

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

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ABSTRACT: The effects of the compatibilization on the toughening of polypropylene (PP) by melt blending with styrene/ethylene-butylene/styrene triblock copolymer (SEBS) in a twin-screw extruder were investigated. The compatibilizers used were an SEBS functionalized with maleic anhydride, a PP functionalized with acrylic acid, and a bifunctional compound, *p*-phenylenediamine (PPD). The effects of the compatibilization were evaluated through the mechanical properties and by 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 to neat PP, which was

likely to have been due to the reaction of the bifunctional compound (PPD) with the acid acrylic and maleic anhydride groups, which rendered both morphological and mechanical stability to these blends. The addition of the PPD to the blends significantly changed their phase morphologies, leading to larger dispersed particles' average diameters, probably due to the morphological stabilization at the initial processing steps during extrusion, with the occurrence of the chemical reactions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1081–1094, 2003

Key words: poly(propylene) (pp)

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, too. Another limitation of PP is its poor adhesion to the surface of other phases such as rubber or polar materials. This is primarily due to the nonpolar nature of PP.¹

The notched impact toughness of the PP matrix can, just like with other polymers, be considerably improved by the presence a dispersed rubber phase. In this way, superductile materials can be obtained.²

The deformation and impact behavior of PP–rubber blends has been studied extensively.^{3–23} Many researches have published works about blends of PP with ethylene–propylene rubber, PP with ethylene–propylene–diene monomer (EPDM),^{2–6,10,12,23} and PP with styrene/ethylene–butylene/styrene triblock co-

polymer (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, which result from unfavorable interactions between the molecular segments of the blend components. These physical blends often exhibit a high interfacial tension and coarse, unstable phase morphologies 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 These problems can be mitigated in many cases by the incorporation of a compatibilizer. This material is usually an appropriate block or graft copolymer, which 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 of an interfacially active species during melt processing through

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TABLE I
Characteristic Properties of the Materials Used in This Study

Material	Trade name	Supplier	MFI (dg/min) ^a	M_n (g/mol)	M_w (g/mol)	Other characteristics
PP	Prolen KM 6100	Polibrasil	3.5	—	—	$T_m = 165^\circ\text{C}$
SEBS	Kraton G 1652	Shell	—	50,000	52,000	S/EB \approx 29/71 wt %
SEBS-g-MA	Kraton FG 1901X	Shell Chemical	—	46,000	57,000	S/EB \approx 28/72 wt % 2 wt % MA
PP-g-AA	Polybond 1001	Uniroyal	40	—	—	$T_m = 161^\circ\text{C}$ 6 wt % AA
PPD	—	—	—	108.14	—	$T_m = 146^\circ\text{C}$ $T_b = 267^\circ\text{C}$

MFI = melt flow index; M_n = number-average molecular weight; M_w = weight-average molecular weight; T_m = melting temperature; S/EB = styrene/ethylene-butylene.

^a ASTM 1238 at 2160 gr and 230°C.

the use of appropriate reactive functionalities. The judicious choice of a compatibilizer can often result in the improvement of the 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 improve the interfacial adhesion between the blend components, which facilitates stress transfer across the interfaces and reduces the possibility of interfacial failure.⁷

SEBSs 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 functionalized with maleic anhydride (SEBS-g-MA) through reactive extrusion resulted in a decrease in particle size and an improvement in impact strength.^{24,25} Investigations on several properties of PP/SEBS blends have shown many advantages in the employment of SEBS to toughen PP,^{13–22} arousing much interest in the exploration of the behavior of this blend. The *in situ* chemical bonding between maleated PP and maleated EPDM rubber was achieved with reactive compatibilizers such as polyether amine; this led to better interfacial adhesion between the PP and EPDM phases and improved mechanical properties.²³

The scope of this work was to investigate the effects of the addition of SEBS-g-MA and of PP functionalized with acrylic acid (PP-g-AA) on the physical and mechanical properties of the PP/SEBS blend. A bifunctional compound [*p*-phenylenediamine (PPD)] 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, (Kraton G 1652) and its maleated version (SEBS-g-MA; Kraton FG 1901X) were used; both were supplied by Shell Chemical.

As reactive compatibilizers, PP-g-AA (Polybond 100), supplied by Uniroyal Chemical, and a bifunctional compound were used.

Characteristic properties of the 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 = 30 mm; length-to-diameter ratio = 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 the materials were fed together. The materials and the blends were dried at 80°C for at least 4 h in a vacuum oven before compounding; only the SEBS-g-MA was dried at 80°C in a vacuum oven for 24 h to remove the humidity because the MA link could 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 was 190, 200, 210, 210, 210, and 200°C from the feed zone to the die, the screw speed was 250 rpm, and the feed rate was 10 g/h.

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

Property	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

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, 10, 15, 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 anhydride was chosen, equivalent to 5 wt % PP-g-AA, and various levels of PPD, 0.5, 1, 1.5 and 2 mol %, 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 replaced 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 All-rounder 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 D 256 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 scanning electron microscopy (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 for analysis of the micrographs.

