2012

Compatibilization of polypropylene/poly(3-hydroxybutyrate) blends

JOURNAL OF APPLIED POLYMER SCIENCE, MALDEN, v. 123, n. 6, pp. 3511-3519, 2012
http://www.producao.usp.br/handle/BDPI/42449

Compatibilization of Polypropylene/Poly(3-hydroxybutyrate) Blends

Roberta K. Sadi,[1] Rafael S. Kurusu,[1] Guilhermino J. M. Fechine,[2] Nicole R. Demarquette[1]

[1]*Metallurgical and Materials Engineering Department, University of São Paulo, Avenida Professor Mello Moraes, 2463, São Paulo 05508-900, Brazil*
[2]*Materials Engineering Department, Mackenzie Presbyterian University, Rua da Consolação, 930, São Paulo 01302-907, Brazil*

Received 22 March 2011; accepted 29 April 2011
DOI 10.1002/app.34853

ABSTRACT: Blending polypropylene (PP) with biodegradable poly(3-hydroxybutyrate) (PHB) can be a nice alternative to minimize the disposal problem of PP and the intrinsic brittleness that restricts PHB applications. However, to achieve acceptable engineering properties, the blend needs to be compatibilized because of the immiscibility between PP and PHB. In this work, PP/PHB blends were prepared with different types of copolymers as possible compatibilizers: poly(propylene-*g*-maleic anhydride) (PP–MAH), poly(ethylene-*co*-methyl acrylate) [P(E–MA)], poly(ethylene-*co*-glycidyl methacrylate) [P(E–GMA)], and poly(ethylene-*co*-methyl acrylate-*co*-glycidyl methacrylate) [P(E–MA–GMA)]. The effect of each copolymer on the morphology and mechanical properties of the blends was investigated. The results show that the compatibilizers efficiency decreased in this order: P(E–MA–GMA) > P(E–MA) > P(E–GMA) > PP–MAH; we explained this by taking into consideration the affinity degree of the compatibilizers with the PP matrix, the compatibilizers properties, and their ability to provide physical and/or reactive compatibilization with PHB. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3511–3519, 2012

Key words: biodegradable; biopolymers; blends; compatibility; polyesters

INTRODUCTION

The accumulation of plastic waste is one of the main current environmental problems. In this scenario, biodegradable polymers have been arising as a nice alternative to reduce the amount of biologically inert plastics in the atmosphere. Besides their biodegradability, most of these materials are obtained from renewable sources; this has also driven much attention and interest toward the so-called bioplastics. Nevertheless, their brittleness, along with their high cost, have limited the use of bioplastics to only certain niche applications. One of the approaches to overcoming this problem is the blending of bioplastics with conventional ones. This technology enhances the properties of the bioplastic and reduces the cost of the final product and the amount of fossil-fuel-based conventional plastic.

Following this track, one can produce a promising blend by mixing polypropylene (PP) and poly(3-hydroxybutyrate) (PHB). PHB is an aliphatic biodegradable polyester produced by a wide range of bacteria from a carbon source, such as plant sugar and oil. On the other hand, PP is a synthetic nonbiodegradable polymer, being the second most consumed thermoplastic in the world. Compared with PHB, PP has a greater toughness, larger processing window, and similar melting temperature (T_m); this favors the processability and properties of a blend between these two polymers. However, PP and PHB form an immiscible and incompatible blend because of differences in their chemical structure and polarity.[1,2] Therefore, it becomes of great importance to study the compatibilization of this mixture.

According to our knowledge, until the moment this article was written, there was only one publication in the literature regarding the compatibilization of PP/PHB blends.[1] In that work, a PP-*g*-PHB was synthesized and tested as a compatibilizer. Although the copolymer could act as an interfacial agent, reducing the size of the PHB domains dispersed in the PP matrix, it could not improve the mechanical properties of the blend. On the other hand, many articles have been written on the compatibilization of analogous blends of polyolefins with polyesters, particularly, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). The most applied compatibilization technique in these systems is the use of compatibilizers containing groups able to

---

Correspondence to: N. R. Demarquette (nick@usp.br).
Contract grant sponsors: Fundação de Amparo à Pesquisa do Estado de São Paulo, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazil).

Journal of Applied Polymer Science, Vol. 123, 3511–3519 (2012)

react with polyester end groups (COOH and OH). Among these compatibilizers, the most frequently used are the ones with glycidyl methacrylate (GMA),[3–16] oxazoline,[17–19] and maleic anhydride (MAH)[11–16,20–26] functions grafted in polymers such as PP, polyethylene, and styrene–ethylene/butylene–styrene rubber (SEBS). The GMA group contains an epoxy moiety at the end of its chain, which is highly reactive with the polyester COOH end group and also able to react with the polyester OH end group, although the reaction with COOH occurs primarily and is 10–20 times faster.[14] The oxazoline function is also capable of reacting with carboxylic acid; however, this reaction presents slower kinetics than the epoxy/COOH system.[27] The MAH molecule can react with the polyester OH groups, but this reaction is reversible, and its equilibrium is shifted to the reactant side with increasing temperature.[14,24] On the contrary, a temperature raise shifts the epoxy/COOH reaction to the product side. Thus, MAH could not be the best choice for compatibilizing polyester blends, although it is commonly used.

