

Effect of Molecular Structure of Styrene–Butadiene Block Copolymers on Morphology, Rheological Properties, and Impact Strength of Polystyrene/Polyethylene Blends

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Received 26 July 2002; accepted 24 January 2003

ABSTRACT: The effect of molecular structure of six model styrene–butadiene (SB) block copolymers with various number of blocks and two lengths of styrene blocks on morphology, rheological properties, and impact strength of polystyrene (PS)/high-density polyethylene (PE) blends was studied. It was found that location of SB copolymers in the blends is determined by the length of styrene blocks. The length of styrene blocks has similar effects on impact

strength and linear viscoelastic properties of the blends. On the other hand, the correlation was not found between the effects of a number of blocks on impact strength and linear viscoelastic properties of the blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2303–2309, 2003

Key words: blends; compatibilization; block copolymers, polyethylene, polystyrene

INTRODUCTION

To improve end-use properties of an incompatible polymer blend, block copolymers with sequences chemically identical or similar to the blend components¹ are usually added. Styrene–butadiene (SB) and styrene–ethene-butene (SEB) block copolymers with a wide scale of molecular parameters are commercially available and, therefore, they are frequently used for compatibilization of polystyrene/polyethylene (PS/PE) and polystyrene/polypropylene (PS/PP) blends. Compatibilized PS/PE and PS/PP blends are of great practical interest, especially as materials for packaging with balanced mechanical and barrier properties. The effect of molecular parameters of SB block copolymers on their compatibilization efficiency in PS/PE and PS/PP blends was studied very intensively. It is impossible to cite all relevant papers here. The results are summarized in reviews.^{1–3} In spite of a number of studies, unexplained discrepancies still exist in the conclusions of various papers.

It follows from some studies that diblock copolymers are the most efficient compatibilizers.^{4–6} On the other hand, some authors refer to triblocks or multiblocks as more effective than diblocks.^{7–11} Recently, Chun and Han¹² made the conclusion that the compatibilization efficiency of SB and styrene–

ethene–butene (SEB) block copolymers in PP/PS and polyisoprene/PS blends is controlled by the temperature of their order/disorder transition. In accord with our previous studies concerning the compatibilization of PS/PP^{8,11,13} and polystyrene/polybutadiene (PS/PB)¹⁴ blends with SB copolymers, the length of styrene blocks and the number of blocks in copolymers are decisive parameters for their efficiency. It was shown that the effect of the styrene blocks length in PS/PP differs from that in PS/PB blends.¹⁵ Using the impact strength as a measure of compatibilization efficiency, SB block copolymers with styrene blocks shorter than the critical length for entanglement formation ($M \approx 18,000$) are more efficient for PS/PP blends than the copolymers with long styrene blocks. The opposite result was obtained for PS/PB blends. With regard to the number of blocks in copolymers, triblock copolymers were found to be more efficient compatibilizers than diblock and pentablock copolymers with the same block lengths for both PS/PP and PS/PB blends.

In most papers, the compatibilization efficiency was measured by the compatibilizer effect on the size of dispersed particles and on mechanical properties. Substantially less attention has been paid to the influence of SB copolymers on rheological properties of PS/PE and PS/PP melts,¹⁶ although correct values of the interfacial tension, determined from flow properties of immiscible polymer blends,^{17,18} showed high sensitivity of small-amplitude oscillatory experiments for evaluation of interface properties.

Recently, we studied the effect of mixing conditions on the morphology, impact strength and flow properties of PS/PE blends compatibilized with S–B diblock

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Grant Agency of the Czech Republic; 106/99/0555, 106/99/0556.

TABLE I
Molecular Characteristics of SB Copolymers

Mark	Type	$M_n \times 10^{-3}$ (kg/mol)	$M_w \times 10^{-3}$ (kg/mol)	PS _{theor} (wt %)	PS _{GPC} (wt %)
SB1	10S-60B	81	86	14.3	14.6
SB2	10S-60B-10S	73	78	25.0	25.6
SB3	10S-60B-10S-60B-10S	135	150	20.0	20.3
SB4	40S-60B	99	105	40.0	39.9
SB5	40S-60B-40S	117	129	57.1	57.7
SB6	40S-60B-40S-60B-40S	206	235	50.0	50.2

M_n : number-average molecular weight; M_w : weight-average molecular weight; PS_{theor}: target molar concentration; PS_{GPC}: PS concentration determined by GPC.

copolymer containing a short styrene block and with a S-B-S-B-S pentablock copolymer with long styrene blocks.¹⁹ It was found that 10 min of mixing is sufficient for the achievement of a steady morphology and properties of all blends under study. However, the morphology and properties of the blends compatibilized with the S-B diblock copolymer were dependent on the rate of mixing.

