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Compatibilization of high-impact polystyrene/polypropylene blends

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Effects of three different linear styrene–butadiene block copolymers on morphology and selected mechanical properties of high-impact polystyrene/polypropylene blends were investigated. Scanning and transmission electron microscopy and small-angle X-ray scattering were used for the determination of the blend morphology. Impact strength, elongation at break and flexural modulus were measured for further evaluation of the compatibilizer efficiency. A similar effect on the particle dispersion was found for all three copolymers but both the styrene-terminated multiblocks influence formation of interfacial layer and consequently the related mechanical properties in a much more pronounced way than the diblock. Small-angle X-ray scattering was found to be the appropriate technique for the determination of triblock concentration necessary for covering a given interfacial area (critical concentration).

(Keywords: polymer blends; morphology; compatibilization)

INTRODUCTION

Blends of immiscible polymers obtained by a simple melt mixing show generally poorer ultimate properties than their individual constituents. This fact is a result of strong separation tendency of immiscible components leading to a coarse phase structure and low interfacial adhesion[1,2]. On the other hand, immiscibility or limited miscibility of polymers enables, dependence on composition and preparation method, formation of various supermolecular structures. Some types of these heterogeneous structures, if stabilized, can impart excellent properties to the final material, hardly attainable by any other way. It is possible to obtain such a stabilized phase structure by the bond formation (physical or chemical) at the polymer interface. This procedure, usually called compatibilization, generally leads to a finer phase structure and enhanced interfacial adhesion. Two main procedures are applied to this purpose. The first one is incorporation of a further component (compatibilizer) into a multiphase system which enhances the physical bonding of dissimilar polymers. Block or graft copolymers (with the same or similar structure to blend components) are suitable as compatibilizers[3–17]. According to the generally accepted idea[3] these copolymers should ensure a finer dispersion during melt blending by decreasing interfacial tension (emulsification effect), should be preferably located at the interface, should provide stabilization against phase structure coarsening during the processing and should improve adhesion between phases. The second approach utilizes functionalized polymers or reactive compatibilizers which react in the melt and form chemical bonds between constituents[18–22]. An alternative to the second process is represented by the peroxide-initiated functionalization leading to grafting or cross-linking reactions[23,24].

Up to now, the first procedure using a non-reactive compatibilizer has been predominantly applied to the preparation of polyolefin/polystyrene blends. Classic examples of such compatibilizers are styrene–butadiene (S–B) block copolymers. Blends prepared with the aid of these components have been extensively studied in the last two decades and fundamental knowledge on their formation, supermolecular structure and properties has been obtained[1–3,6–17]. However, the studies have been carried out mostly with relatively simple systems, in particular with polyethylene/polystyrene, using styrene–butadiene diblocks and triblocks (or these copolymers with hydrogenated polybutadiene blocks) as compatibilizers. Less information can be found on blends of polystyrene/polypropylene (PS/PP)[25–29]; also, the utilization of copolymers with more than three blocks has been studied rather theoretically[30]. No systematic investigation of a more complex system such as high-impact polystyrene/polypropylene (HIPS/PP), which seems to be interesting from the practical point of view[31], has been performed.

Therefore extensive study was carried out with several types of PS/PP blends containing additional components[32–34]. One topic of this study (the effect of three different S–B block copolymers on morphology

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Table 1 Characterization of styrene–butadiene block copolymers

Type	Trade name	PS content (% wt)	$\bar{M}_n$ total ($\times 10^{-3}$)	$\bar{M}_w$ total ($\times 10^{-3}$)	$\bar{M}_n$ PS ($\times 10^{-3}$)	$\bar{M}_w$ PS ($\times 10^{-3}$)
S–B	Buna BL 6533 (Bayer)	30	180	205	23	38
S–B–S	Cariflex TR 1102 (Shell)	28	88	100	8.8	10.2
S–B–S–B–S	TRP 790[a] (Kaučuk Co)	36	76	84	9.1	10.5

[a] Pilot-plant product of Kaučuk Co., CR[34]

and related mechanical properties of HIPS/PP systems) is the subject of this paper.

EXPERIMENTAL

Polymers

HIPS: High/impact polystyrene Krasten 562E (commercial product of Kaučuk Co., Kralupy, Czech Republic). Molecular weight of polystyrene $\bar{M}_w = 190\,000$, $\bar{M}_n = 93\,000$. 7% polybutadiene (particle size 1–10 μm) is dispersed in the polystyrene matrix.

PP: Polypropylene Mosten 52 492 (commercial product of Chemopetrol, Litvínov, Czech Republic). $\bar{M}_w = 330\,000$, $\bar{M}_n = 51\,000$.

Basic characteristics of compatibilizers are listed in *Table 1.*

Sample preparation

The blends were obtained by melt mixing in a laboratory single-screw Goettfert extruder at 80–100 rev min^{-1}. The temperature in the three sections was 160, 190 and 200°C. The temperature at the die was 200°C. The composition of the blends is summarized in *Table 2.*

Specimens for small-angle X-ray scattering (SAXS) were prepared by compression of polymer pellets in Fontijne table presses at 200°C and a load of 100 kN. After 5 min the specimens were transferred from the hot press and cooled to laboratory temperature in a cold press.

Scanning electron microscopy (SEM) observations of fracture surfaces were carried out on specimens fractured in the Charpy impact test. The Balzers Sputter coater was used to coat the surfaces of the specimens with a thin layer of gold.

Samples for transmission electron microscopy (TEM) were prepared from test specimens using cryo-ultramicrotomy technique with a LKB Ultratome III. Samples were stained with osmium tetroxide after cutting.

