Compatibilization Efficiency of Styrene-Butadiene Block Copolymers as a Function of Their Block Number

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ABSTRACT: Effect of block number in linear styrene-butadiene (SB) block copolymers (BCs) on their compatibilization efficiency in blending polystyrene (PS) with polybutadiene (PB) was studied. Di-, tri-, or pentablocks of SB copolymers as well as their combinations were blended with the mentioned homopolymers; supramolecular structure determined by small angle X-ray scattering method (SAXS), morphology using scanning electron microscopy (SEM) combined with image analysis (IA), and stress transfer characteristics of the blends were chosen as criteria of compatibilization efficiency of the copolymers used. It was proved that the addition of SB BCs led to remarkably finer phase structure and substantially higher toughness of PS/PB blends. Triblock copolymer showed to be the compatibilizer with higher efficiency than diblock, pentablock, and the di/triblock copolymer mixture. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 466–472, 2008

Key words: blends; block copolymers; compatibility; morphology; mechanical properties

INTRODUCTION

Polymer blends represent very important field in processing of new materials, which would have better properties in comparison the neat polymers. They are significant also from ecological and economical view. Thus, for example, municipal commingled plastic waste composed from various immiscible polymers can be recycled by mixing in molten state, and so it can be transformed to the material, which would satisfy the relevant application.

High-molecular weight polymers show low entropy of mixing.[1] Therefore, blends of two or more polymers are mostly immiscible systems, whose properties are not only a function of the blend composition but also depend crucially on the degree of dispersion, phase particle size, and phase interaction between the components of the blend. Control of morphology is therefore the control of polymer blend properties.[2] Many polymer pairs are not only immiscible but also incompatible. It means that they show high interfacial tension that leads to rough phase structure, poor adhesion at the interface, and therefore poor mechanical properties. To improve their compatibility and with that their end-use properties we apply the procedures of compatibilization. Two procedures are usually utilized in compatibilization: (1) use of functionalized polymers or reactive compatibilizers to form chemical bonds between the blend components and (2) addition of a block copolymer (BC) or a graft copolymer, the block of which have the same or similar chemical compositions as the blended homopolymers.[3] The addition of compatibilizers such as BCs having their blocks compatible with the pertinent polymers can improve mechanical properties of the blends of immiscible polymers. These copolymers are localized at the polymer interface, reduce the interfacial tension and so provide a finer morphology of the blend. The copolymers, anchored through their blocks in polymers, suppress their separation and improve interface adhesion. Ability of the copolymer to occupy an interface and strength of the formed crossings depend on the structure of the copolymers.[4,5] The total molar mass of the copolymer, the molar mass of particular copolymer blocks, the number of blocks and interaction parameters (χ) between the copolymer blocks and compatibilized polymer chains have generally been accepted as the main parameters affecting the morphology and, consequently, the end-use properties of the blend. It has generally been believed that the proper molar mass of the copolymer blocks should be close to that of the particular homopolymer chain.[6] The results of studies of

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compatibilization of polystyrene/polyolefin blends, where the block lengths of the copolymers are mostly substantially shorter than the lengths of compatibilized chains, appeared so far in literature, are contradictory.[6,7] Still more contradictory are results on the effect of the block number of these copolymers. In some works, diblock copolymers were more efficient than triblock copolymers,[7–9] while in other works the opposite results were obtained.[10–12] High effectiveness was observed also with multiblock (tetrablock, pentablock, or heptablock) copolymers[3,13,14] comparing to diblocks or triblocks and it was supported by some theoretical works.[15,16] Anyway, no theory predicting satisfactorily dependence of compatibilization efficiency of a BC on its molecular structure has been formulated so far.

