

Effect of the Molecular Structure of Ethene–Propene and Styrene–Butadiene Copolymers on Their Compatibilization Efficiency in Low-Density Polyethylene/Polystyrene Blends

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Received 30 April 2007; accepted 17 June 2007

DOI 10.1002/app.27005

Published online 25 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of the molecular structure of styrene–butadiene (SB) block copolymers and ethene–propene (EPM) random copolymers on the morphology and tensile impact strength of low-density polyethylene (LDPE)/polystyrene (PS) (75/25) blends has been studied. The molecular characteristics of SB block copolymers markedly influence their distribution in LDPE/PS blends. In all cases, an SB copolymer is present not only at the interface but also in the bulk phases; this depends on its molecular structure. In blends compatibilized with diblock copolymers, compartmentalized PS particles can also be observed. The highest toughness values have been achieved for blends compatibilized with triblock SB copolymers. A study of the compatibilization efficiency of SB copolymers with the same number of blocks has shown that copolymers with

shorter PS blocks are more efficient. A comparison of the obtained results with previous results indicates that the compatibilization efficiency of a copolymer strongly depends both on the blend composition and on the properties of the components. The compatibilization efficiency of an EPM/SB mixture is markedly affected by the rheological properties of the copolymers. The addition of an EPM/SB mixture containing EPM with a higher viscosity leads to a higher improvement or at least the same improvement in the tensile impact strength of a compatibilized blend as the same amount of neat SB. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 174–186, 2008

Key words: blends; block copolymers; compatibility; impact resistance; morphology

INTRODUCTION

It is well known that block and graft copolymers with blocks that are the same as, are miscible with, or adhere to the related components of a blend are suitable compatibilizers for immiscible polymer blends.^{1–4} Statistical copolymers of monomers that are the same as or miscible with blend components frequently also show a positive effect on the fineness of the phase structure and mechanical properties of immiscible polymer blends, but their effect on the stability of the phase structure during further processing is substantially weaker than that of block or graft copolymers.⁵

Polystyrene (PS)/polyolefin blends are interesting materials, especially for packaging. Moreover, various grades of polyolefins and styrene plastics form a substantial part of municipal plastic waste. Because PS and polyolefins are incompatible and their blends

show poor mechanical properties, their compatibilization is of great interest. It has been found that diblock and triblock copolymers of styrene and butadiene^{6–14} and poly[styrene-*block*-(ethene-*co*-butene)-*block*-styrene]^{10,12,15–20} can serve as compatibilizers for PS/polyolefin blends. Grades of both copolymers, with quite a broad scale of molecular structures, are commercially available. Nevertheless, the copolymers are substantially more expensive than polyolefins or PS. Therefore, the choice of a proper grade of the copolymer with the aim of optimizing the properties and price of polyolefin/PS blends is of great importance.

Many attempts to determine relations between the molecular structure of block copolymers and their compatibilization efficiency for a certain polymer pair can be found in the literature. Attempts to find relations between the molecular structure (number and length of blocks) and the compatibilization efficiency of block copolymers have led to contradictory results. It follows from some studies^{21–23} that diblock copolymers are more efficient than triblocks and multiblocks, but other studies have arrived at the opposite conclusion.^{24–27} Some studies have shown that copolymers with block lengths comparable to

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Contract grant sponsor: Grant Agency of the Czech Republic; contract grant number: 106/06/0729.

the lengths of the related blend components are the most efficient.^{23,28} Other studies have concluded^{27,29,30} that copolymers with substantially shorter blocks can show high efficiency. The rule for the prediction of compatibilization efficiency suggested by Kim et al.³¹ is not applicable to systems with block lengths substantially shorter than the lengths of the compatibilized chains. Recently, the compatibilization efficiency of a set of model block copolymers, with different numbers of blocks and with styrene blocks of different lengths, in blends of PS with various polyolefins has been studied.^{32–39} It has been found that the compatibilization efficiency of a block copolymer depends not only on its molecular structure and interaction parameters with the components of the compatibilized blend but also on the ratio of the blend components and the mixing and processing conditions. The order of copolymers, listed according to their compatibilization efficiency in a certain blend, is a function of their concentration.³⁷ A pronounced migration of copolymers between the interface and bulk phases during blend annealing^{37,38} clearly shows that the distribution of a copolymer between the interface and bulk phases in a steady flow and in the quiescent state is not the same, and it cannot be predicted from the rules of equilibrium thermodynamics. These conclusions seem to be valid at least for systems in which block copolymers are shorter than compatibilized polymers.

Surprisingly, a mixture of a styrene–butadiene (SB) block copolymer with an ethene–propene (EPM) random copolymer is in some cases a more efficient compatibilizer for PS/polyolefin blends than neat SB, even though the compatibilization efficiency of neat EPM is very poor.^{40–42} The effect of the composition of an SB/EPM mixture on its compatibilization efficiency in PS/polypropylene (PP) blends with various component ratios has been studied in detail.⁴³ The positive effect of SB/EPM mixtures on the impact strength of PS/PP blends has in all cases been more pronounced than the additive effects of SB and EPM components. For blends with a high content of PS, the addition of SB/EPM mixtures has led to a larger improvement in the impact strength than the addition of the same amount of neat SB. The cooperative effect of SB and EPM has been explained as a result of the correlation of localization of SB and EPM, which leads to the enhancement of the SB fraction localized at the PS/PP interface.

It has been unclear so far how the dependence of the cooperative effect of SB and EPM copolymers on the structure and mechanical properties of PS/polyolefin blends is affected by the molecular structure of the copolymers. For the elucidation of this problem, the effect of mixtures of six model and three commercial SB copolymers with two commercial EPM copolymers on the structure and tensile impact

strength of low-density polyethylene (LDPE)/PS (75/25) blends is studied in this article.

EXPERIMENTAL

Materials

PS (Krasten 171) was acquired from Kaučuk Co. (Kralupy, Czech Republic); it had a melt flow index of 5.2 g/10 min (ISO 1133, 190°C, 2.16 kg) and a density of 1.05 g/cm³.

LDPE (LD 100 BW) was obtained from ExxonMobil Chemical (Antwerp, Belgium); it had a melt flow index of 1.9 g/10 min (ISO 1133, 190°C, 2.16 kg) and a density of 0.923 g/cm³.

The compatibilizers were as follows. The EPM random copolymers were Exxelor PE X1 703 F1 (EPM1) with a propene content of 27.5% (supplied by ExxonMobil Chemical) and Dutral CO 034 (EPM2) with a propene content of 28% (purchased from Polimeri Europa, Ferrara, Italy). The SB block copolymers (SB1–SB6) were pilot-plant products of Kaučuk with a molecular weight of polybutadiene blocks of about 60 kg/mol and a molecular weight of styrene blocks of about 10 (SB1–SB3) or 40 kg/mol (SB4–SB6). They were prepared by anionic polymerization in *tert*-butyl methyl ether (MTBE) at 50°C with 1,4-dilithiobut-2-ene (formula: Li–CH₂–CH=CH–CH₂–Li) in MTBE as an initiator.^{34,44} The total molecular weights were determined by gel permeation chromatography with a dual refractive index and ultraviolet detection.⁴⁵ The PS content in the copolymers was determined by gel permeation chromatography after the cleavage of styrene blocks with di-*tert*-butyl peroxide and osmium tetroxide. The concentration of the copolymers with a lower number of blocks in the multiblock was lower than 10% in all cases. More detailed characteristic of these copolymers can be found in ref. 34.

