Compatibilization Effects of Styrenic/Rubber Block Copolymers in Polypropylene/Polystyrene Blends

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ABSTRACT: Compatibilizing effects of styrene/rubber block copolymers poly(styrene-*b*-butadiene-*b*-styrene) (SBS), poly(styrene-*b*-ethylene-*co*-propylene) (SEP), and two types of poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS), which differ in their molecular weights on morphology and selected mechanical properties of immiscible polypropylene/polystyrene (PP/PS) 70/30 blend were investigated. Three different concentrations of styrene/rubber block copolymers were used (2.5, 5, and 10 wt %). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the phase morphology of blends. The SEM analysis revealed that the size of the dispersed particles decreases as the content of the compatibilizer increases. Reduction of the dispersed particles sizes of blends compatibilized with SEP, SBS, and low-molecular weight SEBS agrees well with the theoretical predictions based on interaction energy densities determined by the binary interaction model of Paul and Barlow. The SEM analysis confirmed improved interfacial adhesion between matrix and dispersed phase. The TEM micrographs showed that SBS, SEP, and low-molecular weight SEBS enveloped and joined pure PS particles into complex dispersed aggregates. Bimodal particle size distribution was observed in the case of SEP and low-molecular weight SEBS addition. Notched impact strength (a_k), elongation at yield (ε_y), and Young's modulus (E) were measured as a function of weight percent of different types of styrene/rubber block copolymers. The a_k and ε_y were improved whereas E gradually decreased with increasing amount of the compatibilizer. The a_k was improved significantly by the addition of SEP. It was found that the compatibilizing efficiency of block copolymer used is strongly dependent on the chemical structure of rubber block, molecular weight of block copolymer molecule, and its concentration. The SEP diblock copolymer proved to be a superior compatibilizer over SBS and SEBS triblock copolymers. Low-molecular weight SEBS appeared to be a more efficient compatibilizer in PP/PS blend than high-molecular weight SEBS. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 291–307, 1999

Key words: polymer blends; polypropylene blends; polystyrene blends; styrene/rubber block copolymers; compatibilization; phase morphology; mechanical properties

INTRODUCTION

The majority of polymer pairs are immiscible and form multiphase systems with a variety of morphologies. It is well known that the morphology of

polymer blend plays a crucial role on its final properties.[1–4] Therefore, the control of the size, shape, and distribution of the dispersed phase or the degree of cocontinuity in polymer blends means the control of their final properties.

An important part of polymer blends technology is the application of block copolymers as compatibilizers, i.e., polymeric interfacial agents. The

addition of suitable chosen block copolymer can result in modified interfacial characteristics when it locates at the interface between two immiscible polymer phases.[5–7] Namely, in a polymer blend, the interface acts to transmit the stress from one phase to another and the efficiency of stress transfer continuity depends on the nature of the interface. With the proper interfacial modification it is possible to obtain a stable and reproducible morphology, which can lead to desired properties. The clearest interfacial effect of the compatibilizers is control of the sizes of the phase domains in an immiscible polymer blend. According to Datta and Lohse,[8] there are two presumed mechanisms for achieving such effects, which both may be operating in a particular system. The first is thermodynamical in that it lowers the interfacial tension between the phases, whereas the second is kinetic in that the compatibilizer can reduce the coalescence of the dispersed particles. An important effect of the use of compatibilizers also is the improvement of the adhesion between two immiscible phases, which enables to withstand the stress and strains caused by an applied load.[1,9,10] Compatibilizer effectiveness is very much dependent on different structural characteristics like chemical structure of the blocks, molecular weights of homopolymers and copolymer, molecular weights of individual blocks of copolymer, number of blocks in copolymer molecule,[9,10] and the mode of the compatibilizer addition.[11]

Blending of isotactic polypropylene (iPP) and atactic polystyrene (aPS) leads to very brittle blends because of the immiscibility of both components.[12] As shown previously by different authors, PP and PS form two-phase polymer blends for different weight ratios.[13–15] Some authors used block copolymers with one or more PS blocks and rubber blocks in a copolymer molecule as compatibilizers for PP/PS blends. Bartlett et al.[16] studied compatibilization of PP/PS blends with the addition of poly(styrene-b-ethylene-co-butylene-b-styrene) (SEBS) triblock copolymer. They found that the addition of 20 wt % of SEBS increased impact strength and elongation at break but reduced modulus and tensile strength. Compatibilizing effects of SEBS in PP/PS blends were confirmed also by Gupta and Purwar.[17] Appleby et al.[18] synthesized series of hydrogenated styrene/butadiene block copolymers of various structures, which were used as compatibilizers in PP/PS 50/50 blend. For comparison, commercial low-molecular weight SEBS triblock copolymer was added to the same binary blend. It proved to be more effective than high-molecular weight styrenic triblock copolymer as well as synthesized tapered styrenic diblock copolymers. Santana and Müller[19] examined the effects of adding poly(styrene-b-butadiene-b-styrene) (SBS) triblock copolymer to PP/PS blends when PS was a matrix phase. The size of dispersed PP particles did not change with the addition of 2 wt % of SBS. They reported no improvements in the tensile and the impact properties of such blends. However, some differences in crystallization behavior of PP in the blends containing SBS compared with those without SBS were observed. Recently, Fortelny and Michálková[20] studied the effects of SBS compatibilizer, time of mixing, sequence in the mixing chamber filling, and mixing temperature on the development of the phase structure in PP/PS blends. They found that the addition of 5 wt % of SBS led to the decrease in the average size of the dispersed particles but it did not lead to an increase in the phase structure uniformity. Navratilová and Fortelny[21] further confirmed the interfacial activity of SBS copolymer in PP/PS blends. Enhanced adhesion between the phases was observed but, interestingly, SBS did not stabilize particles against coalescence during annealing. Moreover, SBS narrowed the concentration region of the cocontinuous structure in studied blends. Horák et al.[22] used di-, tri-, and pentablock types of styrene/butadiene block copolymers as compatibilizers for blends of high-impact PS (HIPS) and PP. These authors reported that the PS-terminated multiblocks influenced development of the interfacial layer around dispersed PP particles and, consequently, improved mechanical properties compared with diblock copolymer, which showed negligible compatibilization efficiency. Changes in the crystallinity of PP in PP/HIPS blends compatibilized with styrene/butadiene diblock or SBS triblock copolymers were investigated by Hlavatá and Horák.[23] They found that the degree of crystallinity of PP in blends with HIPS did not change with HIPS content and slightly decreased with the addition of styrenic/rubber block copolymers (SRBCs).