Verification of the blend reactivity

The reactivity of the system was evaluated through Fourier transform infrared (FTIR) spectra analyses

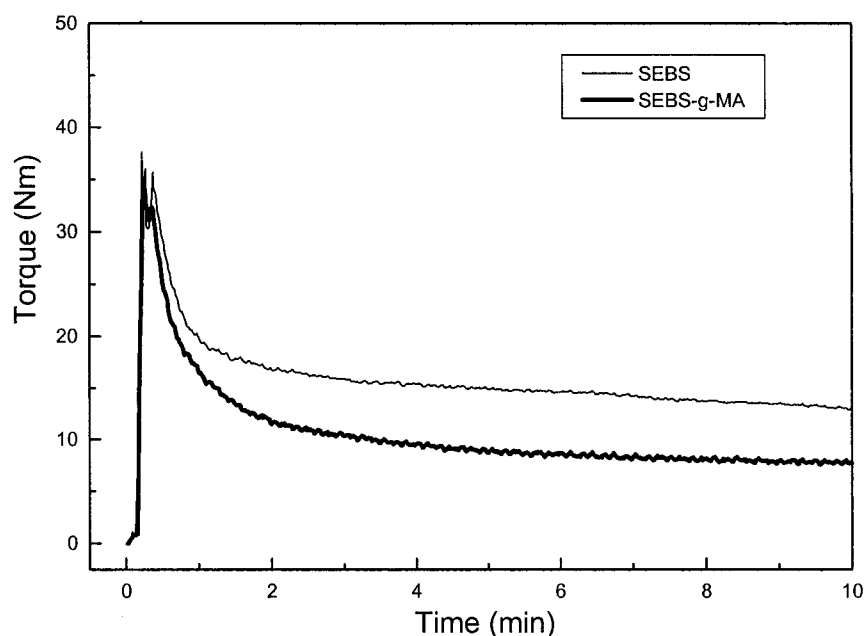


Figure 1 Torque versus time curves obtained with a Haake rheometer for the PP/SEBS (80/20 wt %) and PP/SEBS-g-MA (80/20 wt %) blends (50 rpm, 190°C, 10 min).

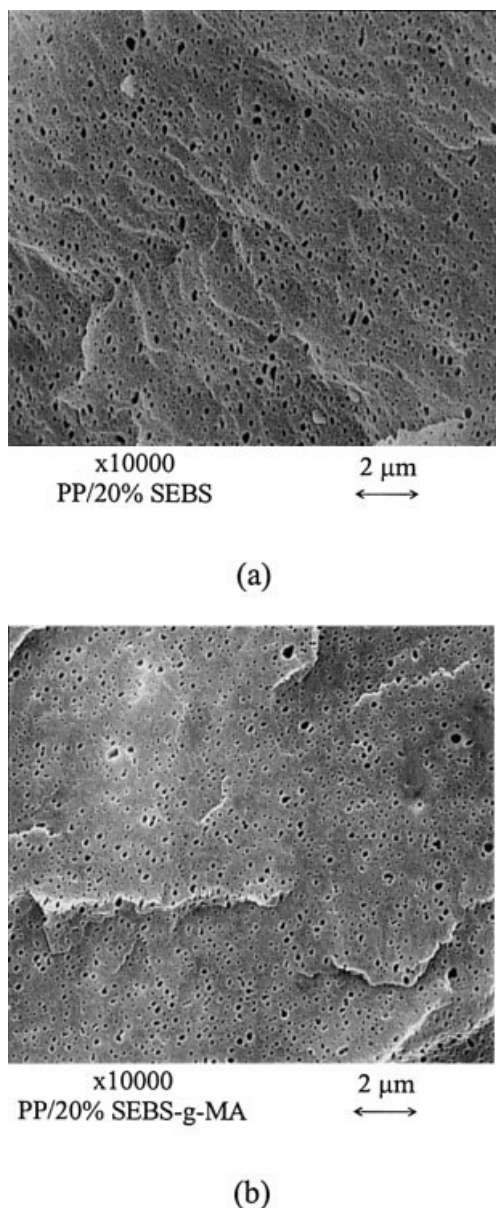


Figure 2 Micrographs of the (a) PP/20 wt % SEBS and (b) PP/20 wt % SEBS-g-MA blends.

and torque curves obtained in a Haake torque rheometer.

The increase in the torque measured with the mixing time was indicative of the occurrence of chemical reactions between the functionalized components, the acid group of PP-g-AA, the anhydride group of 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 IR spectra were taken using a Fourier transform infrared spectrometer (PerkinElmer Spectrum 1000) at 2 cm^{-1} resolution and 24 scans.

RESULTS AND DISCUSSION

PP/SEBS-g-MA blends

In a previous work,²² we reported that the impact strength of PP/SEBS blends was superior to that of pure PP for all of the conditions studied. 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 that of 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 their influence on the mechanical and morphological properties of the blends were studied. Initially, the results for the PP/SEBS-g-MA blend are discussed.

Lower impact strength values were observed for the PP/SEBS-g-MA blend as compared to the PP/SEBS blend with 20 wt % 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 MA functional groups enhanced polarity in the domains of the thermoplastic rubber SEBS-g-MA and consequently hindered interactions between the blocks (ethylene-butylene) of the rubber phase with the matrix of PP, which made adhesion between phases more difficult. Because adhesion was jeopardized by the polarity of the rubber, the transference of stress from the matrix to the dispersed particles was also jeopardized, which caused a smaller impact strength in the SEBS-g-MA blend as compared to the PP/SEBS blend. Probably the strong repulsion of the polar group (MA) of the SEBS-g-MA with nonpolar PP caused this phenomenon.

These results agree with the data obtained for interfacial strength by Setz,²⁶ who observed smaller interfacial resistance for the PP/SEBS-g-MA blend as compared to the PP/SEBS blend.

As shown in Figure 1, SEBS showed torque values that were superior to the ones obtained for SEBS-g-MA, indicating greater resistance to flow under those conditions of mixture, which was related to the viscosity of the material. 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 is, the greater the average size of particles will be. From these observations, one would expect bigger

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

PP-g-AA (wt %)	Izod impact strength (J/m) at 48 h	Izod impact strength (J/m) at 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

particles for the blend prepared with the SEBS rubber as opposed to the SEBS-g-MA rubber. However, the morphologies of both blends showed the same average particles size, 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 (Table II) show that the elasticity modulus did not vary for the blends with SEBS or with SEBS-g-MA. On the other hand, the yield stress of the PP/SEBS blend was slightly inferior, and consequently, the rate of initiation of toughening mechanisms was faster, making the blend with SEBS supposedly more efficient in this aspect when compared with the SEBS-g-MA blend. As to the deformation as failure, the PP/SEBS blend showed a superior value, being thus more efficient in controlling propagation and termination of toughening mechanisms.