The main aim of the paper is to compare the dependences of morphology and impact strength of PS/PE/SB copolymer blends on the number of blocks in the copolymers and on the styrene block length with previous results for PS/PP/SB and PS/PB/SB blends. Another aim is to compare the effect of molecular structure of SB copolymers on impact strength and flow properties of PS/PE/SB blends.

EXPERIMENTAL

Materials

Atactic PS: Krasten 151, commercial product of Kaučuk a. s. (Kralupy, Czech Republic) $M_w = 330,000$, $M_n = 125,000$.

High-density PE: Liten MB 62, commercial product of Chemopetrol a. s. (Litvínov, Czech Republic) $M_w = 87,000$, $M_n = 12,000$, MFI (190°C, 21.2N) = 6 g/10 min, density 961 kg/m³.

Linear SB block copolymers, laboratory products of Kaučuk a. s. Theoretical molecular weight of butadiene blocks is 60,000 for all samples. Two sets of samples with theoretical molecular weight of styrene blocks 10,000 and 40,000 were used. All SB samples contain only very small amounts of copolymers with lower numbers of blocks and styrene homopolymers and they have very narrow molecular weight distribution. Their characteristics are collected in Table I. Detailed description of synthesis and characterization of SB copolymer can be found in Ref.¹⁴

Blend preparation

Binary blends containing 80 wt % of PS and 20 wt % of PE and ternary blends containing 76 wt % of PS, 19 wt

% of PE, and 5 wt % of SB copolymer were prepared by mixing the components in the chamber W 50 EH of a Brabender Plasticorder at constant temperature of the melt 190°C.²⁰ The melts were mixed at 120 rpm for 10 min. The blend specimens used for the determination of the impact strength, rheological measurements, and morphology were shaped from compression-molded plates prepared in a Fontijne press at 200°C and 3.1 MPa.

Electron microscopy

Ultrathin sections of the samples were prepared using Ultratome III (LKB, Sweden). Samples were sectioned at -140°C, the temperature sufficiently low to diminish the possibility of artifacts. After cutting, the sections were stained in OsO₄ vapor for approx. 2 h. For observation and micrographing, transmission electron microscopy (STEM) was used (transmission adapter to JSM 6400, JEOL, Japan).

Rheological measurements

Flow properties were measured on a rotational rheometer Rheometrics SYS 4 in dynamic mode, using parallel plate and coneplate geometries (radius 12.5 and 25 mm; cone angle 0.101 rad). The frequency sweep tests were carried out from 10⁻² to 10² rad/s at 190°C. The experiments were performed in the range of linear viscoelasticity and the deformation amplitude was kept small in order not to destroy the microstructure in studied heterogeneous melts.

Determination of tensile impact strength

The tensile impact strength, a_e , was determined at 23°C with a 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_e were determined as arithmetic means of the measurements on 12 specimens.

RESULTS AND DISCUSSION

Morphology

It was found in our preceding study¹⁹ that PS/PE/SB blends form during the mixing a phase structure which is very sensitive to small differences in manipulation with samples and to the rate of cooling of various parts of the sample. Therefore, quantitative evaluation of the size of dispersed particles of the minor phase cannot be done with needed precision for this system. A qualitative comparison of the phase structure of PS/PE (80/20) with PS/PE/SB1 (76/19/5) and PS/PE/SB6 (76/19/5) blends can be found in a previous paper.¹⁹ Moreover, internal structure of compatibilizers, which was successfully studied by X-ray scattering for PS/PP/SB and PS/PB/SB blends,¹⁵ is masked by long period of PE in PS/PE/SB blends.¹⁹ Therefore, we focused on differences between localization of various SB copolymers as studied by STEM.