Set of our articles[12,14,17–21] have been devoted to the study of the effect of various parameters of molecular structure of styrene-butadiene (SB) BCs on their compatibilization efficiency in polystyrene/polyethylene and polystyrene/polypropylene blends. In these systems, styrene and butadiene blocks were shorter than the length of polyolefin and polystyrene (PS) chains. The results of these studies can be summarized as follows: No unambiguous dependence of the compatibilization efficiency of SB copolymers on their individual structural parameters has been found. This is due to many interfering factors affecting the mechanical and/or morphological blend characteristics, which have been chosen as efficiency criteria. Moreover, it was found that the compatibilization efficiency of SB copolymers depends on mixing[17] and processing[18,22] conditions and on the volume ratio of the compatibilized blend components.[19,22]

Substantially less attention has been paid to the study of compatibilization efficiency of SB copolymers in polystyrene/polybutadiene (PS/PB) blends, where χ parameters between PS and styrene blocks and between PB and butadiene blocks are the same (symmetrical system) in contrast to the relating χ parameters in PS/PE and PS/PP blends (asymmetrical system). Horák et al.[6] found that PS/PB blends compatibilized with BCs containing long styrene block showed better phase structure and improved mechanical properties, comparing to BCs with short styrene blocks. Such a conclusion was applied only on symmetrical systems and the comparable molar masses of the both blocks. As far as the effect of the block number is referred, the most efficient BC was styrene-butadiene-styrene triblock (S-B-S). Mathur and Nauman[23,24] investigated the effectiveness of various PS-PB diblock copolymers in improving the impact strength of PS/PB blends. Low-molecular-weight diblocks provided insufficient adhesion because of lack of entanglements, and high-molecular weight diblocks provided insufficient interfacial concentration because of stearic crowding. The block must be long enough to entangle, but not so long as to lower the areal chain density because of stearic effects.[24] They conclude that the medium-molecular-weight asymmetric tapered diblock, which entangle in both homopolymer phases was the most effective in improving impact strength of the blend. Cavanaugh et al.[25] concluded that for PS/PB system the most effective in improving impact strength was long asymmetric diblock, while multiblock copolymer was successful as an interfacial agent. Joseph et al.[26] evaluated the compatibilising action of S-B random copolymer and S-B-S triblock copolymers in PS/PB blends. The addition of triblock copolymer decreased the interfacial tension and coalescence was suppressed. The result was reduced domain size of dispersed phase and static mechanical properties were increased, while the random copolymer did not give improvement in PS/PB blends, since random copolymer did not localize at the blend interface.

In effort to contribute to elucidation of a role of the block number, an attempt has been made to eliminate, as far as possible, interfering factors confusing evaluation of the compatibilization efficiency of SB BC. Therefore, we determined morphological characteristics and selected mechanical properties of model system PS/PB/SB, where the blocks of the compatibilizer are chemically identical with pertinent homopolymer chains and all blocks have the same length. The set of BCs SB, SBS, and SBSBS was prepared by original procedure of anionic polymerization (Table I), which made possible to achieve high purity of product. Thus only two parameters—the number of blocks and total molecular weight—remained as variables. Molar mass of PS and PB blocks in this set of copolymers were high enough for the formation of entanglements. Moreover, like few of the other studies,[15,16] we tried to verify possible replacement of pentablock copolymer with combination of di- and triblock copolymers.

EXPERIMENTAL

Materials

Two homopolymers were used in the study: polystyrene (PS) Krasten 171, produced by Kaučuk Kralupy, Czech Republic, molecular weight M_w = 332.4 kg/mol, M_n = 61.3 kg/mol, with a melt-flow index of 1.4 g/10 min (5 kg/200°C) and polybutadiene (PB) Seetec BR 1209 H, producer Hyundai Petrochemical, Republic of Korea, molecular weight M_w = 268.4 kg/mol, M_n = 105.2 kg/mol.

Linear styrene-butadiene (SB) BCs with molecular weight M_w of styrene blocks 40 kg/mol and molecular weight M_w of butadiene blocks 60 kg/mol were

TABLE I
Characteristics of Block Copolymers (BCs)

Type	M_{theor} (kg/mol)	M_p (kg/mol)	M_n (kg/mol)	M_w (kg/mol)	PS_{theor} (wt %)	PS_{GPC} (wt %)	PS_{grav} (wt %)
S-B	100	108	99	105	40	39.9	41.2
S-B-S	140	134	117	129	57.1	57.7	58.9
S-B-S-B-S	240	249	206	235	50	50.2	49.4

M_{theor}, target molar mass; M_p, molar mass value for the most probable point on the SEC chromatograph; M_n, number average molar mass; M_w, weight average molar mass; PS_{theor}, target molar mass concentration; PS_{GPC}, concentration of PS determined by GPC; PS_{grav}, concentration of PS determined by gravimetry after cleavage.

prepared by anionic polymerization[6] and were used as compatibilizers. Their characteristics are in Table I. The content of all BCs in PS/PB blends was 5 wt %.