Vector 6241 (V6241), from Dexco Polymers (Houston, TX), is a linear triblock copolymer with a diblock content lower than 1%. Europrene SOL T 6414 (E6414) and Europrene SOL T 168 (E168), supplied by Polimeri Europa, are triblock copolymers with diblock contents of 22 and 10%. The molecular characteristics of the studied block copolymers are summarized in Table I.

Blend preparation

All the blends were prepared through melt mixing in a Brabender Plasticorder W50 EH (Brabender, Duisburg, Germany) internal mixer at 190°C and 60 rpm. The mixing time was 8 min.

Two series of blends with an LDPE/PS weight ratio of 75/25 were made. The first series contained neat SB copolymers at concentrations of 2.5 and 5 wt %. The other set contained a 2.5 wt % concentration

TABLE I
Molecular Characteristics of the SB Block Copolymers

Code	Description	M_n (kg/mol)	M_w/M_n (kg/mol)	M_n of the PS block (kg/mol)	PS (wt %)
SB1	Diblock	81	1.06	11.8	14.6
SB2	Triblock ^a	73	1.07	9.3	25.6
SB3	Pentablock ^b	135	1.11	9.1	20.3
SB4	Diblock	99	1.06	39.5	39.9
SB5	Triblock ^a	117	1.10	33.8	57.7
SB6	Pentablock ^b	206	1.14	34.5	50.2
V6241	Triblock ^a	49	1.10	13.0	52.6
E6414	Triblock ^a	62	1.36	12.9	41.6
E168	Triblock ^a	73	1.13	12.7	34.8

M_n = number-average molecular weight; M_w = weight-average molecular weight.

^a Styrene-butadiene-styrene.

^b Styrene-butadiene-styrene-butadiene-styrene.

of an SB copolymer and a 2.5 wt % concentration of a different EPM. The compatibilizer concentration in the studied blends was based on the total weight of the blends (including the compatibilizer). Uncompatibilized blends and blends compatibilized with neat EPM were also prepared.

Samples were compression-molded into plates with a Fontijne hydraulic press (Fontijne, Vlaardingen, The Netherlands) at 200°C and 1.5 MPa for 2 min and at 3 MPa for another 2 min. Afterwards, the samples were placed in a cool press and cooled to room temperature at 1.5 MPa. Specimens for impact measurements and for morphological investigations were cut from the molded plates.

In some cases described further, quenched samples were prepared. Small pieces of blend melts were immersed in cool water immediately after mixing to preserve their morphology without changes occurring during compression molding.

Measurements of the mechanical properties

The tensile impact strength was measured at 23°C with a Zwick tester (Zwick, Ulm, Germany) according to the ISO 8256 standard. The maximum pendulum energy was 2 J. Ten specimens for all samples were tested, and the presented values are the arithmetical means of these measurements. The variation coefficients of the tensile impact strength values were below 10%.

Morphology

The microstructure of the selected blends was studied by electron microscopy with a scanning electron microscope (Vega TS 5130, Tescan, Brno, Czech Republic) with a transmission adapter. Ultrathin sections were cut with an Ultratome III microtome (LKB, Bromma, Sweden) under cryoconditions (knife temperature = -70°C, specimen temperature = -130°C). After being cut, the sections were stained with OsO₄ vapor for 1.5 h, which ensured the visualization of

polymers containing multiple bonds, particularly styrene-butadiene copolymers and, to a lesser extent, PS. All micrographs were taken at an acceleration voltage of 30 kV.

Rheological measurements

The flow properties were measured on an ARES rotational rheometer (Rheometric Scientific, Piscataway, NJ) in a dynamic mode with parallel-plate and cone-and-plate geometries (radius = 12.5 or 25 mm, cone angle = 0.101 rad). The frequency sweep tests were carried out from 10⁻¹ to 10² rad/s at 190°C. The experiments were performed in the range of the linear viscoelasticity. The frequency dependence of the complex viscosities of the blend components with the EPM copolymers and SB block copolymers is shown in Figures 1 and 2.

RESULTS AND DISCUSSION

Compatibilization with SB copolymers

Our previous studies have shown that the distribution of SB copolymers between the interface and

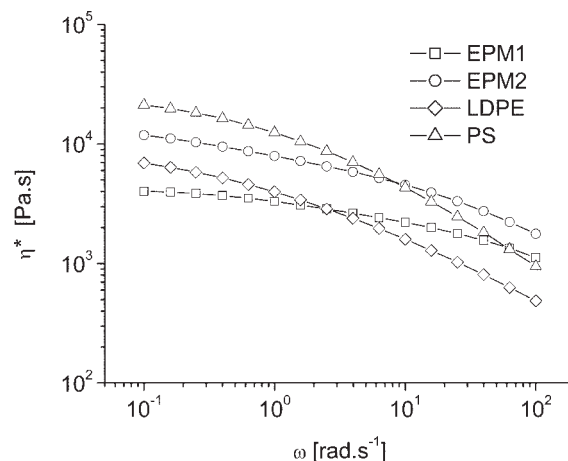


Figure 1 Shear flow curves of the blend components, LDPE and PS, and the EPM copolymers, EPM1 and EPM2, at 190°C (η^* is the complex viscosity, and ω is the frequency).

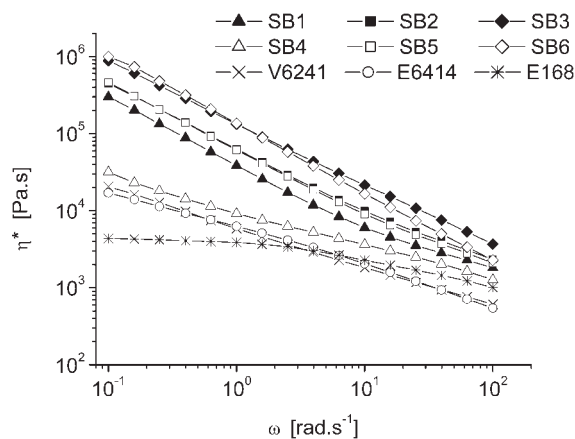


Figure 2 Shear flow curves of SB block copolymers at 190°C (η^* is the complex viscosity, and ω is the frequency).

bulk phases controls their compatibilization efficiency in PS/polyolefin blends.^{36–39} The molecular structure of SB copolymers has only a minor effect on the blend morphology and mechanical properties if the distribution of various SB copolymers in a blend is similar. Moreover, the phase structure in PS/LDPE blends is nonuniform, and a very large number of particles must be evaluated for the achievement of a reliable average particle size.³⁷ Therefore, we have focused our morphological studies in this study on compatibilizer localization in blends. The particle size is discussed only if it is clearly visible from micrographs without quantitative evaluation.

LDPE/PS blends display properties typical of incompatible polymer blends. Therefore, the phase structure of the uncompatibilized blends is coarse, with a sharp and weak interface (Fig. 3) and with a very broad distribution of dispersed particle sizes. These facts provide evidence of low interfacial adhesion between the components.

