Morphology and Mechanical Properties of Polypropylene/High-Impact Polystyrene Blends from Postconsumer Plastic Waste

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ABSTRACT: The compatibilizing effect of the triblock copolymer poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS) on the morphological and mechanical properties of virgin and recycled polypropylene (PP)/high-impact polystyrene (HIPS) blends was studied, with the properties optimized for rigid composite films. The components of the blend were obtained from municipal plastic waste, PP being acquired from mineral water bottles (PP_b) and HIPS from disposable cups. These materials were preground, washed only with water, dried with hot air, and ground again (PP_b) or agglutinated (HIPS). Blends with three different weight ratios of PP_b and HIPS (6:1, 6:2, and 6:3) were prepared, and three different concentrations of SEBS (5, 6, and 7 wt %) were used for investigations of its compatibilizing effect. Scanning electron microscopy showed that SEBS reduced the diameter of dispersed HIPS particles in the globular and fibril shapes and improved the adhesion between the disperse phase and the matrix. However, SEBS interactions with PP_b and HIPS influenced the mechanical properties of the compatibilized PP_b/HIPS/SEBS blends. An adequate composition of PP/HIPS, for both virgin and recycled blends, for applications in composite films with characteristics similar to those of synthetic paper was obtained with a minimal amount of SEBS and a maximal HIPS/PP ratio in the range of concentrations studied. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2861–2867, 2003

Key words: blends; recycling; compatibilization; poly(propylene) (PP)

INTRODUCTION

In recent years, the volume of municipal plastic waste (MPW) has increased greatly, and this has resulted in a critical problem for modern society and future generations. Improved recycling techniques will necessarily be part of the solution for the disposal of this material.[1,2]

A substantial portion of MPW is composed of mixed polymers from unexpurgated monocomponent or laminated and composite materials. The processing of plastic mixtures for recycling has been attempted with some success; however, poor mechanical properties and uncertain economic values can limit more versatile recovery.[3,4] Polyolefins, poly(ethylene terephthalate), polystyrene (PS), and high-impact polystyrene (HIPS) are among the most common components of plastic waste because they are among the most frequently used commercial plastics in our daily lives and in industry.[5] Recycling mixed plastic residues in the form of blends is attractive from academic and industrial points of view because of the improvements in the impact strength (IS), dimensional stability, stress cracking, and processability with respect to virgin blends.[6–9]

A technical problem associated with plastic waste is its heterogeneous composition. The properties of blends are usually inferior because of the lack of compatibility of different polymers when no compatibilizing agent is added.[4,9,10] Compatibilizers must be added to blends for good mechanical characteristics to be achieved, particularly IS. Styrene–butadiene and styrene–ethylene–butane block copolymers are usually used as compatibilizers.[7,9,11] In immiscible polymer blends, such as polypropylene (PP)/PS[6,7] and PP/HIPS blends,[9,11] the adhesion between the phases is, in most cases, very weak.

Horák et al.[11] studied the compatibilizing of HIPS and PP blends with diblock, triblock, and pentablock types of styrene–butadiene copolymers. Multiblock copolymers showed greater improvements in the IS and elongation (tensile strain) at break (ϵ) in comparison with the diblock copolymer. Recently, Melo et al.[9] studied the effect of the concentration of poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS), used as a compatibilizer in a PP/HIPS (70:30) blend, on the

mechanical and morphological properties. They found that an admixture of the SEBS copolymer led to a decrease in the average size of the dispersed PS particles, and the best overall properties were obtained at a 5 wt % concentration.

Santana and Manrich[12] investigated degradative effects in the reprocessing of PP/HIPS blends from postconsumer plastic waste selectively collected through their flow properties. These blends presented melt-flow indices (FIs) higher than those of their individual components, and this indicated light thermomechanical degradation, probably because these blends were submitted to one more extrusion process.

In this work, we report a study of the compatibilizing effects of SEBS on postconsumer and virgin PP/HIPS blends with the aim of investigating some possible specific correlations between the morphological and mechanical properties.

EXPERIMENTAL

The components of the virgin blend were PP (H-603, OPP) with an FI of 1.5 g/10 min (used for mineral water bottles) and HIPS (HIPS 4300, BASF) with an FI of 1.6 g/10 min.

