

In summary, this experiment and its analysis illustrate how basic transport measurements can be used to clarify the physical composition of composite materials.

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Molecular Design of Multicomponent Polymer Systems. III. Comparative Behavior of Pure and Tapered Block Copolymers in Emulsification of Blends of Low-Density Polyethylene and Polystyrene

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Synopsis

Poly(hydrogenated butadiene-*b*-styrene) copolymers are very effective emulsifiers for blends of polystyrene and low-density or high-density polyethylene. It is shown that the extent of improvement in mechanical properties is dependent not only on the molecular weight but also on the structure of the diblock copolymer. A comparative study of the morphology and the mechanical behavior of modified low-density polyethylene/polystyrene blends demonstrates that a tapered diblock is more efficient than a pure diblock with the same composition and molecular weight. It is assumed that the unique behavior of the tapered sample results from its particular miscibility characteristics at the blend interface. The tapered copolymer could behave essentially as a solubilizing agent for the homopolymers at the interface and provide a "graded" modulus responsible for the improved mechanical response of the material.

INTRODUCTION

We have previously reported the beneficial effect of poly(hydrogenated butadiene-*b*-styrene) copolymers (hPB-*b*-PS) on the morphology and mechanical behavior of blends of low-density or high-density polyethylene and polystyrene.^{1,2} Moderate amounts (ca. 3%) of diblock copolymers strongly reduce the particle size of the blends, whatever their composition; furthermore, they stabilize the cocontinuous two-phase structure displayed by PS-rich blends. Both strength (σ_B) and ductility (ϵ_B) of blends are markedly improved and a real synergism is observed in the strength of PS-rich blends. These results support unambiguously the surface activity and the anchoring efficiency of these polymeric emulsifiers. The extent of improvement was found to be largely dependent on the molecular weight of the diblock copolymer.¹ However, even short-block copolymers appeared to be more efficient than longer grafted ones. Similarly, we have observed the superiority of the diblock over the triblock PS-hPB-PS copolymer in improving both σ_B and ϵ_B .³ Undoubtedly, the molecular structure is a key criterion in designing the most efficient emulsifier.

For diblock PB-PS copolymers, the possibility exists of generating two types of sequential distribution, according to the conditions of the anionic copolymerization. While the classical two-step process gives rise to a pure diblock, a so-called tapered block is obtained by polymerizing a mixture of the two monomers in a hydrocarbon solvent.⁴⁻⁶ The higher reactivity of butadiene promotes the formation first of an essentially pure polybutadiene chain, which upon further

growth and butadiene depletion incorporates more and more styrene, until a practically pure PS segment is formed. As a result, a more or less random copolymer section forms the transition between PB and PS blocks.

It is of interest to examine whether this difference in molecular structure has any significant effect on the emulsifying activity of the copolymer. In this paper, we compare the morphology and mechanical behavior of melt-blended low-density polyethylene/polystyrene (LDPE/PS) materials, modified by the addition of a tapered diblock (SE-4) or a pure diblock copolymer (SE-5). Copolymers SE-4 and SE-5 have the same composition and total molecular weight.

EXPERIMENTAL

The tapered block copolymer SE-4 ($\bar{M}_n = 80,000$) was prepared by polymerizing a mixture of equal amounts of butadiene and styrene in toluene at 40°C for 12 h (sec-BuLi initiation). After oxidative degradation of the PB chains in the presence of osmium tetroxide,⁷ pure PS was recovered and amounted to 33 wt % of the whole copolymer. The \bar{M}_n of this PS block was found to be 26,000 as measured by gel permeation chromatography. If the transition zone is assumed to contain equimolar amounts of butadiene and styrene, the copolymer can be described by the sequence of partial molecular weights 26,000-22,000-32,000 for PS-(PS/PB)_{random}-PB.

The pure diblock copolymer SE-5 ($\bar{M}_n = 80,000$) was prepared by the usual two-step copolymerization of the monomers used in equal amounts. Styrene was first polymerized in toluene at room temperature for 6 h with sec-BuLi as initiator; butadiene was added after complete consumption of the first monomer and allowed to polymerize for 12 h at 40°C. Further hydrogenation of the PB chains was performed with Ziegler-type catalysts.⁸

The homopolymers used in this study were a low-density PE, Alkathene XDG 33 from ICI ($\bar{M}_n \approx 40,000$), and a general-purpose PS, Polystyrol 158 K from BASF ($\bar{M}_n \approx 100,000$).