In recent years, some authors reported the differences in compatibilization effectiveness of SRBCs comparing chemical structure of the rubber block,[24–27] number of blocks in a copolymer molecule,[22,25–28] and the molecular weights of different SEBS types.[25,26,28] These studies show that sometimes contradictory results are obtained comparing the effectiveness of SRBCs as interfacial agents in polymer blends. Mostly, the com-

patibilizing effect of SRBCs on dimensions of the dispersed phase was studied, although Schwarz et al.[28] observed that greater reduction in the dispersed phase diameter did not lead necessarily to better mechanical properties. They pointed out the importance of using the physical properties rather than morphology changes alone as a basis for the selection of a proper compatibilizer.

In our previous work we found that poly(styrene-*b*-ethylene-*co*-propylene) (SEP) diblock copolymer is a very effective compatibilizer for PP/PS blends with PP matrix.[29–31] We also observed very clear interfacial activities of SBS block copolymer in PP/PS blends with different weight ratios forming complex PS/SBS aggregates in PP matrix.[32] Besides compatibilization effects, SBS influences the crystallization process of PP changing crystallinity, crystallite sizes, and crystallite orientation.[32]

The aim of the present work is to compare systematically the compatibilizing effects of four different types of SRBCs in immiscible PP/PS blends. Compatibilizing effects were studied through morphological changes (emulsifying ability) and mechanical properties as a function of chemical structure of SRBCs and their concentration.

EXPERIMENTAL

Materials

The homopolymers used in this study were iPP Novolen 1100L (BASF, Germany) and aPS GP-678E (DOKI, Croatia). Four different SRBCs produced by Shell Chemical Co. were used as compatibilizers: SEP Kraton G-1701, SBS Kraton D-1102 CS, high-molecular weight SEBS-1 Kraton G-1651, and low-molecular weight SEBS-2 Kraton G-1652. The SEP is a linear diblock copolymer; SBS and SEBS are linear triblock copolymers with two PS end blocks. Polymer characteristics are summarized in Table I.

Blend Preparation

The PS pellets were dried overnight at 70°C before use and premixed with PP and SRBC pellets before being fed into the kneading chamber. Blends of the different compositions were prepared by melt blending in an oil-heated Brabender kneading chamber at 200°C for 6 min with the rotor speed of 50 rpm. After finishing the

Table I   Characteristics of Used Polymers

Polymer	$M_n{}^a$ (g/mol)	$M_w/M_n{}^a$	*MFI* (g/10 min)	% PS in SRBC[d]
PP	47000	9.3	6.9[b]	—
PS	96000	2.4	12.5[c]	—
SBS	67200	1.7	6.6[c]	29.5[e]
SEP	89500	1.5	0.6[c]	37.0[e]
SEBS-1	162300	1.2	—	33.0[e]
SEBS-2	65900	1.1	0.5[c]	29.0[e]

[a] Measured by size exclusion chromatography with PS standard.
[b] ASTM D 1238 (230°C/2.16 kg).
[c] ASTM D 1238 (200°C/5 kg).
[d] SRBC = styrene/rubber block copolymer.
[e] Manufacturer's data.

blending process, they were transferred rapidly between two aluminium sheets placed in the preheated hydraulic press at 220°C. Blend samples used for investigations of the morphology and mechanical properties were prepared by compression molding. The load of 100 bar was used and after 10 min the plates were moved out and cooled to the room temperature in the air. The weight ratio of PP and PS was 70/30. Compatibilizer contents were 2.5, 5, and 10 wt % for each type of SRBC.

Scanning Electron Microscopy

Scanning electron microscope (SEM) Jeol JSM-840A was used for studying the morphology. Samples were fractured in liquid nitrogen and covered with gold before being examined with the microscope at an acceleration voltage of 10 kV. To provide a better insight into blend morphology, PS and SRBCs were etched off the surface in some samples with xylene at the room temperature. All SEM micrographs are secondary electron images.

The particle size of the dispersed PS phase was determined from several SEM micrographs with the micrometer scale. Five hundred to fifteen hundred dispersed particles were counted for the determination for each studied blend. The particle diameter was obtained from the measurements of hole diameter as a result of the etching of the PS and SRBC phases. The diameter of the dispersed phase was quantified through the definition of the number average particle diameter

$$d_n = \frac{\sum N_i \times d_i}{\sum N_i} \qquad (1)$$

where N_i is the number of the particles with the diameter d_i. Error in the reported diameter is estimated ± 0.2 μm.

Transmission Electron Microscopy

Ultrathin sections (approximately 70 nm thick) were cut at the room temperature from 4-mm-thick plates with Reichert–Jung ultracut E microtome equipment with a diamond knife. Before microtoming, samples were exposed first to the OsO_4 vapor for 3 days. After that, overnight exposure to RuO_4 was performed because of the additional contrasting and hardening of the samples. Microtomed ultrathin sections then were placed on Cu grids and micrographs were taken at an acceleration voltage of 80 kV with a Phillips 3000 microscope.

Mechanical Testing

Test specimens for the notched impact strength were cut from 4-mm-thick compression-molded plates. Testing bars then were machined to the dimensions of 50 × 6 × 4 mm. The U-shaped notch was cut at the center of each specimen with the depth of 1.3 mm. Specimens were fractured according to the Charpy test on Frank apparatus with 0.5 J weight at 23°C (DIN 53453). Ten test specimens for each sample were measured.

Test specimens for the tensile measurements were prepared from 1-mm-thick plates according to ASTM D 638. Young's modulus and elongation at yield were measured by tensile tester Frank 81105 at 23°C with six specimens for each sample. Strain rate was 1 mm/min.

RESULTS AND DISCUSSION

Phase Morphology

Figure 1 shows the morphology of the fracture surface of binary (noncompatibilized) PP/PS 70/30 blend. The SEM analysis revealed two-phase morphology with the polidispersity of spherical PS particles in the PP matrix, which is the result of high interfacial tension and coalescence. From Figure 1 poor adhesion between the phases can be observed. In our previous papers we confirmed two-phase morphologies of binary PP/PS blends in a broader concentration range.[29–32]

The SEM analysis provides an insight of the interfacial activity of block copolymers in polymer
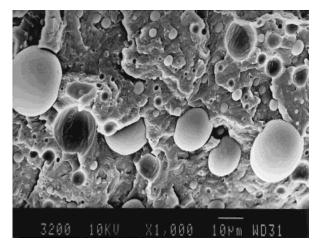

Figure 1 Scanning electron micrograph of the fracture surface of noncompatibilized PP/PS 70/30 blend.

blends. Although we showed previously in the separate studies that diblock copolymer SEP and triblock copolymer SBS have compatibilizing abilities in PP/PS blends,[29–32] no direct comparison of different SRBCs as compatibilizers for PP/PS blends was given. In Figures 2–5 the morphologies of the fractured surfaces of PP/PS 70/30 blends compatibilized with different amounts of SBS, SEP, SEBS-1, and SEBS-2 are shown, respectively. The SEBS-1 and SEBS-2 differ in their molecular weights (Table I). In Figures 2–5, PS and SRBC were etched from the sample surfaces with xylene at the room temperature to get better insight into blend phase morphology.

