Effect of a Styrene–Butadiene Copolymer on the Phase Structure and Impact Strength of Polyethylene/High-Impact Polystyrene Blends

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ABSTRACT: The effect of a styrene–butadiene block copolymer on the phase structure and impact strength of high-density and low-density polyethylene/high-impact polystyrene blends with various compositions was studied. For both the blends, the type of the phase structure was not affected by addition of a styrene–butadiene compatibilizer. The localization and structure of the compatibilizer in the blends were dependent on their composition. Addition of the compatibilizer improved impact strength of the blends in the whole concentration range. The improvement was the largest for blends with a low amount of the minor phase. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 570–580, 2001

Key words: polyethylene; polystyrene; polymer blends; compatibilization; phase structure; toughness

INTRODUCTION

Blends of polyethylene (PE) with high-impact polystyrene (HIPS) are appropriate for various applications (above all, in the automotive industry) as materials with high oil resistance and advantageous barrier properties. Moreover, PE and HIPS are a substantial part of municipal plastic scrap. Therefore, study of the structure and properties of these blends is of great practical importance. It is well known that polyethylene and high-impact polystyrene are incompatible, and their blends have bad mechanical properties.[1] Compatibilizers must be added to the blends to achieve their good mechanical characteristics, in particular impact strength. Styrene–butadiene or styrene–ethylene–butene block co-

polymers are usually used as compatibilizers.[1–3] Compatibilization of blends of PE with unmodified polystyrene (PS) using these copolymers has been studied very extensively (see refs. 1–3 and citations therein). A substantially smaller attention was paid to the study of PE/HIPS blends.

Fayt and Teyssié[4] studied the effect of a tapered hydrogenated poly(butadiene-*block*-styrene) (HPB-*b*-PS) diblock copolymer on the structure and mechanical properties of HIPS/low-density polyethylene (LDPE) blends. They found that the addition of HPB-*b*-PS led to the finer phase structure and to the fixation of cocontinuous structure in blends containing 20% of LDPE. Compatibilized blends showed higher strength and toughness than the related uncompatibilized ones. They did not study localization of the compatibilizer at the interface and in bulk phases. Brahimi et al.[5] studied the effect of block styrene–butadiene copolymers (including tapered types) on rheological properties of HIPS/high-density polyethylene blends. They found that HIPS/HDPE blends without a compatibilizer shows cocontinuous structure in a broad range of compo-

sitions ((70/30)–(30/70)). However, their article is focused mostly on the study of effect of the type and concentration of a compatibilizer on rheological properties of HDPE/HIPS (80/20) and (20/80) blends.

Generally, it can be noted that the achievement of the finer phase structure and improvement of mechanical properties of blends of HDPE or LDPE with PS or HIPS by addition of styrene–butadiene or styrene–ethylene-butene block or tapered copolymers have been documented very well. Less information is available about distribution of the copolymer between the interface and bulk phases. According to the results obtained in a study of polypropylene/polystyrene blends, it seems that the localization and structure of supermolecular objects of styrene–butadiene copolymers have a fundamental effect on mechanical properties of the blends.[6] We believe that the behavior of the supermolecular objects can explain discrepancies in the literature regarding the effects of the block copolymer architecture on their compatibilization efficiency.

Quite recently, studies of the effect of a compatibilizer on the range width of the blend compositions at which the cocontinuous structure is formed were started. In some articles, substantial narrowing of this range was found for compatibilized blends.[7–10] Change in the type of the phase structure due to addition of a compatibilizer was found also in refs. 3 and 11. In other articles, it was found that an admixture of a compatibilizer had no effect on the phase inversion.[12,13]

The aim of this article is to verify the compatibilization efficiency of the styrene–butadiene block copolymer Europrene SOL T 168 in HIPS/HDPE and HIPS/LDPE blends. A further aim of the article is to study the dependence of distribution and structure of supermolecular objects of a compatibilizer on the blend composition and properties of the components. The last aim of the article is the investigation of the effect of a compatibilizer on the composition region width of the blend with the cocontinuous structure.

EXPERIMENTAL

Materials

Low-Density Polyethylene (LDPE)

Bralen RA 2-19, commercial product of Slovnaft a. s., Bratislava, Slovakia; melt flow index MFI 2 g/10 min, density 918 kg/m^3.

High-Density Polyethylene (HDPE)

Liten BB 29, commercial blow molding grade, product of Chemopetrol a. s., Litvínov, Czech Republic; M_w = 420,000, M_n = 110,000, MFI 0.14 g/10 min at 230°C.

High-Impact Polystyrene (HIPS)

Krasten 562E, commercial product of Kaučuk a. s., Kralupy n/V, Czech Republic; M_w = 190,000, M_n = 85,000, 7% polybutadiene (particle size 1–10 μm) is dispersed in the polystyrene matrix.

Styrene–Butadiene Copolymer (SB)

Europrene SOL T 168, commercial product of EniChem; styrene content 43 wt %, M_w = 81,000, M_n = 71,000, molecular weights of styrene block M_w = 13,000, M_n = 10,000.

Sample Preparation

The blends were prepared by mixing the components in the electrically heated W50EH chamber of a Brabender Plasti-Corder at 30 rpm and at constant temperature 190°C in the melt[14] for 20 min. The chamber was filled with a dry blended mixture of all components. The composition of the blends is expressed in wt %. Samples of blends used for investigation of the tensile impact strength were prepared by compression molding. The material from the chamber was placed in a preheated Fontijne table press. Blends were pressed into the shape of plates at 190°C. After 6 min, the plates were transferred into a second press cooled with water. Small pieces of samples for determination of the phase structure were quenched in cold water immediately after the cessation of mixing.

Tensile Impact Strength

The tensile impact strength, a_ε, was determined at 23°C with the Zwick tester, which was equipped with a special fixture for test specimens according to DIN 53448. The maximum energy of pendulum was 4 J. Test specimens were cut from press-molded plates. Values of a_ε were determined as arithmetic means of measurements on 12 specimens.