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

When PP-g-AA was used as compatibilizing agent of the PP/SEBS-g-MA blend, 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 could be related to the nonhomogeneity of the mixtures, lack of interaction between the reactive groups, instability in the possible chemical interactions and so on.

These results also showed a considerable decrease in the values for impact strength throughout a period of 30 days, as shown in Table III and Figure 3. The necessity of further study was justified for the possible interaction between the chemical groups in the mixture and its stability as a function of time. The instabilities could 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 PP/PP-g-AA/SEBS-g-MA. The compositions were the same as those used for the mechanical tests.

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

This study reveals that it is necessary to use a more appropriate material to interact and/or react simulta-

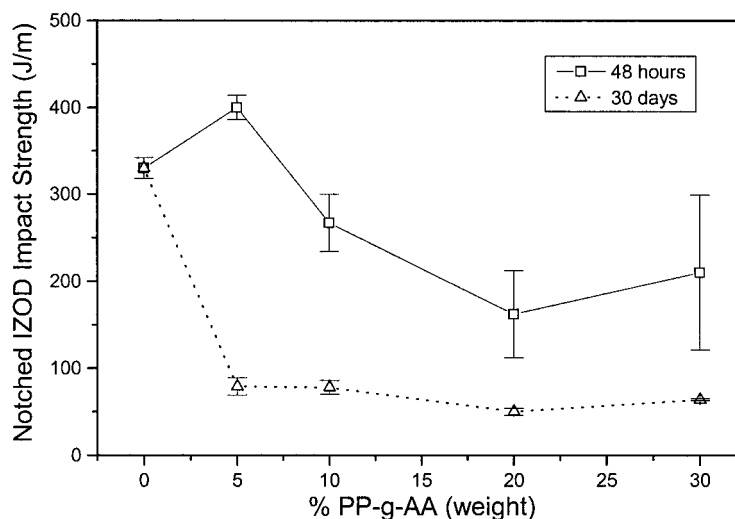


Figure 3 Izod impact strength as a function of the percentage of PP-g-AA tested 48 h and 30 days after injection.

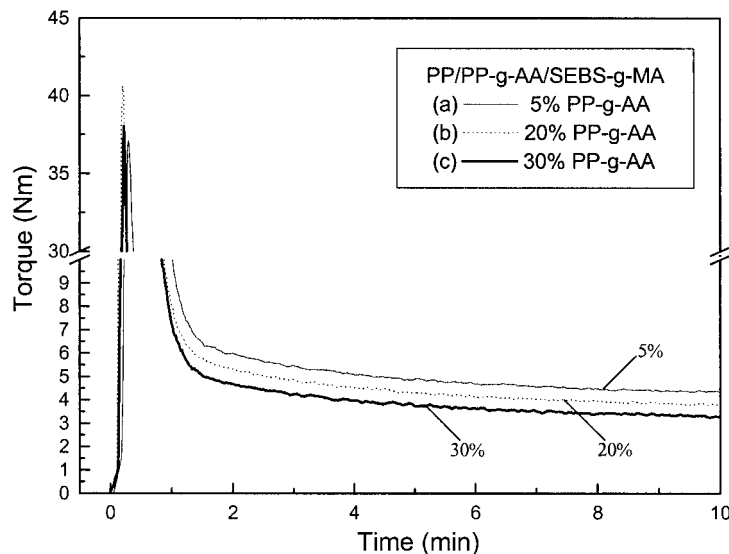


Figure 4 Torque versus time curves obtained for PP/PP-g-AA/SEBS-g-MA blends: (a) 5% wt, (b) 20, and (c) 30 wt % PP-g-AA. (50 rpm, 190°C, 10 min).

neously 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 bifunctional compound (PPD) capable of reacting simultaneously with both functional groups (MA and AA) is a possible way to improve interface adhesion²⁷ and, at the same time, stabilize the properties for the PP/PP-g-AA/SEBS-g-MA blends.

The bifunctional compound that was chosen was PPD because it possesses two amine groups. They could react simultaneously with PP-g-AA and with SEBS-g-MA. Amines, an important class of modifiers, present high reactivity with polymers that contain carboxylic acids or MA.

Table IV shows the values of mechanical properties and the average size of particles for the blends with PPD.

As shown in Figure 5, proportions of 0.5 and 1 wt % PPD in the blends led to a decrease in the values of impact strength in relation to the blend without PPD. However, with bigger proportions, such as 1.5 and 2

wt %, the impact strength improved remarkably. With small amounts of PPD (proportions of 0.5 and 1 wt %), the mating of reactive groups on the surface could become more difficult, and consequently, a smaller incidence of chemical reaction would take place. The small number of bonds was likely to be also due to the presence of some nonreactive functional groups, which might have hampered the performance of the blend, reducing the impact strength.

The impact strength is a mechanical property, which 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 particle size and the adhesion between phases in the system. For each type of material, there is an optimum particle size for toughening. The improvement of adhesion can be achieved by means of chemical reactions because they can reduce interfacial tension and reduce the size of the dispersed particles during the process of preparation of 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