It is clearly demonstrated in Figure 1 that in PS/PE/SB blends, the localization (distribution between the interface and bulk phases) of SB copolymers with short and long styrene blocks differs qualitatively. In blends containing SB with short styrene blocks (SB1–SB3), the PS–PE interface is covered with SB copolymers (black in Fig. 1). Further, a part of SB forms quite large particles. Most of these are localized at the interface. The morphologies of all the samples compatibilized with SB copolymers containing short styrene blocks were very similar; a slight difference was found only in the amount of SB copolymers localized in PE particles. On the other hand, a large part of SB copolymer is localized in small particles dispersed in the PS matrix and only a part of the PS–PE interface is covered with SB in blends containing SB with long styrene blocks (SB4–SB6). SB particles in PS are somewhat larger in blends compatibilized with SB6 than in blends compatibilized with SB4 or SB5. Qualitatively, the same dependence of the localization of SB copolymers on the length of their styrene blocks was found for PS/PP blends.¹⁵

Rheological properties

A 5 wt % addition of the used copolymers into the binary PS/PE blend resulted in an increase in the complex viscosity (η^*) and both dynamic moduli (G' , G''). The highest increase was found in viscosity values.

Figure 2 shows viscosity data for the binary blend and for blends compatibilized with the copolymers containing short styrene blocks (SB1–SB3). Similar flow properties were found for melts containing triblock copolymer SB2 and pentablock copolymer SB3. The highest values of complex viscosity and dynamic moduli (not reproduced here; cf. Ref.¹⁹) were obtained for the blend compatibilized with diblock

copolymer SB1. The short diblock seems to act as an anchoring agent for the studied PS/PE melts, allowing a better adhesion between the melted components. The idea could be supported by results concerning the size of dispersed particles in blends compatibilized with copolymers SB1–SB3. However, due to the above mentioned problems with quantitative evaluation of morphology of studied blends, to explain the measured high increase in viscoelastic data of the PS/PE/SB1 melt is difficult.

In the case of melts containing copolymers with long styrene blocks (SB4–SB6), only a small increase in the viscoelastic characteristics and no effect of the number of SB blocks was found. Within the experimental error, the blends compatibilized with the long diblock, triblock, and pentablock exhibit identical flow properties. The result corresponds with STEM micrographs of the discussed blends where the copolymers with long styrene blocks are not preferentially located between the blend components.

The effect of molecular weight of styrene blocks on flow properties of the blends compatibilized with diblock copolymers is shown in Figure 3. In comparison with the morphology of blends compatibilized with the copolymers containing short styrene blocks, higher values of the complex viscosity show better interface adhesion in the melt containing the diblock with a short styrene block.

Tensile impact strength

The results of measurements of the tensile impact strength, a_e , are collected in Table II. An admixture of all SB copolymers more or less improves impact strength of PS/PE blends. The blends compatibilized with triblock (SB2) and pentablock (SB3) copolymers with short styrene blocks have higher impact strength than those compatibilized with the related SB5 and SB6 copolymers containing long styrene blocks. The same result was found for PS/PP/SB blends.¹⁵ On the other hand, the PS/PE/SB4 (76/19/5) blend has somewhat higher impact strength than the PS/PE/SB1 (76/19/5) blend. However, the difference is not pronounced in comparison with the error of tensile strength measurement. Admixture of SB2 leads to a better improvement of impact strength than that of SB1 or SB3. This agrees very well with the results for PS/PP/SB and PS/PB/SB blends for which triblocks are more efficient compatibilizers than diblocks or pentablocks.¹⁵ On the other hand, the compatibilization efficiency of SB with long styrene blocks decreases with increasing number of blocks. This is somewhat surprising, because in PS/PP and PS/PB blends, the dependence of compatibilization efficiency of SB copolymers on their number of blocks was qualitatively the same for SB with short and long styrene blocks.