Phase Structure

The phase structure of the samples was studied by scanning electron microscopy (SEM) and transmission scanning electron microscopy
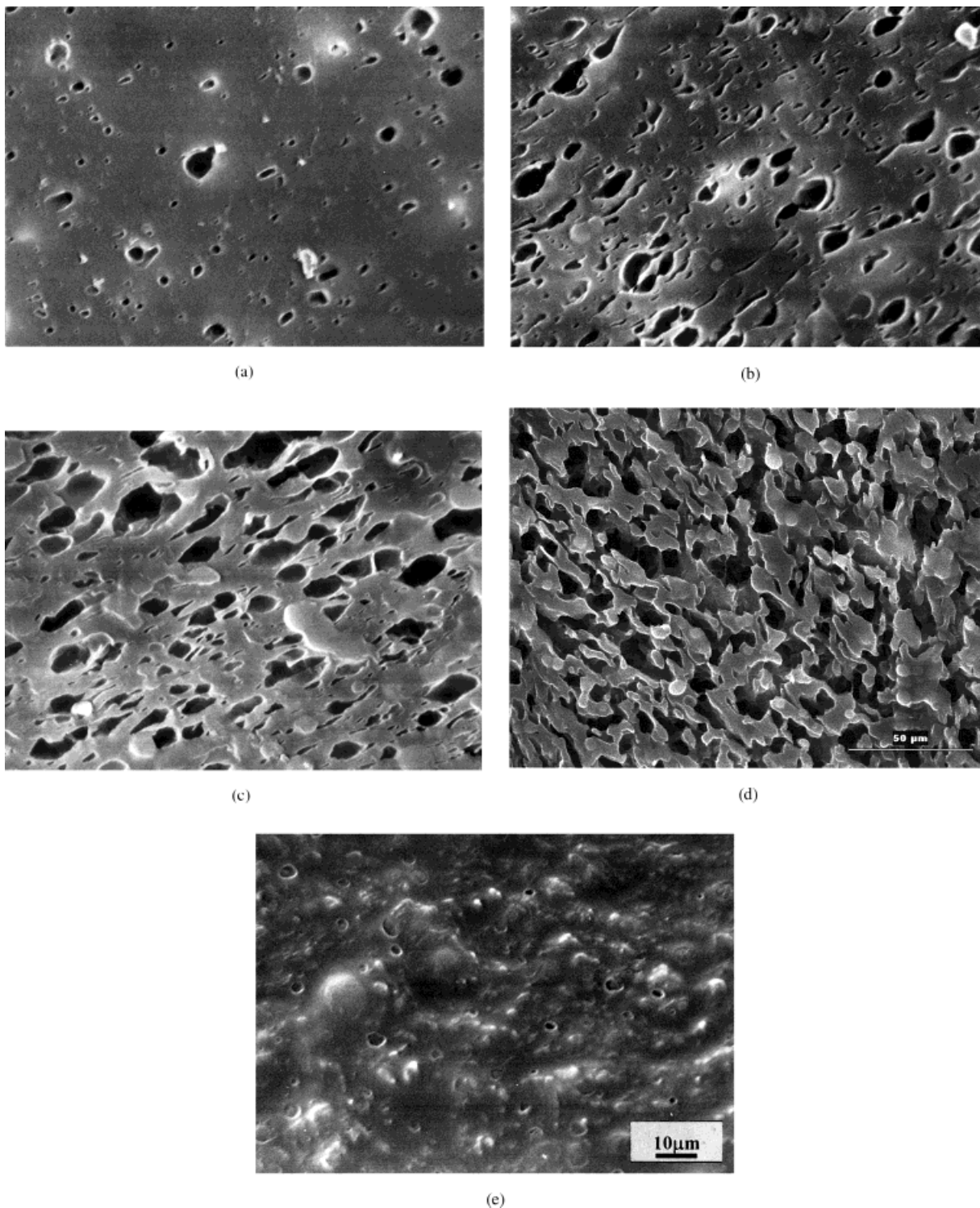
Figure 1 SEM pictures of the phase structure of HDPE/HIPS blends with compositions: (a) (90/10), (b) (70/30), (c) (50/50), (d) (30/70), (e) (10/90).

(STEM). Scanning electron microscopes JSM 35 and JSM 6400 (JEOL, Japan) in the secondary electron mode were used for scanning electron microscopy. Cut surfaces of the samples were pre-