Samples of different compositions were melt blended with 9%* of each block copolymer on a laboratory two-roll mill at 210°C for 5 min. The mixtures were thereafter compression molded (under 2500 psi at 200°C for 5 min) into sheets from which tensile test specimens (DIN 53448) were machined. Control samples without the copolymer were subjected to the same treatment.

Stress-strain measurements were performed on an Instron tensile tester at a crosshead speed of 2 cm/min.

The morphology of the blends was investigated by optical microscopy. Sections 5 μ thick were observed under natural light after selective staining of PS phases using a technique developed in our laboratory.⁹ Fracture surfaces prepared at room temperature were also observed by scanning electron microscopy (Philips PSEM 501-B).

* Similar results can be obtained with lower proportions of block copolymer but this parameter has not yet been optimized.

RESULTS AND DISCUSSION

In agreement with previously reported results,^{1,2} the addition of a pure or a tapered (hPB-*b*-PS) copolymer greatly reduces the microphase size in low-density polyethylene-polystyrene (LDPE/PS) blends at every composition (Fig. 1). The surface activity of these diblock copolymers in polyethylene-polystyrene blends is therefore a quite general feature, whatever their molecular and structural characteristics. However, the PE-rich blends exhibit a finer dispersion of PS particles in a LDPE matrix when modified with the tapered SE-4 than with the pure SE-5 diblock copolymer (Fig. 1). Less significant differences are observed in the cocontinuous two-phase morphology of the modified PS-rich blends.

Tensile mechanical properties of pure and modified blends are presented in Figure 2. The experimental data for the blends modified with a diblock copolymer are arbitrarily extrapolated to those of pure LDPE and PS, respectively.

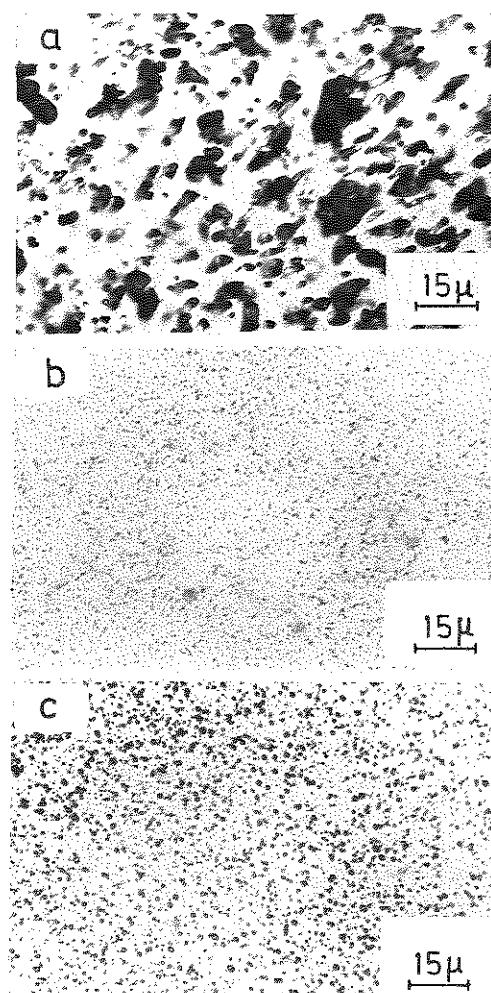


Fig. 1. Optical micrographs of 80 PE/20 PS blends: (a) no copolymer, (b) with 9% SE-4, (c) with 9% SE-5.