When a 5 wt % concentration of a diblock SB copolymer is added to an LDPE/PS (75/25) blend, we obtain a completely different morphology. Figure 4(a,d) shows that a part of the copolymer is located at the interface, but a considerable amount is embedded in PS particles in the form of partitions. Moreover, in the case of SB4 (a diblock with long PS blocks), a part of the copolymer is deposited inside the PS phase as very small particles [Fig. 4(d)]. On the other hand, a small number of somewhat larger particles are localized in the LDPE matrix and at the interface in the case of SB1 [Fig. 4(a)]. This type of morphology, called a honeycomb-like structure, has already been described in PP/PS blends with a PP matrix compatibilized with a commercial triblock SBS^{3,43} or poly(styrene-*block*-ethene-*co*-propene) diblock copolymer.³ With the copolymer content reduced to 2.5 wt %, this morphology is still pre-

served, but the internal structure of the dispersed particles becomes less developed [Fig. 4(b,e)]. These compound particles are thought to be aggregates occurring as a result of coalescence during melt mixing or during compression molding. To determine when this morphology is formed, the phase structure of the quenched samples has also been studied. It is clear from Figure 4(c,f) that immediately after mixing, that is, before compression molding, dispersed PS particles are simple, with no or very little developed internal structure. Furthermore, the droplet size is substantially smaller in comparison with molded samples of the same composition. This implies that the honeycomb-like structure forms predominantly during compression molding; therefore, the diblock copolymers substantially support droplet breakup and/or suppress flow-induced coalescence. At the same time, they do not suppress efficiently coalescence during annealing.

Figure 5(a–d) shows the morphology of blends compatibilized with triblocks and pentablocks with short or long PS blocks. Dispersed PS particles in blends compatibilized with SB2 and SB3 (short PS blocks) are coated with the block copolymer; most of them are simple, and only some particles contain a few SB partitions [Fig. 5(a,c)]. A considerable amount of SB2 or SB3 (i.e., copolymers with styrene contents of 25.6 and 20.3 wt %) is not located at the interface but is dispersed in the polyethylene matrix. In contrast, the amount of diblock copolymer SB1 observed in the polyethylene matrix is very small [Fig. 4(a)]. On the other hand, SB copolymers with long PS blocks (SB4–SB6) and, therefore, with higher styrene contents (see Table I) are partly dispersed inside PS particles [Figs. 4(d) and 5(c,d)] as small particles, and there is no indication of a honeycomb-

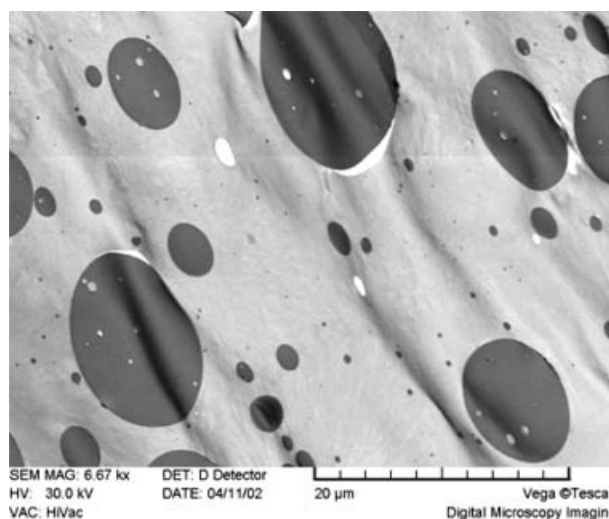


Figure 3 Morphology of an uncompatibilized LDPE/PS (75/25) blend.

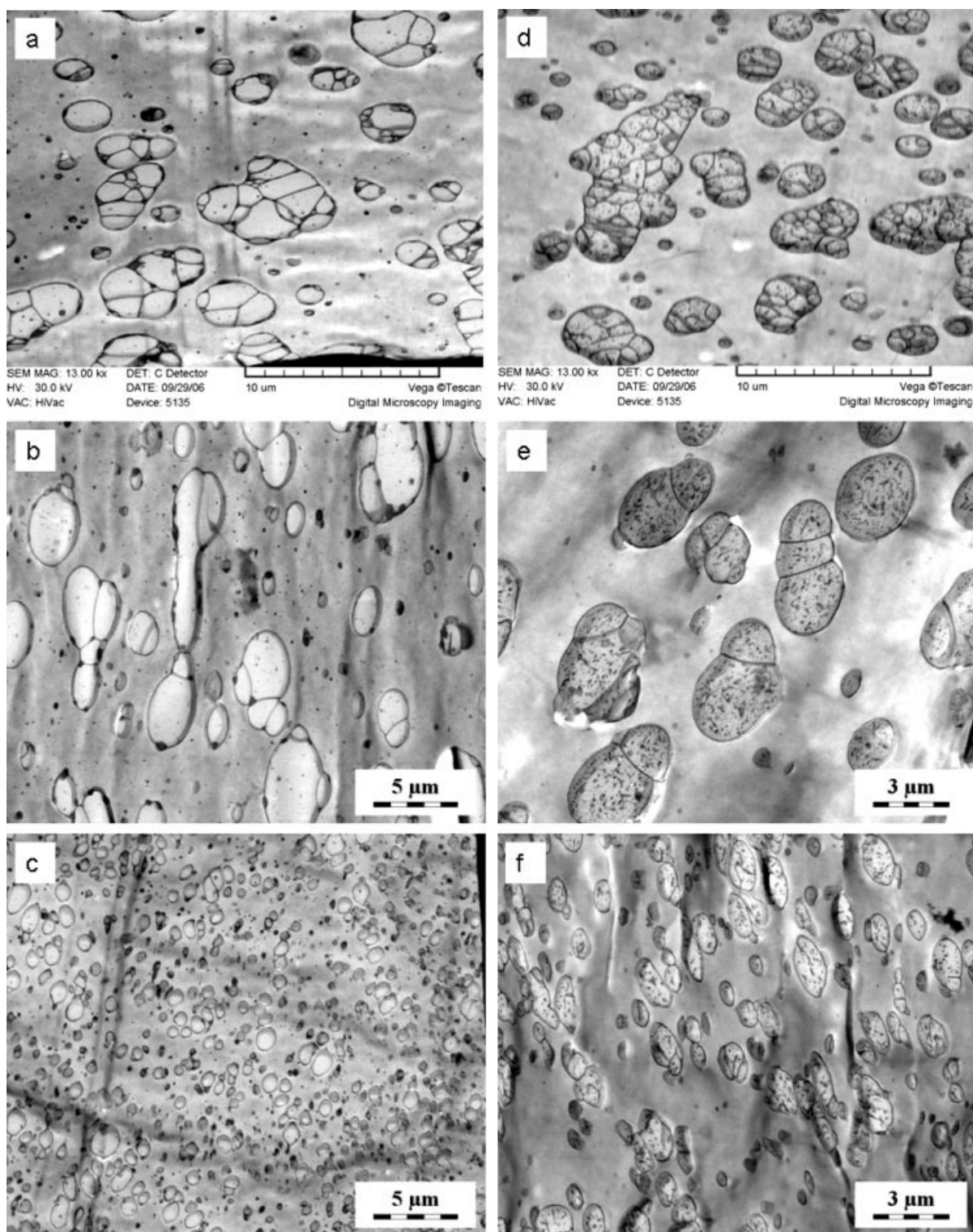


Figure 4 Transmission electron micrographs of LDPE/PS blends compatibilized with diblock SB copolymers: (a) 5% SB1, (b) 2.5% SB1, (c) 5% SB1 (quenched), (d) 5% SB4, (e) 2.5% SB4, and (f) 5% SB4 (quenched).

like structure, with the exception of SB4. The long pentablock SB6 is not located at the interface at all, being trapped inside PS particles in relatively large pieces [Fig. 5(d)]. Therefore, it cannot act as a compatibilizer, and this has been verified with toughness measurements (see Table II).