Figures 2–5 show that the addition of the SRBC compatibilizers changes the phase morphology of PP/PS 70/30 blend compared with the noncompatibilized blend. Even 2.5 wt % of each SRBC added had very noticeable effect in lowering the average diameter of the dispersed phase. From Figures 2(a), 3(a), 4(a), and 5(a) we can observe that when 2.5 wt % of SRBC compatibilizers was added to the blend some dispersed PS particles still have the diameter in the range of that in the noncompatibilized PP/PS 70/30 blend (Fig. 1) indicating that 2.5 wt % of SRBC is still too low of a concentration to cover all dispersed particles with an interfacial layer. Therefore, some of particles coalesce into the bigger ones. From Figures 2 and 4 it is obvious that with the increased amount of the added SBS and SEBS-1 the dispersed PS particles remain spherical, whereas the increasing amount of SEP and SEBS-2 changes their shape and distribution in a completely different manner (Figs. 3 and 5). With
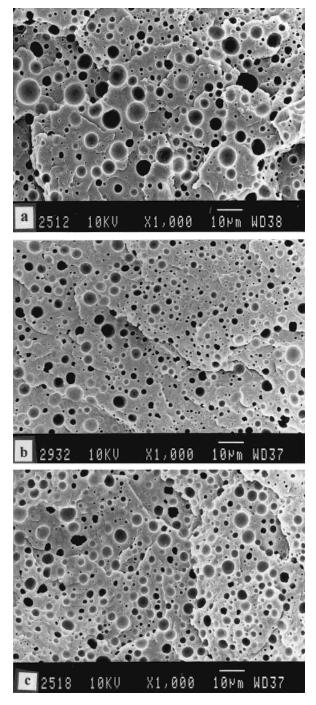
rarely spherical and many of them start to form aggregates [Fig. 3(b)]. Such a trend is pronounced with increasing SEP concentration to 10 wt % [Fig. 3(c)]. The fracture surface morphology of
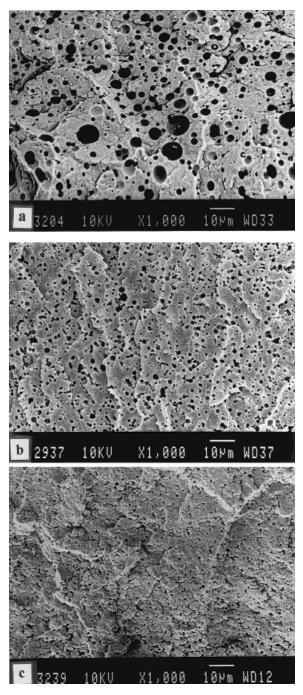

Figure 2 Scanning electron micrographs of the fracture surfaces of PP/PS 70/30 blends compatibilized with different amounts of SBS compatibilizer: (a) 2.5 wt % SBS, (b) 5 wt % SBS, (c) 10 wt % SBS. The PS and SBS etched with xylene.

Figure 3 Scanning electron micrographs of the fracture surfaces of PP/PS 70/30 blends compatibilized with different amounts of SEP compatibilizer: (a) 2.5 wt % SEP, (b) 5 wt % SEP, (c) 10 wt % SEP. The PS and SEP etched with xylene.
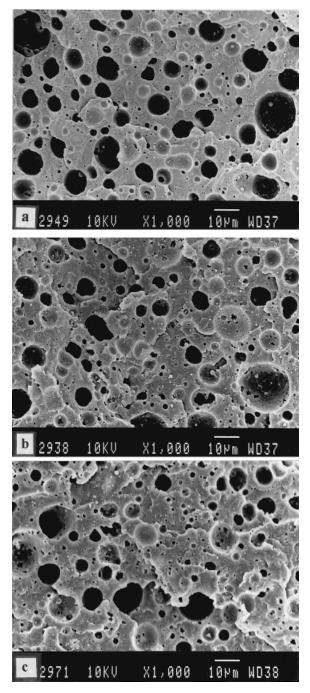
the addition of 2.5 wt % of SEP block copolymer dispersed PS particles remain spherical. The 5 wt % of SEP further reduces dispersed particle size and, moreover, changes their shape. Particles are

centration also is observed with the addition of SEBS-2 block copolymer, although the reduction of the PS particles' diameter is less obvious in this latter case (Fig. 5). The morphology progressively
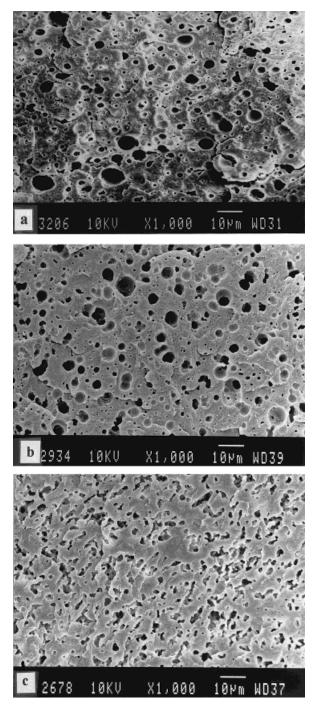

Figure 4   Scanning electron micrographs of the fracture surfaces of PP/PS 70/30 blends compatibilized with different amounts of SEBS-1 compatibilizer: (a) 2.5 wt % SEBS-1, (b) 5 wt % SEBS-1, (c) 10 wt % SEBS-1. The PS and SEBS-1 etched with xylene.

PP/PS 70/30 blend compatibilized with 10 wt % SEP differs completely from the other morphologies observed by SEM. Similar morphology changes as a function of the compatibilizer con-

Figure 5   Scanning electron micrographs of the fracture surfaces of PP/PS 70/30 blends compatibilized with different amounts of SEBS-2 compatibilizer: (a) 2.5 wt % SEBS-2, (b) 5 wt % SEBS-2, (c) 10 wt % SEBS-2. The PS and SEBS-2 etched with xylene.
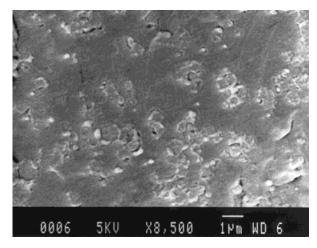
Figure 6 Scanning electron micrograph of the fracture surface of PP/PS 70/30 blend compatibilized with 10 wt % of SEP block copolymer.

changes from dispersed particles of PS [Fig. 5(a)] to an almost cocontinuous morphology as the SEBS-2 content is increased [Fig. 5(c)].