There are also a few works in which compatibilizers used for polyolefin/polyester system were copolymers containing only acrylate groups, such as methyl acrylate (MA), ethyl acrylate, and butyl acrylate,[14,16] and copolymers containing acrylate together with GMA and MAH groups.[9,10,15] Although it is possible that acrylate and polyester undergo transesterification reactions, it has already been pointed out that these reactions are unlikely to occur and are less predominant than the epoxy/COOH reaction.[28]

Some studies have compared the efficiency between GMA, MAH, and acrylate groups; they all converged in indicating the better performance of the epoxy-containing molecule.[11–16] However, it is worth noticing that most publications in which MAH was studied reported some efficiency of this group,[11–13,15,16,20,21,23–25] with only a few exceptions.[14,22,26] Within these later studies, compatibilization could be achieved after the addition of a small amount of epoxy to the PP/PBT/poly(propylene-*g*-maleic anhydride) (PP–MAH) system.[26]

Other compatibilizers found to be used in polyolefin/polyester systems include PP grafted with phenol formaldehyde,[29] isocyanate[30] and itaconate groups,[31] liquid-crystalline ionomers and polymers,[32,33] epoxidized ethylene propylene diene rubber,[34] and bismaleimide[35] and silane[36] molecules. These publications reported the existence of specific interactions between those materials and PET or PBT that caused some level of blend compatibilization.

In this work, the efficiency of PP–MAH, poly(ethylene-*co*-methyl acrylate) [P(E–MA)], poly(ethylene-*co*-glycidyl methacrylate) [P(E–GMA)], and poly(ethylene-*co*-methyl acrylate-*co*-glycidyl methacrylate) [P(E–MA–GMA)] as compatibilizers for the PP/PHB system was tested as PHB presents the same terminal groups of PET and PBT. The blends obtained were characterized by means of their morphological, chemical, and mechanical properties (tensile and impact tests).

EXPERIMENTAL

Materials

The materials used in this work were: poly(propylene-*co*-ethylene) (PP) containing a low ethylene content from Suzano Petroquímica (Mauá, Brazil), PHB from Biocycle (Serrana, Brazil), the compatibilizers PP-MAH, P(E-MA), and P(E-MA-GMA) from Arkema (Colombes, France), and P(E-GMA) from Sigma Aldrich (St. Louis, MO). The materials were used without further purification. Their main characteristics and their codes are summarized in Table I.

Preparation of the blends

PHB in powder form was pelletized as received with a twin-screw extruder Haake Rheomix PTW 16 (Waltham, MA) operating at 160°C at a screw speed of 110 rpm and a feeding speed of 50 rpm. With all materials in pellet form, three mixtures of PP with each of the copolymers were obtained at a screw speed of 50 rpm and a feeding speed of 10 rpm at 160°C in the same equipment. These premixtures were then mixed with PHB using the same processing conditions.

The following compositions (in weight percentage) were tested: the neat blend PP/PHB (80/20) and the blends with compatibilizers PP/PHB/PP–MAH, PP/PHB/P(E–MA), PP/PHB/P(E–GMA), and PP/PHB/P(E–MA–GMA), all according to the proportion 80/20/10, that is, 10 wt % compatibilizer with regard to the neat blend PP/PHB (80/20). The premixtures PP/PP–MAH, PP/P(E–MA), PP/P(E–GMA), and PP/P(E–MA–GMA) were also tested in the same proportion found in the blends (8 : 1). In some cases, the PHB/compatibilizer mixture was analyzed also in the same content found in the blends (2 : 1).

The materials were injection-molded in a Demag Ergotech machine (Schwaig, Germany) at 170°C and at a screw speed of 160 rpm.

Characterization techniques

Tensile testing was performed with a Kratos K10.000MP machine (Cotia, Brazil). The specimens were dumbbell-shaped according to ASTM D 638 with dimensions of 165 × 19 × 3 mm^3 approximately (Type I). The clamp separation was 100 mm, and the test speed was 1 mm/min for tensile modulus measurements until 0.5% strain. After that, the

TABLE I
Materials Used in This Study

Material (code)	Composition (wt %)[a]	MFI (g/10 min)[b]	T_g (°C)[c]	T_m (°C)[d]	E (GPa)[e]	σ_{UTS} (MPa)[e,f]	ε (%)[e]	Notched Izod impact strength (J/m)[e]
PP (RP200L)	Ethylene: 2.5	6	2.6	150	0.75	27.0	71.5	50.0
PHB (B1000)	—	13	14.8	175	1.95	29.0	2.0	18.0
PP–MAH (Orevac PPC)	MAH: 2	2	2.3	151	0.50	18.5	118.0	Did not break
P(E–GMA) (430862)	GMA: 8	5	1.7	99	0.080	8.5	120.0	Did not break
P(E–MA) (Lotryl© 29 MA 03)	MA: 29	2–3.5	−21.4	61	0.015	5.0	423.0	Did not break
P(E–MA–GMA) (Lotader© AX8900)	MA: 24 GMA: 8	6	−20.9	65	0.010	3.0	327.0	Did not break

[a] Ethylene content in PP was measured in this work by ^{13}C-NMR according to the method described in the literature.[37] The composition of the other materials was informed by the suppliers.

[b] MFI, melt flow index. Information from the product datasheet. The MFI test was carried out with 2.16 kg and at 190°C for PHB, P(E–MA), P(E–GMA), and P(E–MA–GMA) and at 230°C for PP and PP–MAH.

[c] Measured by DMA in this work.

[d] Measured in this work for PP and PHB by differential scanning calorimetry. The other values were taken from the product datasheet.

[e] The mechanical properties were obtained according to the methods described in the following sections.

[f] σ_{UTS}, ultimate tensile strength.

test was carried out at 20 mm/min for all materials containing PHB and at 50 mm/min for the others. About 10 specimens of each composition were tested.

The Izod impact strength was determined using a Tinius Olsen 104 machine (Horsham, PA) at room temperature and with 2.82 J of pendulum energy. The specimens were notched according to ASTM D 256. About 15 specimens of each composition were tested with dimensions of 60 × 13 × 3 mm^3.

The morphology of the blends was investigated using a scanning electron microscope Philips XL 30 (Hillsboro, OR) with a voltage of 20 kV. The samples were cryofractured after they were cooled in liquid nitrogen and then coated by gold sputtering. In some cases, extraction of the dispersed phase was performed in chloroform at 55°C for 2.5 h.