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

Property	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

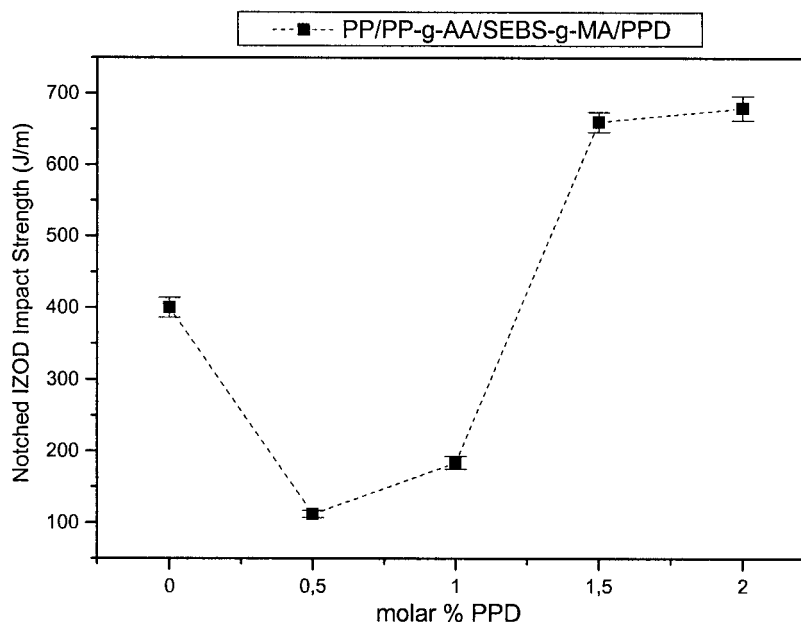


Figure 5 Izod impact strength in relation to the proportion of PPD (mol %) added to the PP/PP-g-AA/SEBS-g-MA/PPD blends.

the PP/SEBS and PP/SEBS-g-MA binary blends. The morphologies and the average diameters of the particles are presented in Figures 6 and 7, respectively.

Hu²⁸ 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 due to the action of the final segments of the extrusion screw. The chemical reactions that take place are able to stabilize the morphology of the blend at the beginning of the extrusion process, whereas this fact was not observed for the mechanical blend without a chemical reaction. In conventional nonreactive mechanical blends, rubber particles only reach their final morphology when leaving the extruder; that is, their morphology is developed throughout the way within the extruder.

In this study, it was verified that for the reactive system, there was no such strong reduction in the size of particles as compared to the nonreactive blends. The final morphology of the blends with PPD showed rubber particles with average sizes superior to the blends without PPD. This phenomenon could be related to the observations made by Hu,²⁸ who suggested that at the beginning of the process, soon after the melting zone, the rubber particles could have larger average diameters because they would not have passed the shearing zone of the extruder yet. Subsequently, with the occurrence of chemical reactions, this morphology could stabilize with larger average diameters and, thus, pass through the other shearing zones without changing their diameters. After the morphology of the reactive blends are established, they do not change through-

out the mixture because 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 the 1:1:0.5 and 1:1:1 PP/PP-g-AA/SEBS-g-MA/PPD blends. Therefore, this was indicative 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, consequently, 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 efficient to initiate and terminate toughening mechanisms, leading to excellent mechanical properties.

As discussed previously, the PP/PP-g-AA/SEBS-g-MA blends showed a decrease in impact strength with time. Consequently, a bifunctional compound, which was able to interact simultaneously with both the acid and anhydride groups of the PP and SEBS, respectively, 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/