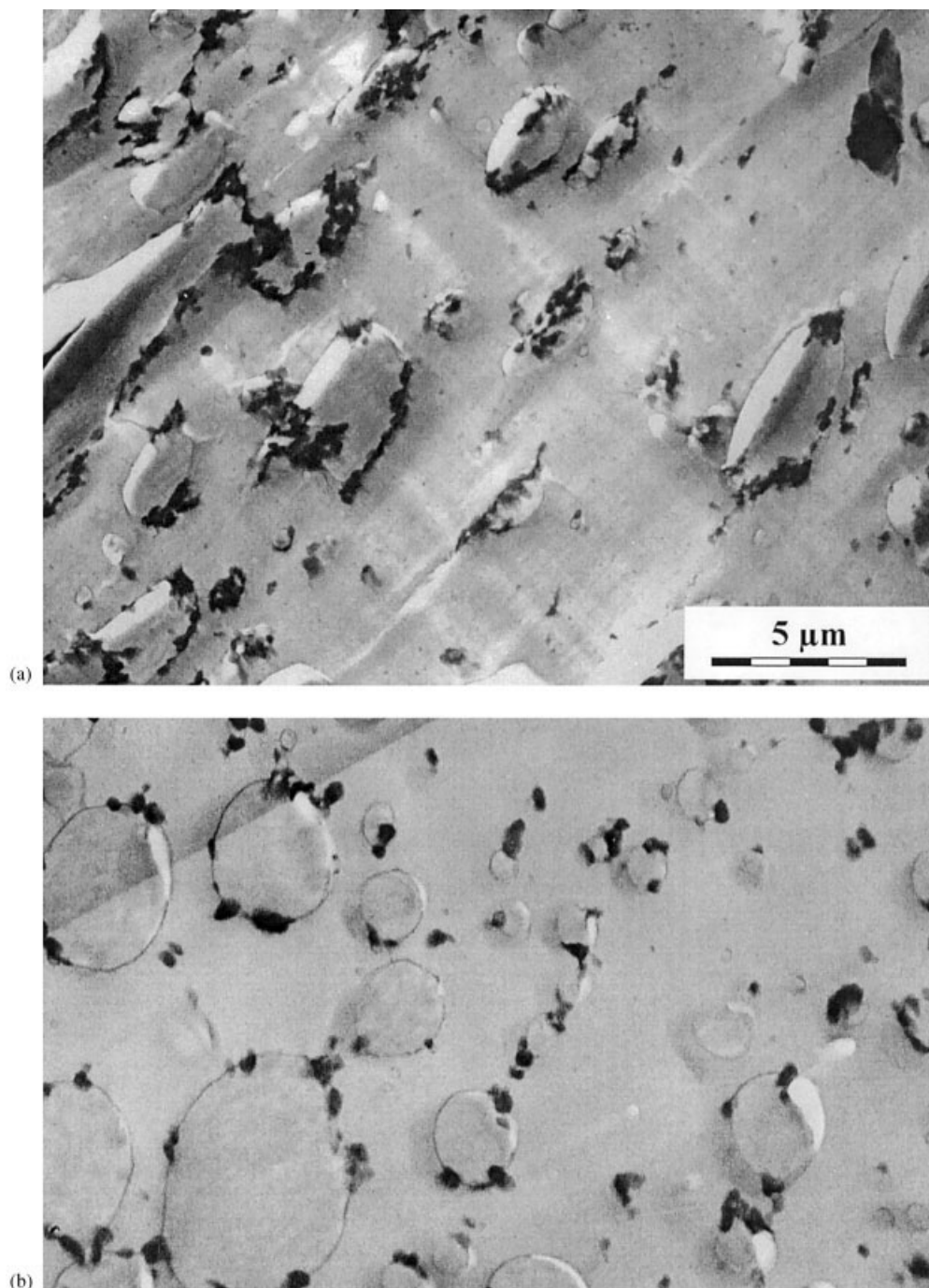


Figure 1 STEM micrographs of PS/PE/SB (76/19/5) blends compatibilized with (a) SB1, (b) SB2, (c) SB3, (d) SB4, (e) SB5, and (f) SB6.