To observe whether there was a reaction between the components, Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet Magna 560 spectrophotometer (Waltham, MA). The analysis was made with thin films by transmission, and 64 scans were accumulated at a resolution of 4 cm^{-1}.

RESULTS

In this section, the results obtained by the chemical, morphological, and mechanical analyses of the blends are presented, along with brief comments and evaluations. A more detailed discussion about these results and a classification of the compatibilizer efficiency is presented in the Discussion section.

Chemical reaction

FTIR analyses were carried out to investigate the occurrence of the reaction illustrated in Figure 1 in the case of the compatibilizers containing the GMA group. Figure 2 presents the FTIR spectra of PHB, P(E–MA–GMA), and PHB/P(E–MA–GMA) with the same proportion found in the ternary blends (2 : 1). It could be seen that the three vibration bands corresponding to the epoxy group of GMA (997, 911, and 847 cm^{-1}) were not present in the PHB/P(E–MA–GMA) mixture; this indicated that the epoxy ring was opened due to the chemical reaction between GMA and the terminal groups of PHB chains.[4,15] Such analysis could not be done with the ternary blend PP/PHB/P(E–MA–GMA), as the lack of vibration bands specific to the epoxy group in this case could either be caused by the chemical reaction or by a dilution effect of P(E–MA–GMA) in the final blend. The nonexistence of the epoxy vibration bands in the case of the PHB/P(E–MA–GMA) blend could not be attributed to a dilution effect as the example vibration band at 720 cm^{-1} presented a high intensity in the pure compatibilizer spectrum, a low intensity in the pure PHB spectrum, and also a high intensity in the PHB/compatibilizer mixture. The disappearance of the epoxy bands was also observed for the PHB/P(E–GMA) mixture in this work and by other researchers who employed P(E–GMA) as a compatibilizer for the PET/high-density polyethylene (HDPE) blend.[15]

Morphology

The scanning electron micrographs of the blends are shown in Figure 3. The blend PP/PHB without compatibilizer presented a typical morphology of an immiscible and incompatible blend, with poor adhesion between the phases due to differences in their chemical structure. Similar features have already been reported in the literature for PP/PHB blends.[38]

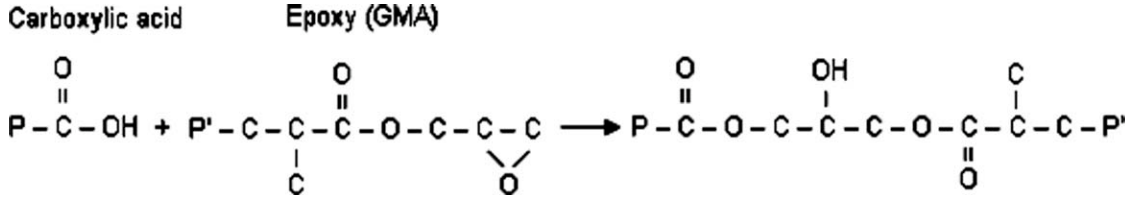


Figure 1 Chemical reaction of the polyester carboxylic acid end group with the epoxy moiety contained in the GMA group (adapted from ref. [27]).

All of the blends containing the compatibilizers still presented two phases but showed some differences in their morphologies when compared with the binary blend. In all cases, a decrease of the size of the PHB dispersed phase was observed. However, the emulsifying effect was different for each of the compatibilizers added to the blend. A rough quantitative analysis of the micrographs indicated that P(E–MA–GMA) and P(E–MA) were more efficient in reducing the diameter of the dispersed phase than P(E–GMA), which, in turns, was more efficient than PP–MAH. The micrographs indicated that the diameter of the dispersed phase for the noncompatibilized blend ranged from 2 to 7 μm, whereas the ones for the blends to which either P(E–MA–GMA) or P(E–MA) was added ranged from 1 to 2 μm and the ones for the blends to which P(E–GMA) was added ranged from 3 to 4 μm. Also, the micrographs indicated that the best adhesion between the matrix and dispersed phase was obtained when P(E–MA–GMA) was added to the blend [see Fig. 3(f)]. Different polyolefin/polyester blends have also shown a reduction in the size of the dispersed phase in several studies that used compatibilizers containing MAH,[11–13,16,21,23–25] GMA solely,[4–8,10–13,15,16,39] and GMA along with other types of acrylates (MA, ethyl acrylate, butyl acrylate).[9,10,15,39] A more homogeneous morphology[5,6] and with better adhesion[6,9,16,23,39] was also commonly observed in these same studies. The decrease in the dispersed phase size seen in this work and in the ones reported in the literature could be attributed to reductions in both the interfacial tension and the dispersed phase coalescence, which occurs when compatibilizers are employed.[40–47]

