14 shows a comparison between the impact strength of the ternary blend PP/PP-g-AA/SEBS-g-MA and the quaternary blends PP/PP-g-AA/SEBS-g-MA/SEBS. It is possible to verify increased impact strength with increased content of SEBS. This is be-

cause the pending functional groups in PP and in SEBS-g-MA may be hindering the interaction between PP and SEBS. To keep the proportion of acid and anhydride in the quaternary blend with the addition of the elastomer SEBS, both contents of PP-g-AA and SEBS-g-MA were reduced. The decrease in the content of the functional groups (acid and anhydride) has probably facilitated the approximation between PP and SEBS, which resulted in improved impact
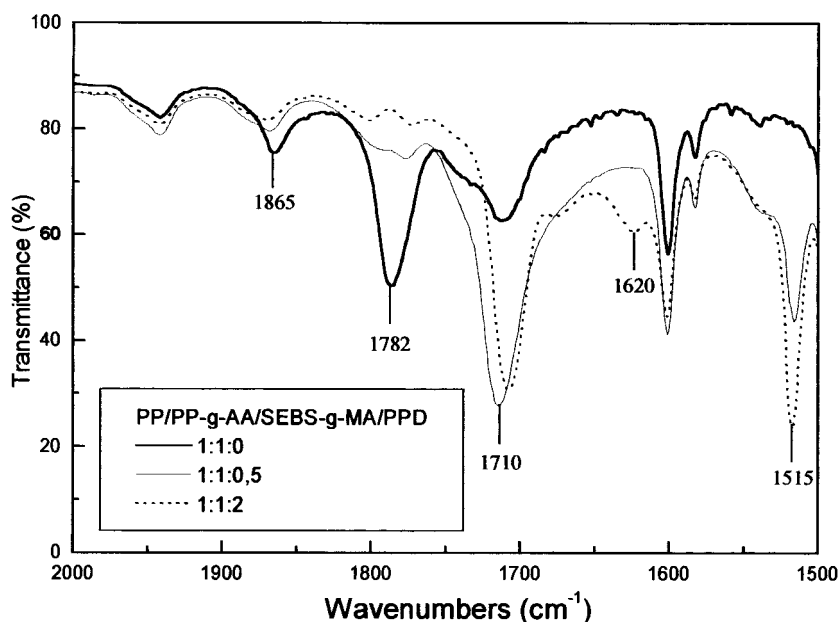

Figure 11 Fourier transform infrared spectra obtained from pressed films of the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/p-phenylenediamines blends for the range of wavelength 2000 to 1500 cm^{-1}.
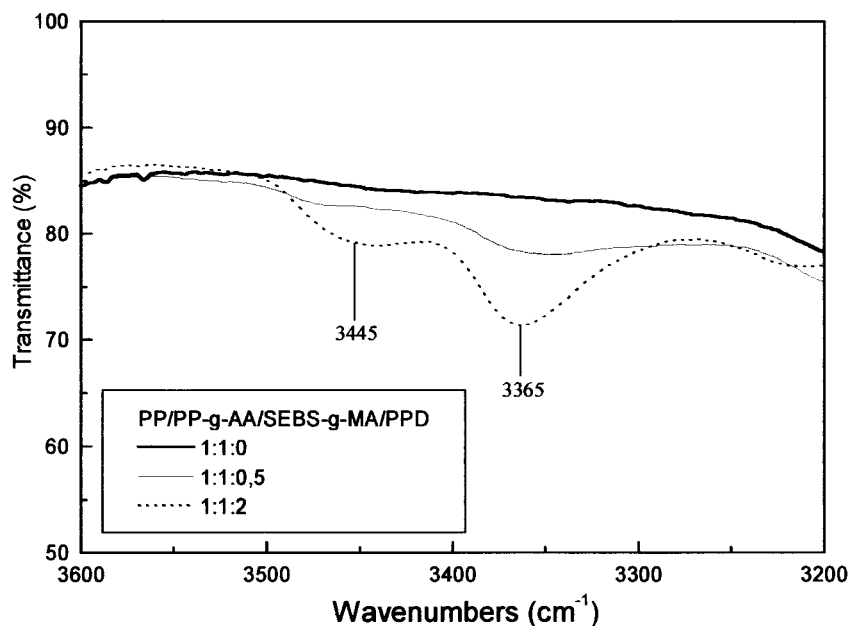
Figure 12 Fourier transform infrared spectra obtained from pressed films of the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/p-phenylenediamines blends for the wavelength range of 3600 to 3200 cm^{-1}.

strength. As to the results of the tensile test, the elasticity modulus did not show significant change, the yield strength showed a slight decrease, and the deformation at failure increased. The addition of SEBS provided for better actuation of the toughening mechanisms and, consequently, for better absorption of mechanical energy.