General note

It should be mentioned that the study is focused on the dependence of morphology, impact strength, and flow properties of PS/PE/SB blends on the number of blocks and length of styrene blocks in SB copolymers. In addition to diblocks and triblocks, also the effect of pentablocks was studied because multiblocks were recognized as efficient compatibilizers for PS/PE⁷ and PS/PP⁸ blends. Moreover, the high efficiency of

multiblocks was predicted from thermodynamic considerations.²¹ The consequence of our choice of the set of SB copolymers is a strong difference in their PS/PB ratios (see Table I). It is well known that the PS/PB ratio strongly affects the bulk structure of SB copolymer. It cannot be *a priori* excluded that the PS/PB ratio is one of the parameters controlling the effect of SB on the structure and properties of PS/PE/SB blends. On the other hand, it seems from thermodynamic analysis

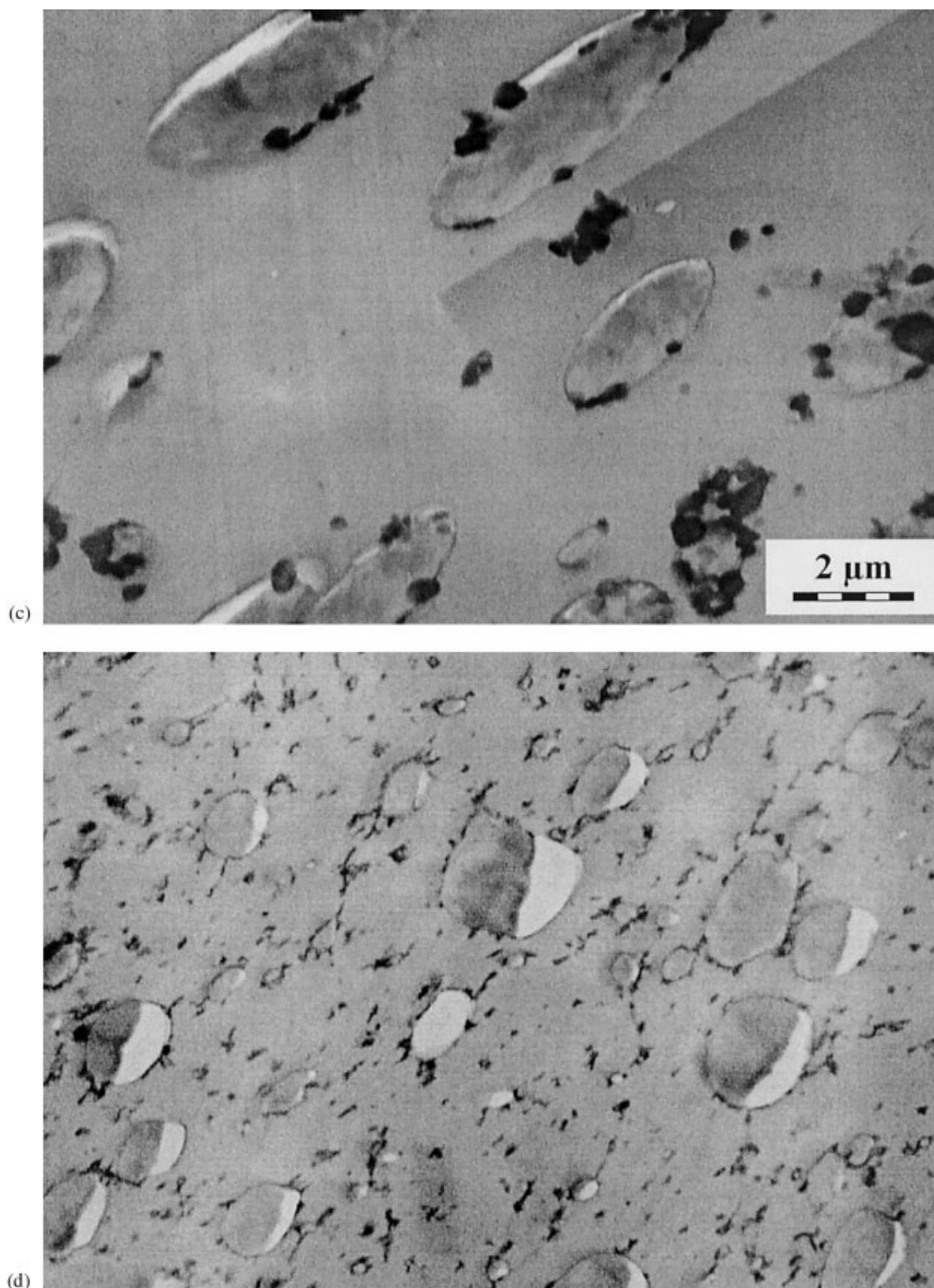


Figure 1 (Continued from the previous page)

that the distribution of a block copolymer between the interface and bulk phases is determined by the ratios of the block length and the related blend components and their interaction parameters.²² The direct effect of the ratio of plastic PS and rubbery PB in SB copolymers on the impact strength of PS/PE/SB blends should be apparently stronger than that on their morphology and flow properties. However, we did not find correlation between the tensile impact strength of PS/PE/SB blends and the PS/PB ratio in SB copolymers (cf. Tables I and II). Therefore, we believe that

the above interpretation of the effect of molecular structure of SB copolymers on structure and properties of PS/PE blends is plausible.