pared with a glass knife of the knife angle 90° in a vessel filled with liquid nitrogen.[14] HIPS and SB were etched off from sample surfaces with toluene.
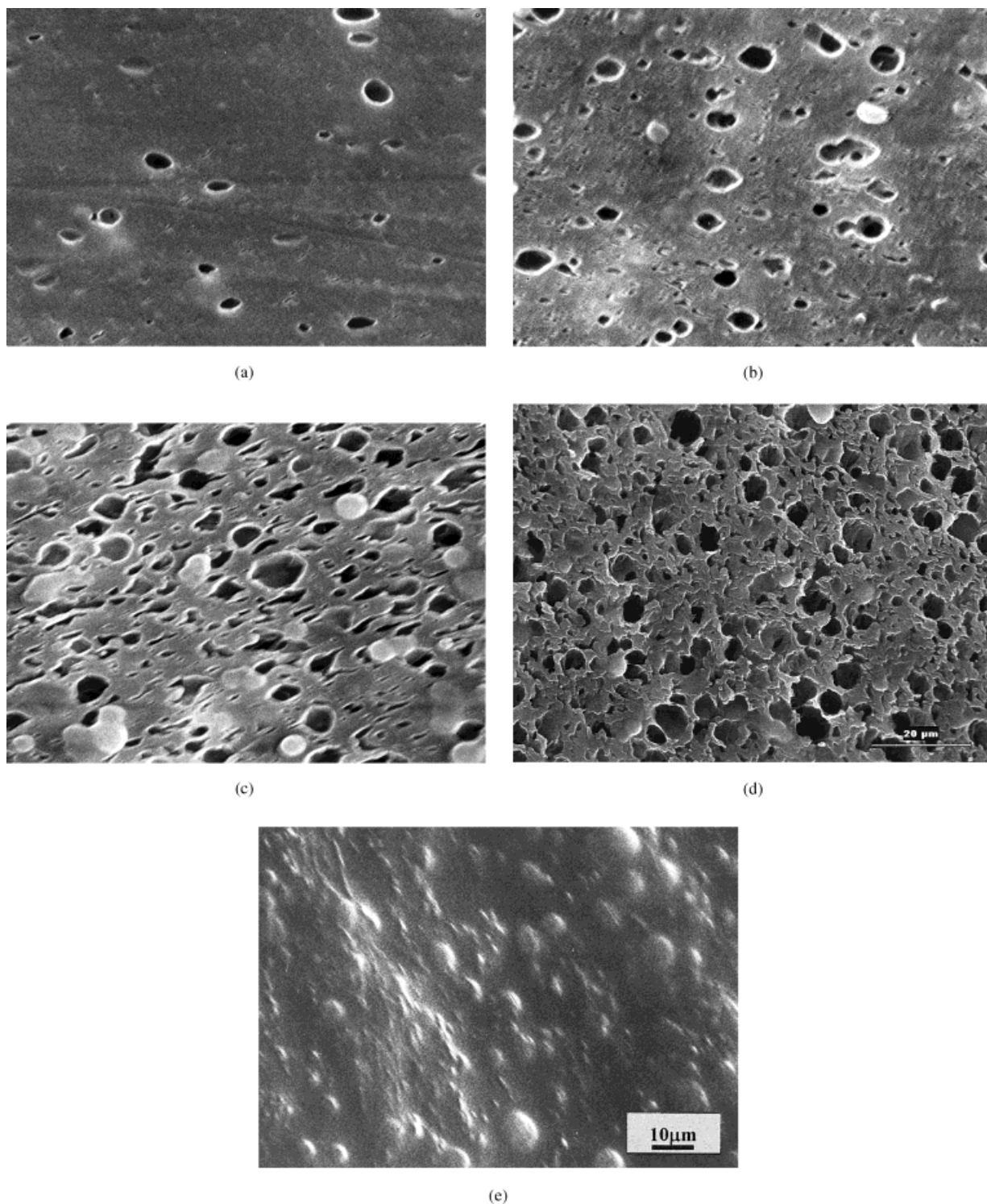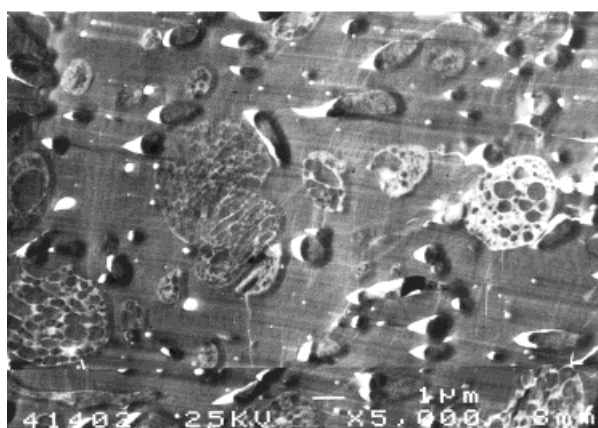
Figure 2 SEM pictures of the phase structure of HDPE/HIPS/SB blends with compositions: (a) (85.5/9.5/5), (b) (66.5/28.5/5), (c) (47.5/47.5/5), (d) (28.5/66.5/5), (e) (9.5/85.5/5).

Ultrathin sections were prepared to analyze the phase structure by transmission scanning electron microscopy. After cutting the sections at low temperature ($-130°C$) with a glass knife using ultramicrotome Ultrotome III (LKB), they were stained in OSO_4 vapor. For observation and

(a)

(b)

Figure 3 STEM pictures of the phase structure of HDPE/HIPS blends with compositions: (a) (70/30), (b) (10/90).

micrographing, scanning electron microscope JSM 6400 with a transmission adapter was used.

RESULTS AND DISCUSSION

In an HDPE/HIPS (90/10) blend, HDPE forms the matrix in which HIPS particles are dispersed [see Fig. 1(a)]. The sizes of HIPS particles have clear bimodal distribution. A similar structure can be seen in an HDPE/HIPS (70/30) blend [Fig. 1(b)]. Small particles in this blend are somewhat larger than those in the preceding case. It follows from comparison with Figure 3 that the large particles contain polybutadiene (PB) inclusions but small particles are formed by PS only. The HDPE/HIPS (50/50) blend [Fig. 1(c)] contains anisometric HIPS particles in the HDPE matrix. The HDPE/HIPS (30/70) blend [Fig. 1(d)] has a rough cocon-

tinuous structure. The HDPE/HIPS (10/90) blend consists of HDPE particles with diameter about 1 μm dispersed in the HIPS matrix [cf. Figs. 1(e) and 3(b)].