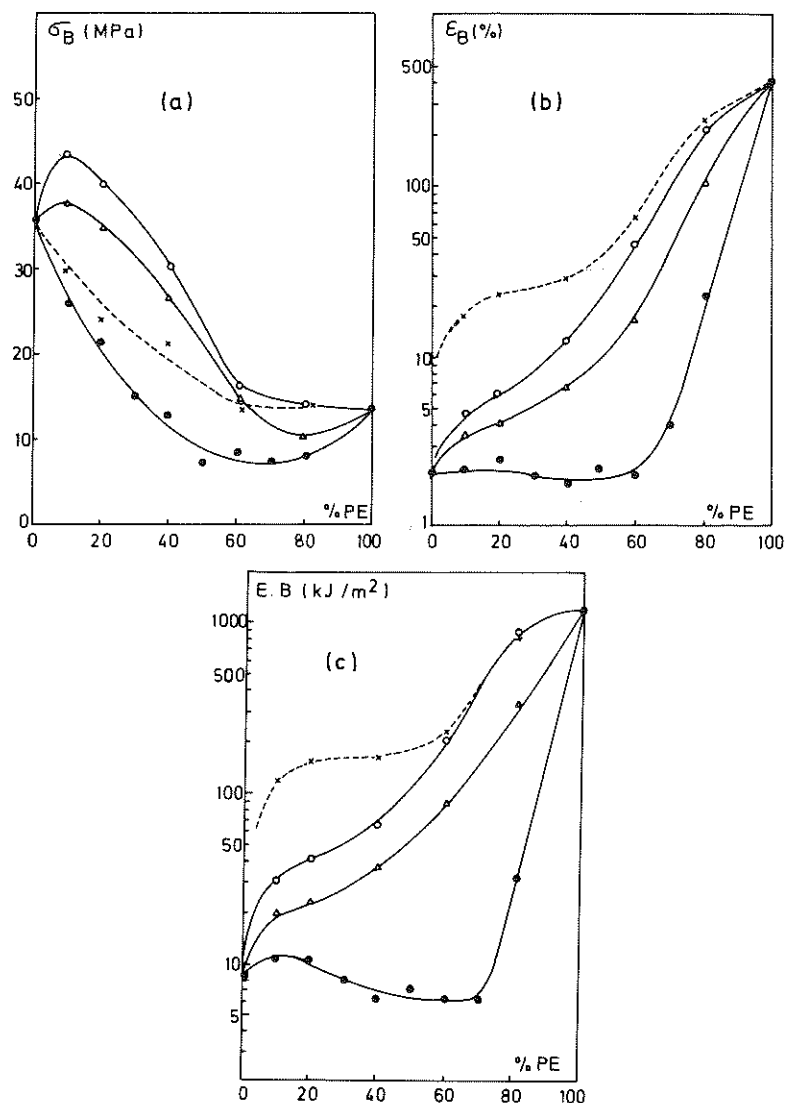


Fig. 2. (a) Ultimate tensile strength σ_B , (b) elongation ϵ_B at break, and (c) energy EB to break (area under the stress-strain curve at break) for LDPE/PS blends: (●) without copolymer, (○) with 9% SE-4, (△) with 9% SE-5, and (×) with 9% SE-2. Every point is the average of 8–12 measurements.

In that respect, the copolymer has been assumed to be a linking agent for the binary blends, rather than a third component. Nevertheless, the mechanical behavior of each homopolymer is certainly altered by the addition of the copolymer in a way which could provide information about the mechanism of modifications in the LDPE/PS blends. Therefore the mechanical characteristics of each homopolymer blended with a hPB-*b*-PS copolymer will be investigated in the near future. In order to allow a comparison of the effectiveness of the copolymers studied here with that of a previously reported high-molecular-weight copolymer SE-2 (pure diblock hPB-*b*-PS, $\overline{M}_n = 155,000$),¹ data for it have been

included in Figure 2. In spite of the shorter block lengths than in SE-2, the copolymers SE-4 and SE-5 generally exhibit marked effects on the mechanical properties of LDPE/PS blends. The superiority of the tapered SE-4 over the pure SE-5 diblock is a general feature. SE-4 gives rise to the highest strength in both PS- and PE-rich blends, even when the effect of SE-2 is considered [Fig. 2(a)]. In particular, the minimum in the σ_B curve disappears at the 80 PE/20 PS composition and strength close to that of pure PE is recorded in this range. SE-4 is also responsible for a significant synergism in σ_B in blends containing 20% PE or less; such an effect is not observed with SE-2. Moreover, a greater improvement in ductility is obtained at every composition when SE-4 is used instead of SE-5. Finally, the superiority of SE-4 over SE-5 is unambiguously demonstrated when the total energy to break EB is considered [Fig. 2(c)]. EB values more than twice those reported with SE-5 are recorded at every composition. It is noteworthy that the efficiency of the tapered SE-4 copolymer is similar to that of the high-molecular-weight material SE-2 in improving both strength and ductility of the 80 PE/20 PS blend. All these results suggested that the emulsifying ability of diblock copolymers in polymer blends depends more on their molecular structure than on their block length.

As already discussed,^{1,2} the significant increase in both strength and elongation of the modified PS-rich blends is due not only to the improvement of the interfacial adhesion but also to the interlocked-phase morphology. This type of behavior has also been reported for some IPNs.¹⁰ If the low-modulus PE component were dispersed as discrete particles anchored into a PS matrix, a mechanical behavior close to that of a classical toughened PS would be expected, i.e., a higher elongation but a lower strength than those of the pure PS.¹¹ PS-rich blends containing the copolymer SE-2 behave in this way despite a morphology apparently similar to that observed when SE-4 or SE-5 is used as modifier. This conclusion suggests subtle but definite differences in the cocontinuous two-phase morphology of the modified PS-rich blends, in relation to the molecular characteristics of the polymeric emulsifiers. Attempts to explain this situation are in progress.