In Figure 6 it is shown the morphology of the fracture surface of PP/PS 70/30 blend compatibilized with 10 wt % of SEP and in Figure 7 the morphology of the fracture surface of PP/PS 70/30 blend compatibilized with 10 wt % of SEBS-2. From Figures 6 and 7 we can see that the dispersed PS particles are embedded strongly in the PP matrix indicating good interfacial adhesion. It can be seen that the structure and shape of the dispersed particles are very complex. In our previous study we described more detailed improve-
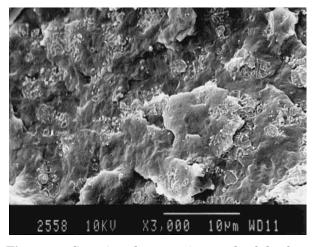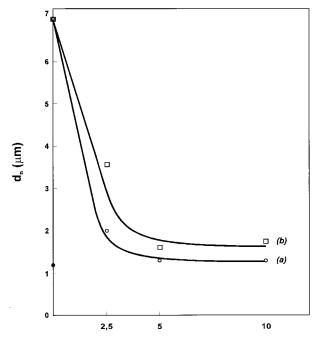

Figure 7 Scanning electron micrograph of the fracture surface of PP/PS 70/30 blend compatibilized with 10 wt % of SEBS-2 block copolymer.

Weight percent of compatibilizer

Figure 8 Dependence of the number average diameter (d_n) of the dispersed PS particles in PP/PS 70/30 blends measured as a function of the compatibilizer content: (a) SBS block copolymer and (b) SEBS-1 block copolymer.

ments of the interfacial adhesion in the compatibilized PP/PS/SBS blends as a result of localization of SBS block copolymer at the interface.[32]

Figure 8 shows the dependence of the number average diameter of the dispersed PS particles as a function of the compatibilizer content. Because the shapes of the dispersed particles in the samples containing SEP and SEBS-2 are too complex (Figs. 3 and 5), determination of the particle diameter in these cases is impossible. Thus, we present the results for blends compatibilized with SBS and SEBS-1 block copolymers only. Values for the number average diameter (d_n) were determined by the eq. (1). As can be seen from Figure 8, major effects of the particle size reduction is observed by the addition of the first 2.5 wt % of the copolymers, whereas beyond 5 wt % of the compatibilizer no significant reduction results anymore. From Figure 8 it appears that approximately 5 wt % of SBS and SEBS-1 is sufficient to produce a maximum reduction of the dispersed PS-phase size. No further decrease in the dispersed phase diameter is achieved by adding more SBS or SEBS-1 compatibilizer. This can be

concluded from the shape of the curves in Figure 8, which achieve a plateau for the concentrations higher than 5 wt %. From Figure 8 it also is interesting to note that even 2.5 wt % of the added compatibilizer significantly reduces the number average particle diameter compared with non-compatibilized blend. The SBS is a more effective interfacial agent in PP/PS blend than SEBS-1.

Diagrams, such as those in Figure 8, enable us to estimate the concentration of the compatibilizer needed for the maximum diameter reduction of the dispersed phase and are defined as emulsification curves.[33,34] Some authors propose that the concentration of the compatibilizer beyond where no reduction of the dispersed particles size is observed corresponds to the interfacial saturation by the block copolymer molecules.[6,27,33–35] Both curves in Figure 8 also are in accordance with the observations of Anastasiadis et al.[36] who determined the lowering of the intarfacial tension as a function of the compatibilizer concentration in polymer blends. They found that the interfacial tension is lowered with the increasing amount of compatibilizer to the limiting value beyond which no significant reduction of interfacial tension is observed. According to the authors, this can be the result of the interfacial saturation at the higher concentrations of the block copolymers.

George et al.[35] reported that too high concentration of the added compatibilizer may increase the average dispersed particle size. They attributed this effect to the formation of micelles of the compatibilizer in the matrix phase. This also might be the reason for a bit higher d_n value when 10 wt % of SEBS-1 was added compared with 5 wt % SEBS-1 as seen in Figure 8. Namely, an effective compatibilizer must have a high enough molecular weight to lower interfacial tension as well as to improve the interfacial adhesion, but not too high molecular weight to prevent the formation of micelles in a matrix phase.

A possible interpretation of the compatibilization effectiveness of SRBC in PP/PS blends may consider the thermodynamic aspect, which includes the Flory–Huggins interaction parameter concept widely used in the theory of polymer blends.[12,37,38] Flory–Huggins interaction parameter χ_{12} can be estimated from the solubility parameters of the blend components. The relation between the interaction parameter χ_{12} and the solubility parameters of the individual components of polymer blend is given by the following equation[12,37]:

$$\chi_{12} = \frac{V_r}{R \times T} (\delta_1 - \delta_2)^2 \qquad (2)$$

where V_r is the reference volume, which is taken as close to the molar volume of the polymer repeat unit as possible; R is the gas constant; T is the temperature; and δ_1 and δ_2 are solubility parameters of polymers 1 and 2. The closer the match of solubility parameters of the two polymers, the greater the probability of their miscibility. In spite of the obvious shortcomings,[12] this approach allows practical predictions of polymer miscibility to be made. From the literature it is known that the interaction parameter χ_{12} also can be related with so-called interaction energy density B defined as[37,39]

$$B = \frac{R \times T \times \chi_{12}}{V_r} \qquad (3)$$

From eqs. (2) and (3) a simple correlation between interaction energy density and solubility parameters is obtained;

$$B = (\delta_1 - \delta_2)^2 \qquad (4)$$

Paul and Barlow[39] derived an expression for the estimation of the interaction energy density for the blends that contain copolymer as the blend component. This model is based on the fact that the net exothermic heat of mixing required for miscibility of high-molecular weight polymer blends may result from appropriate considerations of both intermolecular and intramolecular interactions of the component units without exothermic interactions existing between any individual pair of the monomer units. According to this binary interaction model, Paul and Barlow[39] obtained an expression for the interaction energy density $B_{h/c}$ of the polymer blends composed of the copolymer with monomer units 1 and 2 and homopolymer with monomer units 3, which is given by the following equation:

$$B_{h/c} = B_{13}\phi_1^c + B_{23}\phi_2^c - B_{12}\phi_1^c\phi_2^c \qquad (5)$$

where B_{13} and B_{23} are interaction energy densities of copolymer monomer units 1 and 2 with homopolymer monomer units 3, B_{12} is interaction energy density between monomer units 1 and 2 in a copolymer macromolecule, and ϕ_1^c and ϕ_2^c are volume fractions of the monomer units 1 and 2 in

Table II   Solubility Parameters (δ) of Used Polymers

Polymer	δ (J$^{1/2}$ cm$^{-3/2}$)[a]
PP	15,1
PS	19,4
PB	16,6
PBu	16,1
PE	16,4

[a] Ref. 38.

a copolymer macromolecule. If B_{12} is a large enough positive value, i.e., there are strong repulsion interactions between monomer units in a copolymer, mixing of the homo- and copolymer in a blend is preferred. According to Paul and Barlow,[39] this phenomenon occurs because the addition of homopolymer 3 to the copolymer dilutes the unfavorable interactions between monomer units 1 and 2 leading to a exothermic mixing condition even though no individual binary interaction is exothermic.