HDPE/HIPS/SB (85.5/9.5/5) and (66.5/28.5/5) blends contain (similarly to the related HDPE/HIPS blends) HIPS particles with bimodal size distribution [see Fig. 2(a) and (b)]. Small particles, containing neat PS, are smaller in compatibilized than in uncompatibilized blends. Also, the structure of the HDPE/HIPS/SB (47.5/47.5/5) blend [Figs. 2(c) and 4(a)] is not much different from the structure of HDPE/HIPS blends. Cocontinuous structure of the HDPE/HIPS/SB (28.5/66.5/5) blend is finer than that of the HDPE/HIPS (30/70) blend [cf. Figs. 1(d) and 2(d)]. In the HDPE/HIPS/SB (9.5/85.5/5) blend, HDPE particles are dispersed in the HIPS matrix [Figs. 2(e) and 4(b)]. Somewhat surprising is the fact that
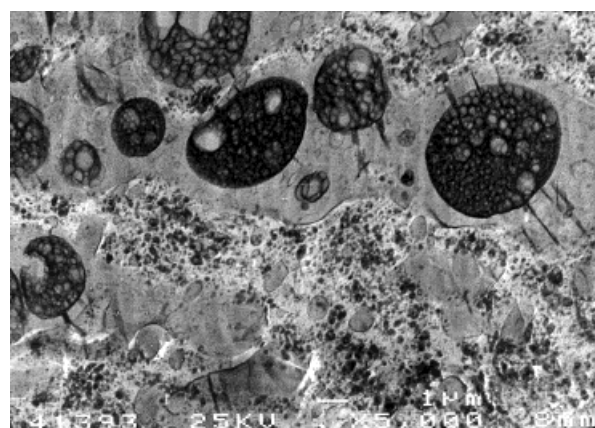
(a)
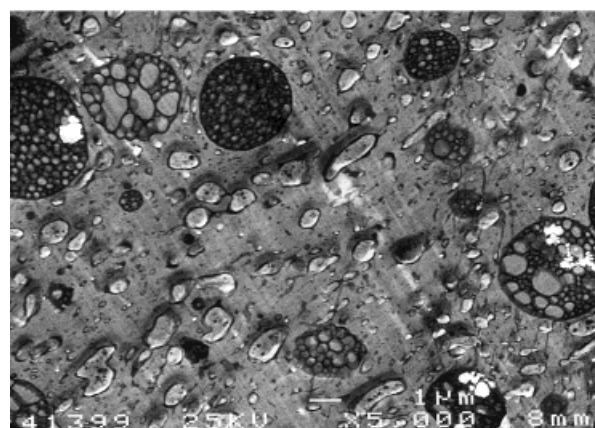
(b)

Figure 4 STEM pictures of the phase structure of HDPE/HIPS/SB blends with compositions: (a) (47.5/47.5/5), (b) (9.5/85.5/5).
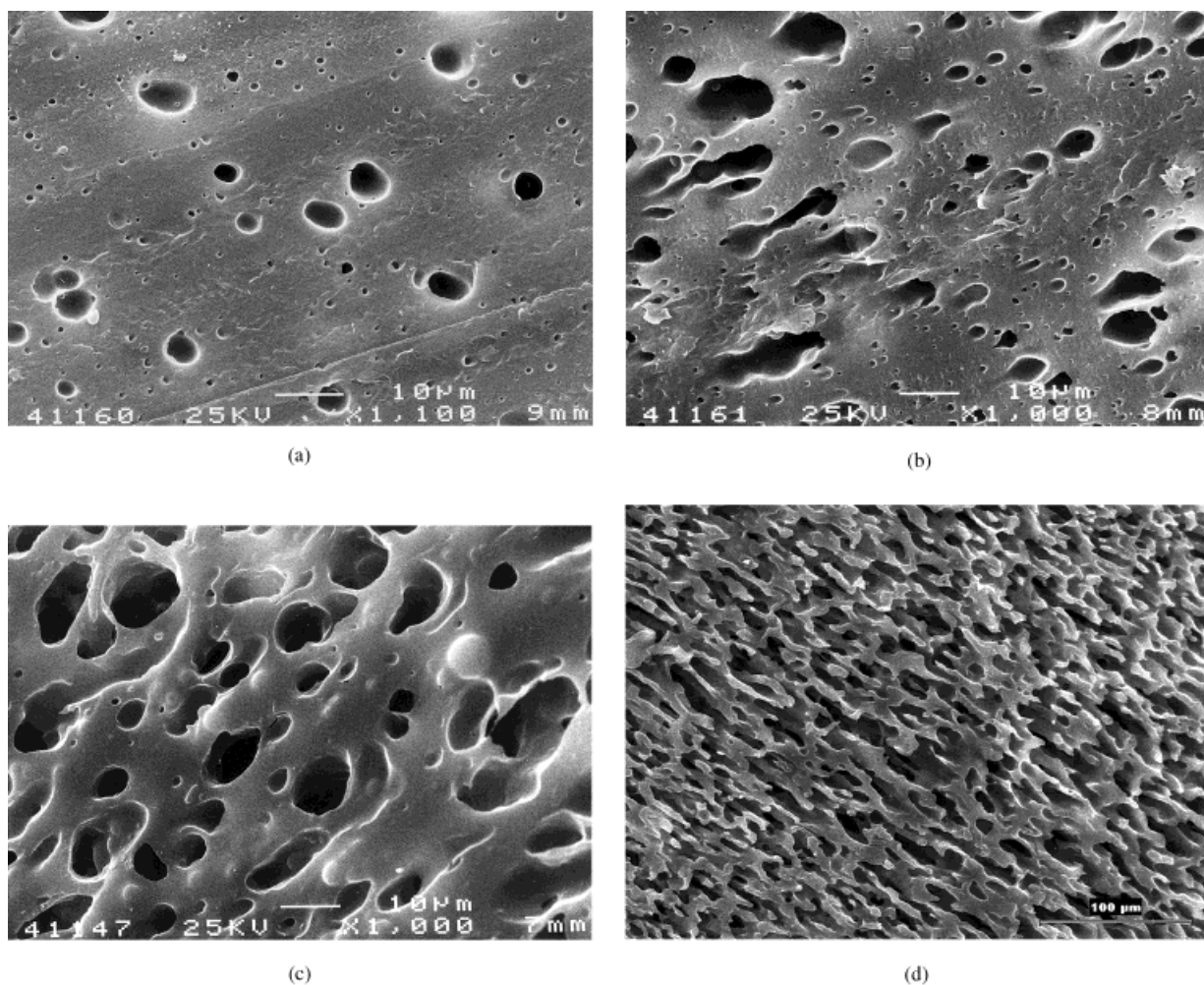
Figure 5 SEM pictures of the phase structure of LDPE/HIPS blends with compositions: (a) (90/10), (b) (70/30), (c) (50/50), (d) (30/70).

the size of HDPE particles is similar to that in the HDPE/HIPS (10/90) blend, i.e., SB copolymer has only a negligible emulsification effect [cf. Figs. 1(e), 2(e), 3(b), and 4(b)].