Test specimens for the determination of mechanical characteristics were prepared in accordance with the principles of ISO 294, using a Battenfeld injection moulding machine (Type BA 500/200 CD). The temperatures of the plastic material and the mould were 200°C and 60°C respectively, the injection time was 3 s and the total moulding cycle was 1 min. Test specimens were conditioned for 24 h at 23°C and 50% relative humidity.

Possible degradation of polymer components (especially polypropylene) was monitored by determining changes in viscosity and yellowness index of polymers during blending in an extruder, and during moulding when the test specimens were prepared. No observable changes in the mentioned characteristics were found after the first regranulation and up to 5 min of residence time in the injection moulding machine.

Table 2 Blend composition (wt %)

Code	HIPS	PP	Styrene-butadiene Diblock	Triblock	Pentablock
A	80	20	0	0	0
B	76	19	5	0	0
C	76	19	0	5	0
D	76	19	0	0	5
E	72	18	10	0	0
F	68	17	15	0	0
G	64	16	20	0	0
H	79.2	19.8	0	1	0
I	77.6	19.4	0	3	0
J	72	18	0	10	0

Determination of morphology and mechanical properties

SAXS curves were taken on Kratky camera. Cu $K\alpha$ radiation was monochromatized by a Ni filter and pulse-height analyser. Measured intensities were registered with a proportional counter in the range of scattering vector $q = (4\pi/\lambda)\sin\Theta$ from 0.04 to 2.00 nm^{-1} (λ is wavelength and 2Θ is the scattering angle). SEM observations were carried out using a JEOL JSM 6 400. For TEM investigations, a JEOL JEM 200 CX was used at an acceleration voltage of 100 kV or a JEOL JSM 6 400 with a STEM adapter.

Impact strength and notched impact strength were determined by the Charpy method (Czech Standard, CSN 64 0610), elongation at break was measured using the Instron tester (CSN 64 0605) and flexural modulus using the Instron tester (CSN 64 0614). Each value reported is the average from ten tests.

RESULTS AND DISCUSSION

SEM micrographs (*Figure 1*) show substantial differences in the morphology of fracture surfaces of the blend without a compatibilizer (Sample A) or the blend containing the diblock (Sample B) on the one hand and the blends containing the tri- or pentablock (Samples C, D) on the other hand. In the case of A and B the fracture path follows the phase boundary while blends C and D show transformed zones and perspicuous fractures predominantly in the polystyrene (PS) matrix. Furthermore, the phase structure of blend A is coarser in comparison with blend B. This means that the presence of the latter compatibilizer leads to a finer structure but the adhesion between phases does not appear to be improved. Thus, the adhesion between PS and PP phases depends on the type of the incorporated copolymer.

However, the SEM technique does not make it possible to distinguish other morphology features, in particular the character of the presumed interface layer. Therefore, we used the presence of double bonds in the PB block of all the compatibilizers, and after staining the blends with osmium tetroxide we observed ultrathin sections using TEM (*Figure 2*). The refinement of phase structure caused by the compatibilizers, already observed partially by SEM, was verified. The particle size of PP in blends B, C and D is not very different and hence we can state that the compatibilizers used can be regarded as emulsifiers of a similar efficiency. However, the black layer of the stained tri- and pentablocks at the interface (blends C and D) is much better developed than that in blend B containing the diblock. Moreover, in the case of blend B it is possible to see a large number of very small particles dispersed in the matrix which obviously correspond to the dispersed diblock. Thus the results of both SEM and TEM indicate that the tri- and pentablocks are preferentially fixed between two phases and so they improve their mutual adhesion.

We verified the assumed compatibilization effect of these block copolymers by the determination of some mechanical properties. *Figures 3* and *4* demonstrate the effect of compatibilizers on impact strength and elongation at break of HIPS/PP blends. A marked increase in both the mechanical characteristics for the blends containing copolymers terminated by styrene blocks shows that a well-developed interlayer formed by the compatibilizer is essential for good impact and tensile properties of this multiphase polymeric system. Fine dispersions of the minority phase need not necessarily bring about an improvement in mechanical properties, as is evident from *Figures 3* and *4*.