The symbols for polymer blends were as follows: SB4: PS/PB/S-B; SB5: PS/PB/S-B-S; SB45: PS/PB/(S-B+S-B-S); SB6: PS/PB/S-B-S-B-S; SB7: PS/PB.

Sample preparation

Blends were prepared by double extrusion of the components, in twin-screw extruder Berstorff ZE-25 D, L/D 40/1, with the following temperatures in zone: extrusion zones were set to 180°C and temperature of the die was 200°C. The frequency of rotation was 100 rpm. Samples were obtained by Battenfeld injection molding machine at the temperature of 220°C. The temperature of cavity was 45°C and time of the injecting, including cooling, was 60 s.

In all blends ratio of PS/PB was 4 : 1. Irganox 1076 (0.3 wt %) was used to stabilize the system.

Scanning electron microscopy and image analysis

Scanning electron microscope (SEM) Vega (Tescan, Czech Republic) was used to observe morphology of polymer blends. Samples (dog bones) were cut in the middle and perpendicular to the injection direction. The cut surfaces, thus obtained were smoothed with a glass knife (angle 90°) in liquid nitrogen. We use to call that technique as ''cryogenic scratching.'' Solvable fraction (PB phase) was removed from the sample surfaces in heptane at room temperature (5 min). Surfaces obtained that way were mounted on a substrate, covered with 4 nm thick layer of platinum, and then micrographed. Image analysis (IA) was performed with software Lucia (Laboratory Imaging, Czech Republic). Equivalent particle diameter (d_{eq}) was calculated from the particle cross section area S as $d_{\text{eq}} = (4\ S/\pi)^{1/2}$.

Small angle X-ray scattering method

Small angle X-ray scattering (SAXS) measurements were preformed with a reconstructed Kratky camera with a 60 μm entrance slit and a 42 cm flight path. Ni filtered Cu Kα radiation (wavelength $\lambda = 1.54$ Å) was used; it was recorded with a position-sensitive detector (Joint Institute for Nuclear Research, Dubna, Russia) for which the spatial resolution was ~ 0.1 mm. The intensities were taken in the range of the scattering vector, $q = (4\pi/\lambda) \sin \Theta$, from 0.006 to 0.2 Å^{-1} (where 2 Θ is the scattering angle). The measured intensities have been corrected for background, the constant sample thickness, primary beam flux, and camera geometry. Plates of 2 mm thickness, obtained by compression molding, were used for this measurement.

Mechanical properties

The tensile impact strength was measured with a Zwick tester equipped with a special fixture for the test specimen according to DIN Standard 53448. The maximum pendulum energy was 2 J. The values obtained are presented as arithmetical means of measurements of 10 specimens. Dimensions of beams that were used for testing were 4 mm × 10 mm × 80 mm.

For Charpy impact test we used bar specimens, dimension of 80 mm × 10 mm× 4 mm, which were notched in their narrow side using Notchvis Ceast Comp. machine to the depth of 2 mm. Specimens were tested at a speed of 2.9 ms^{-1} on a PSW 4 instrumented impact tester with 4 J work capacity with support span of 40 mm. The tests were carried out at room temperature. For each material sample, 10 specimens were tested.

RESULTS AND DISCUSSION

The effect of BCs as compatibilizers in PS/PB blends was determined by SEM micrographs and IA. SEM microphotograph of PS/PB blend without compatibilizer [Fig. 1(a)] shows voids (remaining from the dissolved particles), which are corresponding to the PB phase in PS matrix. Thus, we can state that presence of all the BCs leads to substantially finer particles of the dispersed PB phase [Fig. 1(b–e)]. The