In comparison with block copolymers prepared as pilot-plant products, three commercially available triblock copolymers have been examined in this study. All the used commercial SB copolymers have short PS blocks (Table I), and the morphology of the blends compatibilized with these copolymers is simi-

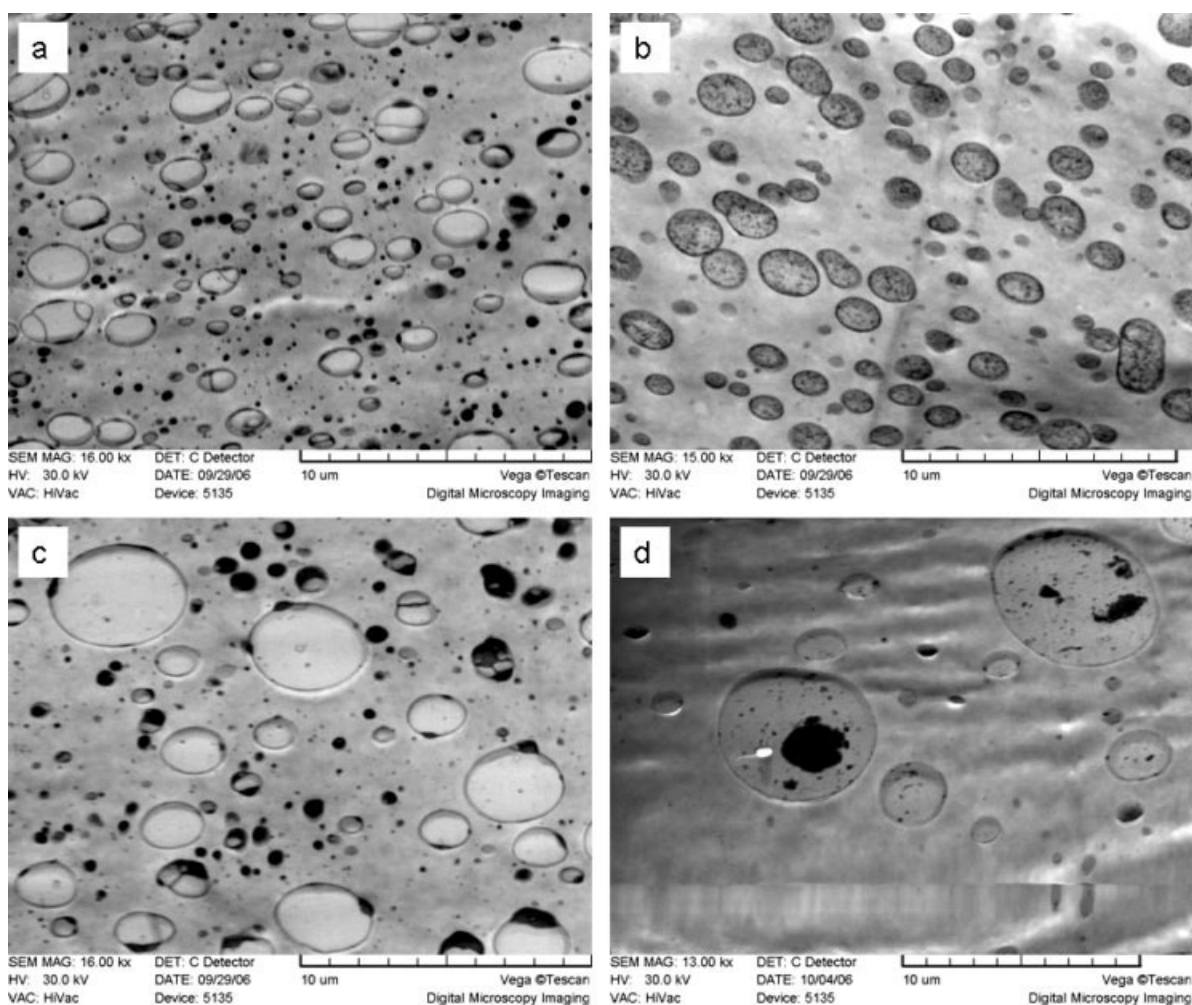


Figure 5 Transmission electron micrographs of LDPE/PS blends compatibilized with triblock and pentablock SB copolymers (5 wt %): (a) SB2, (b) SB5, (c) SB3, and (d) SB6.

lar to that of the blend with SB2 [Fig. 5(a)]. The phase structure of the blends compatibilized with a 5 wt % concentration of these copolymers is shown in Figure 6. In all these blends, a more or less developed honeycomb-like structure is inside the PS par-

ticles, and a part of the copolymer is dispersed in the polyethylene matrix.

Block copolymers SB1–SB3 and the commercial triblocks have PS blocks shorter than the minimal length necessary for the formation of entanglements

TABLE II
Influence of the Composition of the Compatibilization System on the Tensile Impact Strength (kJ/m^2) of the LDPE/PS (75/25) Blends

Code	Compatibilization system			
	2.5% SB	5% SB	2.5% SB + 2.5% EPM1	2.5% SB + 2.5% EPM2
SB1	40.6 ± 3.0	62.3 ± 6.1	54.5 ± 4.9	72.9 ± 2.6
SB2	60.9 ± 2.1	81.8 ± 2.1	60.8 ± 2.4	86.3 ± 3.4
SB3	41.7 ± 1.5	63.4 ± 4.8	47.1 ± 4.4	67.5 ± 4.4
SB4	45.3 ± 3.8	54.8 ± 3.8	71.1 ± 2.6	73.8 ± 6.3
SB5	52.3 ± 2.9	66.7 ± 5.7	54.8 ± 4.7	75.1 ± 5.1
SB6	17.6 ± 1.3	17.3 ± 1.3	18.4 ± 1.7	18.3 ± 0.7
V6241	63.1 ± 3.4	74.5 ± 2.0	75.6 ± 1.8	74.1 ± 2.8
E6414	64.8 ± 2.9	78.0 ± 3.6	74.3 ± 3.0	71.7 ± 2.9
E168	73.6 ± 4.4	87.2 ± 5.0	83.7 ± 3.2	80.2 ± 3.5

For the uncompatibilized blend, the tensile impact strength was $14.7 \pm 1.4 \text{ kJ/m}^2$.