Localization of a compatibilizer in HDPE/HIPS/SB blends is rather unexpected. In the HDPE/HIPS/SB (47.5/47.5/5) blend [Fig. 4(a)], apparently only a small amount of SB is located on the interface between HDPE and PS. A part of SB copolymer forms aggregates of very small particles in the HDPE phase and another part forms fibers in the PS phase. The fibers frequently link two PB inclusions, a PB inclusion with the HDPE/PS interface or two points on the HDPE/PS interface [see Fig. 4(a)]. On the other hand, a substantial part of SB is localized on the surface of HDPE particles in the HDPE/HIPS/SB (9.5/85.5/5) blend [Fig. 4(b)]. The rest of SB forms small particles in the PS matrix or in HDPE par-

ticles. It cannot be decided from the micrographs whether a part of the compatibilizer is located in PB inclusions.

It follows from the above results that the dependence of the type of the phase structure of HDPE/HIPS blends on their composition, i.e., the composition region with cocontinuous structure, is virtually not affected by the presence of a compatibilizer. For blends with the HDPE matrix, the size of large HIPS particles is apparently controlled by the size of partially crosslinked PB particles containing small PS inclusions that are not broken in the mixing of any blend. The presence of SB compatibilizer leads to a decrease in size of the particles formed by neat PS. The SB compatibilizer causes a finer cocontinuous structure of the blend with the HIPS/HDPE ratio 7/3. It has surprisingly a small effect on the size of HDPE particles in HIPS-rich blends, but it strongly af-
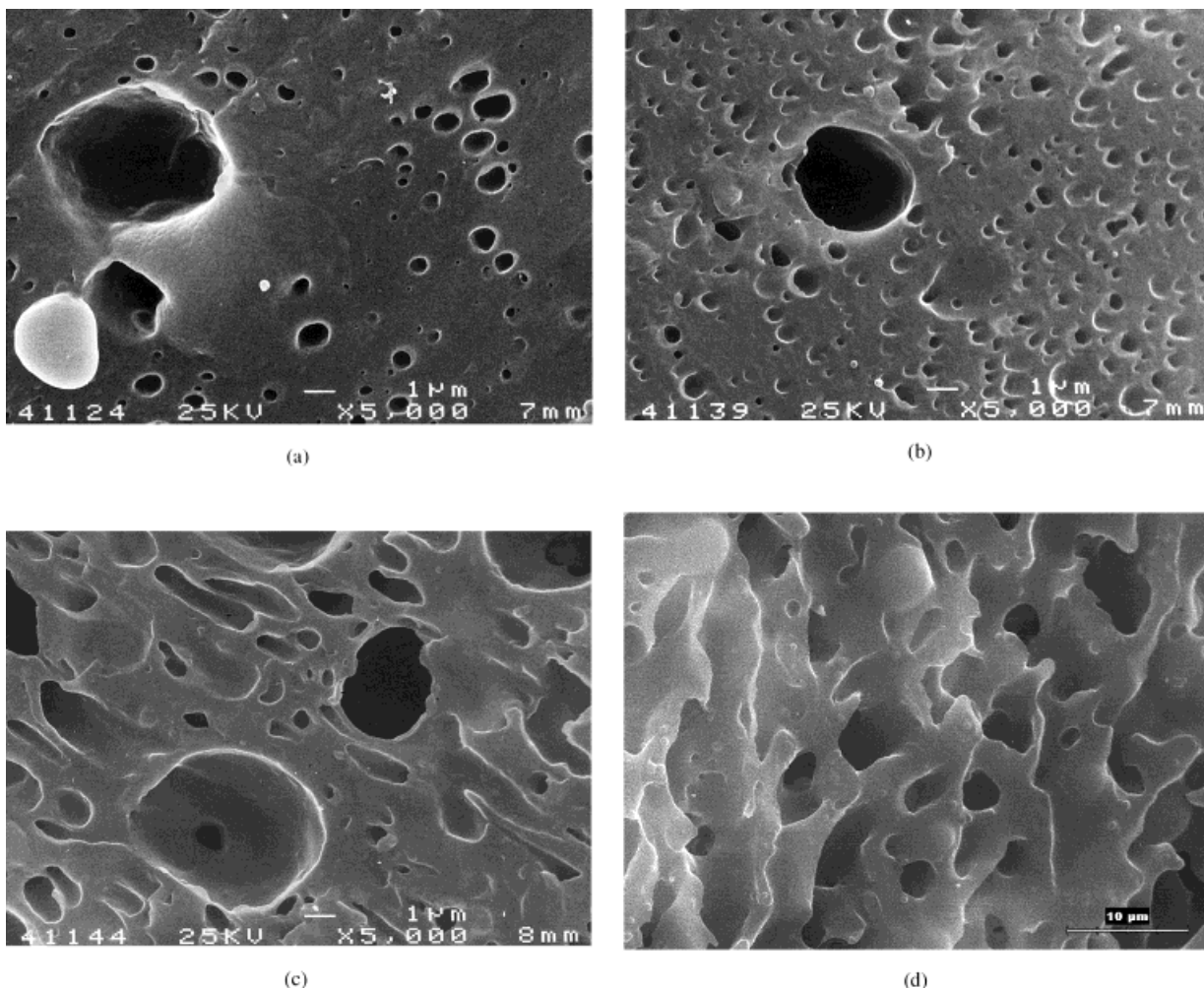
Figure 6 SEM pictures of the phase structure of LDPE/HIPS/SB blends with compositions: (a) (85.5/9.5/5), (b) (66.5/28.5/5), (c) (47./47.5/5), (d) (28.5/66.5/5).

fects adhesion of these particles to the HIPS matrix [see voids in Fig. 3(b) and cf. Fig. 4(b)].