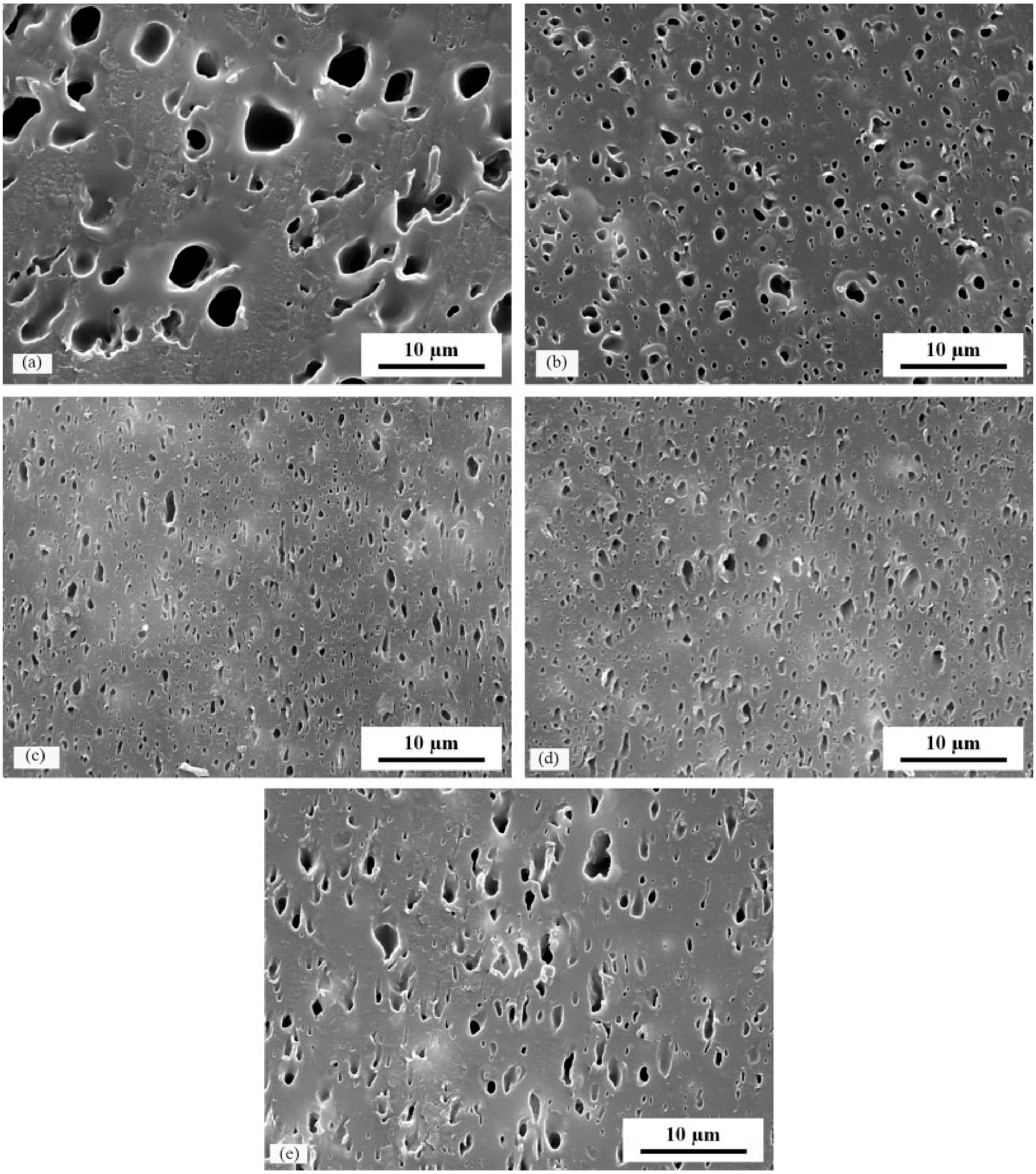

Figure 1 SEM micrographs of: (a) PS/PB; (b) PS/PB/S-B; (c) PS/PB/S-B-S; (d) PS/PB/(S-B+S-B-S); and (e) PS/PB/S-B-S-B-S.

influence of diblock, triblock, and their combination is similar. Larger PB particles in the blend compatibilized with the pentablock signalize lower emulgation effect of this copolymer in comparison with the copolymers mentioned earlier. This is apparently the results of less coverage of interface due to steric limits with location of these large pentablock. Elongation of some particles occurred because of stress during injection molding of the samples.