The components of the recycled blends were obtained from selectively collected plastic waste at the Federal University of São Carlos (São Carlos, Brazil). PP (average FI = 2.0 g/10 min) was from 0.5-, 1.5-, and 3.5-L mineral water bottles (PP_b), and HIPS came from disposable cups with an average FI of 2.3 g/10 min. These materials were preground (average size was ca. 10 cm – 5 cm) in a knife mill (Kie model MAK 250), washed only in water, and dried with hot air to 50°C[13–15] in a washing–drying centrifuge system.[16] Then, PP_b was ground again into flakes, and HIPS was agglutinated (Lombard model 162).[15] PP_b/HIPS blends were prepared in three weight ratios (6:1; 6:2, and 6:3) and in the presence of 7, 6, and 5% SEBS (Kraton G, Shell Chemical Co.), respectively (used as a compatibilizer agent). The mixture processing of the PPb/HIPS blends was performed with a Gerst model 25X24D single-screw extruder at 130 rpm and with a temperature profile of 180, 190, and 200°C in the three sections.

An LO Stereoscan 440 scanning electron microscopy (SEM) instrument was used for studying the morphology. The samples were fractured in liquid nitrogen and covered with gold before being examined with the microscope at an acceleration voltage of 20 kV. Specimens for the mechanical test were prepared in a Pic Boy injection-molding machine (model Boy 15).[17,18] Flexural and tensile (type I) tests were carried out with an Instron machine (model 1122). For the impact tests, the notched Izod IS was measured with an impact-testing machine (Ceast model Resil 25 P/N 6545.500) at room temperature according to ASTM D 256-93. The variations of the heat deflection temperature (HDT) were obtained in an apparatus for deflection temperature testing (Ceast model HDT 6 VIC) based on ASTM 648-96.

RESULTS AND DISCUSSION

Morphology study

SEM micrographs of binary PP/HIPS blends (6:1) containing 7 wt % of the SEBS compatibilizer are shown in Figure 1(a,b) for recycled and virgin materials, respectively. The magnifications in Figure 1 are all the same (25,000×), with the white bar representing 1 μm. The HIPS particles (disperse phase) can be found in low concentrations, and some holes and pulled particles with droplets and threads formed from the stretching in the fracture. The presence of SEBS in excess,[9,11] located at the interface between PP and HIPS, can better be observed in Figure 1(a) than in Figure 1(b). A large size distribution is shown in both micrographs, the particle dispersions of the virgin blends being higher than those of the recycled blends.

Figure 1(c,d) shows micrographs of fractured surfaces of PP/HIPS blends (6:2) containing 6 wt % of the SEBS compatibilizer. In both blends, the size of the dispersed HIPS particles is reduced with a small decrease in the SEBS triblock copolymer content and with a small increase in the HIPS content. The size reductions and a better adherence of the disperse phase in the matrix are particularly visible in the recycled blend, rather than in the virgin blend. The higher average interfacial area of HIPS particles (diameter = 0.08–0.15 μm) is the reason for the more efficient interfacial activity of SEBS at this level. However, in Figure 1(d), the virgin blend shows a higher concentration of holes and particles of HIPS being pulled by the stretching in the fracture, indicating weak adherence. This weak adherence of the virgin blend could be due to the grade of HIPS or the mixture processing conditions of the blend.

Structural and morphology differences among HIPS resins result from different production processes and elastomer-phase concentrations. There are many types and grades of HIPS commercially available. The most common has a particle average size of the elastomer phase of up to 5 μm and a salami-type morphology. This morphology consists of particles of different sizes (with PS wrapped by an elastomeric membrane) dispersed in a PS matrix, and it is commonly obtained in the process of mass polymerization.[19]