LDPE/HIPS (90/10) and (70/30) blends consist of HIPS particles with bimodal size distribution, dispersed in the LDPE matrix (cf. Figs. 5 and 7). The large particles contain one or more PB inclusions [see Fig. 7(a) and (b)]. A similar structure also has an LDPE/HIPS (50/50) blend [Fig. 7(c)]. However, it contains only a small number of particles, which consists of neat PS only. LDPE/HIPS (30/70) has a cocontinuous structure with thread widths of several micrometers [Figs. 5(d) and 7(d)]. In LDPE/HIPS (10/90) blends [Fig. 7(e)], ellipsoidal particles, with a longer semiaxis of several μm, dispersed in the HIPS matrix were detected.

LDPE/HIPS/SB (85.5/9.5/5) and (66.5/28.5/5) blends [Fig. 6(a) and (b)] have finer structure than the related LDPE/HIPS (90/10) and (70/30)

blends [Fig. 5(a) and (b)]. Distribution of the particle size in SB containing blends is not strictly bimodal [see Fig. 6(a) and (b)]. It is caused by the fact that large particles in compatibilized blends mostly do not contain more than one PB inclusion [see Fig. 8(a) and (b)]. In these blends, only a small part of the SB copolymer is located on the interface (see Fig. 8). SB fibers located in PS particles are another part of the whole amount of the SB. The rest of SB is located in the LDPE matrix as small particles. In this case cannot we decide whether a part of SB copolymer is located on the surface and/or in PB inclusions. The LDPE/HIPS/SB (47.5/47.5/5) blend contains quite large, sometimes anisometric, particles of HIPS dispersed in the LDPE matrix. The large particles frequently contain several PB inclusions [see Fig. 8(c)]. Large PS particles are separated by SB fibers. They have character of aggregated subpar-
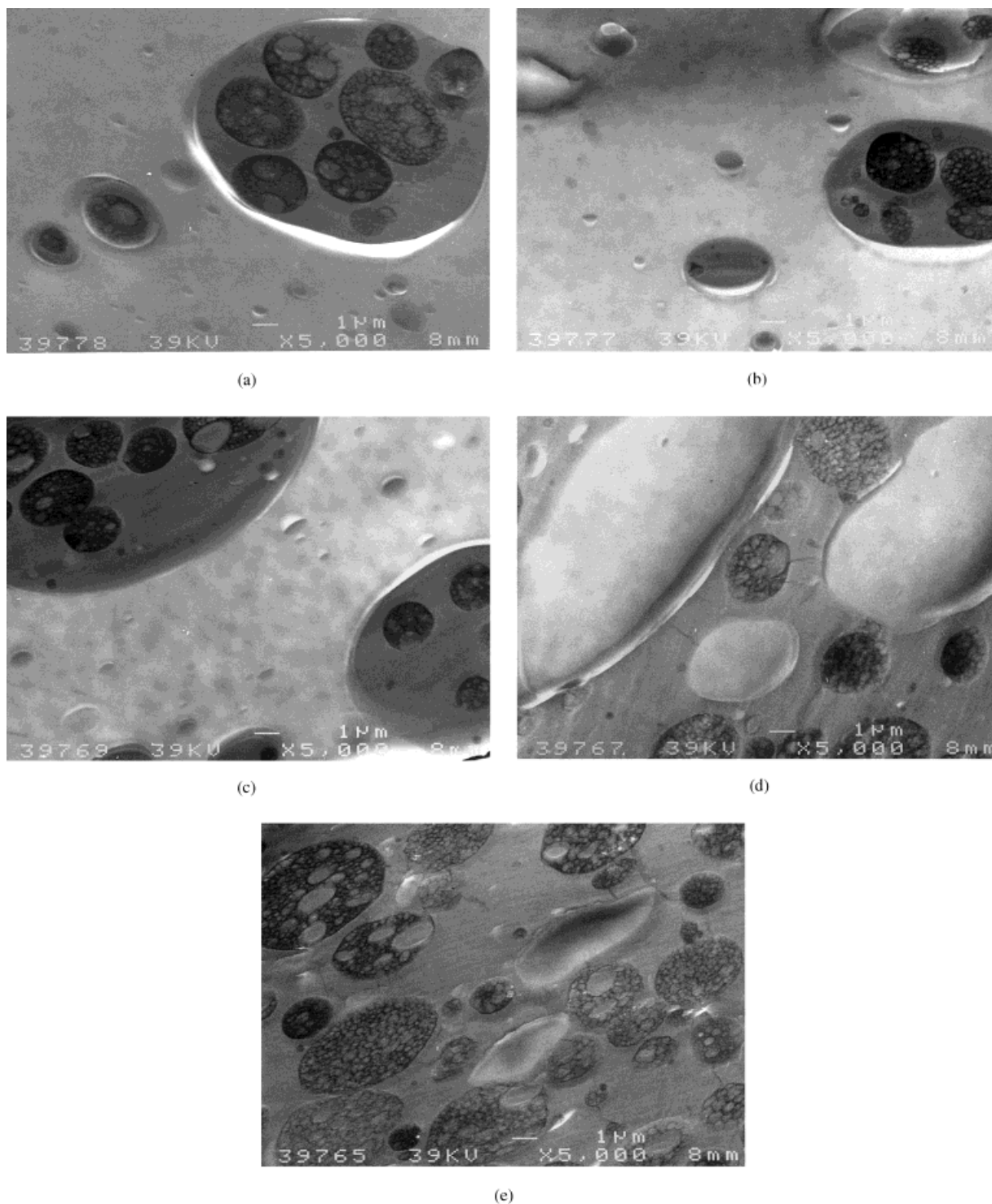
(a)

(b)

(c)

(d)

(e)

Figure 7 STEM pictures of the phase structure of LDPE/HIPS blends with compositions: (a) (90/10), (b) (70/30), (c) (50/50), (d) (30/70), (e) (10/90).

ticles surrounded by the SB copolymer. A similar structure was found by Radonjič et al.[15] in polypropylene/polystyrene blends compatibilized with triblock copolymer poly(styrene-*block*-butadiene-*block*-styrene). The LDPE/HIPS/SB (28.5/