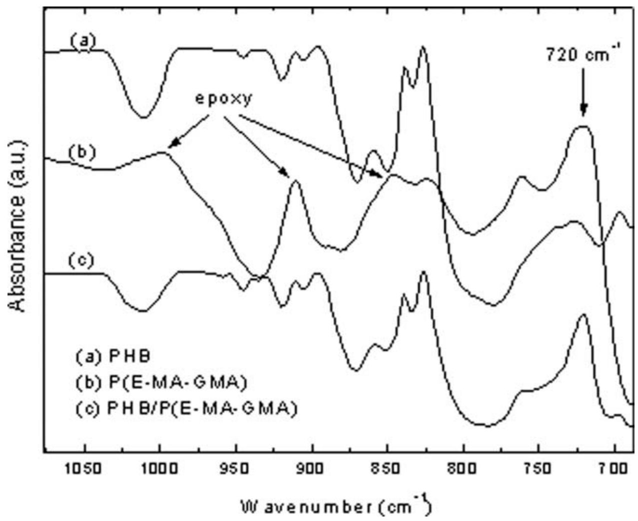
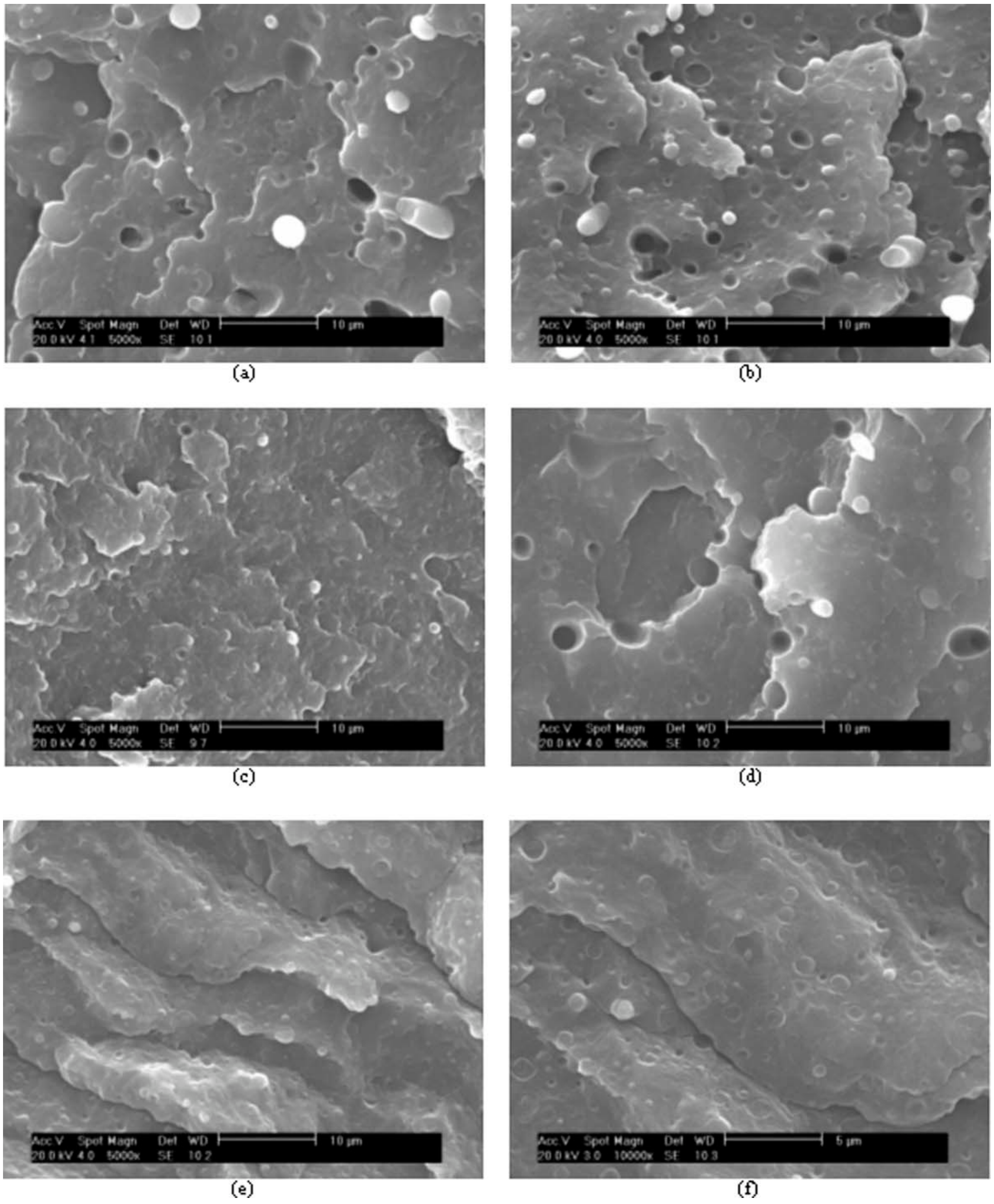


Figure 2 FTIR spectra of PHB, P(E–MA–GMA), and the mixture 2 : 1 PHB/P(E–MA–GMA).

Mechanical properties

The mechanical properties of the blends and of PP and PHB are illustrated in Figure 4. Pure PP and PHB presented typical ductile and brittle behavior, respectively. All of the compatibilizers had an elastomeric character, with low values of elastic modulus (*E*) and high values of elongation at break (ε) and impact strength because they did not break during the impact test (Table I). When compared to PP and to the binary blend PP/PHB, these materials caused decreases in the modulus and tensile strength of the ternary blends, which is a typical result found in the literature for polyolefin/polyester blends with elastomeric compatibilizers containing the acrylate[9,10,13,39] and MAH groups.[13,23]

The parameters commonly used to evaluate the efficiency of compatibilization are ε and impact strength; thus, the analysis presented here after will focus on these properties. As expected, PHB presented the lowest value of impact strength and elongation, whereas the PP/PHB blend without compatibilizer presented intermediary properties between those of pure PP and PHB. When any of the compatibilizers was incorporated, the impact strength and elongation of the ternary blends increased significantly when compared to the PP/PHB blend, which is a typical result found in the literature when an elastomeric compatibilizer is added to a mixture.[4,7,9–11,13,16,23,39] This result could be due to toughening by addition of a material with elastomeric character and/or the occurrence of effective compatibilization. Nevertheless, the toughening effect is rarely considered, and the increase in the mechanical properties is usually only attributed to the occurrence of compatibilization. Figure 4 shows that the simple presence of the compatibilizers was already able to improve the toughness of the materials, as seen in a comparison between the properties of PP and the PP/



(a) (b) (c) (d) (e) (f)

Figure 3 Final morphology of the PP/PHB blends containing or not the compatibilizers: (a) PP/PHB (80/20, 5000×), (b) PP/PHB/PP–MAH (80/20/10, 5000×), (c) PP/PHB/P(E–MA) (80/20/10, 5000×), (d) PP/PHB/P(E–GMA) (80/20/10, 5000×), (e) PP/PHB/P(E–MA–GMA) (80/20/10, 5000×), and (f) PP/PHB/P(E–MA–GMA) (80/20/10, 10,000×).

compatibilizer premixtures. To separate the two possible contributions mentioned, in this study, the impact strength and ε of the final blends PP/PHB and PP/PHB/compatibilizer were compared with those of pure PP and of the premixtures PP/compatibilizer (respectively), as shown in Table II. Because PHB causes a deterioration in the mechanical performance of the materials, we calculated the decrease in the cited properties after PHB addition.