The HIPS morphology obtained through the process of emulsion polymerization generally presents spherical elastomeric particles and particles with structures of the core–shell kind; these particles are composed of a nucleus of PS (core) covered by a membrane of PB (shell). This morphology does not significantly affect
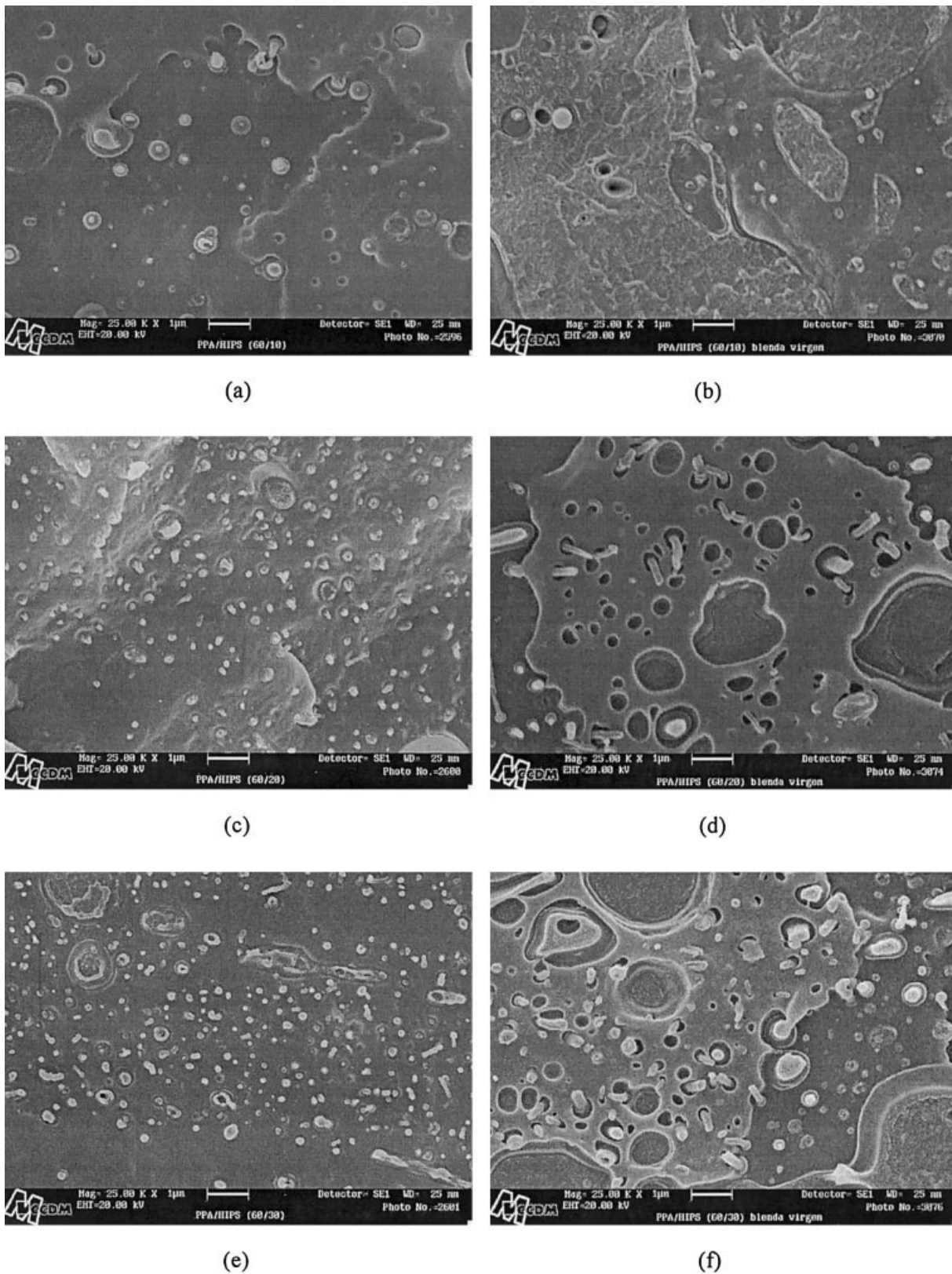
Figure 1 SEM micrographs of recycled and virgin PP/HIPS blends: (a,b) B1 (6:1), (c,d) B2 (6:2), and (e,f) B3 (6:3) compatibilized with SEBS concentrations of 7, 6, and 5 wt %, respectively, at a magnification of 25,000×.
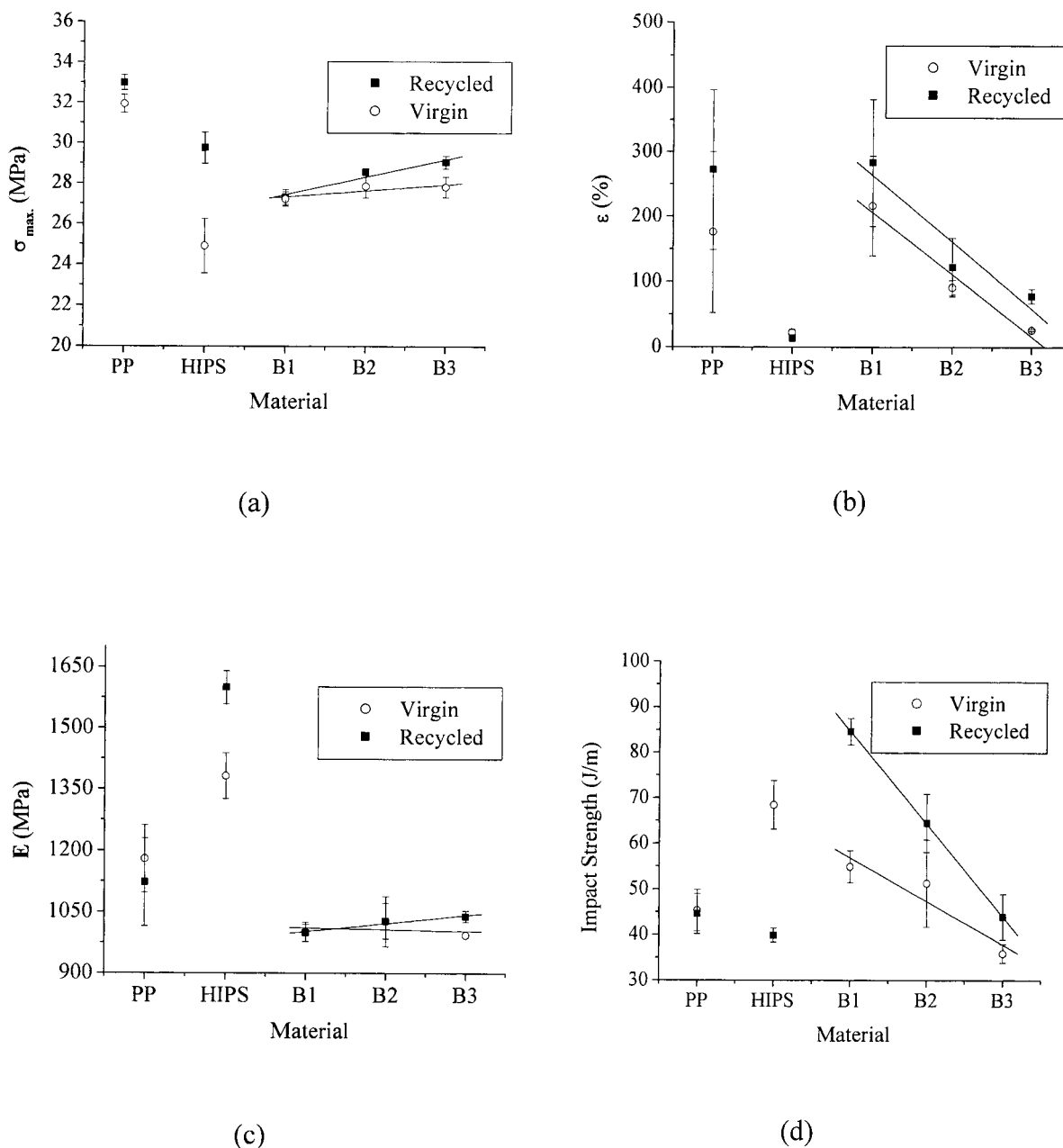
(a)