The size of dispersed PB particles as well as their particle size distribution is obtained by IA (Fig. 2 and Table II). Analysis revealed that noncompatibilized

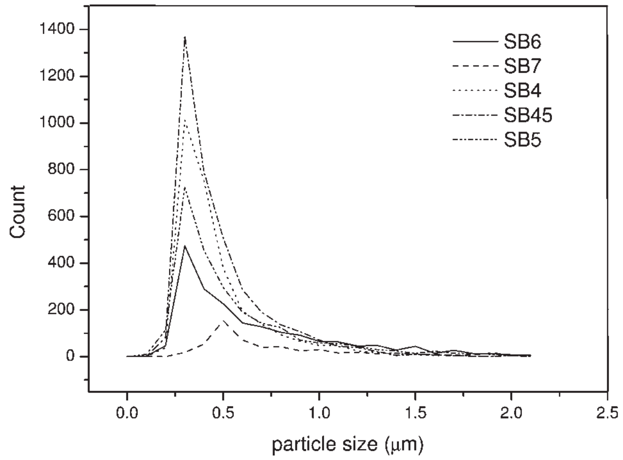

Figure 2 Image analyses (IA) of PS/PB blends.

blend of PS/PB has the largest size of PB phase (0.9 μm) in PS matrix, while the compatibilized blends of PS/PB/BC show a reduction in particle size of PB phase. The mean particle size for PS/PB/S-B and PS/PB/(S-B+S-B-S) blends is the same (0.4 μm), while for the PS/PB/S-B-S is 0.5 μm. The mean particle size of PB phase in PS/PB/S-B-S-B-S blend is 0.6 μm, which indicates that the influence of S-B-S-B-S as compatibilizer on the reduction of the size of the dispersed PB particles is less expressed. Reason for the weaker influence of pentablock on particle size is less coverage of interface with this copolymer, and follows from thermodynamics. For high-molecular weight pentablock copolymer is apparently more difficult to localize at the interface comparing with di- or triblock copolymer.

Particle size distribution for PS/PB blend is broader, while the compatibilized blends have a narrow distribution, which indicates suppressed coalescence. All compatibilized blends have a similar particle size distribution of PB phase with the maximum at 0.3 μm, while the maximum of particle size distribution of PS/PB blend is at 0.5 μm.

The efficiency of SB compatibilizers was also studied by SAXS measurements. The regular two-phase structure of BCs can be detected by maximum at scattering curve in the region of scattering vector, *q*. In previous published articles[3,6,20,21] were obtained the SAXS curves of the neat SB BCs. The SAXS curves of all investigated blends show heterogeneous systems and do not have any maxima (Fig. 3), corresponding to the formation of ordered BCs.

TABLE II
The Mean Particle Size of PB Phase in PS/PB Blends

Sample	Mean particle size (μm)
SB4	0.43
SB45	0.43
SB5	0.51
SB6	0.62
SB7	0.93

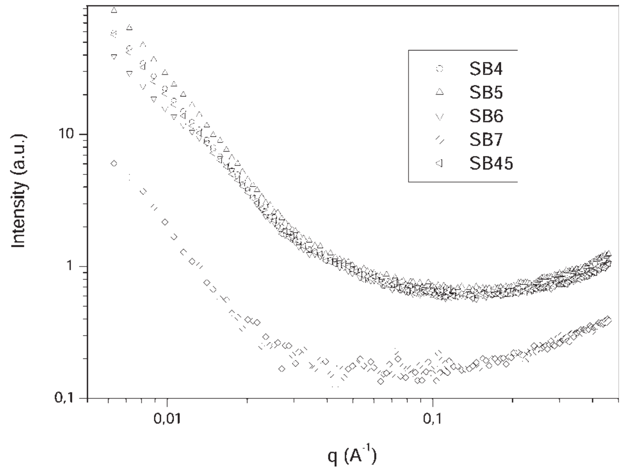

Figure 3 SAXS curves of PS/PB (4/1) blends without and with the addition of 5 wt % SB BC.

The disappearance of these maxima points out either the dissolution of the BC separate phase to a molecular level or at least partial disorder of its separate phase because of some kind of interactions of BC with one of the blend component.[3] Since there is no maxima in SAXS curves, BCs do not form the ordered separate phase in blends of PS/PB.[3] This means that the BCs participated in the formation of a PS/PB interfacial layer and should be good compatibilizers.[6]

The effect of SB BCs as compatibilizer in PS/PB blend and the effect of different number of their blocks on the mechanical properties were verified by tensile impact test (Fig. 4).