Before we analyze the data contained in Table II, it is important to point out that the resulting properties of a blend generally do not follow a linear law of mixture. The quantitative analysis performed here, therefore, was only a rough approximation. We noticed that when PHB was added to any of the PP/compatibilizer premixtures or to PP solely, the impact strength and elongation decreased, except for the PP/P(E–MA–GMA) premixture, considering the

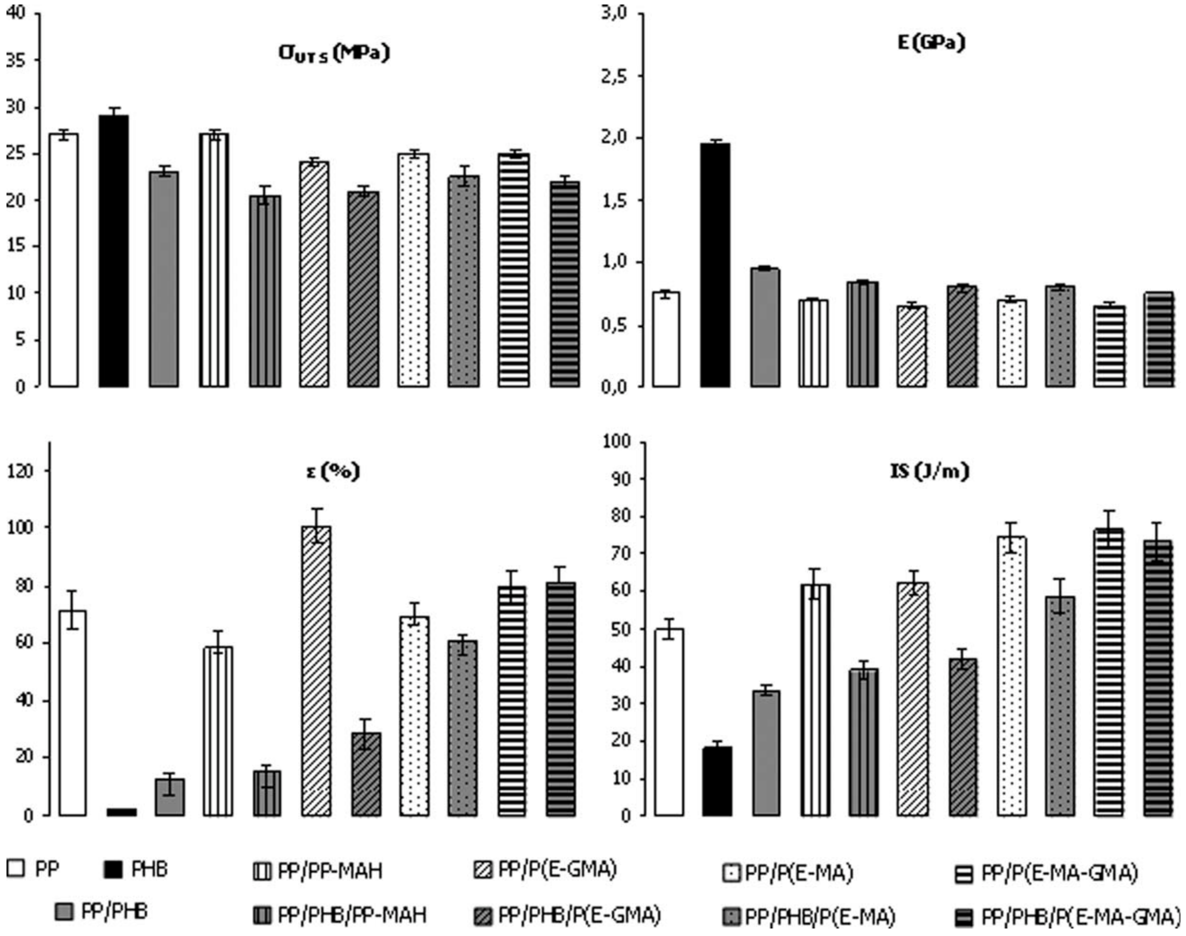


Figure 4 Mechanical properties of the materials (σ_{UTS} = ultimate tensile strength, IS = notched izod impact strength).

standard deviation from the measurements. The steadiness of these properties after PHB addition for the PP/PHB/P(E–MA–GMA) blend could be seen as an evidence of the occurrence of reactive compatibilization through the GMA group of the copolymer and PHB. The same effect could not be observed when P(E–GMA) was used. In fact, this copolymer, together with PP–MAH, presented the weakest performance among the four compatibilizers tested. The decrease in the properties analyzed for the blends with P(E–GMA) and PP–MAH was similar to the neat blend PP/PHB (there was only a small improvement for the elongation); this indicated a low efficiency of compatibilization in these cases. The compatibilizer P(E–MA) presented the second best performance, with a smaller decrease in the properties of the premixture after PHB addition.

DISCUSSION

The morphological and mechanical properties data presented an excellent correlation because the best mechanical properties were obtained for the blends containing the finest morphologies. Such results allowed us to classify the efficiency of the compatibilizer in this order: P(E–MA–GMA) $\gg$ P(E–MA) $>$ P(E–GMA) $\geq$ PP–MAH.