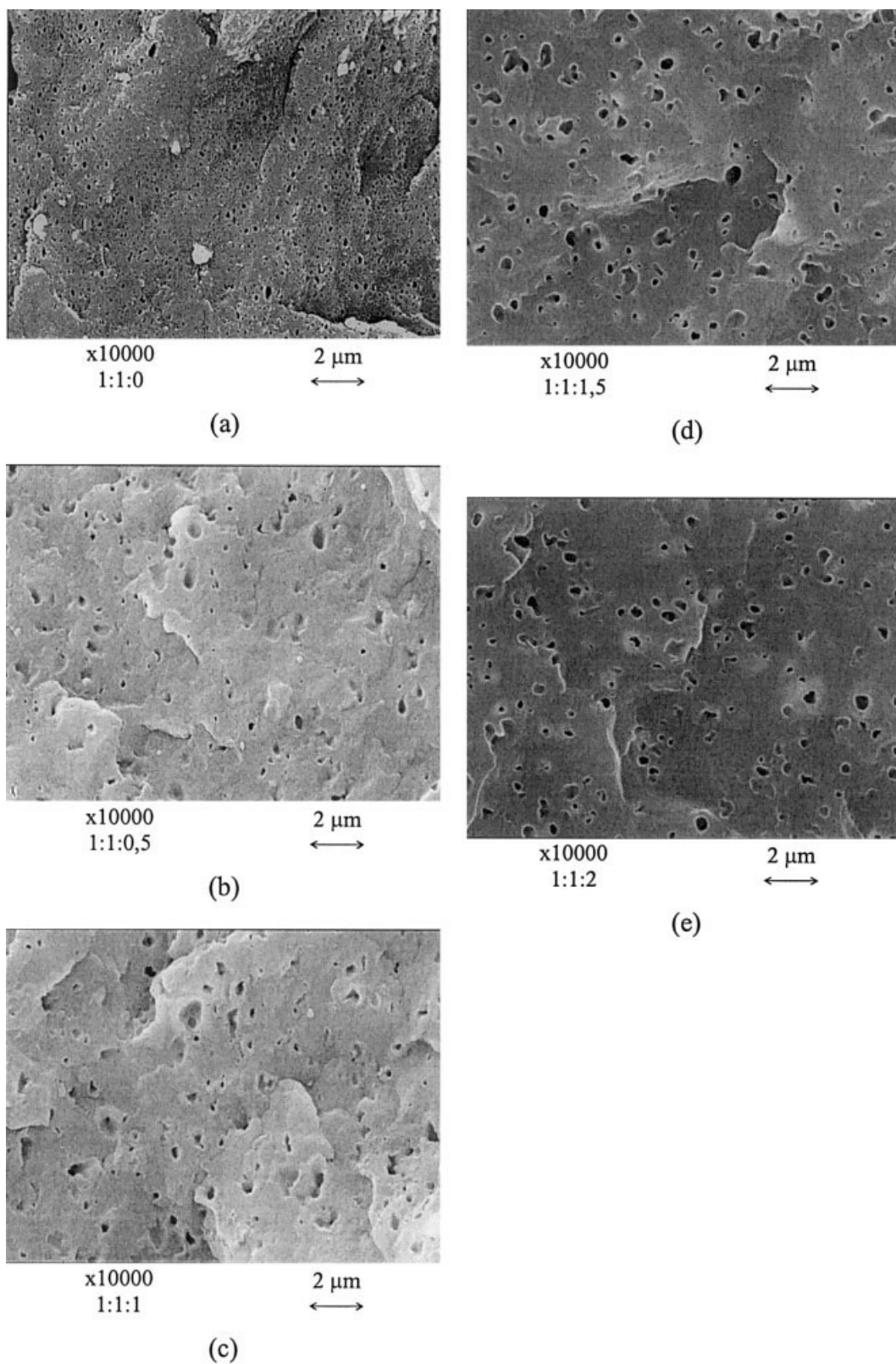


Figure 6 Micrographs of the PP/PP-g-AA/SEBS-g-MA/PPD blends with proportions: (a) 1:1:0, (b) 1:1:0,5, (c) 1:1:1, (d) 1:1:1,5, (e) and 1:1:2.

SEBS-g-MA/PPD blends (1:1:2) remained around 680 J/m for different intervals of time between the preparation of specimens and testing. These systems did

not show any decrease in this property as observed previously without the bifunctional compound. No changes were observed in the morphology of the

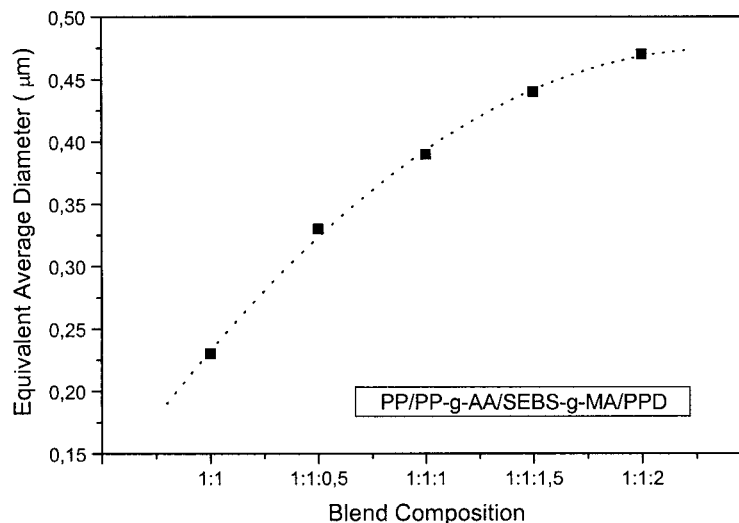


Figure 7 Equivalent average diameter of the dispersed phase as a function of the proportion of PPD added to the PP/PP-g-AA/SEBS-g-MA/PPD blends.

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 should cause higher molecular weights and viscosities in the system. For this reason, we expected higher torque during the processing in the melt state. The torque versus time values 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-

tained from the blends prepared in the twin-screw extruder. The evaluation of the most likely chemical reactions was done through the observation of the behaviour of peaks corresponding to the absorption of the functional groups of each component and through verification of verifying the development or lack of development 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 IR 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 the PP/PP-g-AA/SEBS-g-MA blend with different contents of PPD.

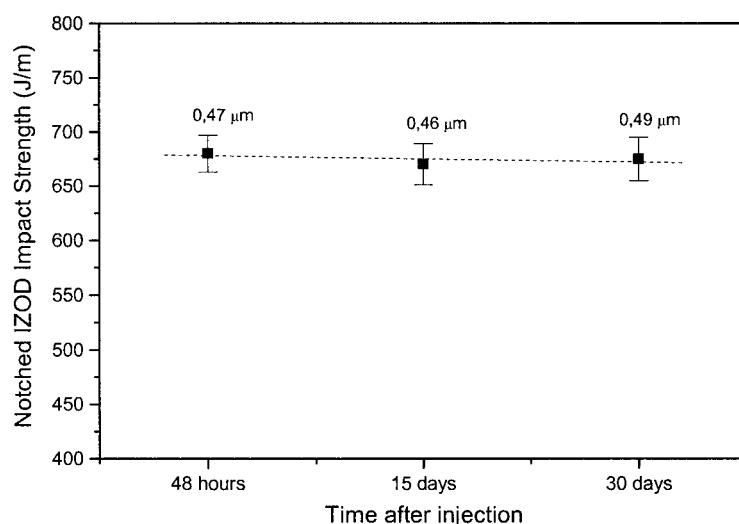


Figure 8 Izod impact strength for the PP/PP-g-AA/SEBS-g-MA/PPD blend (1:1:2) as a function of time and its equivalent average diameter of the dispersed phase.