PS/PB 80/20 blend showed the lowest value of tensile impact test, 47.01 kJ/m^2. The impact strength of PS/PB blend increased with the addition of compatibilizers, which is in accordance with its effect on

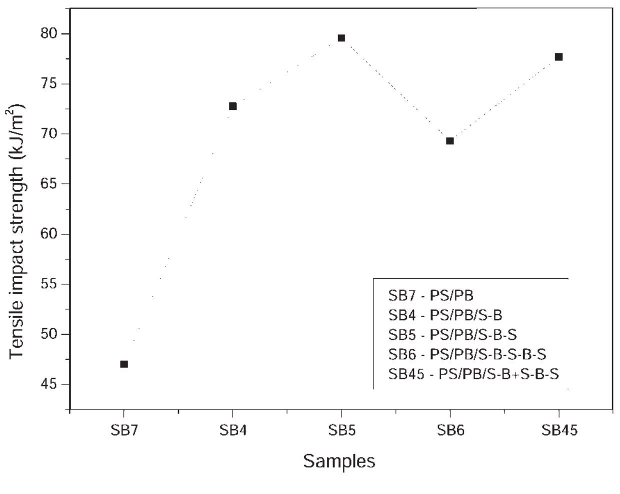

Figure 4 Tensile impact strength of PS/PB blends.

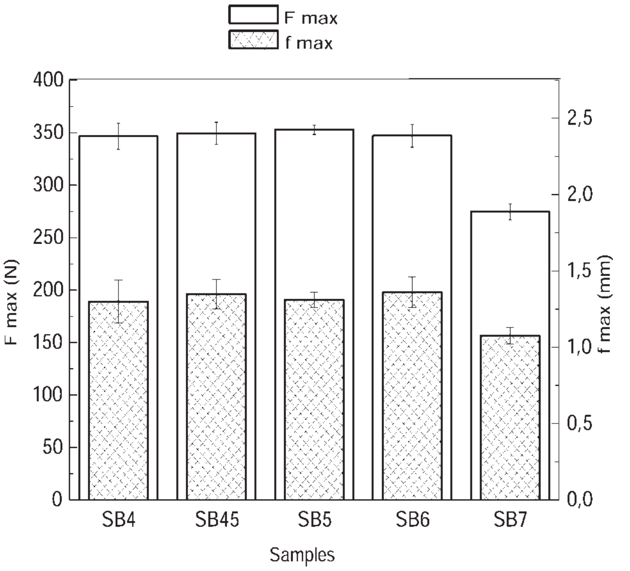

Figure 5 Values of maximum load ($F_{\max}$) and maximum deflection ($f_{\max}$) of PS/PB blends.

fineness of phase structure as well as on improved interfacial adhesion. The highest impact strength showed the blend containing triblock copolymer; the lowest value had the blend compatibilized with pentablock. It can be tentatively explained by results obtained from SEM micrographs and IA, which indicates that the blend with S-B-S-B-S has the highest mean particle size. Although, PS/PB/SBS blend has higher mean particle size of the dispersed PB particles than PS/PB/SB blend, its tensile impact strength is higher. This surprising results can be explain as follows: Besides the contradictory results from various studies of the effects of the molecular parameters of copolymers, some data in the literature show that the results comparing the compatibilization efficiency of the copolymers in a system are dependent on the property that is chosen for comparison because the results for the fineness of the phase structure and for the mechanical properties may be significantly different. Fine dispersions of the minority phase need not necessarily bring about an improvement in mechanical properties.[12] Interface adhesion depends on the homopolymer areal chain density at the interface and on the molar mass of the block anchored to the homopolymer and its relation to the molar mass necessary for entanglement formation. The diblock copolymers make it possible to achieve a higher chain density at the interface but only with simple links. Diblock provided insufficient adhesion because of lack of entanglement, while adhesion in SB5 was higher as consequence of better entanglement formation, and result was higher tensile impact strength of SB5.

The particle size affects the rate of crack initiation and propagation energy in compatibilized blends. The toughness can be influenced by distribution of the compatibilizer between interface and bulk phases in form of micelles or metaphases and also by degree of crosslinking of PB particles. One of the reasons of less efficiency of the pentablock is the higher number of blocks that restricts the copolymer chain density at the interface because of steric effects.[24]

The second indicator of SB BCs efficiency was impact strength obtained by Charpy impact test. Typical load-deflection curves of PS/PB blends are illustrated in Figures 5 and 6.