PP–MAH had the weakest performance as a compatibilizer for the PP/PHB system. Despite that, the blend with this compatibilizer presented some change in its morphology and improvement in its mechanical properties. Because the compatibilization effect in this system was unlikely to proceed from a reactive nature, it could be mainly related to the occurrence of physical interactions. These consist of hydrogen bonds between oxygen atoms of MAH with hydrogen atoms of polyester OH and COOH

TABLE II
Decrease in the Mechanical Properties with PHB

Material	Decrease in the mechanical properties after the addition of 20% PHB	
	ε (%)	Notched Izod impact strength (%)
PP/PHB	82.0	33.0
PP/PHB/PP–MAH	72.5	37.0
PP/PHB/P(E–GMA)	71.5	33.0
PP/PHB/P(E–MA)	12.5	22.0
PP/PHB/P(E–MA–GMA)	None	None

end groups or between hydrogen atoms of hydrolyzed MAH with oxygen atoms of carbonyl groups presented in the repeating unit of polyesters.[22,23]

The efficiency of P(E–MA) as a compatibilizer for the PP/PHB system could also be attributed to physical effects, and it was greater than PP–MAH, possibly because of the higher amount of functional groups contained in P(E–MA) (29 vs 2 wt %, see Table I). Transesterification reactions were unlikely to have occurred between acrylate and polyester as they are very slow kinetically and can be neglected unless long residence times or catalysts are employed.[10,14,23] In fact, in a previous study of PBT/P(E–MA) blends, the authors could not find the existence of grafted PBT, which indicated the absence of a reaction in this system.[48] Nevertheless, a decrease in the size of the dispersed phase could be observed, but it was less pronounced than when P(E–MA–GMA) was used instead of P(E–MA); this was similar to the results found in this work.

The best performance was achieved when we used P(E–MA–GMA) because this copolymer could sum both physical compatibilization provided by the MA groups and reactive compatibilization provided by the GMA groups. However, if the presence of the reactive epoxy group from GMA was the most important factor in determining the efficiency of the compatibilizer, P(E–GMA) should have had a better performance than P(E–MA). Instead, the blend compatibilized with P(E–MA) presented a finer morphology and better mechanical properties than the one containing P(E–GMA). This result could have arisen from a series of reasons discussed next.

Although P(E–GMA) contained 8 wt % GMA, P(E–MA) contained 29 wt % MA. The chemical reaction between the epoxy group of GMA and the carboxylic acid group of PHB generates a covalent bond with 358 kJ/mol of energy, whereas MA groups should have formed hydrogen bonds with PHB containing a bond energy ranging from 1 to 20 kJ/mol.[49] A very simple calculation showed that if all of the epoxy groups of P(E–GMA) and all of the MA groups of P(E–MA) interacted with PHB, the total strength between the P(E–GMA) and PHB bonds should have been stronger than the ones between P(E–MA) and PHB. However, P(E–GMA) presented a worse performance as a compatibilizer than P(E–MA).

The smaller size decrease of the dispersed phase upon addition of P(E–GMA) could neither be explained rheologically because no viscosity differences between the premixtures PP/compatibilizer were observed (data not shown here), which means that the viscosity ratio between the matrix and the dispersed phase remained constant in all systems.

The worse performance of P(E–GMA) when compared to the one of P(E–MA) may have originated from the better affinity that the first presented with PP. Figure 5 presents a morphological analysis of the premixtures of PP with the compatibilizers containing the MA and the GMA groups. In this case, the images correspond to samples subjected to extraction of the dispersed (compatibilizer) phase in chloroform to improve morphology visualization.

It can be seen from Figure 5 that in the case of PP/P(E–GMA), the compatibilizer was dispersed in PP in the form of smaller and more spherical particles than either P(E–MA) or P(E–MA–GMA). This result suggests that P(E–GMA) had a greater affinity with the PP matrix than the other copolymers. This could have been due to the lower copolymerization degree of P(E–GMA) (8%) when compared with P(E–MA) and P(E–MA–GMA) (29 and 32%, respectively). Similar results have already been reported in the literature.[25,39] The greater affinity of P(E–GMA) with HDPE compared to other copolymers with higher comonomer contents made this compatibilizer unable to locate in the interface matrix/dispersed phase and to efficiently compatibilize the HDPE/PET blend.[39] The authors of another study concerning PP/PET/SEBS-MAH blends pointed out that the PP/SEBS–MAH premixture diluted the compatibilizer in the PP phase and reduced its availability for interacting with PET in the second stage of the mixing process.[25] Analogously, it is possible that in this work, PHB had more difficulty finding the GMA reactive groups when it was added to the PP/P(E–GMA) premixture. Such a problem did not take place when P(E–MA–GMA) was used, probably because of its lower affinity with the PP matrix. Tests carried out with the blends obtained in a single step seemed to confirm this hypothesis (data not shown here). Although the mechanical properties of the PP/PHB/P(E–GMA) blend were improved when the material was obtained in a single step (in a comparison with the blend obtained in two steps shown here), the PP/PHB/P(E–MA–GMA) blends obtained in one and two steps presented identical properties.

The better mechanical properties obtained upon addition of P(E–MA) and P(E–MA–GMA) could also be explained in light of the glass-transition temperatures (T_g's) of the compatibilizers. The values of T_g of the different compatibilizers used were measured by dynamic mechanical analysis (DMA) and are presented in Table I. It can be seen that both P(E–MA–GMA) and P(E–MA) presented very low values of T_g, whereas P(E–GMA) and PP–MAH had T_g's a few degrees above zero. To achieve a significant toughening by addition of a rubbery phase to a matrix, it is necessary that the elastomeric material have a T_g well bellow room temperature.[50] Thus, this could have contributed to the impact strength results because the blends containing the compatibilizers with the lowest T_g presented the higher values of this property. However, although T_g can influence