If we consider rubber blocks of SRBCs as individual random copolymer molecules oriented in the PP matrix phase of PP/PS blends, we can estimate the values of $B_{h/c}$ between PP and rubber blocks from eq. (5). With the same prediction we assume that PS end blocks of SEP and SEBS block copolymers are oriented into the PS homopolymer phase because of their chemical structure similarity. Using the approximations in eqs. (4) and (5), the interaction energy densities $B_{h/c}$ between PP and different rubber blocks of SRBCs can be estimated using the values of the solubility parameters of homopolymers, obtained from the literature data and that are given in Table II.

Solubility parameters data in Table II show that the differences between the values of solubility parameters of polybutadiene (PB), polybutylene (PBu), and polyethylene (PE) with PP are all less than the difference of solubility parameters between PP and PS. Because rubber blocks of SRBCs are composed of PB or random ethylene/butylene (E/B) or ethylene/propylene (E/P) copolymer blocks this might be the driving force for the localization of SRBC in the PP–PS interfacial region although there is no chemical identical PP block in any of the SRBCs used. The reported solubility parameter values for the individual polymers in the literature may differ because they are dependent on the method of determination. Therefore, some authors, like González–Montiel

et al.,[40] presented interaction energy density rather as a region than a single line, reflecting the uncertainties in the interaction energy density due to the range of the values estimated for the solubility parameters. Calculated $B_{h/c}$ values between PP and rubber blocks of SRBCs are shown in Figure 9 as a function of the volume fraction of the ethylene monomer unit in a rubber block of SRBCs, as calculated by eqs. (4) and (5). On the basis of the calculated $B_{h/c}$ values it is possible to compare the compatibilizing effectiveness of SRBC in PP/PS blends from the thermodynamic point of view, based on the compatibility between PP and rubber blocks of SRBCs.

Figure 9 shows that $B_{h/c}$ values for the rubber block of SEP and PP as well as SEBS and PP increases with the increased amount of ethylene monomer units. From the calculated $B_{h/c}$ values it can be concluded that compatibility between E/P blocks of SEP with PP segments is higher than compatibility between E/B blocks of SEBS or PB blocks of SBS. Such calculation agrees well with compatibilizing effectiveness of SEP, SBS, and SEBS-2 block copolymers if the comparison of the dispersed particle size reduction is a criterion for the higher interfacial activity of SRBCs. But
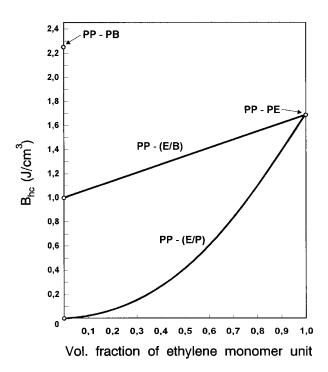

Figure 9 Calculated interaction energy density ($B_{h/c}$) between PP and different rubber blocks of SRBCs as a function of volume fraction of the ethylene monomer unit in a rubber block.
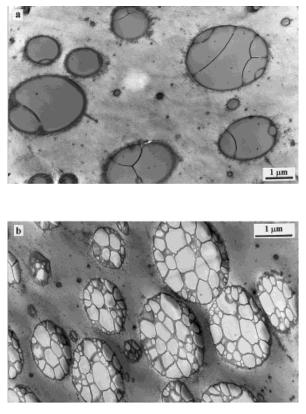
Figure 10 Transmission electron micrographs of PP/PS 70/30 blends compatibilized with SBS block copolymer and stained with OsO_4 and RuO_4: (a) 2.5 wt % SBS and (b) 10 wt % SBS.

the morphology analysis with SEM only partly confirms theoretical calculations. Namely, SEBS-1 shows the least compatibilizing effect in spite of the lower calculated $B_{h/c}$ values compared with SBS (Figs. 2–5 and 8). Moreover, interfacial activity between SEBS-1 and SEBS-2 differs significantly indicating some other influential factors. Number average molecular weight of SEBS-1 is approximately 2.5 times higher than that of SEBS-2 (Table I). On the other hand, SEP, SBS, and SEBS-2 have all comparable values of number average molecular weights. Considering these facts, it is obvious that molecular weight plays one of the crucial roles in the compatibilizing effectiveness of SRBC compatibilizers. A separate study is necessary to evaluate the role of the number of blocks in SRBCs as an influential compatibilizing factor.

Transmission electron microscopy (TEM) provides additional insight into the phase morphology of compatibilized PP/PS blends. Before analyzed, samples were prepared using combined OsO_4 and RuO_4 staining technique. Because of

this procedure, rubber blocks of SRBCs appear dark grey or black in TEM micrographs. The PS blocks of SRBCs, pure PS homopolymer, and PP homopolymer remained brighter.

In our previous study[32] we already described some details of the morphology of PP/PS blends compatibilized with 10 wt % of SBS. In this paper some further morphological features of PP/PS/SBS blends are presented and commented on. Figure 10 shows TEM micrographs of PP/PS 70/30 blends compatibilized with 2.5 and 10 wt % of SBS. The TEM analysis reveals that SBS is not located only at the interface between PP and PS phases but forms, together with pure PS particles, complex dispersed structures. Figure 10 shows that the dispersed particles in PP matrix actually are the aggregates of PS particles, which are surrounded and joined together with SBS triblock copolymer. Such aggregates start to form even when only 2.5 wt % of SBS is added [Fig. 10(a)]. With the increasing amount of SBS compatibilizer, the internal structure of dispersed particles becomes more developed. Moreover, the major amount of SBS is not located at the PP–PS interface but inside the aggregates where it partly preserves the characteristic two-phase microstructure of pure styrenic/rubber triblock copolymers.[41] Namely, SBS and SEBS are, at room temperature, phase-separated linear thermoplastic elastomers with two PS end blocks and a central rubber block. Styrenic/rubber triblock copolymers may form spherical, rodlike, or lamellar nanometer-scale domains whose size and shape depend on PS content in triblock copolymers. Such microphase separation is a consequence of strong incompatibility between chemically different blocks.[42] Figure 11 shows a detailed structure
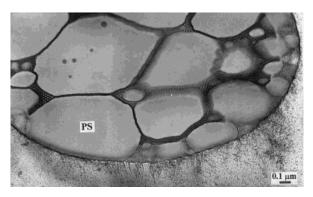

Figure 11 Transmission electron micrograph of PP/PS 70/30 blend compatibilized with 10 wt % SBS block copolymer and stained with OsO_4 and RuO_4.

of the dispersed PS/SBS aggregates. The SBS layers surround pure PS particles and mostly preserve phase-separated morphology. Part of the PS end blocks of SBS obviously penetrates into pure PS particles and joins them into complex aggregates.