CONCLUSIONS

The localization of SB block copolymers in PS/PE/SB blends is strongly affected by molecular weight of styrene blocks in the copolymer. The copolymers with short styrene blocks are preferentially located at the

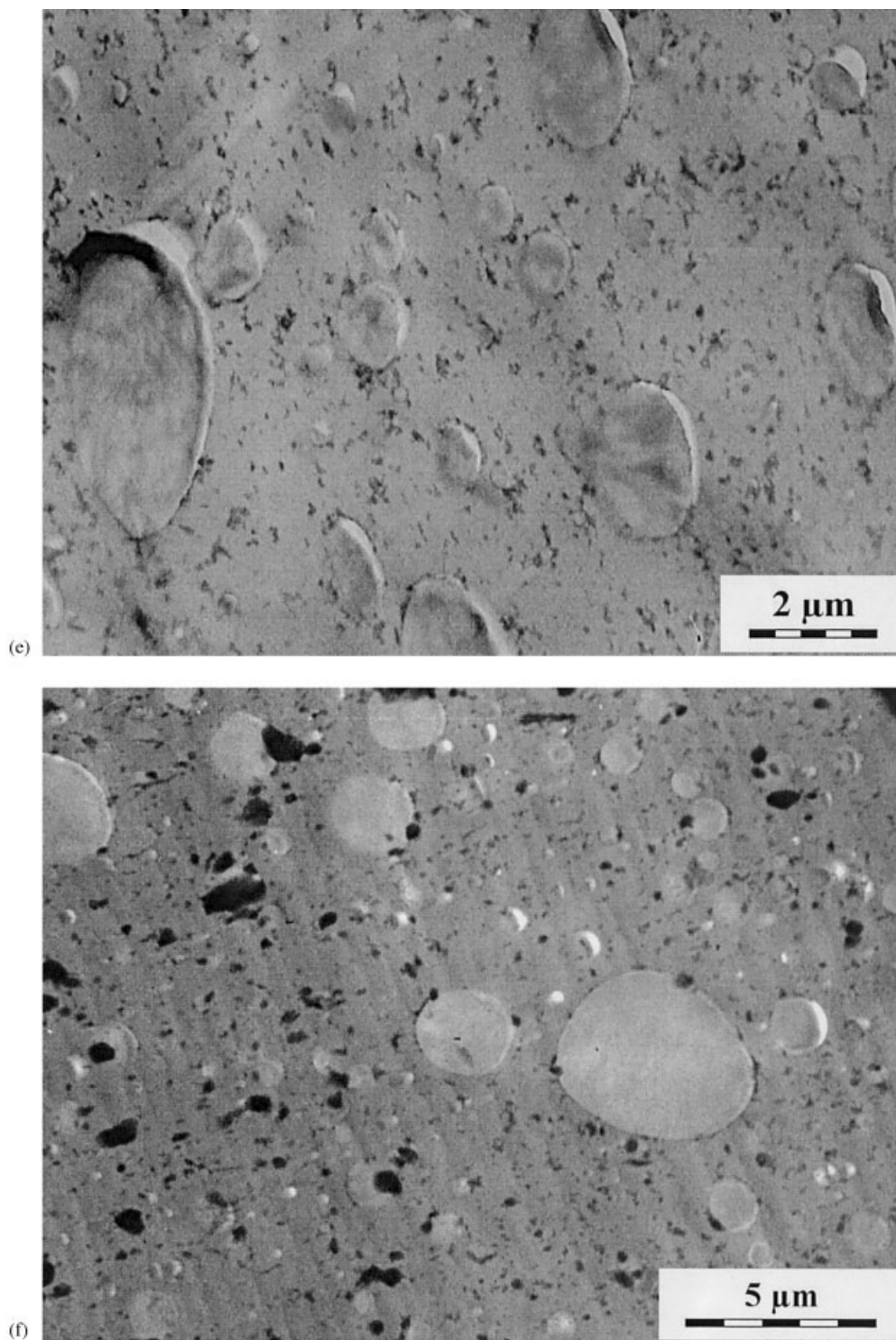


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interface, the copolymers with long styrene blocks are mostly located in the PS phase.