Present experience with blends if immiscible polymers

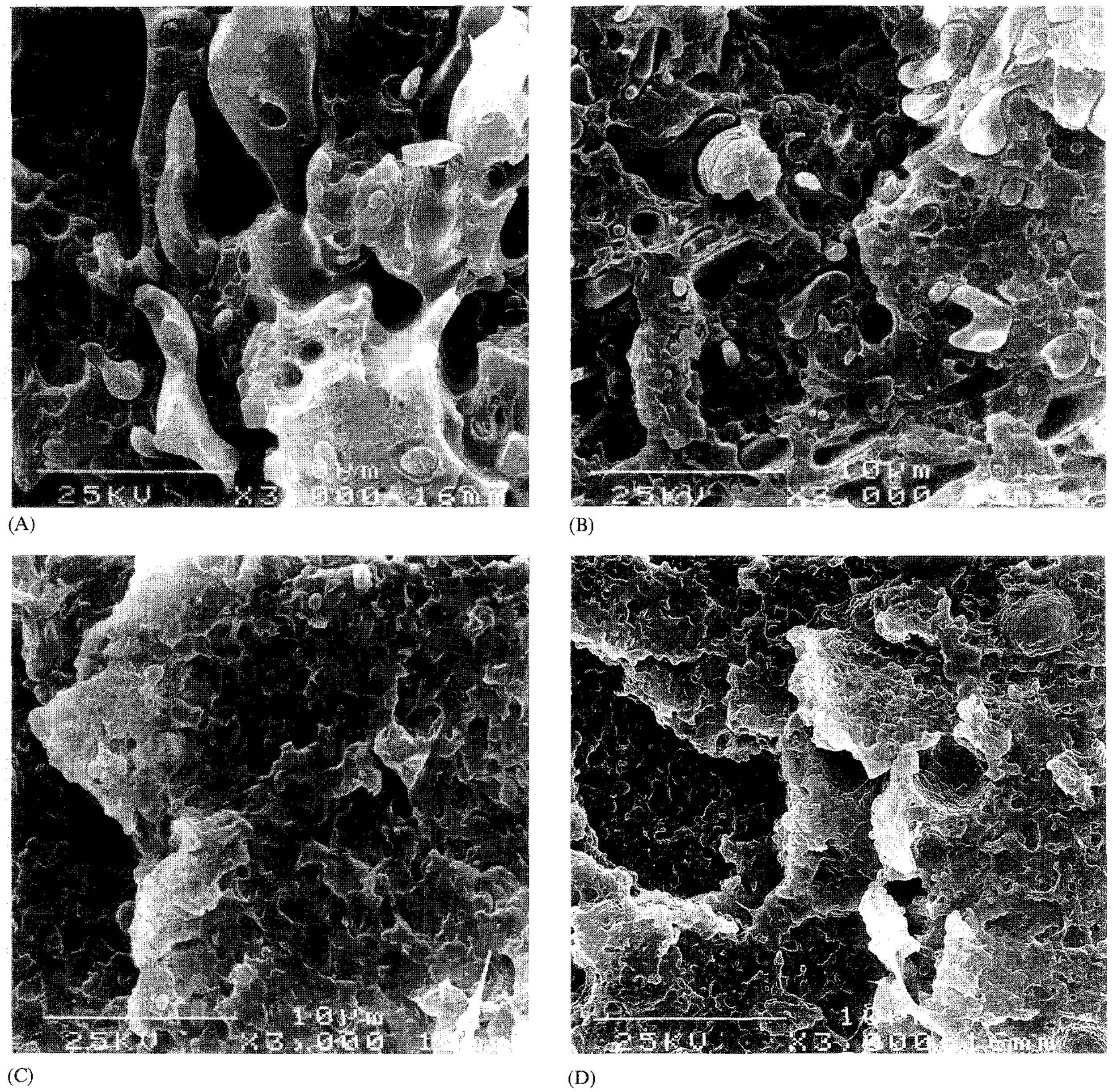
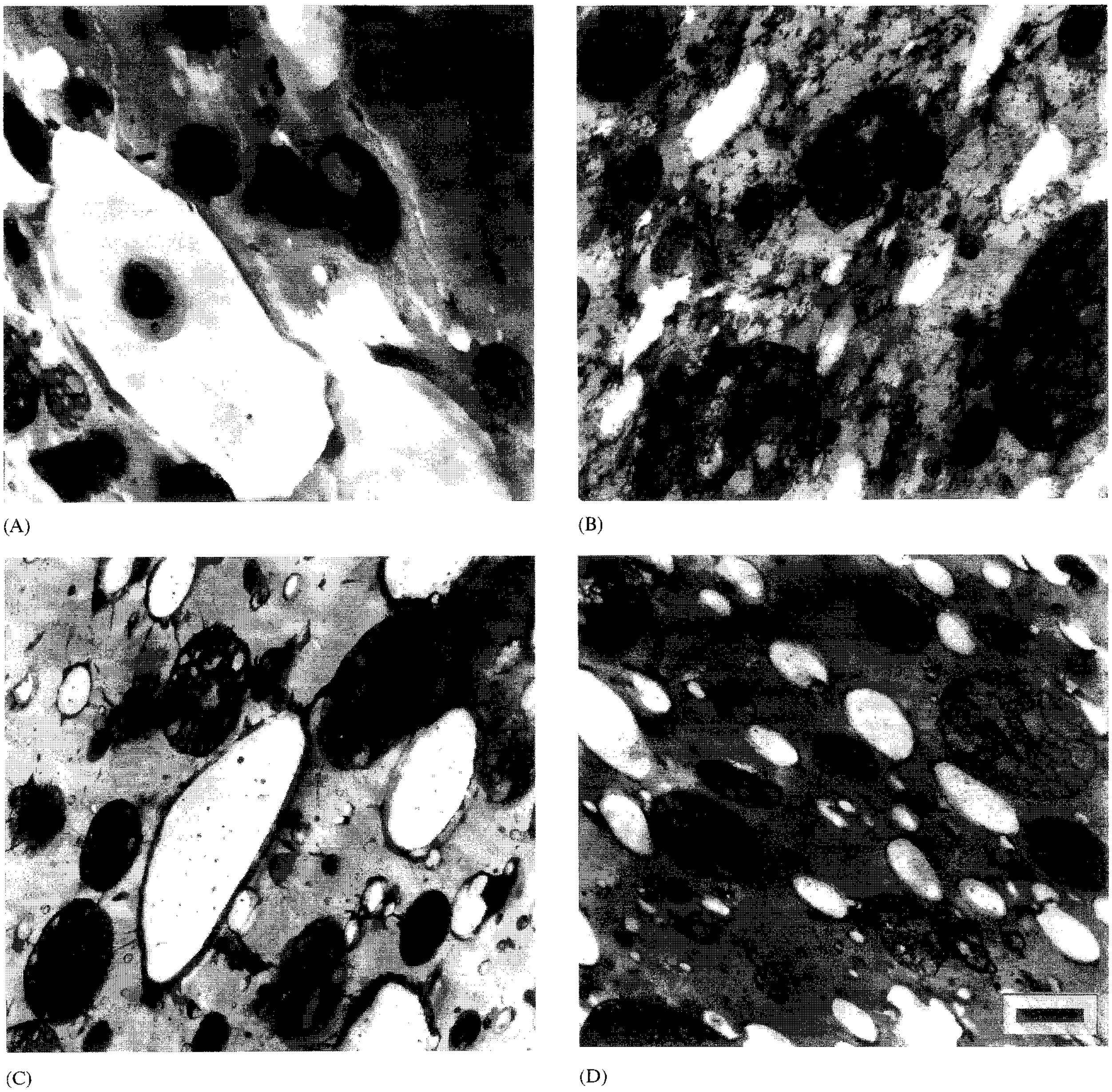