Considering the internal structure of the dispersed aggregate particles in PP matrix, three basic conformations of SBS triblock copolymer are suggested. Mostly in the vicinity of smaller and spherical PS particles, PS end blocks form spherical microdomains. Such PS microdomains occur where SBS layer is somewhat thicker. Thus, from the thermodynamical point of view, it is most advantageous that chemical identical PS end blocks segregate into spherical microdomains. A different situation occurs in an SBS internal layer between bigger and more elongated PS particles in the aggregates. In such cases, lamellar structure of SBS occurs with one or more PS and PB layers. In Figures 10 and 11 we also can see the completely black layers of SBS in the aggregates. It can be assumed that one PS end block of SBS penetrates into one pure PS particle, and the second PS end block penetrates into another pure PS particle and joins them. It also is possible that different SBS blocks freely penetrate into corresponding phases in the disordered regions without forming ordered SBS two-phase microstructures. It is worth mentioning that such SBS phase-separated microstructures occur only inside dispersed aggregates and not at the PP–PS interface region. Proposed conformations of SBS in the PS/SBS aggregates are shown in Figure 12.

The TEM micrographs of PP/PS 70/30 blends compatibilized with 2.5 and 10 wt % of SEP diblock copolymer are shown in Figure 13. The SEP forms a continuous interface layer around the dispersed PS particles even when only 2.5 wt % of SEP is added. As seen in Figure 13(a), the particle size distribution is distinctly bimodal. Bimodality of PP/PS/SEP blends is much clearer to observe in TEM micrographs than in SEM micrographs. When the concentration of the SEP compatibilizer is increased to 10 wt %, dispersed PS particles start to form aggregates joining together smaller and bigger particles [Fig. 13(b)]. Bimodal distribution becomes more evident when 10 wt % of SEP is added. The average size of the small particles seems to remain constant as the SEP concentration increases, but their number is increased. Bigger PS particles are surrounded partly with the aggregates of smaller PS particles as shown clearly in Figure 14. Figure 14 repre-
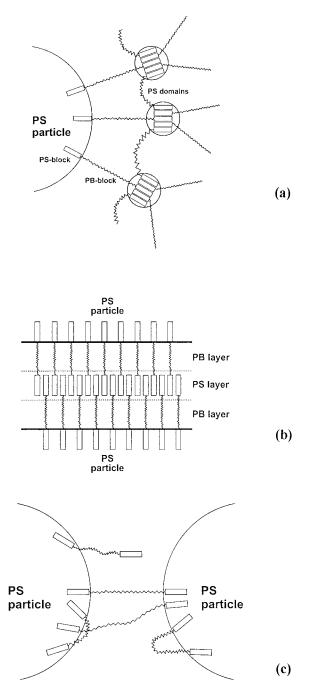

(a)

(b)

(c)

Figure 12 Proposed SBS block copolymer conformations in the dispersed PS/SBS aggregates: (a) formation of spherical PS microdomains, (b) formation of lamellar microdomains, and (c) disordered interparticle region.

sents the interfacial region of PP/PS 70/30 blend compatibilized with 10 wt % of SEP at the higher magnification. Morphologies of PP/PS/SEP blends are completely different from the morphologies of PP/PS/SBS blends. Namely, SEP diblock copolymer mostly locates at the PP–PS interface, which is not the case with SBS.
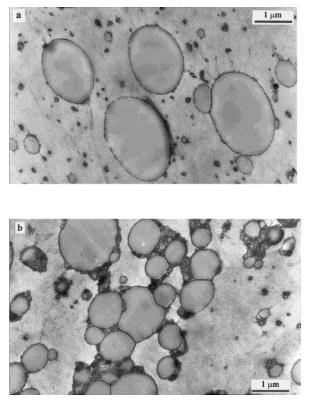
Figure 15 Transmission electron micrographs of PP/PS 70/30 blends compatibilized with 10 wt % SEBS-1 block copolymer and stained with OsO_4 and RuO_4.

Figure 13 Transmission electron micrographs of PP/PS 70/30 blends compatibilized with SEP block copolymer and stained with OsO_4 and RuO_4: (a) 2.5 wt % SEP and (b) 10 wt % SEP.

Figure 15 shows the TEM micrograph of PP/PS 70/30 blend compatibilized with 10 wt % of SEBS-1 triblock copolymer. The SEBS-1 forms a continuous interfacial layer around the dispersed PS particles with no tendency of forming aggregates even at higher compatibilizer concentra-
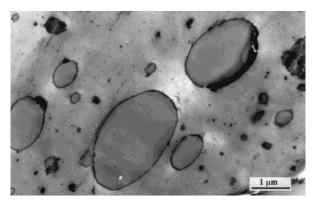
tion. The TEM micrograph in Figure 16 shows that the interfacial layer is very sharp, indicating that interpenetration between copolymer blocks and corresponding homopolymer phases, especially between E/B blocks and PP segments, is limited at the interface.