It is usually expected for the reactive blends to show more elevated impact strength than the blends without reactive compatibilization. However, the system that was studied is very complex, and this phenomenon was not observed. Fewer chemical reactions may

have occurred because of the addition of SEBS to the blend. This fact could possibly explain the less significant impact strength of quaternary blends with PPD as compared with the PP/PP-g-AA/SEBS-g-MA/PPD blend (1 : 1 : 2), as seen in Figure 15. The level of interfacial chemical reactions may have rested below a minimum, which would affect the toughness of the system satisfactorily because of the reduction of the contents of functionalized PP and SEBS, and this may be detrimental to the performance of the blend.

The different properties of impact strength between the quaternary blends with and without PPD may
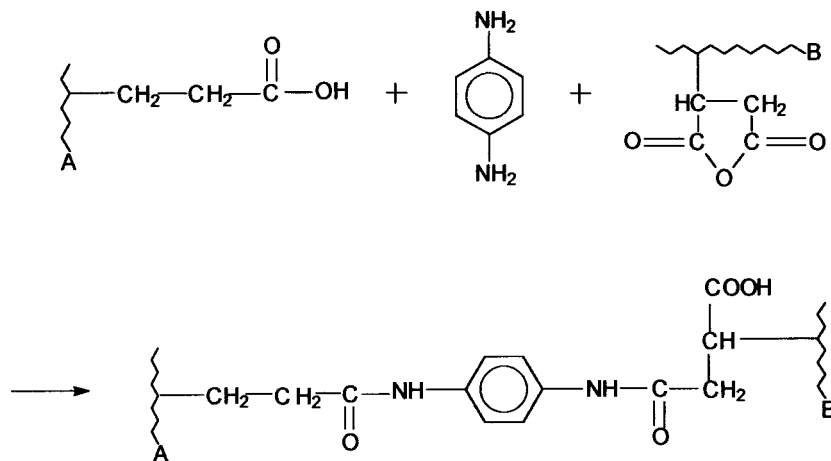

Figure 13 Probable chemical reaction between the acid groups of the polypropylene (PP) (PP functionalized with acrylic acid [PP-g-AA]) and anhydride groups present in SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA) with the diamines of p-phenylenediamine, where (A) represents the chain of PP and (B) the chain of SEBS.

Properties	Q15/5	Q10/10	Q5/15	Q15/5-2	Q10/10-2	Q5/15-2
Izod impact strength (J/m)	540 ± 16	567 ± 18	598 ± 16	570 ± 12	535 ± 14	179 ± 18
Tensile modulus (MPa)	1068 ± 51	1081 ± 41	1069 ± 28	1130 ± 50	1115 ± 57	1194 ± 60
Tensile yield stress (MPa)	24.9 ± 0.1	24.6 ± 0.1	24.0 ± 0.1	25.3 ± 0.1	25.2 ± 0.1	25.5 ± 0.1
Strain at break (%)	182 ± 6	191 ± 18	200 ± 14	140 ± 60	74 ± 7	71 ± 7
Equivalent average diameter (μm)	0.18 ± 0.09	0.19 ± 0.09	0.22 ± 0.11	0.63 ± 0.23	0.67 ± 0.32	0.45 ± 0.27

possibly be explained by the fact that, although the elastomer SEBS does not show reactive functional groups capable of reacting with PPD, it has more affinity with PP than the elastomer SEBS-g-MA, owing to its lack of polarity, which can consequently lead to improved mechanical properties.

CONCLUSIONS

The blend with functionalized elastomer with maleic anhydride (PP/SEBS-g-MA) showed reduced impact strength. This is attributed to the polarity of the elastomer, which is detrimental to the interactions between PP and the blocks (ethylene-butylene) of the SEBS copolymer.

The impact strength of the ternary blends with PP functionalized with acrylic acid showed a slight increase compared with PP/SEBS-g-MA, but it varied with time. It was thus necessary to use a bifuncional component with amine groups capable of reacting simultaneously with the acid groups of the PP and maleic anhydride of the SEBS, as evidence of chemical

reactions between acid and anhydride was not observed by torque rheometry.

The mechanical performance showed by the ternary blend with the bifuncional component (PPD) in the proportion 1 : 1 : 2 was superior when compared with the other blends studied. The impact strength reached a value approximately 30 times that of pure PP, which is 680 J/m. This blend also showed stability in both morphology and impact strength.

The occurrence of chemical reactions between the components was verified through both torque rheometry and infrared spectroscopy (FTIR). It was possible to detect the increase in the values of torque and the formation of amine groups from the reactions involving the amine from PPD, the maleic anhydride of the SEBS, and the acrylic acid of the PP.