To gain further insight into their morphology, the 20 PE/80 PS blends added with SE-4 and SE-5 were fractured at room temperature and the fracture surfaces examined by scanning electron microscopy. The response of the blends to applied stress is found to be quite similar. Craze and shearing both contribute to deformation of the samples [Figs. 3(a),(b)]. Adhesion between the phases is also evidenced in both cases. Closer examination reveals, however, that the tapered copolymer provides stronger adhesion than does the pure diblock. Consequently, the former stabilizes a more homogeneous interlocked structure [Fig. 4(a)], whereas the latter enables the coalescence of some PE domains into discrete particles more weakly bonded to the PS [Fig. 4(b)]. These morphological results together with optical microscopy observations are consistent with the superiority of the tapered copolymer in improving the mechanical properties of the LDPE/PS blends. Defects in the interfacial region which appear more frequently when a pure diblock is used would therefore promote earlier rupture of the sample.

The apparently lower interfacial activity of the pure diblock SE-5 compared to that of the tapered SE-4 copolymer could mean that a larger part of the former solubilizes or forms its own domains in one or the other homopolymer phase. It

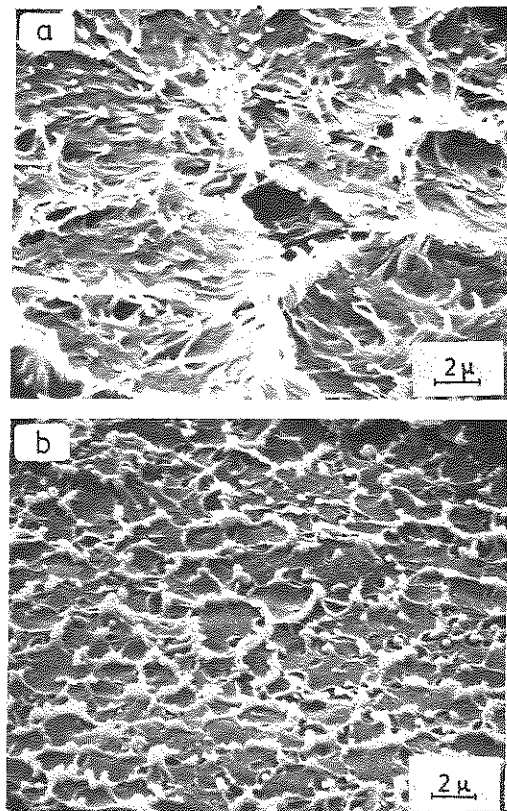


Fig. 3. Scanning electron micrographs of the room-temperature fracture surface of a 20 PE/80 PS blend with 9% SE-5 exhibiting both microshear (a) and crazing (b). The SE-4-modified blend displays similar behavior.

is well known that block copolymers containing highly incompatible sequences segregate into distinct domains in which very little mixing occurs.¹² This supramolecular structure can persist even in the melt (at least partly) well above the glass transition temperature of the two partners.^{13,14} As a result, the melt viscosity of a block copolymer is much higher than that of a homopolymer with the same molecular weight.^{13,14} Accordingly, high temperature and high shear rate are necessary to disrupt the domains and to allow the copolymer chains to be dispersed at the blend interface. In other words, the driving force for domain formation limits the emulsifying activity of the copolymer. Reducing the "blockiness" of the diblock copolymer by formation of a tapered structure enhances the mixing of the two blocks.¹⁵ As a result, the tendency of the tapered copolymer to form domains in the melt is reduced. Tsukahara et al.¹⁵ observed that the weakening of the repulsive interactions between the blocks causes the critical temperature of miscibility T_c to be much lower for a tapered structure than for the corresponding pure diblock. For instance, these authors demonstrated by SAXS measurements that the melting of the microphases into a homogeneous mixture occurred around 170°C for a tapered PS-*b*-PIP copolymer ($\bar{M}_n = 43,000$), whereas it appeared only well above 220°C for the corresponding pure diblock. Therefore, thermodynamic arguments could be proposed to ex-