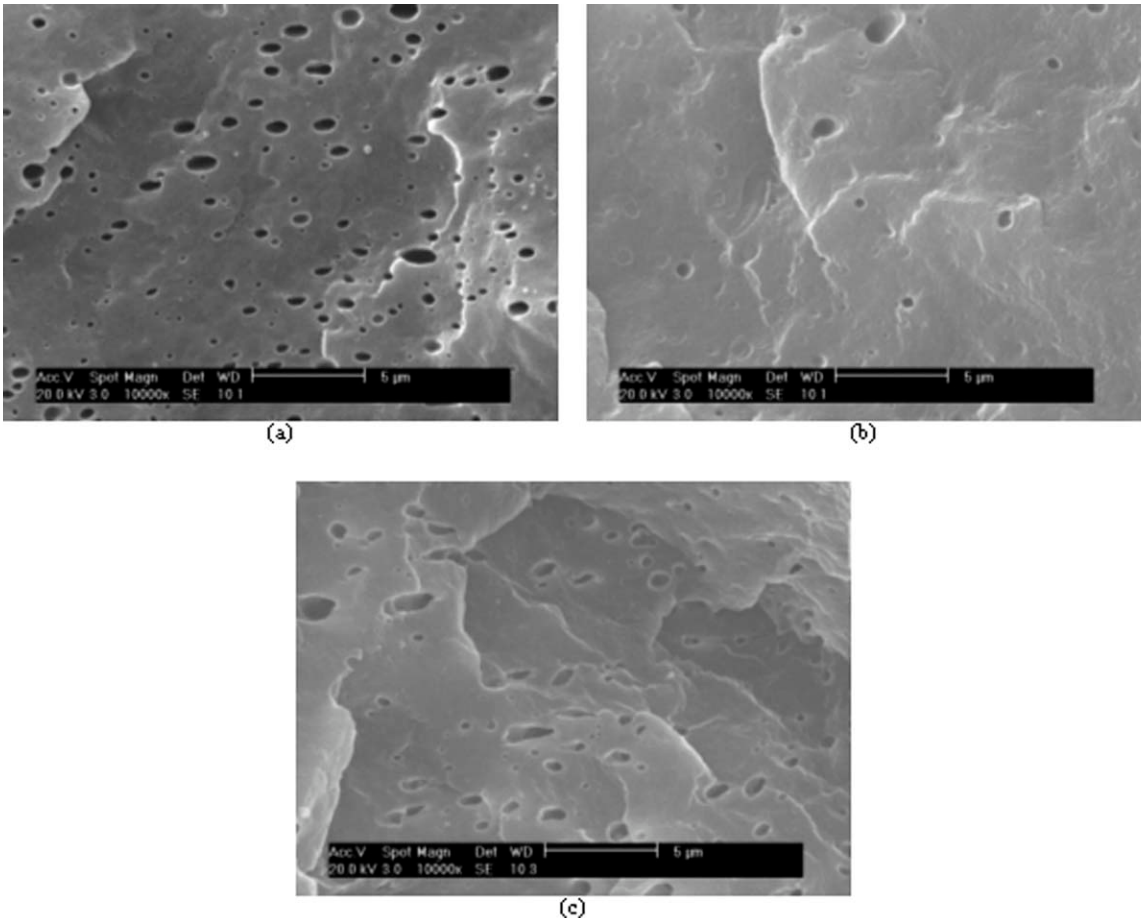


Figure 5 Scanning electron micrographs after dispersed-phase extraction in chloroform of the PP/compatibilizer premixtures. The proportion of all of the mixtures was 8 : 1, and the magnification was 10,000×: (a) PP/P(E–MA), (b) PP/P(E–GMA), and (c) PP/P(E–MA–GMA).

the mechanical properties, it does not account for the differences seen in the morphology analysis, which can only be explained in light of the mixture protocol discussion just presented.

CONCLUSIONS

The mechanical properties and morphology results allowed us to classify the efficiency of the materials tested to compatibilize PP/PHB blends in this order: P(E–MA–GMA) $\gg$ P(E–MA) $>$ P(E–GMA) $\geq$ PP–MAH.

The slight improvement in the mechanical properties and changes in morphology observed upon addition of PP–MAH were probably due to hydrogen-bond interactions between its groups and PHB. This physical effect was more evident when P(E–MA) was used because of the higher concentration of functional groups in this compatibilizer, which helped it to greatly improve the properties of the PP/PHB blend.

The weak performance of P(E–GMA) could have been due to its higher T_g compared to P(E–MA) and P(E–MA–GMA). The higher affinity degree of P(E–GMA) with the PP matrix also greatly accounted for such behavior because the PP/P(E–GMA) premixture possibly hindered the interaction of the compatibilizer with PHB in the second stage of the mixing process.

The strongest adhesion between the phases was obtained with P(E–MA–GMA) and the mechanical properties of the PP/PHB/P(E–MA–GMA) blend were equivalent to that of the PP/P(E–MA–GMA) premixture; this showed that the reactive compatibilization provided by the GMA groups and the physical effects provided by the MA groups were very effective. This result is of great importance when we consider that it makes it possible to add a certain amount of a fragile biodegradable polymer to a ductile matrix and maintain the mechanical performance of the final material.

The authors thank the companies Quattor, Arkema, and Midland Química for supplying materials.

References

1. Graebling, D.; Bataille, P. Polym Plast Technol Eng 1994, 33, 341.
2. Arcana, I. M.; Sulaeman, A.; Pandiangan, K. D.; Handoko, A.; Ledyastuti, M. Polym Int 2006, 55, 435.