(b)

(c)

(d)

Figure 2 Mechanical properties: (a) σ_{max}, (b) ϵ, (c) E, and (d) IS.

the transparency of HIPS, it being a semitransparent resin used in package manufacturing. The particles of PS covered by the elastomer are 0.2 μm in diameter.[19]

In this study, the virgin blends present a morphology of a salami form [Fig. 2(d,f)], and the recycled blends show a core–shell form [Fig. 2(c,e)]. The recycled blends present a morphology with better homogeneously dispersed fine particles than the virgin blends.

However, Fortelny et al. studied the mixture processing conditions of blends and concluded that the particle size decreased with an increasing rate of mixing for blends with a low content of the disperse

phase. This conclusion was followed by an analysis of the theoretical expressions for the particle size in a steady flow.[20] They showed that the increasing viscosity of the PP matrix influenced the decreasing particle size of the disperse phase.[6]

The recycled and virgin HIPS/PP blends B3 (6:3) with 5 wt % SEBS present characteristics of dispersion and adherence similar to those of the HIPS/PP blends B2 (6:2) with 6 wt % SEBS, as shown in Figure 1(e,f). Good adherence of the disperse phase in the matrix of the recycled blend can be observed, and the virgin blend again presents a weak adherence of HIPS particles in the matrix. Despite the presence of some holes
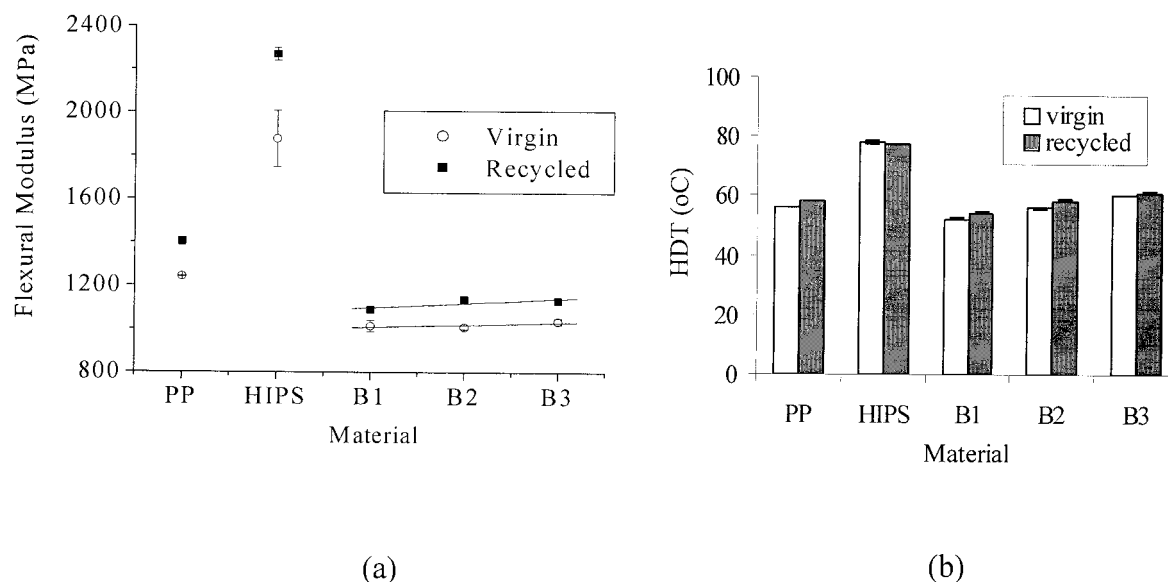
(a)   (b)

Figure 3 Thermomechanical properties: (a) *M* and (b) HDT under a flexural load.

in the fracture surface of the recycled blends, these can be considered negligible in number in comparison with the virgin blends. B3 blends have higher concentrations of HIPS and lower concentrations of SEBS than the B2 blends. The disperse-phase size of B3 was reduced one more time, with averages diameters of 0.04–0.12 μm, and this led to a higher average interfacial area of the HIPS particles.

Mechanical properties

Figure 2 shows the mechanical properties of virgin and recycled PP and HIPS and their binary compatibilized PP/HIPS blends. Recycled PP presents higher tensile stress at the maximum load (σ_{max}) and ϵ than virgin PP and recycled and virgin HIPS. However, recycled HIPS presents higher tensile strength, ϵ, and IS than virgin HIPS (H4300). The result is attributable to the different grades of the polymers.

In relation to the blends, the optimization of the blend composition, that is, the SEBS content decreasing from 7 to 5 wt % and the HIPS content increasing from 10 to 30 wt %, improves the interfacial adhesion (previously analyzed by morphological studies); therefore, σ_{max} is increased, as shown in Figure 2(a). Also, the recycled blends demonstrate slightly higher σ_{max} and tensile modulus (*E*) values [Fig. 2(a,c)] than the virgin blends.

However, in relation to the IS property in Figure 2(d), we observe that the virgin resin presents higher values than recycled HIPS. This result can be explained by the morphology because HIPS with elastomeric core–shell particles, with an average diameter of 0.2 μm, does not present the same toughness[21] as HIPS with salami-type particles. The core–shell-type HIPS

presents an IS lower than that of the salami-type HIPS and slightly higher than that of the PS homopolymer.[19]

Also shown in Figure 2(b,d), the IS and ϵ properties decrease with decreasing SEBS contents and increasing HIPS contents for both the virgin and recycled blends. This behavior is expected because the proportion of the elastomer component SEBS decays and the proportion of the most brittle component in the blend, HIPS, increases.