66.5/5) blend has a cocontinuous structure, which is somewhat finer than that of the LDPE/HIPS (30/70) [cf. Figs. 6(d) and 5(d)]. The compatibilizer is localized in the HIPS phase as fibers, separating various parts of the PS matrix and small
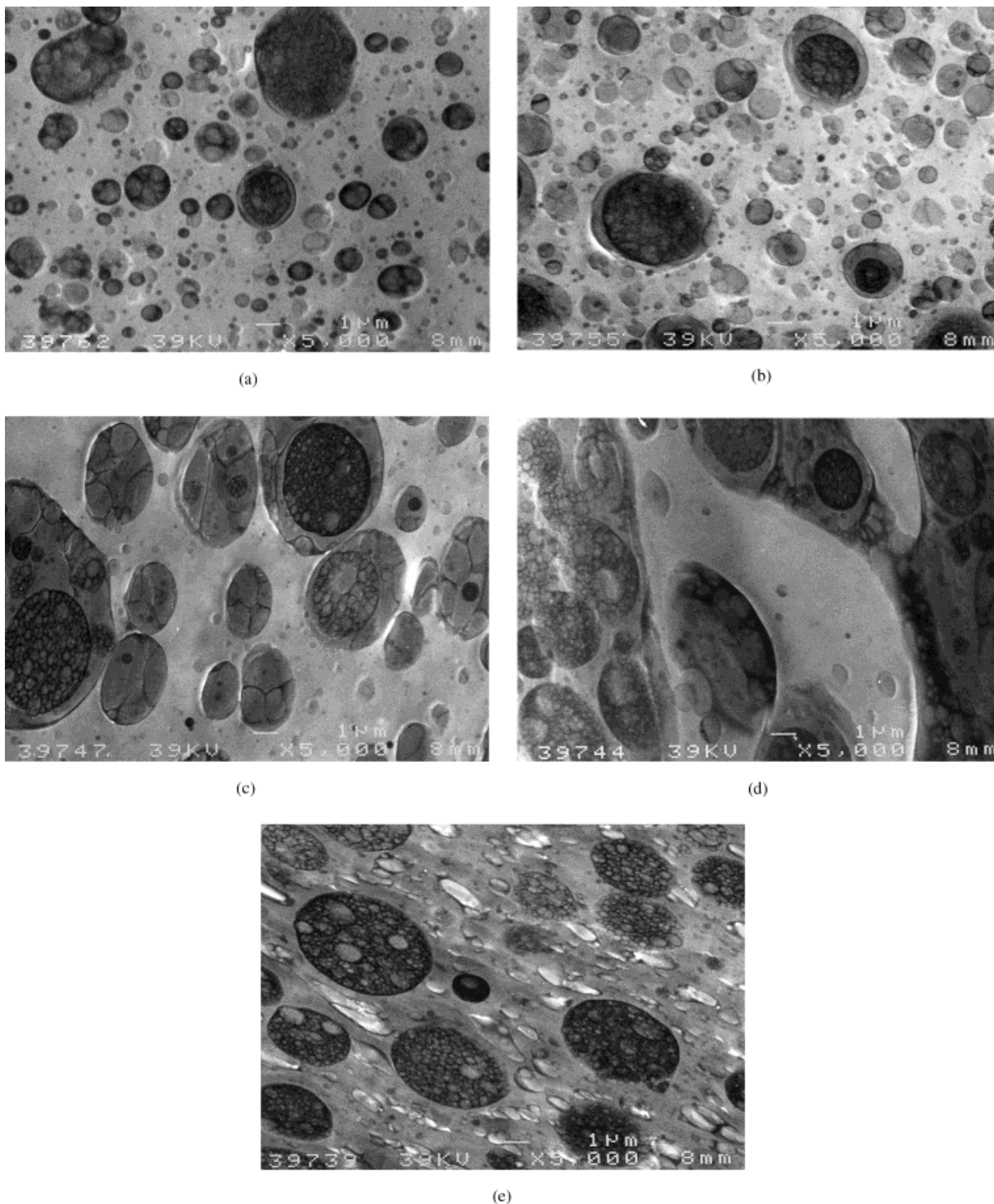
Figure 8   STEM pictures of the phase structure of LDPE/HIPS/SB blends with compositions: (a) (85.5/9.5/5), (b) (66.5/28.5/5), (c) (47./47.5/5), (d) (28.5/66.5/5), (e) (9.5/85.5/5).

particles [see Fig. 8(d)]. Small anisometric LDPE particles dispersed in the HIPS matrix are characteristic of LDPE/HIPS/SB (9.5/85.5/5) blends [see Fig. 8(e)]. The particles are substantially smaller than those in LDPE/HIPS (10/90) blends [see Fig. 7(e)]. A part of the SB copolymer is located on the surface of the LDPE particles. In some cases, LDPE particles form aggregates sep-
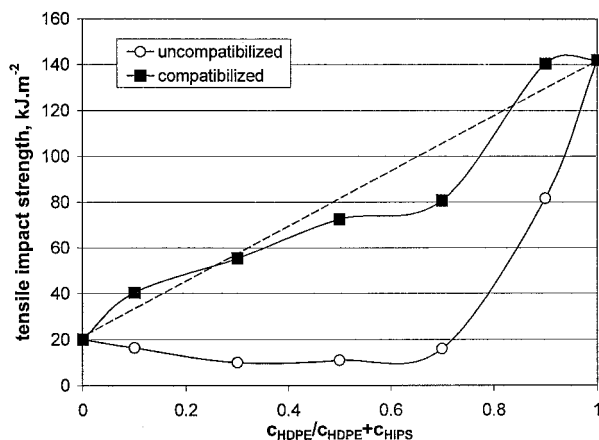
Figure 9 Dependences of the tensile impact strength, a_ε, on the $c_{HDPE}/c_{HIPS+HDPE}$ ratio in HDPE/HIPS (○) and HDPE/HIPS/SB (■) blends. Broken line assumes the additivity of a_ε of HDPE and HIPS.

arated by the SB layers. The other part of the SB is located in the HIPS matrix.