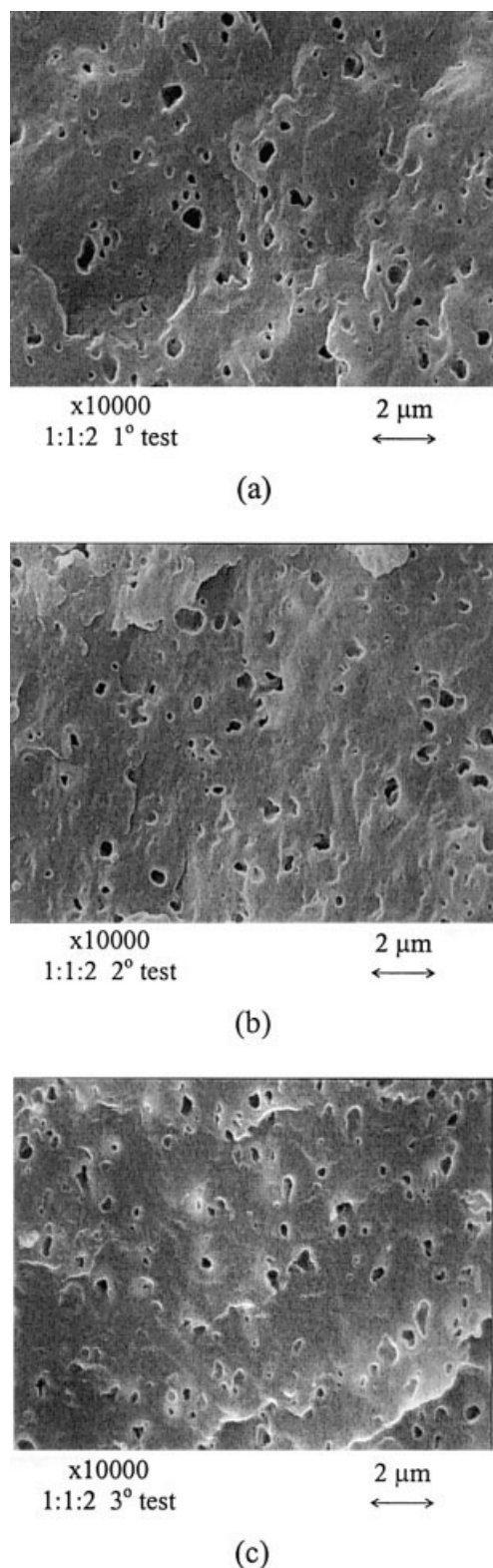


Figure 9 Micrographs of the PP/PP-g-AA/SEBS-g-MA/PPD blend (1:1:2) used to verify the stability with time: (a) 48 h, (b) 15 days, and (c) 30 days after injection.

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 1865 cm^{-1} , which correspond to the stretching of the carbonyl of MA in SEBS. There was also an increase in the intensity of the peak of absorption at 1710 cm^{-1} , which corresponds to the vibration of carbonyl of carboxylic acid in the PP. The fact that the peaks of absorption at 1865 and 1782 cm^{-1} were totally absent for the PP/PP-g-AA/SEBS-g-MA/PPD blend (1:1:2) indicated a considerable extension of the reaction. The intensification of the absorption around 1710 cm^{-1} suggested the conversion of anhydride into carboxylic acid groups and amide. Figure 13 illustrates the possible reactions that took 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 the PP/PP-g-AA/SEBS-g-MA/PPD blend (1:1:0.5). However, there was a peak of absorption in the spectra of the PP/PP-g-AA/SEBS-g-MA/PPD blend (1:1:2) at 1620 cm^{-1} . Amide groups can also show IR absorption peaks between 3360 and 3445 cm^{-1} , corresponding to the vibration of the N-H group of a 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 the PP/PP-g-AA/SEBS-g-MA/PPD (1:1:2) samples, whereas for the PP/PP-g-AA/SEBS-g-MA sample, 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 was related to the vibrations of angular deformation of N-H groups of secondary amides.

It is believed that the possibility of the existence of nonreacted MA was minimum due to the total disappearance of absorption at 1865 and 1782 cm^{-1} for the PP/PP-g-AA/SEBS-g-MA/PPD (1:1:2) blend. However, it is difficult to make any statement about the AA because with the opening of anhydride for the reactions, there was also the formation of an acid group, causing superposition of peaks, which hindered the identification of nonreactive acid. The PP/PP-g-AA/SEBS-g-MA/PPD blends (1:1:0.5 and 1:1:1) did not show any traits of the formation of amide groups due to 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 fact 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 spoiled this property.

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

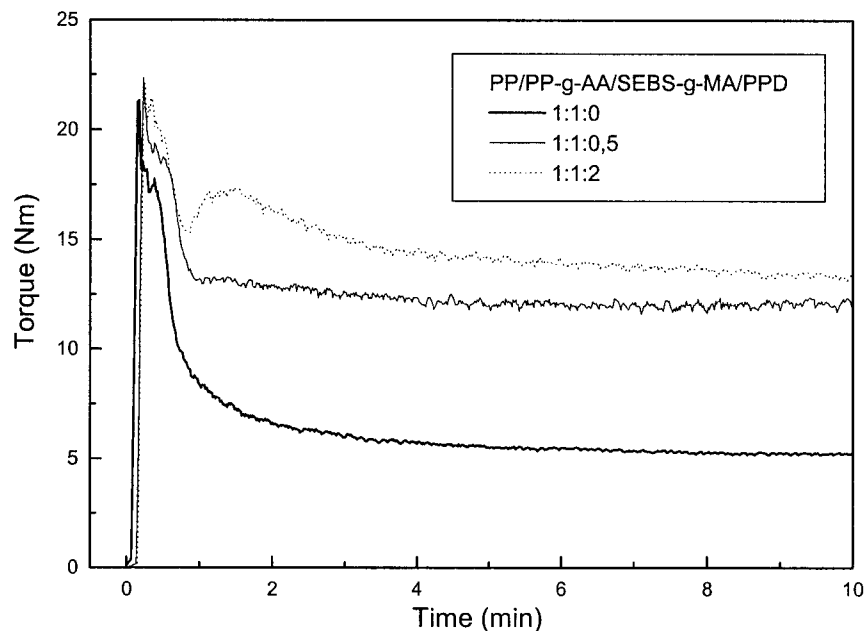


Figure 10 Torque versus time curve obtained by with a torque rheometer for the blend PP/PP-g-AA/SEBS-g-MA/PPD blends (1:1:0), (1:1:0.5), and (1:1:2).

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

For economical reasons and also because of the possibility to dilute the concentration of MA, the blends were prepared with both elastomers (SEBS and SEBS-g-MA), where the functionalized elastomer was replaced in concentration by the elastomer without functionalization. Blends both with PPD and without PPD were prepared. The proportion of acid to anhydride

was kept as 1:1, and the proportion of PPD was 2. We established these proportions while taking into consideration our previous work.

The mechanical and morphological properties are shown on Table V.