3. Hu, G. H.; Sun, Y. J.; Lambla, M. Polym Eng Sci 1996, 36, 676.
4. Tsai, C. H.; Chang, F. C. J Appl Polym Sci 1996, 61, 321.
5. Champagne, M. F.; Huneault, M. A.; Row, C.; Peyrel, W. Polym Eng Sci 1999, 39, 976.
6. Pracella, M.; Chionna, D. Macromol Symp 2003, 198, 161.
7. Friedrich, K.; Evstatiev, M.; Fakirov, S.; Evstatiev, O.; Ishii, M.; Harrass, M. Compos Sci Technol 2005, 65, 107.
8. Fuchs, C.; Bhattacharyya, D.; Friedrich, K.; Fakirov, S. Compos Interfaces 2006, 13, 331.
9. Kaci, M.; Benhamida, A.; Cimmino, S.; Silvestre, C.; Carfagna, C. Macromol Mater Eng 2005, 290, 987.
10. Barhoumi, N.; Jaziri, M.; Massardier, V.; Cassagnau, P. Polym Eng Sci 2008, 48, 1592.
11. Heino, M.; Kirjava, J.; Hietaoja, P.; Seppälä J. J Appl Polym Sci 1997, 65, 241.
12. Pluta, M.; Bartczak, Z.; Pawlak, A.; Galeski, A.; Pracella, M. J Appl Polym Sci 2001, 82, 1423.
13. Pracella, M.; Chionna, D.; Pawlak, A.; Galeski, A. J Appl Polym Sci 2005, 98, 2201.
14. Sun, Y. J.; Hu, G. H.; Lambla, M.; Kotlar, H. K. Polymer 1996, 37, 4119.
15. Kalfoglou, N. K.; Skafidas, D. S.; Kallitsis, J. K.; Lambert, J. C.; Stappen, L. V. Polymer 1995, 36, 4453.
16. Pracella, M.; Pazzagli, F.; Galeski, A. Polym Bull 2002, 48, 67.
17. Vocke, C.; Anttila, U.; Heino, M.; Hietaoja, P.; Seppälä, J. J Appl Polym Sci 1998, 70, 1923.
18. Vainio, T.; Hu, G. H.; Lambla, M.; Seppälä, J. J Appl Polym Sci 1997, 63, 883.
19. Vainio, T.; Hu, G. H.; Lambla, M.; Seppälä, J. V. J Appl Polym Sci 1996, 61, 843.
20. Yoon, K. H.; Lee, H. W.; Park, O. O. J Appl Polym Sci 1998, 70, 389.
21. Arencón, D.; Velasco, J. I.; Rodríguez-Pérez, M. A.; Saja, J. A. J Appl Polym Sci 2004, 94, 1841.
22. Cheung, M. K.; Chan, D. Polym Int 1997, 43, 281.
23. Chiu, H. T.; Hsiao, Y. K. J Polym Res 2006, 13, 153.
24. Lepers, J. C.; Favis, B. D.; Lacroix, C. J Polym Sci Part B: Polym Phys 1999, 37, 939.
25. Papadopoulou, C. P.; Kalfoglou, N. K. Polymer 2000, 41, 2543.
26. Shieh, Y. T.; Liao, T. N.; Chang, F. C. J Appl Polym Sci 2001, 79, 2272.
27. Macosko, C. W.; Jeon, H. K.; Hoye, T. R. Prog Polym Sci 2005, 30, 939.
28. Duin, M. V.; Gurp, M. V.; Leemans, L.; Walet, M.; Aussems, M.; Martin, P.; Legras, R.; Machado, A. V.; Covas, J. A. Macromol Symp 2003, 198, 135.
29. Børve, K. L.; Kotlar, H. K.; Gustafson, C. G. J Appl Polym Sci 2000, 75, 361.
30. Bae, T. Y.; Park, K. Y.; Kim, D. H.; Suh, K. D. J Appl Polym Sci 2001, 81, 1056.
31. Yazdani-Pedram, M.; Vega, H.; Retuert, J.; Quijada, R. Polym Eng Sci 2003, 43, 960.
32. Zhang, A.; Zhang, B.; Feng, Z. J Appl Polym Sci 2002, 85, 1110.
33. Zhang, B. Y.; Sun, Q. J.; Li, Q. Y.; Wang, Y. J Appl Polym Sci 2006, 102, 4712.
34. Ao, Y. H.; Sun, S. L.; Tan, Z. Y.; Zhou, C.; Xu, N.; Tang, K.; Yang, H. D.; Zhang, H. X. Polym Bull 2007, 58, 447.
35. Zhang, H. X.; Hourston, D. J. J Appl Polym Sci 1999, 71, 2049.
36. Oyman, Z. O.; Tinçer, T. J Appl Polym Sci 2003, 89, 1039.
37. Tang, L. M.; Li, Y. G.; Ye, W. P.; Li, Y. S. J Polym Sci Part A: Polym Chem 2006, 44, 5846.
38. Pachekoski, W. M.; Agnelli, J. A. M.; Belem, L. P. Mater Res 2009, 12, 159.
39. Pietrasanta, Y.; Robin, J. J.; Torres, N.; Boutevin, B. Macromol Chem Phys 1999, 200, 142.
40. Wu, S. Polym Eng Sci 1987, 27, 335.
41. Sundararaj, U.; Macosko, C. W. Macromolecules 1995, 28, 2647.
42. Demarquette, N. R.; Kamal, M. R. J Appl Polym Sci 1998, 70, 75.
43. Macaubas, P. H. P.; Demarquette, N. R. Polymer 2001, 42, 2543.
44. Souza, A. M. C.; Demarquette, N. R. Polymer 2002, 43, 3959.
45. Yee, M.; Calvão, P. S.; Demarquette, N. R. Rheol Acta 2007, 46, 653.
46. Yee, M.; Souza, A. M. C.; Valera, T. S.; Demarquette, N. R. Rheol Acta 2009, 48, 527.
47. Garmabi, H.; Demarquette, N. R.; Kamal, M. R. Int Polym Processing 1998, 13, 183.
48. Martin, P.; Devaux, J.; Legras, R.; Gurp, M. V.; Duin, M. V. Polymer 2001, 42, 2463.
49. Lele, A. K.; Hirve, M. M.; Badiger, M. V.; Mashelkar, R. A. Macromolecules 1997, 30, 157.
50. Valera, T. S.; Demarquette, N. R. Eur Polym J 2008, 44, 755.