It follows from the above results that addition of the SB copolymer does not lead to the change in the dependence of the phase structure type on the blend composition for LDPE/HIPS blends either. The addition of SB, however, leads to a finer phase structure of these blends in the whole range of compositions.

It is apparent that for the blends under study, the presence of the SB compatibilizer had no substantial effect on the type of the phase structure. However, the range of compositions with cocontinuous structure was not broad for the HDPE/HIPS and LDPE/HIPS blends under study. Somewhat surprising is the fact that the distribution of a compatibilizer between the interface and bulk phases depends not only on the type of polyethylene but also on the composition of a particular blend. The dependence on the composition cannot be explained by differences in the available interfacial area. This dependence is in clear disagreement with the broadly accepted assumption that the density of a copolymer at the interface, measured by the amount of the copolymer localized on the unit area of the interface, is controlled only by molecular parameters of the copolymer and blend components. The reason for the formation of SB fibers in the PS phase is unclear.

Samples for the measurement of tensile impact strength, prepared by compression molding, were cooled more slowly than the samples quenched immediately after the cessation of mixing. Therefore, their structures can somewhat differ. It follows from a comparison of micrographs of

quenched and compression-molded samples (not reproduced here) that compression molding leads to a slight coarsening but not to a change in the phase structure type.

Dependences of the tensile impact strength, a_ε, on the composition of HDPE/HIPS and LDPE/HIPS blends are typical of incompatible blends. They have broad minimum around the 50/50 composition and all values of a_ε are lower than those related to additivity rules. An addition of 5 wt % of SB always leads to an increase in the blend impact strength. For the contents of minor components about 10 wt %, both the blends have higher values of a_ε than those resulting from the additivity of a_ε of the components. LDPE/HIPS/SB (85.5/9.5/5) blends have higher a_ε than the neat LDPE. HDPE/HIPS/SB and LDPE/HIPS/SB blends have lower values of a_ε than the additive ones in the range of HDPE/HIPS and LDPE/HIPS ratios 8/2–3/7 and 7/3–1/9, respectively. The minimum in the dependence of a_ε on the PE/HIPS ratio is deeper for the LDPE/HIPS/SB than for the HDPE/HIPS/SB blend.

CONCLUSIONS

The dependence of the phase structure type on the composition of HDPE/HIPS and LDPE/HIPS blends is not affected by addition of 5 wt % of a SB copolymer.

The distribution of the SB copolymer between the interface and bulk phases depends on the type
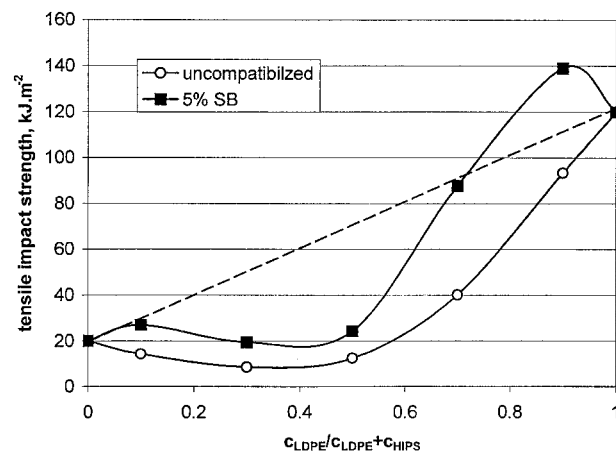

Figure 10 Dependences of the tensile impact strength, a_ε, on the $c_{LDPE}/c_{LDPE+HIPS}$ ratio in LDPE/HIPS (○) and LDPE/HIPS/SB (■) blends. Broken line assumes the additivity of a_ε of LDPE and HIPS.

of PE (HDPE or LDPE) and, surprisingly, also on the PE/HIPS ratio.

Admixture of SB copolymer improves the impact strength of both HDPE/HIPS and LDPE/HIPS blends, especially of blends with lower content of the minor phase. For blends with a composition of about 1/1, the SB copolymer is a better compatibilizer (from the point of view of the impact strength) for HDPE/HIPS than for LDPE/HIPS blends.

REFERENCES

1. Bonner, J. G.; Hope, P. S. In Polymer Blends and Alloys; Folkes, M. J.; Hope, P. S., Eds.; Blackie Academic and Professional: London, 1993.
2. Fayt, R.; Teyssié, P. Polym Eng Sci 1990, 30, 937.
3. Hermes, H. E.; Higgins, J. S. Polym Eng Sci 1998, 38, 8477.
4. Fayt, R.; Teyssié, P. Polym Eng Sci 1990, 30, 937.
5. Brahimi, B.; Ait-Kadi, A.; Ajji, A.; Jérôme, R.; Fayt, R. J Rheol 1991, 35, 1069.
6. Hlavatá, D.; Horák, Z.; Hromádková, J.; Lednický, F.; Pleska, A. J Polym Sci B Polym Phys 1999, 37, 1647.
7. Navrátilová, E.; Fortelný, I. Polym Networks Blends 1996, 6, 127.
8. Lyngaae-Jørgensen, J.; Lunde Rasmussen, K.; Chtcherbakova, E. A.; Utracki, L. A. Polym Eng Sci 1999, 39, 1060.
9. Dedecker, K.; Groeninckx, G. Polymer 1998, 39, 4993.
10. Bourry, D.; Favis, B. D. J Polym Sci B Polym Phys 1998, 36, 1889.
11. Taha, M.; Frerejean, V. J Appl Polym Sci 1996, 61, 969.
12. Hietaoja, P. T.; Holsti-Miettinen, R. M.; Sepälä, J. V.; Ikkala, O. T. J Appl Polym Sci 1994, 54, 1613.
13. Zhang, X.; Yin, Z.; Yin, J. J Appl Polym Sci 1996, 62, 893.
14. Fortelný, I.; Michálková, D.; Koplíková, J.; Navrátilová, E.; Kovář, J. Angew Makromol Chem 1990, 179, 185.
15. Radonjič, G.; Musil, V.; Šmit, I. J Appl Polym Sci 1998, 69, 2625.