The quaternary blends PP/PP-g-AA/SEBS-g-MA/ SEBS with PPD showed inferior impact performance compared with the ternary blend PP/PP-g-AA/SEBS-g-MA with PPD (1 : 1 : 2). This is a result of the decrease in the content of functionalized components,
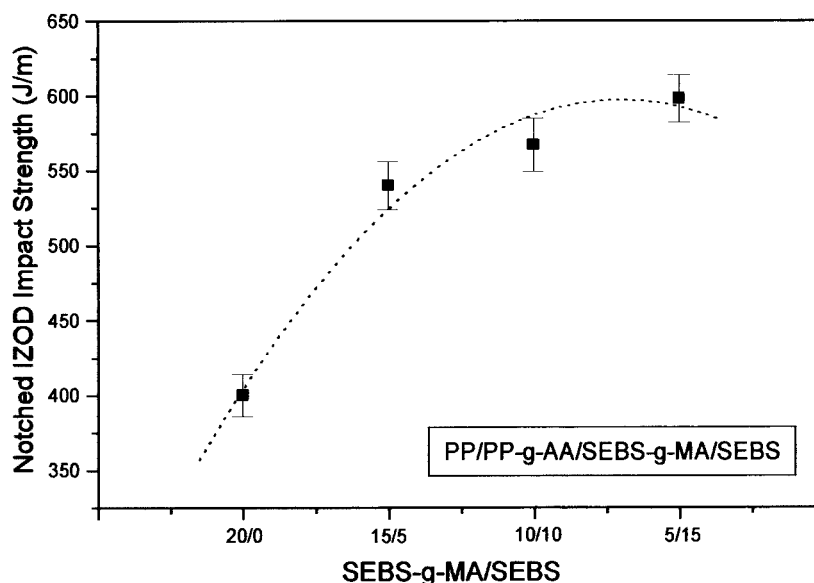

Figure 14 Izod impact strength of the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA) ternary blend (20/0) and the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA)/SEBS quaternary blends (15 : 5, 10 : 10, and 5 : 15) with p-phenylenediamine. Proportions of SEBS-g-MA/SEBS were 20 : 0, 15 : 5, 10 : 10, and 5 : 15.
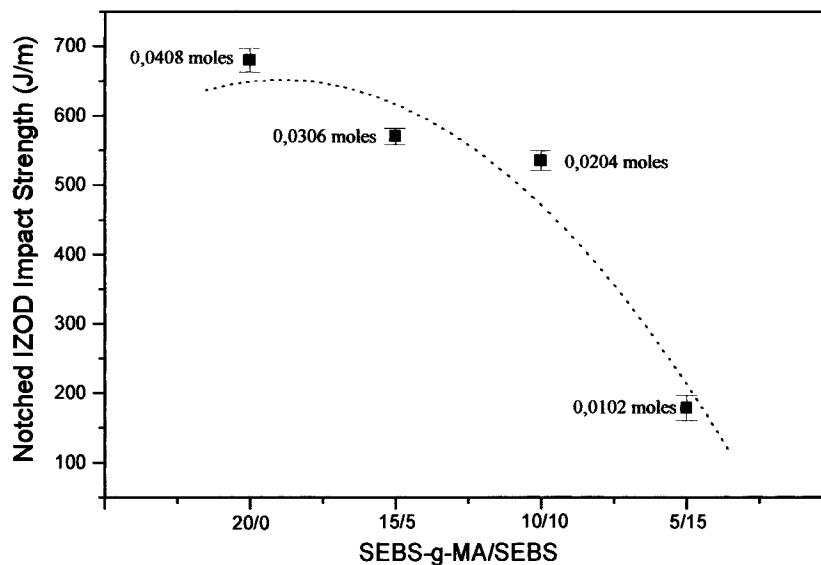
Figure 15 Izod impact strength of the polypropylene (PP)/PP functionalized with acrylic acid (PP-g-AA)/SEBS (styrene/ethylene-butylene/styrene tri-block copolymer) functionalized with maleic anhydride (SEBS-g-MA) blends and the PP/PP-g-AA/SEBS-g-MA/SEBS blends with p-phenylenediamine (1 : 1 : 2), where the respective molar values of the contents of acid and maleic anhydride are presented.

which led to the reduction of the number of chemical reactions.

The addition of PPD to the blends with functionalized components caused the increase, in terms of average diameter, of dispersed particles as compared with the blends without the bifunctional components. This is likely to the result of to the stabilization of the morphology in the initial steps of processing with the chemical reactions.

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