(A) (B) (C) (D)

Figure 1 SEM micrographs of HIPS/PP (4/1) blends: (A) without compatibilizer; (B) with diblock; (C) with triblock; (D) with pentablock such as polyolefins and polystyrenes has shown that S–B–S triblocks are for some polymers better compatibilizers than S–B diblocks[32,34,35] even though other results indicate the opposite effect[10]. The efficiency of compatibilizer depends, of course, on its other structural features such as the molecular weight of individual blocks, the total molecular weight or chemical microstructure (e.g. tapered or pure diblock, ratio of 1,2 and 1,4 structures in the PB block, etc.). Therefore, it is generally believed that a block copolymer acts as an efficient compatibilizer only when molecular weights of the blocks are comparable with the molecular weight of the corresponding homopolymer. However, some results show that even considerably shorter blocks of copolymer provide efficient compatibilization[10]. The fact that this experimental rule is not so stringent is also shown in this contribution. From the further mentioned characteristics, the tappered S–B diblock was proved to be more efficient than a pure diblock[7] whereas the difference in the content of 1,2 and 1,4 structures in the PB sequence did not play an important role in the systems studied[34].

Nevertheless, the number of blocks in the copolymer seems to be extraordinarily important. This problem was theoretically analysed by Nooland[30], who assumed that the diblock and triblock are oriented perpendicularly to the interface plane (dumb-bell-like conformation) and therefore the macromolecule covers a smaller part of the surface than the macromolecule of multiblock copolymer which can lie in the plane of the interface (pancake-like conformation). Further, he assumes that less multiblock copolymer than diblock copolymer would be lost, because of its structure, in bulk phases such as micelles or mesophases. Thus, one can conclude that a smaller amount of multiblock copolymer is required to cover a given interfacial area than in the case of di- or triblock copolymers. Our results show, however, that the effect of the triblock is similar to that of the pentablock, but different from that of the diblock (see *Figures 1–4*).



(A) (B) (C) (D)

Figure 2 TEM micrographs of HIPS/PP (4/1) blends: (A) without compatibilizer; (B) with diblock; (C) with triblock; (D) with pentablock. Scale bar 2.5 μm

Further significant results obtained in polystyrene/polyolefin blends with various concentrations of the pentablock copolymer which support our conclusions have been submitted for publication[32].

Therefore, it seems that, at least for the studied system, it is possible to distinguish two groups of S–B block copolymers according to their compatibilization efficiency:

(i) diblock copolymer;
(ii) copolymers containing three or more blocks terminated with PS.

Except for this fact, Noolandi's idea appears plausible, as will be seen later. Anyway, a question arises of how the concentration of block copolymers with different numbers of blocks can influence the build-up of interface layer and related properties.

A set of samples with increasing concentration of S–B diblock (*Figure 5*) show an increasing number of small particles dispersed in the bulk phase. However, the interface layer does not become better developed (if traceable, the layer is incoherent and thin). Insufficient concentration of the diblock at the interface probably also leads to an anisometric shape of the PP particles in these blends (see *Figure 5*). In the blends containing the S–B–S triblock (*Figure 6*), the interface layer is already perceptible at lower concentrations and the number of black spots (corresponding to small particles of dispersed copolymer) is in accordance with Noolandi's idea, much smaller than in the case of the diblock-containing blend. Thus, it appears that a smaller percentage of triblock gets lost into bulk phase than in the case of the diblock-containing blend[30].

Indirect evidence of a different character of the interface layer, as a result of varying compatibilizer

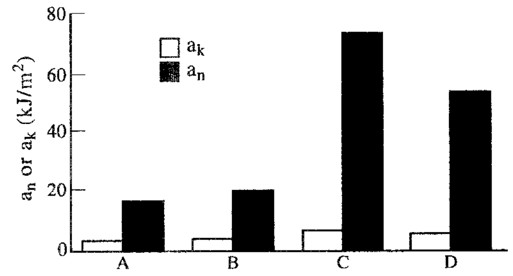


Figure 3 Impact strength a_n and notch impact strength a_k of HIPS/PP (4/1) blends A, B, C, D