Figure 14 shows a comparison between the impact strength of the PP/PP-g-AA/SEBS-g-MA ternary blend and the PP/PP-g-AA/SEBS-g-MA/SEBS qua-

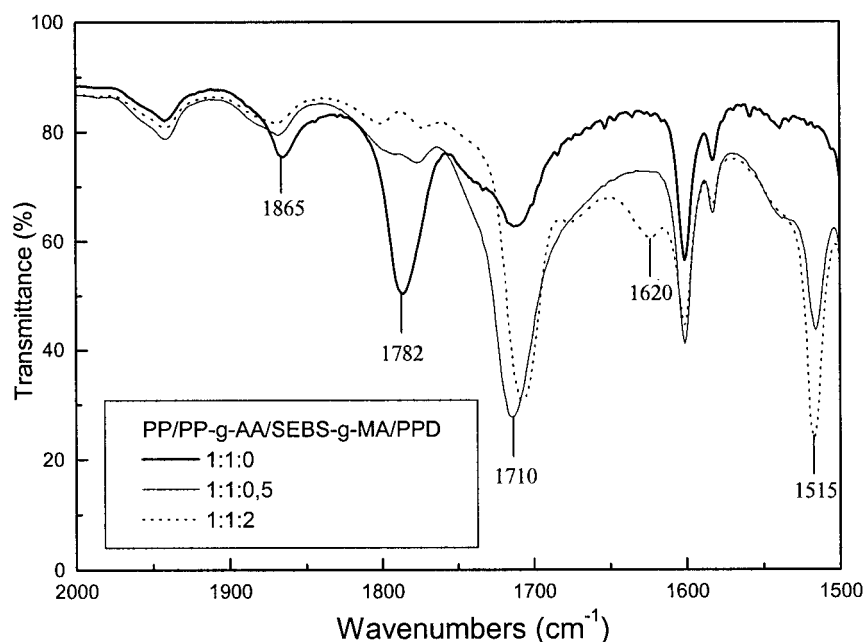


Figure 11 FTIR spectra obtained from pressed films of the PP/PP-g-AA/SEBS-g-MA/PPD blends for the range of wavelength from 2000 to 1500 cm^{-1} .

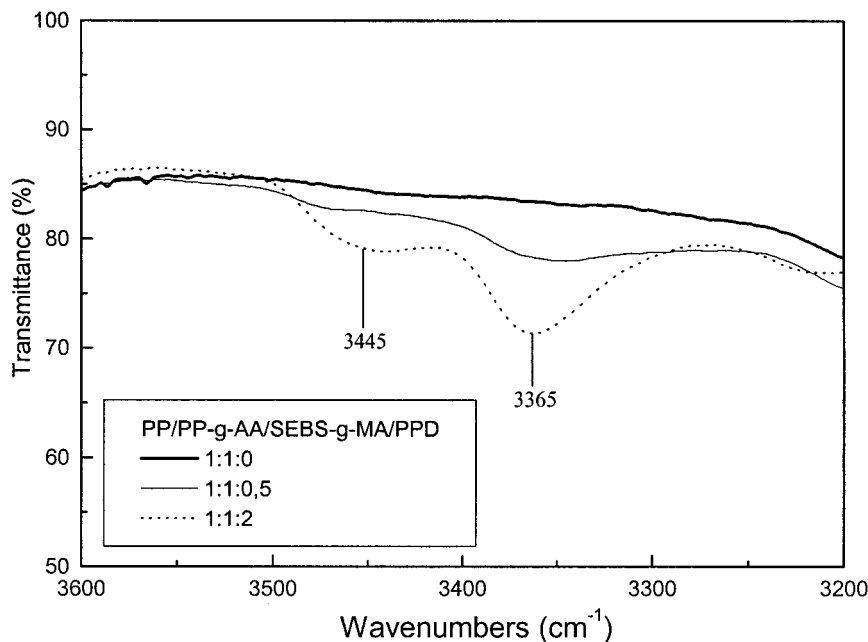


Figure 12 FTIR spectra obtained from pressed films of the PP/PP-g-AA/SEBS-g-MA/PPD blends for the wavelength range from 3600 to 3200 cm^{-1} .

ternary blends. It is possible to verify an increased impact strength with increased content of SEBS. This fact can be explained because the pending functional groups in PP and in SEBS-g-MA maybe have been 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) probably facilitated the approximation between PP and SEBS, which resulted in improved impact 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.

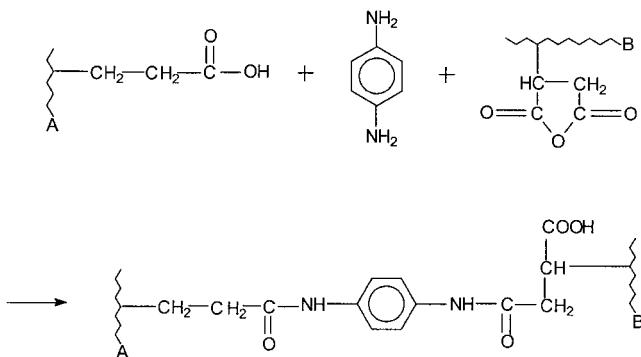


Figure 13 Probable chemical reaction between the acid groups of the PP (PP-g-AA) and anhydride groups present in SEBS-g-MA with the diamines of PPD, where A represents the chain of PP and B represents the chain of SEBS.

The addition of SEBS provided for better actuation of the toughening mechanisms and, consequently, better absorption of mechanical energy.

The reactive blends are usually expected to show elevated impact strength compared to the blends without reactive compatibilization. However, the system that was studied was very complex, and this phenomenon was not observed. Fewer chemical reactions may have occurred due to the addition of SEBS to the blend. This fact could possibly explain the less significant impact strength of quaternary blends with PPD as compared to the PP/PP-g-AA/SEBS-g-MA/PPD (1:1:2) blend, as shown in Figure 15. The level of interfacial chemical reactions may have rested below a minimum, which would have affected the toughness of the system satisfactorily due to the reduction of the contents of functionalized PP and SEBS, and this may have been detrimental to the performance of the blend.