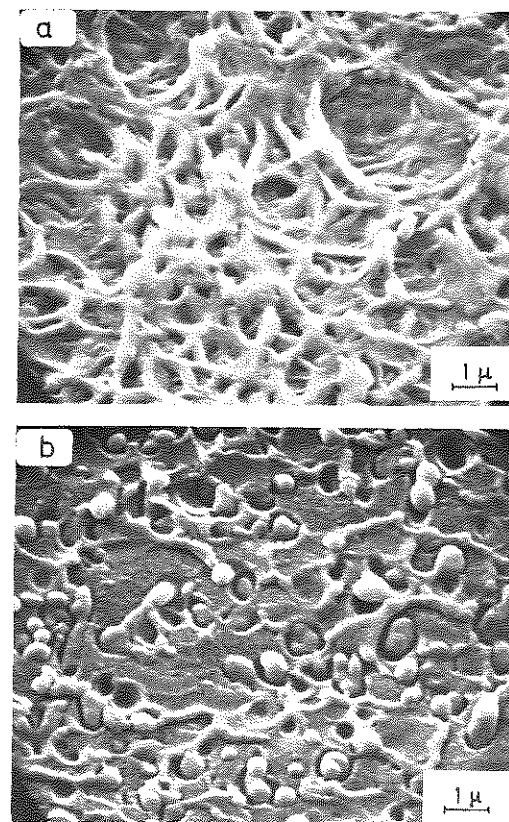


Fig. 4. Scanning electron micrographs of the room-temperature fracture surface of a 20 PE/80 PS blend with 9% SE-4 (a) and 9% SE-5 (b).

plain, at least partly, the difference in the interfacial activity of the tapered SE-4 and pure SE-5 diblock copolymers. Nevertheless, kinetic parameters could also contribute to the difference in emulsifying effectiveness. In that respect, the melt-flow indices (MFI) of SE-4 and SE-5 are, respectively, 3.13 and 0.23 g/10 min (210°C, 17,185 kg). A more complete evaluation of the melt-flow behavior of these samples is in progress; however, these MFI values are already significant as they indicate that at the same molecular weight the tapered copolymer has a much higher MFI, i.e., a lower melt viscosity, than the pure diblock copolymer. As all the blends are prepared under the same conditions, the less viscous tapered SE-4 sample is expected to disperse more easily in the LDPE/PS mixtures than SE-5. In this respect, it would be meaningful to estimate the effect of a longer mixing time or melt blending at higher temperature or shear rate on the interfacial activity of SE-4 and SE-5 copolymers.

When the melt viscosity of the pure and tapered copolymers is discussed, the question arises as to what would happen if these polymeric emulsifiers were of different molecular weight but the same viscosity. Useful information can be found in the comparison of the tapered SE-4 copolymer ($\bar{M}_n = 80,000$ and MFI = 3.13 g/10 min) with the pure diblock copolymer SE-1 ($\bar{M}_n = 58,000$ and MFI = 3.77 g/10 min), the behavior of which has been previously investigated under

the same experimental conditions.¹ The copolymer SE-1 behaves just like the pure diblock SE-5, but unlike the tapered SE-4 sample. Therefore the efficiency of the studied emulsifiers is surely not controlled by their melt viscosity, at least under the present conditions of melt blending.

It could be assumed that a partial coalescence of the pure copolymer SE-5 takes place at the interface during the compression molding of the roll-milled blends. This situation would lead therefore to the formation of PE and PS phases tied together only at a few points, as shown in Figure 4(b). In the tapered copolymer, the intermediate, more or less random block would prevent the rearrangement of the emulsifier at the blend interface, and allow the stabilization of a diffuse interface between pure PE and PS phases. Thanks to its molecular structure, the tapered copolymer would act as a solubilizing agent for the homopolymers in the interfacial region rather than as an effective anchoring agent. A large transition zone with a modulus intermediate between the low modulus of PE and the high modulus of PS can favorably decrease the stress concentration around the dispersed domains and induce the improved response of blends to the applied stresses. The beneficial effect of such a "gradual" modulus at an interface has been demonstrated in thermoplastics reinforced with mineral fillers.¹⁶

Additional investigations are certainly in order to sharpen the arguments proposed in this article. The characterization of the morphology of blends at different stages of mixing and after suitable thermal treatments is desirable. The localization of the copolymer in the blends is of course of prime importance. Finally, dynamic mechanical investigations of selected blends could provide information on the characteristics of sufficiently developed interfacial regions.

Whatever the results of further investigations, it is evident that the versatile catalytic synthesis of PB-*b*-PS copolymers* offers a unique and very attractive route towards the modeling of an emulsifier for PE/PS blends. Thanks to the present results, further optimization of properties can be expected upon adjusting the length of both pure and transition blocks of tapered copolymers.

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* See also the results obtained with a hydrogenated PB-*b*-PS copolymer obtained by coordination polymerization with bis(trifluoroacetato-nickel allyl) complex.¹⁷

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