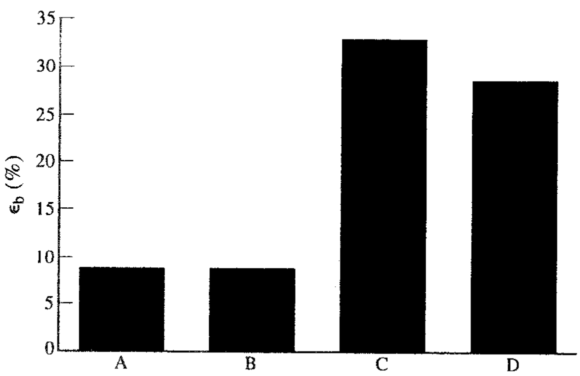


Figure 4 Elongation at break ϵ of four HIPS/PP (4/1) blends A, B, C, D

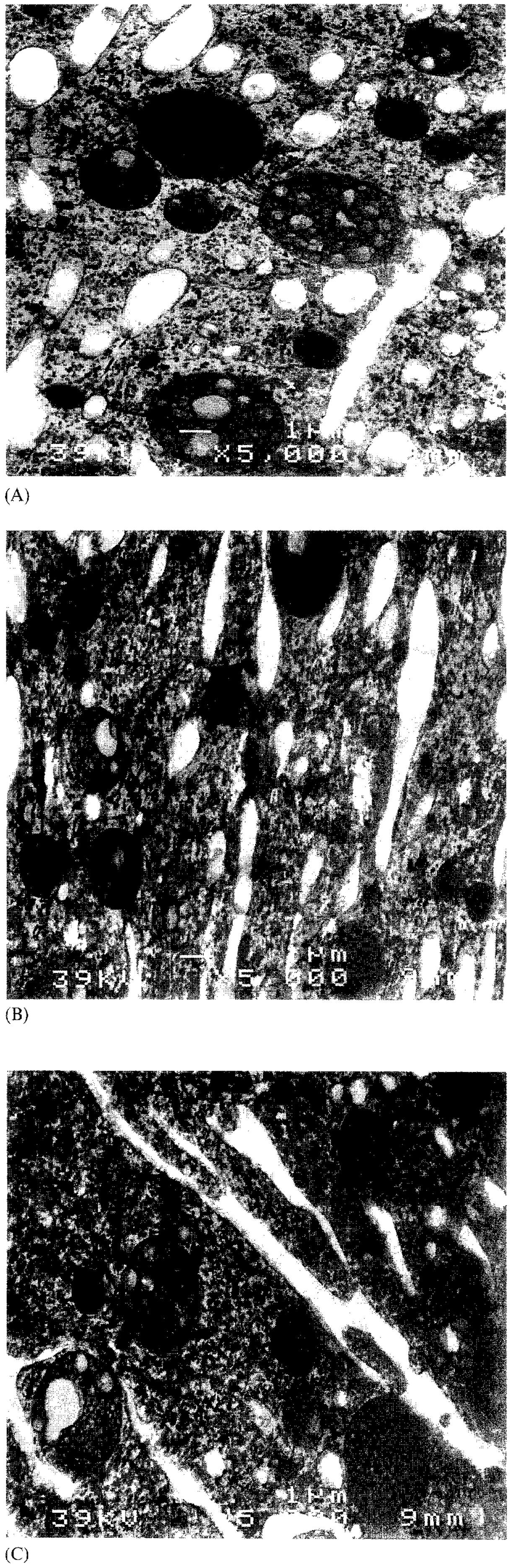
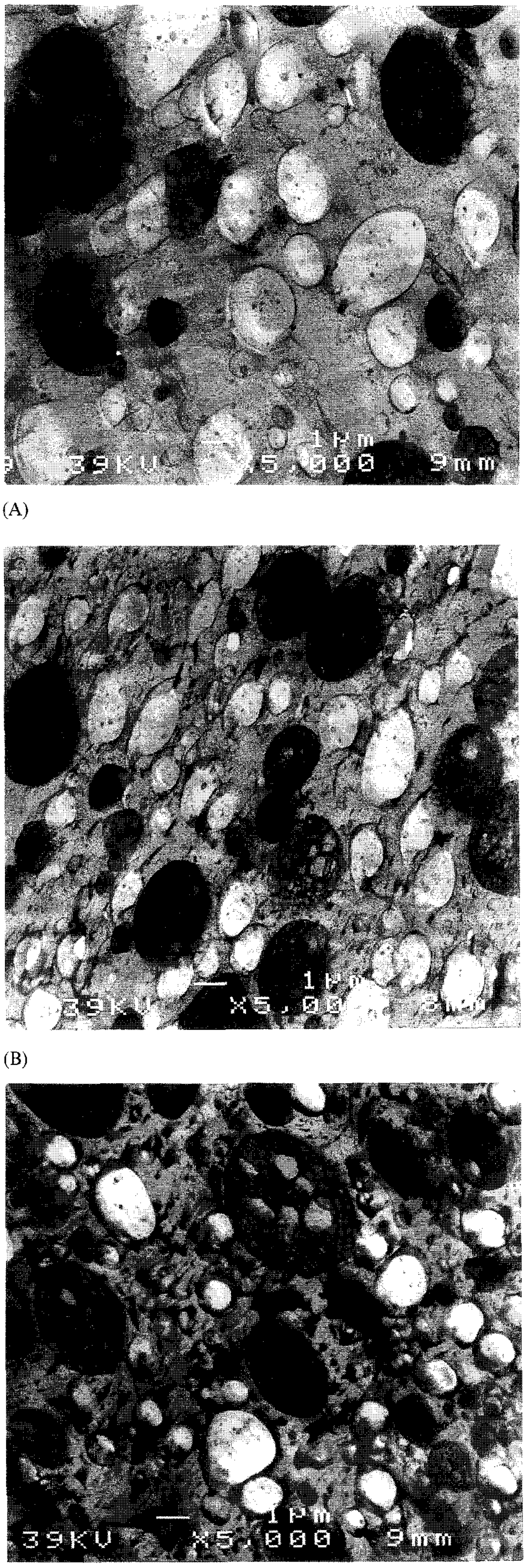


Figure 5 TEM micrographs of HIPS/PP (4/1) blends containing various concentrations of the S–B diblock: (A) 10%; (B) 15%; (C) 20%

structure, was brought by the determination of impact strength and elongation for all the studied blends. Simple comparison of *Figures 7* and *8*, and *Figures 9* and *10* shows that, unlike the S–B diblock, the S–B–S triblock is an efficient compatibilizer for blending HIPS with PP.