The different properties of impact strength between the quaternary blends with and without PPD may possibly be explained by the fact that although the elastomer SEBS did not show reactive functional groups capable of reacting with PPD, it had more affinity with PP than the elastomer SEBS-g-MA, because of its lack of polarity, which could have consequently led to improved mechanical properties.

CONCLUSIONS

The blend with the functionalized elastomer with MA (PP/SEBS-g-MA) showed reduced impact strength.

TABLE V
Mechanical and Morphological Properties of the PP/PP-g-AA/SEBS-g-MA/SEBS Quaternary Blends Used in This Study

Property	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

This fact was attributed to the polarity of the elastomer, which was detrimental to the interactions between PP and the blocks (ethylene-butylene) of the SEBS copolymer.

The impact strength of the ternary blends with PP-g-AA showed a slight increase as compared to the PP/SEBS-g-MA blend, but it presented variations with time. It was necessary, thus, to use a bifunctional component with amine groups capable of reacting simultaneously with the acid groups of the PP and MA of the SEBS because evidence of chemical reactions between acid and anhydride was not observed by torque rheometry.

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

The occurrence of chemical reactions between the components was verified both through torque rheom-

etry and IR spectroscopy (FTIR). It was possible to detect an increase in the values of torque and the formation of amine groups from the reactions involving the amine from PPD, the MA of the SEBS, and the AA of PP.

The PP/PP-g-AA/SEBS-g-MA/SEBS quaternary blends with PPD showed inferior impact performance as compared to the PP/PP-g-AA/SEBS-g-MA ternary blend with PPD (1:1:2). This fact was due to the decrease in the content of functionalized components, 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 to the blends without the bifunctional components. This fact was likely to be due to the stabilization of the morphology in the initial steps of processing with the chemical reactions.

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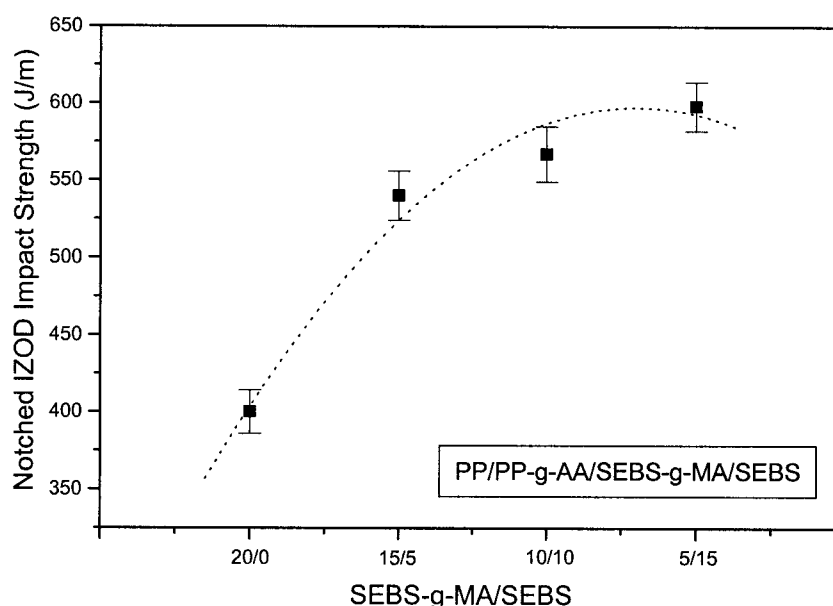


Figure 14 Izod impact strength of the PP/PP-g-AA/SEBS-g-MA ternary blend (20/0) and the PP/PP-g-AA/SEBS-g-MA/SEBS quaternary blends (15/5, 10/10, and 5/15) with PPD. The proportions of SEBS-g-MA/SEBS were 20/0, 15/5, 10/10, and 5/15.

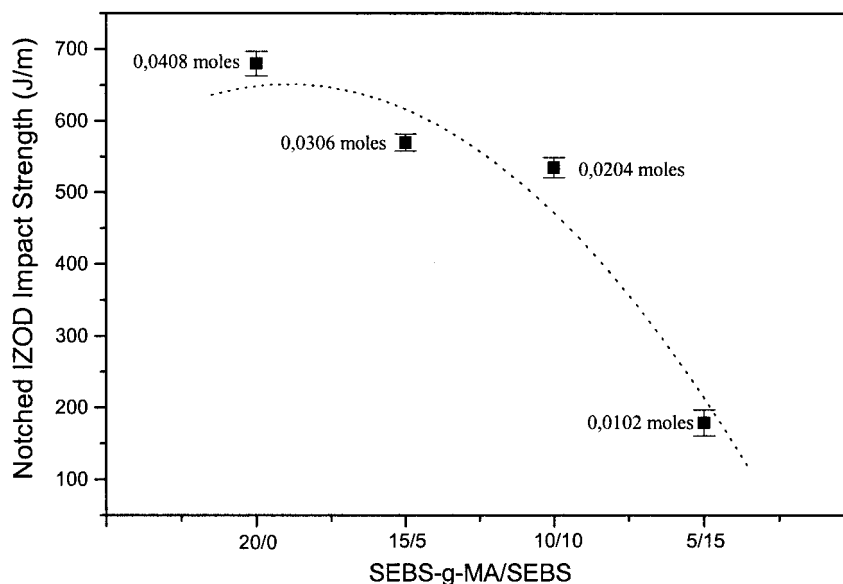


Figure 15 Izod impact strength of the PP/PP-g-AA/SEBS-g-MA blends and the PP/PP-g-AA/SEBS-g-MA/SEBS blends with PPD (1:1:2) where the respective molar values of the contents of acid and MA are presented.

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