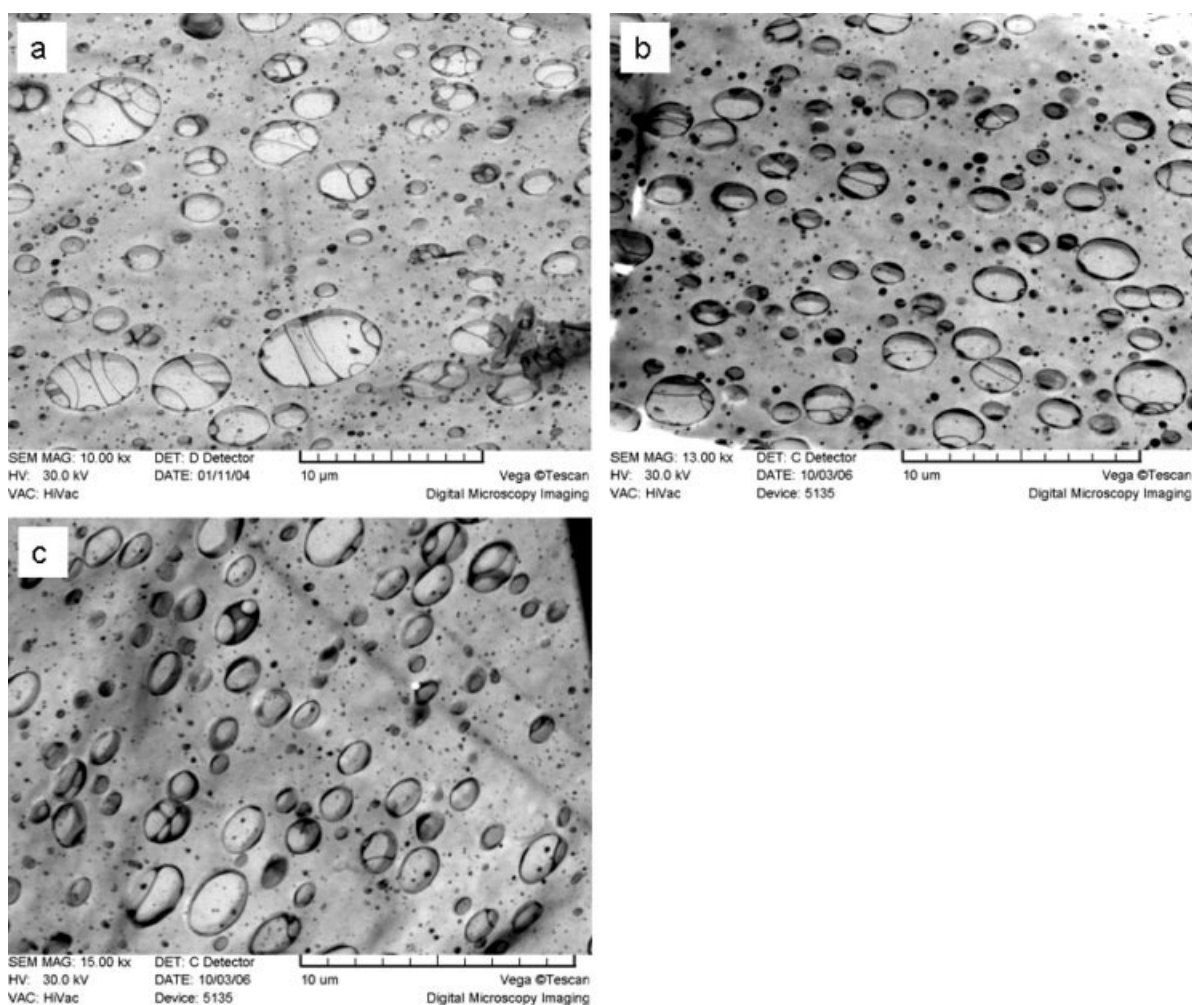


Figure 6 Transmission electron micrographs of LDPE/PS blends compatibilized with commercial triblock SB copolymers (5 wt %): (a) V6241, (b) E6414, and (c) E168.

at the interface, that is, 18 kg/mol (refs. 46 and 47). On the other hand, all the copolymers used in this study have polybutadiene blocks considerably longer than this minimal length, which has been estimated to be 6 kg/mol (ref. 48). The obtained results show that copolymers with short PS blocks are located partly at the interface and partly in both bulk phases of the LDPE/PS blends. Inside PS particles, these copolymers form partitions. These compound PS particles are a result of droplet coalescence during molding; the block copolymers forming partitions are primarily deposited at the interface. Copolymers with long PS blocks do not form their own phase in the polyethylene matrix, and inside PS particles, they form small nanoscale particles, which are already generated during melt mixing.

As a criterion of compatibilization efficiency, the tensile impact strength has been chosen. The tensile impact strength of polymer blends is generally affected by many factors. If the effects of various compatibilizers on the tensile strength of a certain

blend are compared, the particle size and adhesion on the interface are the most important parameters. As discussed previously, the particle size is controlled mainly by copolymer localization in a blend. Also, for interfacial adhesion, the presence of a compatibilizer at the interface is decisive.

The values of the tensile impact strength of all the prepared blends are summarized in Table II. From the obtained results, it follows that, despite theory, block copolymers with short PS blocks are better compatibilizers than copolymers with long PS blocks and with the same number of blocks. Regardless of the length of the PS blocks, triblock copolymers are the most efficient compatibilizers for LDPE/PS (75/25) blends in terms of toughness. This is in good agreement with the morphological study because the dispersed particle size in these blends is considerably lower than that in the blends compatibilized with diblocks and pentablocks. With 5 wt % SB2, the toughness of the blend can be enhanced more than 5 times in comparison with an uncompatibilized

TABLE III
Influence of EPM on the Tensile Impact Strength (kJ/m²) of the Blend Components and LDPE/PS Blends

	EPM content				
	0%	2.5% EPM1	5% EPM1	2.5% EPM2	5% EPM2
LDPE	155.1 ± 13.5	154.2 ± 13.3	168.8 ± 14.5	157.8 ± 11.5	168.6 ± 7.0
PS	13.7 ± 2.0	14.1 ± 0.9	14.5 ± 1.1	16.9 ± 1.9	16.0 ± 2.1
LDPE/PS blend	14.7 ± 1.4	17.1 ± 1.7	25.9 ± 4.8	19.3 ± 1.5	31.0 ± 5.7

blend. In all cases except SB6, an increase in the SB content from 2.5 to 5 wt % leads to a considerable increase in the toughness of the blend. From the obtained results, it follows that the compatibilization efficiency, based on the enhancement of the toughness, cannot be derived only from the localization of the SB copolymer in the blend, that is, when the copolymer forms partitions or small particles inside the PS dispersed phase.

Interesting results are provided by a comparison of the aforementioned results with the results of our previous article,³⁹ in which the effect of SB1–SB6 copolymers on the morphology and impact strength of LDPE/PS (80/20) is reported. The same PS and LDPE with a somewhat higher viscosity (LDPE1; cf. Fig. 1 and Fig. 1 in ref. 37) were used in the previous study. Figure 4 in ref. 39 shows that no compound particles are formed in compatibilized LDPE1/PS (80/20) blends. Small SB particles are dispersed in the LDPE1 matrix in LDPE1/PS blends compatibilized with SB containing short styrene blocks (SB1–SB3). A similar morphology was found in LDPE/PS (75/25) blends compatibilized with SB2 and SB3. LDPE1/PS/SB4 contains small SB4 particles in both bulk phases—the PS particles and the LDPE1 matrix. A similar morphology, but only with a smaller number of SB particles in the matrix and larger PS particles, was detected in an LDPE1/PS/SB5 blend. Large pieces of SB6 in PS particles were found in LDPE1/PS/SB6, similarly to the related blend in this study.