The existence of an interface layer demonstrated on the TEM micrograph of the blend compatibilized by the triblock (*Figure 2c*) raises the question of the optimum content of a compatibilizer and, also, why this layer was not observed in the blend compatibilized by the diblock. For elucidation of these questions we tried to use the SAXS method in addition to TEM. From the tail of the SAXS curve we can theoretically determine the thickness of the interface layer[36] which certainly depends on the amount and character of the compatibilizer present on the interface boundary. In such complex systems, as in the case of a semicrystalline polymer and an amorphous polymer with inclusions of another polymer, this



(A)

(B)

(C)

Figure 6 TEM micrographs of HIPS/PP (4/1) blends with various concentrations of the S–B–S triblock: (A) 1%; (B) 3%; (C) 10%

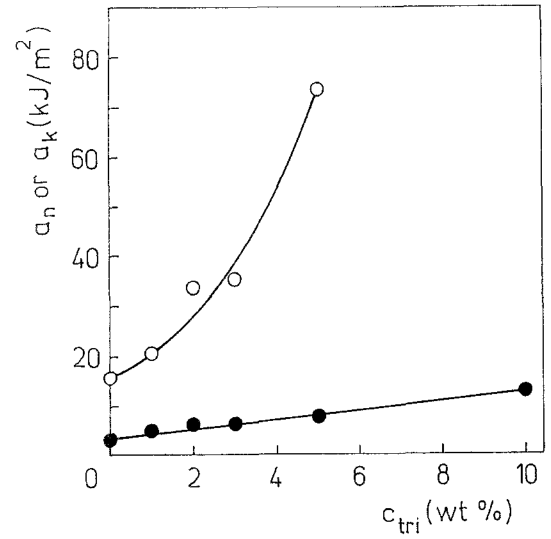


Figure 7 Impact strength a_n (○) and notch impact strength a_k (●) of HIPS/PP (4/1) blends *versus* S–B–S; concentration c_{tri}

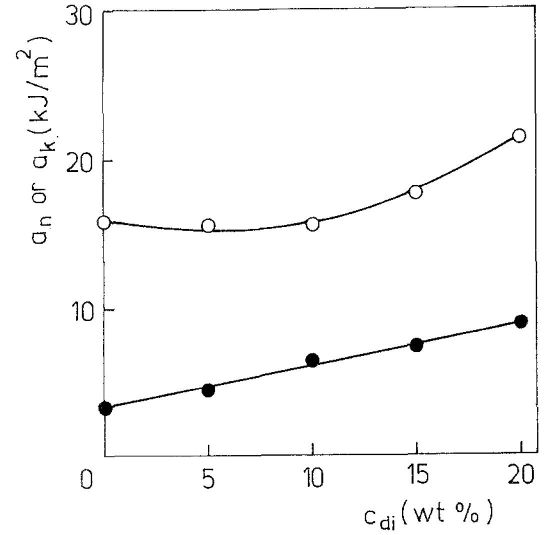


Figure 8 Impact strength a_n (○) and notch impact strength a_k (●) of HIPS/PP (4/1) blends *versus* S–B; concentration c_{di}

procedure cannot be used because the tail of the scattering curve is influenced by many factors.

Fortunately, SAXS curves give us further evidence of structural parameters that can be exploited. The scattering curve of the blend containing 5% triblock exhibits maxima at $q = 0.40$ and $0.20\,\mathrm{nm}^{-1}$ (see *Figure 11*). The maximum at $q = 0.40\,\mathrm{nm}^{-1}$ corresponds to a long period in the semicrystalline PP component of the blend[33]. The other maximum can be attributed to an excess of the triblock phase which no longer participates in interface covering. The maximum was detected at the same scattering vector as the interference maximum on the SAXS curve of S–B–S triblock, corresponding to a regular structure of this copolymer. We suppose that the excessive triblock is present in the blend as a separate phase having the same morphology as the virgin S–B–S copolymer. To determine the concentration of the triblock necessary for covering a given interfacial area (critical compatibilizer concentration) we carried out measurements of the blends with a lower concentration of this copolymer. We found that the SAXS curve of the sample with 3% S–B–S still suggests a maximum at $q = 0.20\,\mathrm{nm}^{-1}$ (*Figure 12*). Assuming that the resulting intensity is given by a linear combination of intensities scattered by individual phases, we calculated this

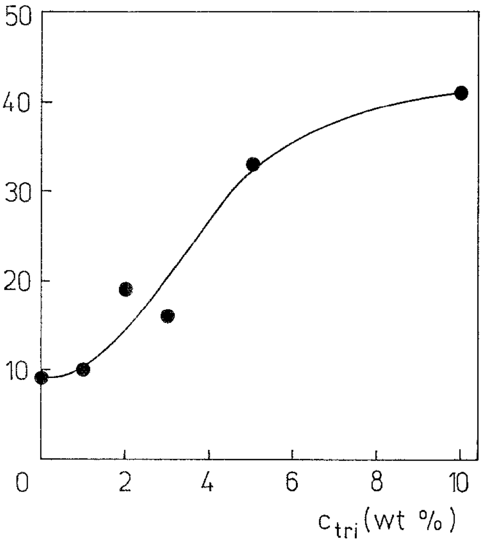


Figure 9 Elongation at break ϵ_b of HIPS/PP (4/1) blends *versus* S–B–S concentration c_{tri}