By recording the load-deflection curves, we determined the stages of the fracture process. In principle, the total fracture energy (A_T) can be split into the initiation (A_G) and propagation (A_P) fracture energies as energy portions measured up to maximum load ($F_{\max}$) and from $F_{\max}$ to full break of the specimen.[27] The overall fracture process may be divided into crack initiation and crack propagation stages. During crack initiation stress concentrates at the notch tip, but it is too low to enable crack propagation.[28] Charpy impact test of the noncompatibilized PS/PB blend exhibits brittle fracture ending in a sharp drop after reaching the maximum load (Fig. 6).

PS/PB 80/20 blend did not show propagation fracture energy, as a result of low adhesion between phases, which was confirmed by SEM and IA. The compatibilization brings about a dramatic increase in total fracture energy. The total fracture energy obtained from the area of load-deflection curve showed that their value is higher with BC addition (Fig. 6); thereby their initiation and propagation fracture energies were higher.

The compatibilizer contributes a strong interfacial layer to be formed that alters the local stress distribution and thus the deformation and fracture mechanism are also changed.[29] Corresponding load-deflection curves obtained by Charpy impact test

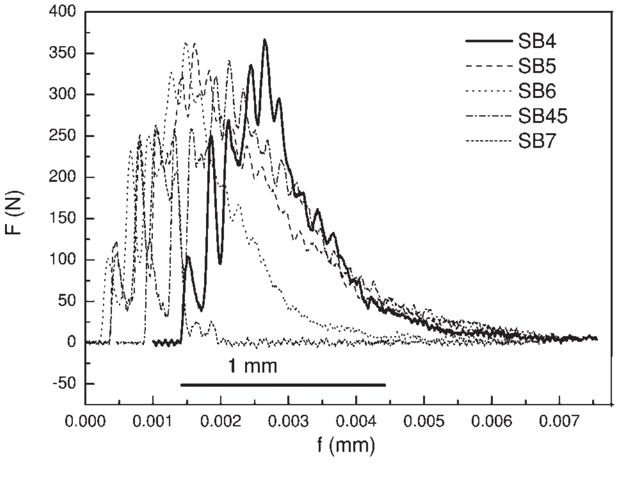

Figure 6 Loaf (F)-deflection (f) curves of PS/PB blends.

TABLE III
Ductility Index of PS/PB Blends

Sample	A_P (N/mm)	A_T (N/mm)	A_P/A_T
SB4	9.52	17.51	0.54
SB45	13.42	21.05	0.63
SB5	14.38	22.07	0.65
SB6	9.5	16.75	0.57
SB7	–	4.46	–

show that the onset of the crack initiation occurs at substantially higher level of both force ($F_{\max}$) and deflection ($f_{\max}$). The values of $F_{\max}$ and $f_{\max}$ do not depend on the compatibilizer type.

Crack initiation energies are higher in PS/PB/BC blends. The PS/PB blend does not show crack propagation energy. The compatibilized blends indicated non-negligible propagation energy, which enhances the total fracture energy. The crack propagation energy and the total fracture energy increase in the order PS/PB/S-B ≈ PS/PB/S-B-S-B-S < PS/PB/(S-B+S-B-S) < PS/PB/S-B-S.

The competition between initiation and propagation phase could be expressed by the ratio of propagation energy to the total energy, A_P/A_T, ductility index (Table III). The highest ductility index had the PS/PB/S-B-S blend (0.65), and the lowest value had PS/PB/S-B blend.

CONCLUSIONS

1. The particle size quantitative evaluation of statistically significant number of PB particle size made possible by the used technique of SEM and so reliable determination of SB copolymer effect on their size distribution.
2. Incorporation of all the used SB copolymers leads to a significant decrease in the PB particle size as well as in width of their size distribution. This effect grows in sequence: pentablock < triblock < diblock + triblock ≈ diblock copolymer.
3. Impact strength of the PS/PB blends compatibilized by four different copolymers is in all cases higher than that of uncompatibilized one and decreases in order (in block sequence): triblock, diblock + triblock, diblock, pentablock copolymer.
4. The study did not prove that multiblock is the better compatibilizer than diblock copolymer.
5. The combined compatibilizer S-B+S-B-S (1/1) shows the higher effect as the pentablock copolymer.

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