The LDPE1/PS (80/20) blend has substantially higher tensile impact strength than LDPE/PS (75/25; cf. Table III with Table I in ref. 39). This is apparently the result of the higher viscosity of LDPE1, which leads to smaller PS particles and a smaller content of PS. The addition of 5% SB1–SB4 to the LDPE1/PS (80/20) blend remarkably improves its impact strength. However, this improvement is substantially smaller than that for the related LDPE/PS (75/25) blends. This difference can be explained by a stronger tendency of the SB copolymer to occupy the interface in LDPE/PS (75/25) blends, which manifests itself by the existence of smaller or compound PS particles and better developed SB envelopes around them. The addition of SB6 leads to a slight decrease in the impact strength for the LDPE1/PS

blend and to a negligible increase in the LDPE/PS blend in agreement with their similar morphologies. The most striking difference is between the impact strengths of LDPE/PS (75/25) and LDPE1/PS (80/20) blends compatibilized with 5% SB5 (cf. Table II and Table I in ref. 39). In LDPE/PS (75/25), the addition of 5% SB5 leads to a 4.5 times higher value of a_{ϵ} , the tensile impact strength. On the other hand, 5% SB5 leads even to a slight decrease in the LDPE1/PS (80/20) blend. This clearly proves that the compatibilization efficiency of a copolymer depends strongly on the composition of the compatibilized blends and/or the molecular weights of their components and that it cannot be predicted even qualitatively from the knowledge of the molecular parameters of a compatibilizer and χ parameters describing the interaction of the copolymer blocks with chains of compatibilized polymers only. This statement is apparently valid at least for systems in which the lengths of the copolymer blocks are smaller than the lengths of the compatibilized polymer molecules.

Compatibilization with the EPM/SB system

In our previous work, we have shown that the combination of an SB block copolymer and an EPM random copolymer can be a more efficient compatibilization system than a neat SB copolymer for polyolefin/PS blends, even though neat EPM does not act as a compatibilizer at all.^{40–43} Furthermore, it has been proved that this synergic activity is caused by the formation of an EPM/SB double layer at the interface; EPM is located on the polyolefin side and SB is located on the PS side of the interface.⁴³ However, no systematic study of the influence of EPM properties on the compatibilization efficiency of EPM/SB systems has been carried out. In this work, we have chosen two types of EPMS with the same content of propene but different viscosities (Fig. 1). Unfortunately, all attempts to visualize EPM in the presence of LDPE through staining with RuO₄ have been unsuccessful. Nevertheless, the results of toughness measurements have led us to the conclusion that EPM is concentrated at the interface as in the case of PP/PS blends, for which the presence of EPM at the interface has been found with electron

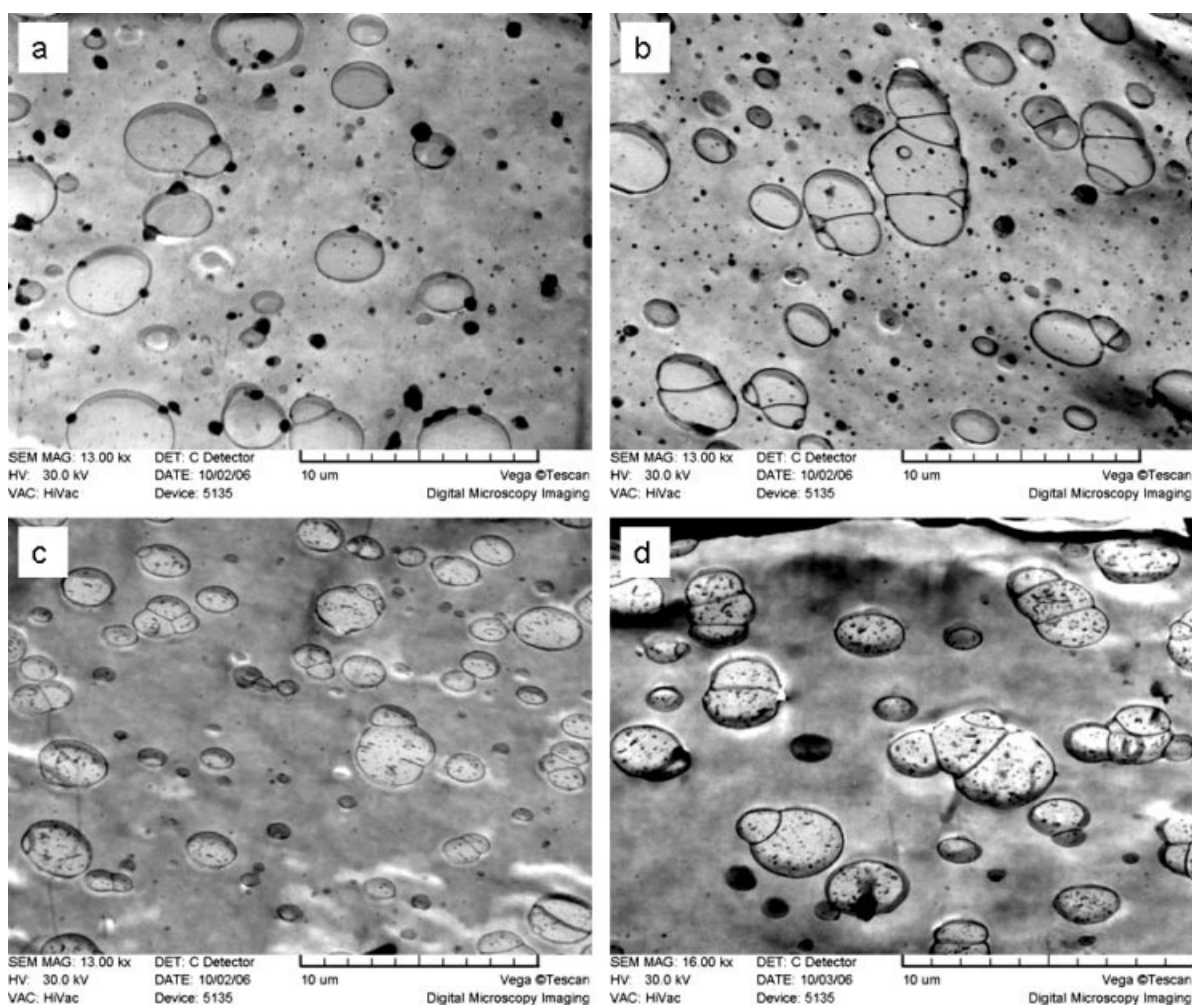


Figure 7 Phase structures of blends compatibilized with 1/1 EPM/SB systems (5 wt %) containing diblock copolymers: (a) EPM1/SB1, (b) EPM2/SB1, (c) EPM1/SB4, and (d) EPM2/SB4.

microscopy.⁴³ The activity of EPM can be also deduced from the SB behavior at the interface. As can be seen in Table III, a 2.5 wt % concentration of neat EPM does not affect the tensile impact strength of LDPE/PS (75/25) or blend components considerably. Only the incorporation of 5 wt % EPM leads to a noticeable increase in the blend toughness.

The phase structure of the blends compatibilized with a 2.5 wt % concentration of diblock SB copolymer and a 2.5 wt % concentration of EPM is shown on Figure 7. The type of EPM markedly influences the morphology of the blend compatibilized with SB1 (a diblock with a short PS block). When the compatibilization system containing EPM1 is used [Fig. 7(a)], a major amount of SB1 is localized at the interface in the form of particles, and practically no SB partitions are inside the PS particles [cf. Fig. 4(b)]. On the other hand, blends with EPM2 display a morphology with well-developed SB envelopes around PS particles with SB partitions [Fig. 7(b)]. This morphology difference is reflected in toughness

values: the tensile impact strength of the blend compatibilized with EPM2/SB1 is about 20 kJ/m² higher than the value for the blend with EPM1/SB1 (see Table II). However, no substantial differences have been found in blends compatibilized with EPM/SB4 [Fig. 7(c,d)]. In these blends, some SB4 is concentrated at the interface, and some is located inside the PS phase as partitions or small particles. Also, the toughness of these blends is basically the same (Table II).