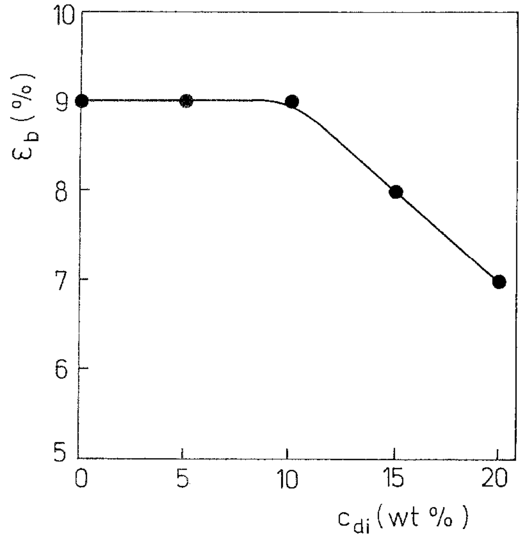


Figure 10 Elongation at break ϵ_b of HIPS/PP (4/1) blends *versus* S–B concentration c_{di}

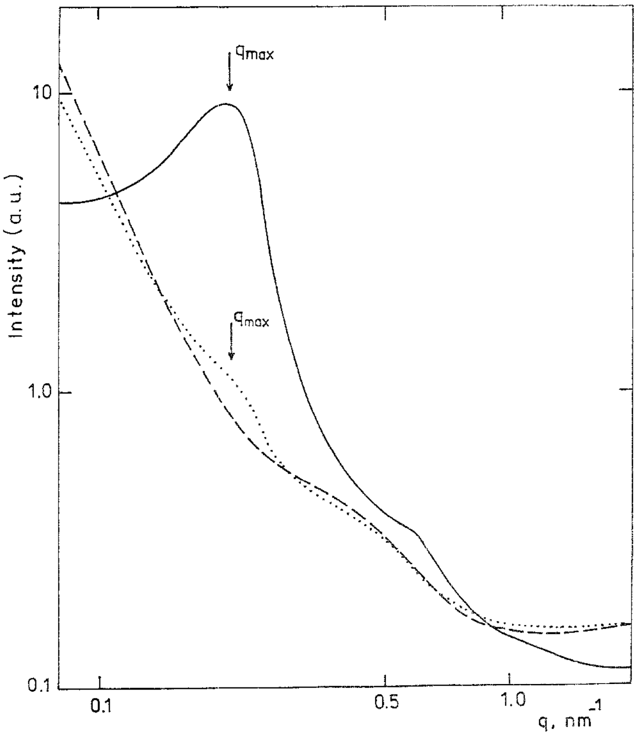


Figure 11 SAXS curves for neat S–B–S copolymer (—), and for HIPS/PP (4/1) blends without compatibilizer (- - -) and with 5% S–B–S (···)

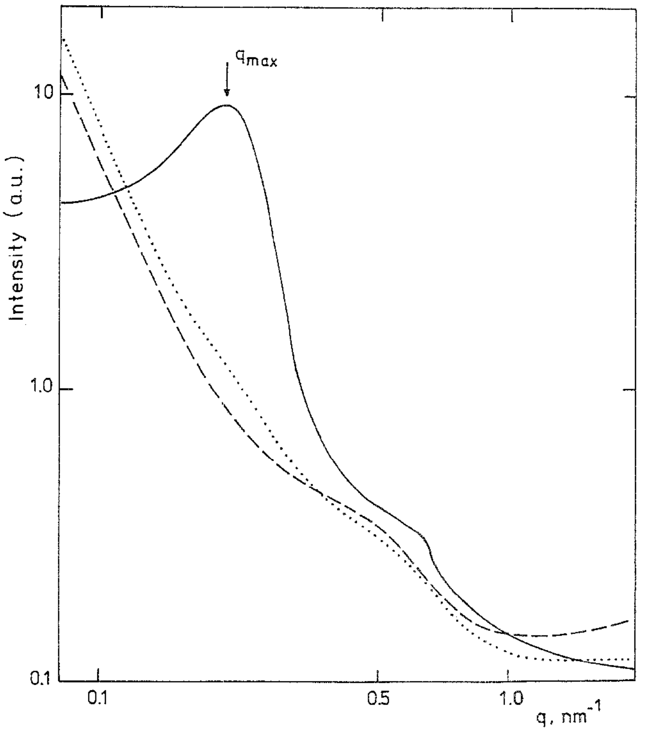


Figure 12 SAXS curves for neat S–B–S copolymer (—) and for HIPS/PP (4/1) blends without compatibilizer (- - -) and with 3% S–B–S (···)