It can be observed in Figure 2(d) that the recycled blends present better IS than the virgin materials; this is due to the best adherence and compatibilization of the disperse phase on the matrix. However, IS decreases with an increasing HIPS concentration in the blends. This behavior can be explained by the high *E* [Fig. 2(c)] and low ϵ [Fig. 2(b)] values of HIPS.

In Figure 2(a–d), all the mechanical properties of the virgin blends are shown to be lower than those of the recycled blends. This can be explained by the grade of HIPS,[19] with consideration given to the composition and morphology variations. Composition differences have not yet been analyzed, but it is well known that the differences in the phase morphology affect the mechanical properties. The weak adherence of the disperse phase (HIPS) in the matrix, morphologically analyzed, probably also influences these properties [Fig. 1(c,d)].

Figure 3 shows the flexural modulus (*M*) and HDT results for virgin and recycled PP and HIPS and binary PP/HIPS blends compatibilized with SEBS at 7 (B1), 6 (B2), and 5 wt % (B3). The same behavior observed in tensile tests occurred in both tests. The recycled blends show higher *M* and HDT values than

TABLE I
Thermo mechanical Properties of PP, HIPS, and Their Recycled and Virgin Blends

Material	σ_{max} (MPa)	ε (%)	E (MPa)	M (MPa)	IS (J/m)	HDT (°C)
PP_b	33.0	272.2	1122	1404	44.6	58.3
PP_v	31.9	176.1	1179	1243	45.3	56.1
$HIPS_r$	29.8	13.6	1599	2271	39.9	77.3
$HIPS_v$	24.9	22.3	1382	1879	68.5	78.2
$B1_r$ (6:1) with 7 wt % SEBS	27.3	283.6	998	1090	84.6	54.3
$B1_v$ (6:1) with 7 wt % SEBS	27.2	216.5	1009	1014	54.9	52.3
$B2_r$ (6:2) with 6 wt % SEBS	28.5	121.9	1027	1137	64.5	58.4
$B2_v$ (6:2) with 6 wt % SEBS	27.9	90.9	1027	1009	51.3	55.9
$B3_r$ (6:3) with 5 wt % SEBS	29.1	77.8	1039	1132	43.9	61.3
$B3_v$ (6:3) with 5 wt % SEBS	27.8	26.3	993	1036	35.9	61.3

v = virgin; r = recycled.

the corresponding virgin materials, and the values increase from blend B1 to B3.

Finally, we can conclude that the knowledge of the compatibilizer concentration is important for the development of multiphase polymer materials with well-balanced properties according to specific requirements.[11]

All the thermomechanical properties can be better visualized in Table I, in which blend B3 presents increases in σ_{max}, E, M, and HDT properties and decreases in ϵ and IS with an increasing concentration of HIPS and a decreasing excessive concentration of SEBS.

Despite IS and ϵ decreasing for B3 with respect to the values for the other blends, these values are higher than those of recycled HIPS and similar to those of recycled PP. Furthermore, for rigid composite films, these properties are less critical than the others analyzed. This finally brings us to the conclusion that the most appropriate blend composition, with balanced properties, is presented by the B3 recycled blend.

CONCLUSIONS

We have compared the compatibilization efficiency of the SEBS copolymer and the HIPS content in virgin and recycled PP/HIPS blends with high rigidity and better mechanical properties because this blend will be used as a raw material for preparing composite films with characteristics similar to synthetic paper.

Morphological studies have provided evidence for the interfacial activity of block copolymers attributable to the stronger interactions of SEBS between the disperse phase (HIPS) and the matrix (PP), which reduce the average particle size of HIPS and increase the interfacial adhesion between the both phases.

The B3 recycled blend (6:3 PP/HIPS) with 5 wt % SEBS presents the highest reduction in the disperse-phase particle size, with average diameters of 0.04–

0.12 μm, which lead to a higher average interfacial area of HIPS particles.

An excessive triblock copolymer concentration brings about observable changes in the property–concentration dependence, and so the compatibilizer and disperse-phase concentration are important for the development of multiphase polymer materials with well-balanced properties according to specific requirements.

In this work, the most appropriate composition for a PP/HIPS blend for rigid composite films, based on improvements in the majority of the thermomechanical properties, has been found to be as follows: 6:3 PP/HIPS compatibilized with 5 wt % SEBS.

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