Figure 8 shows electron micrographs of the blends with a compatibilization system consisting of EPM and a triblock or pentablock SB copolymer. In all these blends, the compatibilization system containing EPM2 exhibits higher toughness (ca. 20 kJ/m²) like SB1, and so this system is more efficient (Table II) in the studied blends. However, changes in the phase structure can be observed well only in blends containing triblock copolymer SB2 [Fig. 8(a,b)]. The incorporation of EPM2 leads to a finer morphology with smaller PS particles with a more developed honeycomb-like structure. In other cases [Fig. 8(c-f)],

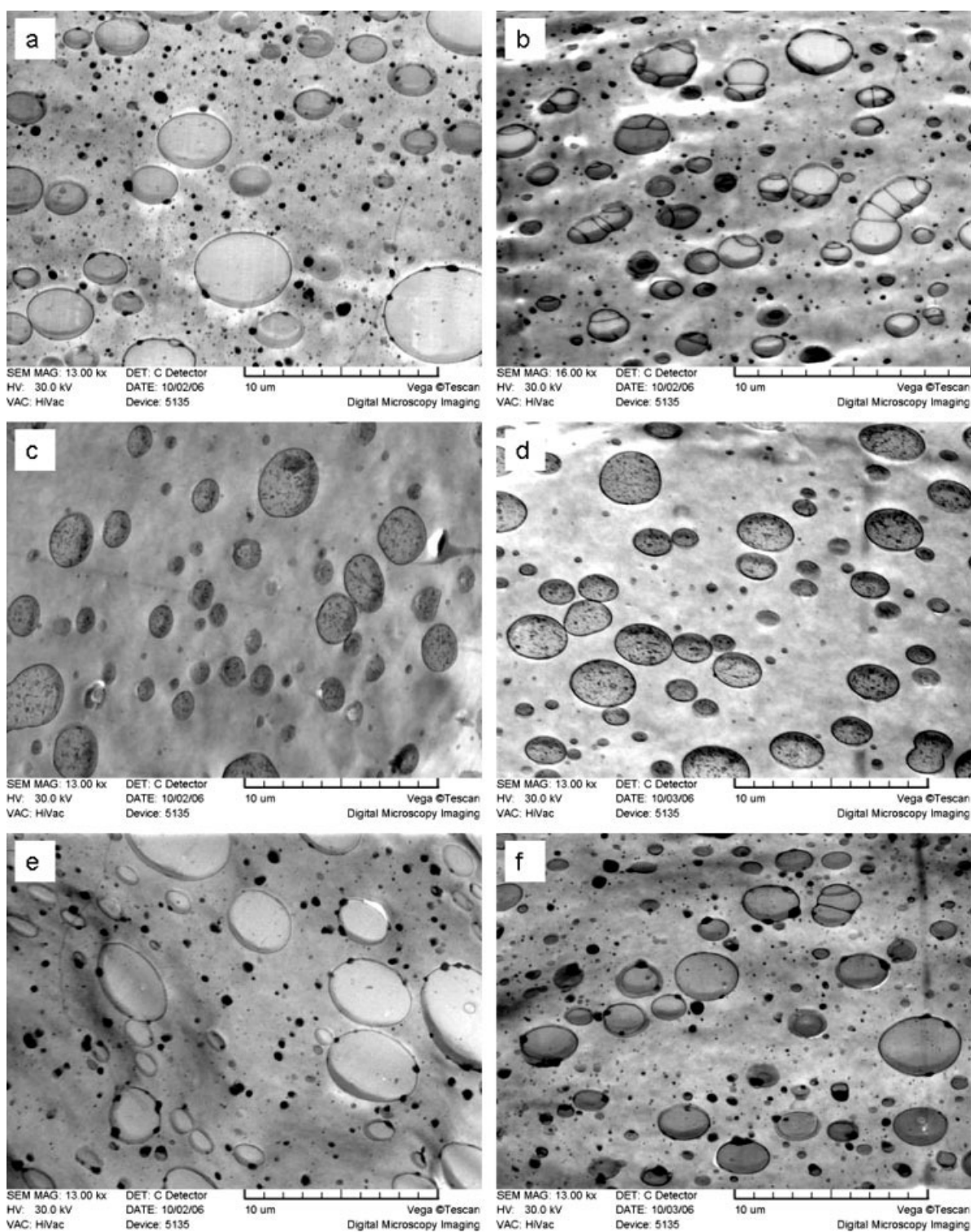


Figure 8 Phase structures of blends compatibilized with 1/1 EPM/SB systems (5 wt %) containing triblock or pentablock copolymers: (a) EPM1/SB2, (b) EPM2/SB2, (c) EPM1/SB5, (d) EPM2/SB5, (e) EPM1/SB3, and (f) EPM2/SB3.

the size of the dispersed PS particles and distribution of the SB particles between the interface and bulk phases do not depend on the type of EPM; only SB envelopes of PS particles seem to be somewhat clearer and more continuous in blends containing EPM2. On the other hand, the tensile

impact strength is considerably higher when EPM2 is used. The most efficient compatibilization system for LDPE/PS (75/25) blends from the point of view of toughness is a combination of EPM2 and the triblock copolymer with short PS blocks (SB2).