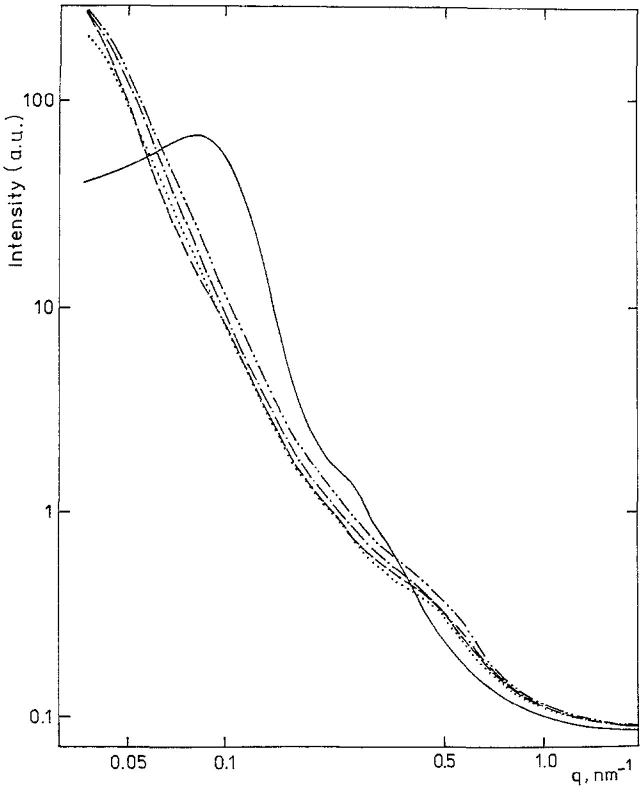


Figure 13 SAXS curves for neat S–B copolymer (—) and for HIPS/PP (4/1) blends without compatibilizer (- - -), with 5% (·-·-·), with 10% (-·-·) and with 15% (· · · ·) S–B

triblock excess to be about 0.5%. This means that approximately 2.5% of S–B–S is localized in the interface layer.

SAXS curves of the blend with the S–B diblock are quite different (*Figure 13*). Even at high concentrations, only one maximum, corresponding to the long period in PP, is observed, even though the SAXS curve of the diblock suggests a regular structure, similarly to the case of the triblock. Thus, the existence of an individual S–B phase in the blend was not proved, but we cannot say whether this copolymer is dispersed in the interface layer or in the bulk of the present polymers. As mentioned above, black spots of dimensions about 50 nm are observed on TEM micrographs, in addition to much larger PB particles dispersed in the PS matrix, even at very low concentrations. The assumption that they can be ascribed to PB micelles, dispersed in the bulk, is not in contradiction to the SAXS measurements.

The determination of the critical compatibilizer concentration, however, raises the question of its practical relevance. From *Figures 7* and *9* it is evident that both measured mechanical characteristics increase even after exceeding critical concentration. The reason for this lies in the fact that the triblock copolymer occupies preferentially the interfacial area forming a certain type of bondage between phases and thus increasing their adhesion. The result of this process is an improvement in the mechanical properties. After exceeding the critical concentration of the compatibilizer the excessive copolymer dispersed in the bulk polymers contributes further to an enhancement of these mechanical characteristics which is in accordance with present knowledge[37]. (It is well known that S–B–S copolymers are used for modification of these mechanical properties.) Thus, without further information one cannot distinguish the contribution of the interlayer and that of the dispersed particles in the bulk phase.

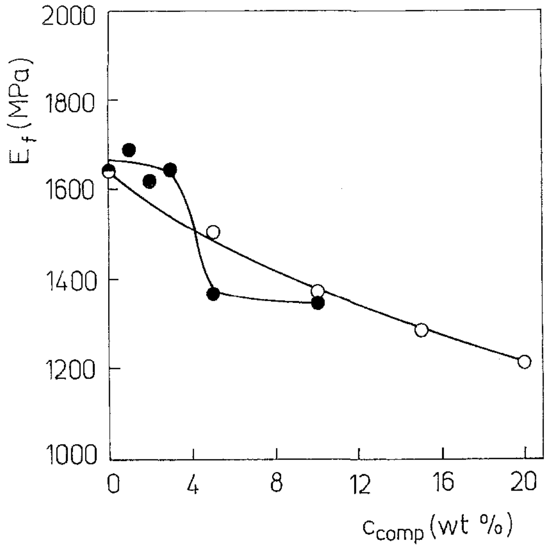


Figure 14 Flexural modulus E_f of HIPS/PP (4/1) blends as function of compatibilizer concentration c_{comp}. (●) S–B–S; (○) S–B

However, there are some properties where an excessive triblock copolymer concentration brings about observable changes in the property–concentration dependence. Thus, e.g. flexural modulus falls after exceeding a limiting compatibilizer concentration (*Figure 14*). A similar phenomenon can be observed in the case of yield strength[32]. Therefore, we can conclude that the knowledge of critical compatibilizer concentration is important for development of multiphase polymer materials with well-balanced properties according to specific requirements.

CONCLUSIONS

This study compares the compatibilization efficiency of three types of styrene–butadiene linear block copolymers in HIPS/PP blends. In addition to currently used S–B and S–B–S copolymers, the styrene-terminated pentablock copolymer was included in the investigation.

Electron microscopy techniques show the differences in the appearance of PS/PP interfacial layers in the blends compatibilized by the diblock and those containing the multiblock compatibilizers. Determination of impact strength, elongation and flexural modulus of all the blends also shows the fundamental differences in the effect of diblock and multiblocks.

It is possible to conclude that the diblock has a negligible compatibilization efficiency while both multiblocks are efficient compatibilizers giving similar results. This difference appears to result from preferential localization of multiblocks at the interface and probably different bonding when compared with the diblock.

The developed SAXS method makes it possible to determine the critical compatibilizer concentration, i.e. the concentration necessary for covering the present interfacial area. This concentration is important for the control of some ultimate properties of multiphase polymer materials.

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