Figure 17 shows the morphologies of PP/PS 70/30 blends compatibilized with 2.5 and 10 wt % SEBS-2 triblock copolymer. Addition of SEBS-2 causes the formation of complex multiphase morphology. Like the SEP diblock copolymer, SEBS-2 triblock copolymer promotes bimodal PS particles distribution. Bigger PS particles are joined together with SEBS-2 and are surrounded partly by the aggregates of smaller particles. Such trend is emphasized when SEBS-2 concentration is increased to 10 wt % [Fig. 17(b)]. At this SEBS-2 content dispersed PS/SEBS-2 aggregates start to
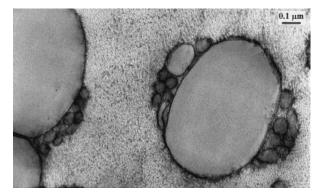

Figure 14 Transmission electron micrograph of PP/PS 70/30 blend compatibilized with 10 wt % SEP block copolymer and stained with OsO_4 and RuO_4.
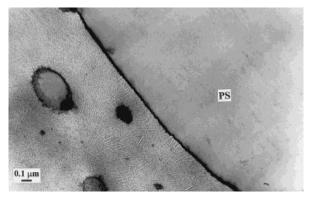

Figure 16 A detail of the interfacial region of PP/PS 70/30 blend compatibilized with 10 wt % SEBS-1 block copolymer taken by TEM and stained with OsO_4 and RuO_4.
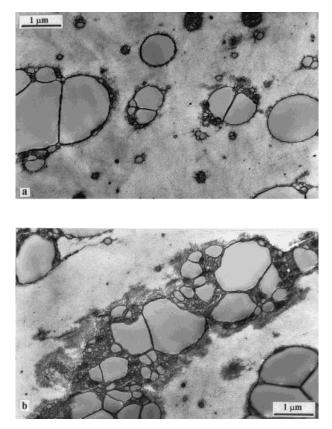
Figure 17 Transmission electron micrographs of PP/PS 70/30 blends compatibilized with SEBS-2 block copolymer and stained with OsO_4 and RuO_4: (a) 2.5 wt % SEBS-2 and (b) 10 wt % SEBS-2.

generate morphology, which is almost cocontinuous with the PP phase. In TEM micrographs (Figs. 17 and 18), the typical two-phase morphology of styrenic/rubber triblock copolymers is not observed as in the case of PP/PS/SBS blends where SBS partly preserves characteristic phase microstructure (Figs. 10 and 11). Lee et al.[43] reported that one of the distinctions between SBS and SEBS was the segregation strength between PS blocks and rubber blocks in SBS and SEBS. SEBS is found to have higher segregation strength between the PS blocks and E/B blocks in SEBS than that between the PS blocks and PB blocks in SBS. Interestingly, we observed the opposite case: SBS compatibilizer partly preserves two-phase morphology whereas SEBS does not. The reason may be stronger interactions between E/B rubber blocks of SEBS with PP segments compared with PB rubber blocks of SBS (Fig. 9). Stronger interactions then cause such two-phase morphology to be broken and the existence of only SEBS layers. We can classify the morphologies of

PP/PS/SEBS-2 blend somewhere between PP/PS/ SBS and PP/PS/SEP blends morphologies.

From Figure 18 it can be seen the interfacial region of PP/PS 70/30 blend compatibilized with 10 wt % of SEBS-2. It is clearly seen that the transcrystallinity of PP lamellae, more or less perpendicular to the interface region, occurs. This is caused by higher nucleation density near the interface.[44,45] Setz et al.[45] also observed similar transcrystallinity effect at the binary PP/SEBS-2 blend interface. These authors clearly showed that SEBS-2 tended to diffuse into the PP phase under formation of micelles. The fact that the SEBS-2 block copolymer showed a reorientation phenomenon of large domains at the interface before the diffusion process into the PP phase proved that different phenomena can occur at the PP-SEBS interfaces.

To our knowledge, aggregated dispersed phase morphology of compatibilized blends as observed in this study is reported rarely in the literature. Rösch et al.[46] and Horiuchi et al.[47] observed similar dispersed aggregates of polyamide (PA) and SEBS grafted with malein anhydride (SEBS-g-MA) in PP/PA/SEBS-g-MA and polycarbonate/ PA/SEBS-g-MA blends. The PA microparticles were found embedded in SEBS-g-MA shells and formed clusters of such core/shell dispersed particles ("honeycomblike morphology").

From TEM micrographs of PP/PS 70/30 blends compatibilized with different SRBC we estimated the thickness of the interfacial layer. Table III summarizes the maximum estimated thickness of the interfacial layer for two SRBC concentrations. Considering the values in Table III we must point out two facts influencing such determination.
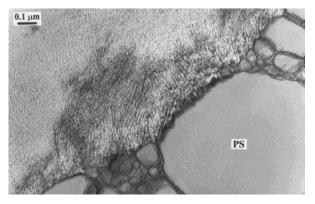

Figure 18 A detail of the interfacial region of PP/PS 70/30 blend compatibilized with 10 wt % SEBS-2 block copolymer taken by TEM and stained with OsO_4 and RuO_4.

Table III Maximum Estimated Thicknesses of Interfacial Layer (in nm) of PP/PS 70/30 Blends Compatibilized with Different Types of SRBCs[a]

SRBC	Compatibilizer Content (wt %)	Interfacial Thickness (nm)
SBS	2.5	—
	10	30
SEP	2.5	35
	10	42
SEBS-1	2.5	—
	10	56
SEBS-2	2.5	22
	10	50

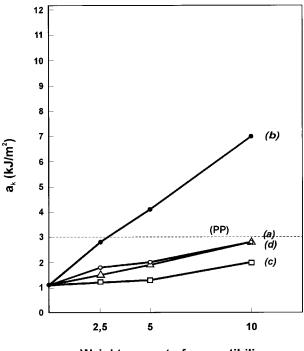[a] The values are estimated from TEM micrographs.

First, when SEP and SEBS-2 are used as compatibilizers the interfacial layer is much more diffuse. Consequently, it is more difficult to estimate accurately the interfacial layer thickness. Second, the thicknesses of the interfacial layers change, more or less, around dispersed PS particles. Therefore, we report the maximum thickness values in this article.

Our results support the work of some other authors. The importance of molecular weight on compatibilizing efficiency of block copolymers was pointed out already by Paul.[9] Fayt et al.[6,10] believed that a diblock copolymer is more effective than triblock because its blocks can penetrate more easily into corresponding homopolymer phases and provide strong entanglements whereas triblock copolymers mainly adsorb onto the phase because of conformational restraints. Taha and Frerejean[26] compared the compatibilizing effectiveness of SEP, SEBS-1, and SEBS-2 in low-density PE/PS blends. The finest and more stable dispersion was obtained with the addition of SEP diblock copolymer. Also, SEBS-2 was more effective than SEBS-1. Akkapeddi and Van Buskirk[25] and Schwarz et al.[28] found the superiority of SEBS-2 over SEBS-1 in improving mechanical properties of different polymer blends. In some cases, opposite results are obtained. Namely, Horák et al.[22] observed that multiblock styrene/butadiene copolymers showed higher improvements in impact strength and elongation at break in comparison with diblock copolymer in HIPS/PP blends. All these results confirm that molecular weight and the structure of the block copolymer molecule together with molecular weights of corresponding homopolymers very much influence compatibilizing effectiveness.
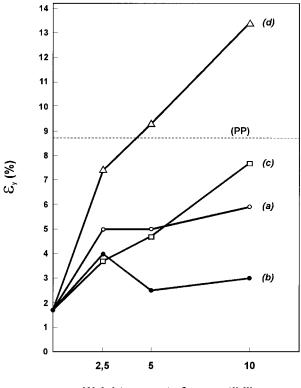
Mechanical Properties

Figure 19 shows the notched impact strength of compatibilized PP/PS 70/30 blends as a function of the concentration of different types of SRBC. Noncompatibilized PP/PS 70/30 blend has poorer impact properties compared with pure PP. Large dispersed PS particles sizes and the apparent lack of interfacial adhesion between PP and PS (Fig. 1) seem to be primary factors resulting in the weak and brittle behavior observed for this blend.