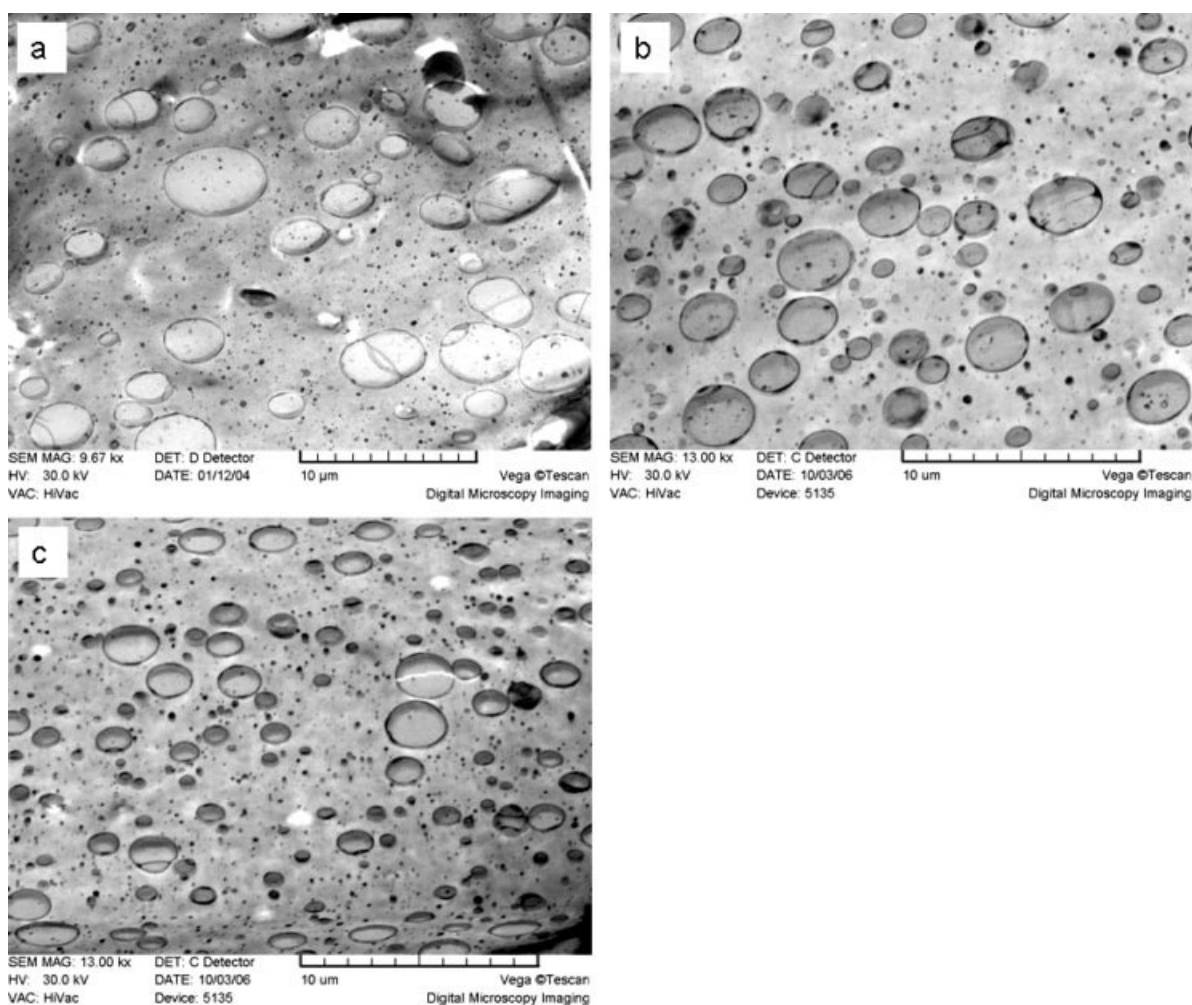


Figure 9 Phase structures of blends compatibilized with 1/1 EPM/SB systems (5 wt %) containing commercial triblock SB copolymers: (a) EPM1/V6241, (b) EPM1/E6414, and (c) EPM1/E168.

The compatibilization efficiency of the EPM/SB system has also been studied with commercially available triblock copolymers. From the values in Table II, it follows that the tensile impact strength of the final blend is not affected by the type of EPM, in contrast to the systems containing nearly all model SB copolymers. Therefore, electron micrographs were taken to observe the phase structure of the blends compatibilized only with EPM1/SB [Fig. 9(a–c)]. In all cases, the SB copolymer is preferentially located at the interface, and a minor part is scattered in the polyethylene matrix. In comparison with the blends compatibilized with a 5 wt % concentration of commercial SB copolymers (Fig. 6), only a few PS particles contain SB partitions.

Generally, the incorporation of a 5 wt % concentration of an EPM/SB compatibilization system results in materials with a considerably higher tensile impact strength than the use of a 2.5 wt % concentration of the neat SB copolymer, even though 2.5 wt % EPM has only a negligible effect on blend

toughness. It follows from the results previously discussed that the viscosity of the EPM can play an important role in the compatibilization efficiency of EPM/SB systems. In this study, nine SB copolymers and their combinations with two EPMS were tested as compatibilizers for the LDPE/PS (75/25) blend. The used SB copolymers can be divided into two groups according to their rheological properties (Fig. 2). All three commercially available triblocks (V6241, E6414, and E168), together with SB4, fall into the first group, with lower absolute values of the complex viscosity. The compatibilization efficiency of the EPM/SB system containing these copolymers is independent of the viscosity of the used EPM, and high values of toughness are reached already with EPM1, that is, EPM with a lower viscosity. On the other hand, SB copolymers with a higher complex viscosity (SB1–SB3 and SB5) are much more efficient in combination with EPM2, that is, EPM of a higher viscosity, whereas a combination with EPM1 displays a markedly lower compatibilization efficiency.

For all the studied model SB copolymers, with the exception of SB6, their combination with EPM2 is more efficient than the incorporation of the same amount of the neat SB copolymer. The correlation between the viscosity of SB and EPM copolymers and the compatibilization efficiency of their mixtures is very interesting because no correlation of the viscosity of neat SB copolymers and their compatibilization efficiency has been found.

On first sight, the enhancement of the impact strength of LDPE/PS/SB blends by the addition of EPM, which is a poor compatibilizer for LDPE/PS, is surprising. Unfortunately, no satisfactory theory predicting the compatibilization efficiency of block copolymers is available. Therefore, the prediction of the effect of an even mixture of two types of copolymers is difficult. Qualitatively, the cooperative effect of SB and EPM copolymers is apparently caused by the correlation of their previously mentioned localization. This correlation can lead in some cases to the enhancement of the amount of SB localized at the interface; for example, the correlation with the localization of EPM can pull at the interface some SB that is localized in the PS phase in blends compatibilized with neat SB copolymers.

CONCLUSIONS

The molecular characteristics of SB block copolymers markedly influence the distribution of the copolymers in LDPE/PS blends. A morphological study has proven that SB copolymers with short PS blocks, that is, with PS blocks with a molecular weight lower than the critical molecular weight required for entanglement formation, are partly located at the interface and partly dispersed in the LDPE matrix. Moreover, all these copolymers, more or less, tend to form partitions inside dispersed PS particles. These partitions are residues of the copolymer originally deposited at the interface of the primary PS particles, which aggregate during compression molding. On the other hand, SB copolymers with long PS blocks are located at the interface and partly inside the PS phase in the form of small particles, in which they are deposited already during melt mixing. Only SB4 (long diblock with low viscosity) displays both forms inside the PS phase, partitions and particles. The amount of the SB copolymer located at the interface and therefore its efficient usage as a compatibilizer are considerably influenced by the processing history in the case of copolymers with short PS blocks. Therefore, a change in the processing conditions can lead to a further increase in the compatibilization efficiency of these copolymers.

The obtained results show that the compatibilization efficiency based on the enhancement of tough-

ness cannot be predicted only on the basis of localization of the SB copolymer in the blend, that is, whether the copolymer forms partitions or small particles inside the PS dispersed phase or is partly dispersed in the matrix. In general, blends compatibilized with triblock SB copolymers display the highest toughness values, whereas copolymers with short PS blocks are more efficient than those with long PS blocks and the same number of blocks.

The rheological properties of the EPM and SB copolymers can affect the compatibilization efficiency of the EPM/SB system. SB copolymers with a low viscosity exhibit a high compatibilization efficiency with both types of EPMs, regardless of the EPM viscosity. In contrast, SB copolymers with a high viscosity are pronouncedly more efficient in combination with more viscous EPM. The addition of a mixture of SB copolymers with more viscous EPM to LDPE/PS (75/25) blends leads in all cases to a higher impact strength or at least the same tensile impact strength as the addition of the same amount of neat SB. The role of the viscosity of EPM and SB in their cooperative compatibilization will be the aim of a future study.

The authors thank I. Novotná and J. Pelcman for their help with the blend preparation and J. Mikešová for the viscosity measurements.

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