A correlation between the localization of block copolymers in the interface layer and linear viscoelastic characteristics of PS/PE/SB melts was observed. The highest values of complex viscosity and dynamic moduli were measured for the melt containing the diblock with short styrene blocks.

A higher tensile impact strength was found for the blends compatibilized with the copolymers containing short styrene blocks rather than with those containing long styrene blocks. With the copolymers with short styrene blocks, addition of the triblock led to the best improvement of the impact strength. The effect of SB copolymers with long styrene blocks on the impact strength decreased with their number of blocks.

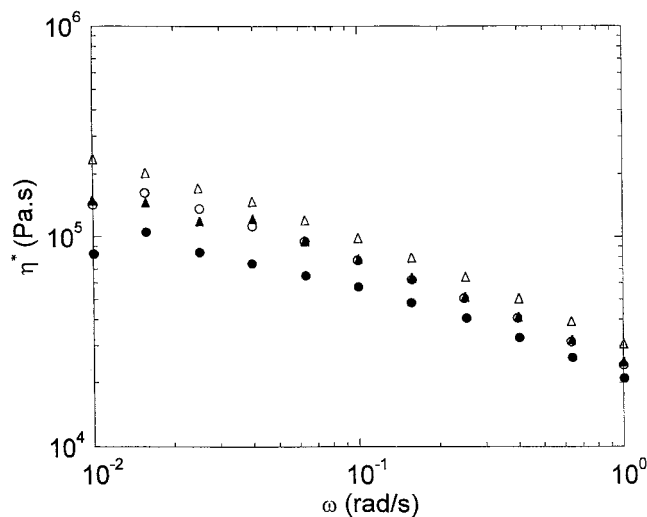


Figure 2 The dependence of complex viscosity on the angular frequency for PS/PE melts: without compatibilizer (●) and with 5 wt % of copolymers containing short styrene blocks: diblock SB1 (△), triblock SB2 (○), pentablock SB3 (▲).

The effects of the length of styrene blocks on linear viscoelastic properties and tensile impact strength of PS/PE/SB blends are in accordance. However, a discrepancy exists between the effects of the block number on the properties.

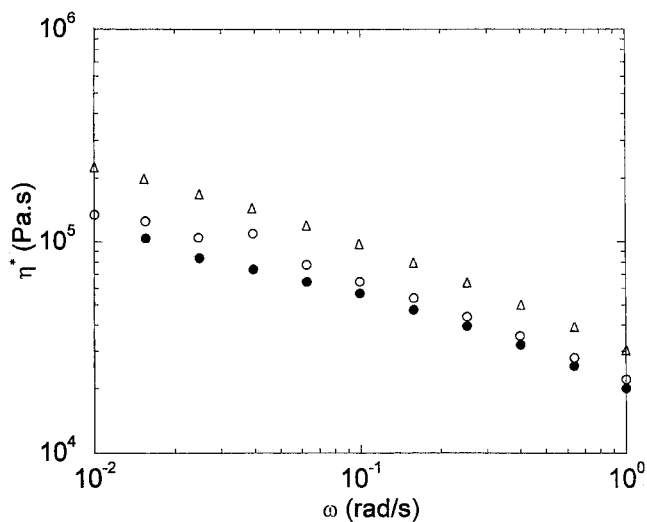


Figure 3 The dependence of complex viscosity on the angular frequency for PS/PE melts: without compatibilizer (●), with 5 wt % of short diblock SB1 (△), and with 5 wt % of long diblock SB4 (○).

TABLE II
Tensile Impact Strength of PS/PE (80/20) and PS/PE/SB (76/19/5) Blends

Compatibilizer	a_e (kJ/m ²)
—	13.1
SB1	26.6
SB2	36.3
SB3	18.0
SB4	29.1
SB5	21.7
SB6	16.6

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