With increasing amount of SRBC the notched impact strength almost linearly increases for all SRBC types. There is a distinct difference in notched impact strength improvements for blends compatibilized with SEP compared with other SRBC used. The 10 wt % of SEP causes an almost sevenfold increase in the notched impact strength, whereas 10 wt % of SBS and SEBS-2, added to PP/PS 70/30 blend, increases notched impact strength close to the value of pure PP. Even larger improvements in impact resistance were observed when SEP was added to PP/PS 90/10 blend.[29] Addition of SEBS-1 causes negligible improvements of the notched impact strength

Figure 19 Notched impact strength (a_k) of PP/PS 70/30 blends compatibilized with different types of SRBCs as a function of compatibilizer content: (a) SBS, (b) SEP, (c) SEBS-1, and (d) SEBS-2.

Figure 20 Elongation at yield (ε_y) of PP/PS 70/30 blends compatibilized with different types of SRBCs as a function of compatibilizer content: (a) SBS, (b) SEP, (c) SEBS-1, and (d) SEBS-2.

of PP/PS 70/30 blend. These results are in accordance with the morphology observations reported in a previous chapter. The increase of the notched impact strength can be explained in the terms of better interfacial adhesion and finer dispersion of PS particles caused by the addition of the compatibilizers, especially when SEP is added. Considering the reduction of the dispersed particles sizes from Figures 2–5 we conclude that SEBS-1 is the least effective compatibilizer. Also, the very sharp interface layer observed by TEM (Fig. 16) indicates poor interpenetration of rubber blocks with PP segments. According to Park et al.,[48] the strength of the adhesive bond formed is related to the extent that polymer chains traversing the interface are anchored into each phase.

Variations of elongation at yield as a function of the concentration of different types of SRBC are shown in Figure 20. Elongation at yield is increased most evidently when SEBS-1 or SEBS-2 is added to the PP/PS 70/30, whereas SEP is not effective in improving this mechanical

property. But it must be pointed out that SEP is much more effective in improving elongation at break than SBS, SEBS-1, or SEBS-2.[29,32,49]

Figure 21 shows that Young's modulus decreases gradually with the increasing amount of different SRBC types. The PP/PS 70/30 blends compatibilized with SBS, SEP, and SEBS-2 have very similar values of Young's modulus, whereas blends compatibilized with SEBS-1 are more rigid. Additional investigation should be carried out to explain this behavior.

Although some authors showed that elongation at yield can be used as a measure of polymer blends miscibility[50] it also is very important to include the changes of supermolecular structure of PP matrix caused by the addition of different SRBCs interpreting mechanical properties. It means, it is necessary to include observations of the changes of supermolecular PP structure to comment accurately mechanical behavior of compatibilized PP/PS blends.[32,49] This is particularly important because PP may exhibit wide crystalline variances, which result in changes of mechanical properties.
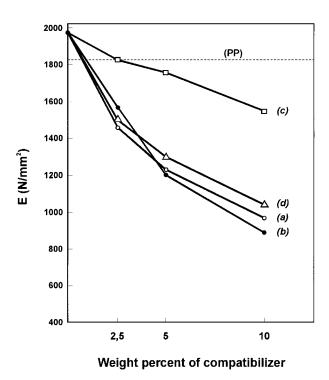

Figure 21 Young's modulus (E) of PP/PS 70/30 blends compatibilized with different types of SRBCs as a function of compatibilizer content: (a) SBS, (b) SEP, (c) SEBS-1, and (d) SEBS-2.

CONCLUSIONS

The results presented in this study show that different SRBCs can act as compatibilizers in immiscible PP/PS 70/30 blend. The SBS, SEP, high-molecular weight SEBS (SEBS-1), and low-molecular weight SEBS (SEBS-2) develop an interfacial layer around dispersed PS particles. Nevertheless, when comparing the phase morphology of blends compatibilized with different types of SR-BCs, several differences were observed. The SBS, SEP, and SEBS-2 connect particles of pure PS into complex dispersed aggregates, whereas a smaller portion of these SRBCs locates at the interface between PP matrix and dispersed phases. The SEBS-1 does not show tendencies of forming such aggregates. Bimodal particle distributions were observed for blends compatibilized with SEP and SEBS-2 block copolymers. Average dispersed PS particle size decreases significantly with the addition of small amounts (2.5 wt %) of SRBC compatibilizers followed by a leveling off as the compatibilizer content is increased. Approximately 5 wt % of SBS or SEBS-2 is sufficient to produce a maximum reduction of the dispersed PS-phase size. It was found that the chemical structure of the SRBCs rubber block and the molecular weight of block copolymer play an important role in the compatibilizing effectiveness in studied PP/PS blends. Diblock copolymer SEP proved to be the most effective compatibilizer among SRBCs used considering the reduction of the dispersed particles size. The SBS and SEBS-2 triblock copolymers also are distinguished as relatively efficient polymeric intarfacial agents. Determination of interaction energy densities between PP and rubber blocks of different SRBCs indicates that compatibility between PP and E/P block of SEP should be the highest whereas PB block of SBS is the least compatible with PP. This is in accordance with morphological observations considering the reduction of the dispersed particle sizes caused by the addition of SEP, SBS, and SEBS-2.

Interfacial activity of SEBS-1 and SEBS-2 differs significantly, indicating that besides the chemical structure of rubber block, molecular weight of block copolymer is an important influential compatibilization factor. The SEBS-2 appears to be a more efficient compatibilizer than high-molecular weight SEBS-1. It is believed that SEBS-2 is more effective than SEBS-1 because its blocks can penetrate more easily into corresponding homopolymer phases and provide strong entanglements whereas SEBS-1 mainly adsorbs onto the phases because of conformational restraints.

As a result of interfacial activities of SRBC, the notched impact strength and elongation at yield of compatibilized PP/PS blends are improved in comparison with the brittle binary PP/PS 70/30 blend. The degree of improvement largely depends on the characteristics of the block copolymer selected and its content. The most evident improvement of mechanical properties is the sevenfold increase of the notched impact strength by the addition of 10 wt % of SEP.

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