Molecular Design of Multicomponent Polymer Systems. VII. Emulsifying Effect of Poly(ethylene–b–styrene) Copolymer in High-Density Polyethylene/Polystyrene Blends

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Synopsis

Poly(butadiene–b–styrene) copolymers containing a pure 1,4-PB block have been synthesized by a "living" coordination process. The complete hydrogenation of the PB chain leads accordingly to a high-density polyethylene (HDPE) block. The emulsifying efficiency of such a copolymer (H-7) in HDPE/PS blends is compared with that of a previously reported poly(ethylene–butene–b–styrene) copolymer (SE-7) obtained by the PB hydrogenation of an anionically prepared PB–b–PS. Microscopy examinations demonstrate unambiguously the interfacial activity of both copolymers in HDPE/PS blends. The tensile mechanical properties of the blends are significantly but also differently modified by the two emulsifiers. The copolymer H-7 gives rise to the highest strengths, but, contrary to the copolymer SE-7, provides a poor ductility to the blends. This different behavior is assumed to result in part from the different characteristics of the hydrogenated PB blocks. The elastomeric HPB chain of SE-7 should form at the interface a more or less extended soft zone whereas a rigid interface would result from the cocrystallization of the HPB chain of H-7 with the HDPE homopolymer.

INTRODUCTION

Well-designed block copolymers can act as efficient emulsifiers bridging the "compatibility gap" which exists in many polymer blends.[1,2] In that context, current research in our laboratory has demonstrated the beneficial influence of moderate amounts (as low as 1–2%) of a suitable diblock copolymer [i.e., poly(hydrogenated butadiene–b–styrene), or HPB–b–PS] in blends of polystyrene with low or high-density polyethylene (LD or HDPE/PS). It reduces significantly their particle size, improves interfacial adhesion, and markedly enhances their tensile mechanical properties[3-5]: These results clearly demonstrate the important interfacial activity of the macromolecular emulsifier.

It is to be noted, however, that the HPB–b–PS copolymers used up to now were obtained from anionic block copolymerization of styrene and butadiene, using s-butyllithium as an initiator in toluene solution; accordingly, the PB chains contain ca. 10% of 1.2 vinyl-type units and further hydro-

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genation leads to the formation of a poly(ethylene–co–butene) block quite similar to some linear low-density polyethylenes.

Recently, we succeeded in synthesizing PB–PS diblock copolymers by a "living" coordination process,[6-8] that leads to a pure 1,4-PB chain (ca. 1 mol % of 1.2 units); upon complete hydrogenation, it yields therefore a block whose characteristics are very close to those of a HDPE with approximately less than 5 ethyl branches per 1.000 carbon atoms. It was thus of obvious interest to examine the performances of such a copolymer as emulsifier for HDPE/PE blends, in comparison with an already efficient, anionically prepared HPB–b–PS.

EXPERIMENTAL

The 1,4-PB-b–PS copolymer was prepared using a bis(η^3-allyl trifluoroacetato nickel) catalyst $(ANiTFA)_2$; the *cis*-1,4-polybutadiene chain was synthesized first at 25°C using a chloranil/$(ANiTFA)_2$ molar ratio equal to 0.5 and a low nickel concentration (5×10^{-3} mol L^{-1}) in toluene solution. Butadiene polymerization was stopped at the desired conversion by distillation of the residual monomer; styrene monomer was added in the medium together with a further amount of ligand, and allowed to polymerize between -10 and 0°C. Infrared analysis, ^{1}H-NMR, GPC, and fractionation experiments before and after hydrogenation clearly proved that a *cis*-1,4-PB–b–PS block copolymer had been obtained in at least 75% yield.

Details of that procedure are published elsewhere[6-8]; the particular sample used throughout this study (H-7) has the following molecular characteristics: 1,4-PBD block, 39.000/PS block, 10.400. It was compared with a PB–b–PS (SE-7) prepared by *s*-BuLi-initiated polymerization of an equimolar mixture of butadiene and styrene monomers in toluene: A "tapered" structure is so obtained,[9] where a more or less random copolymer section forms an important transition (ca. 22,000 $\overline{M}_n$) between PB (26,000 $\overline{M}_n$) and PS (22,000 $\overline{M}_n$) pure blocks.

Further hydrogenation of the PB segments of both H-7 and SE-7 was performed using a Ziegler-type catalyst.[10] The blends were prepared on a laboratory two-roll mill using a HDPE Eltex B2008 from Solvay ($\overline{M}_n$ = 18,000, $\overline{M}_w$ = 190,000) and a PS Polystyrol 158 K from BASF ($\overline{M}_n$ = 100,000). Processing conditions were chosen as 5 min at 200°C, providing for reproducible results; the added block copolymer (9 wt %) was mixed first with the minor component (1 min). Tensile bars were machined from sheets prepared by compression molding at 200°C for 5 min. Stress–strain measurements were performed at room temperature on DIN 53.448 specimens with an Instron instrument at a crosshead speed of 2 cm min^{-1}; each value is the average of 4–6 experiments. Control samples without copolymer were also prepared and submitted to the same treatment. The morphology of the blends was investigated by optical microscopy. Sections 5 μm thick were observed under natural light after selective staining of PS phases using an original technique developed in our laboratory.[11]

Fracture surfaces prepared at liquid nitrogen temperature were also observed by scanning electron microscopy (Philips 501-B).

RESULTS AND DISCUSSION

As already mentioned, HDPE and PS form highly incompatible mixtures which undergo macrophase separation [Fig. 1(a)]. Addition to the blends of either the anionically prepared block copolymer (SE-7) or the linear sample (H-7) markedly reduces their particle size as shown by Figures 1(b) and (c). That effect is observed at every composition. PE-rich blends exhibit a fine dispersion of PS particles in a HDPE matrix whereas a practically cocontinuous two-phase structure is stabilized by the emulsifier in PS-rich blends (up to 80–90 wt % PS). These results demonstrate unambiguously the interfacial activity of both emulsifiers in HDPE/PS blends. However, the optical micrographs also put in evidence that the SE-7 copolymer promotes a somewhat finer dispersion of the phases than does the H-7 copolymer.

Tensile mechanical properties of the blends are presented in Figure 2. As expected, those containing no copolymer exhibit a poor mechanical behavior, and are indeed brittle at every composition. Both SE-7 and H-7 emulsifiers modify significantly, but also differently the behavior of these blends. The H-7 copolymer gives rise to the highest strength (σ_Y or σ_B) except for the 20 PE/80 PS blend, and a significant synergistic effect is to be noted in the 30–60 wt % PE composition range. However, the samples remain rather brittle, as much as the pure blends (low ϵ_B values). On the other hand, the SE-7 copolymer improves significantly the ductility of the blends, whereas σ_B is only moderately increased.

Scanning electron microscopy of fracture surfaces prepared at liquid nitrogen temperature demonstrates that both block copolymers greatly improve the adhesion between the phases (Figs. 3–4).

No significant difference was observed in the morphology of the PS-rich blends (20 PE/80 PS) modified by either copolymer. Considering the HDPE-rich blends (80 PE/20 PS), we observe that both the matrix and the dispersed PS particles are fractured when the samples contain an emulsifier, whereas the PS particles remain unbroken in pure blends [compare Fig. 3(a) with

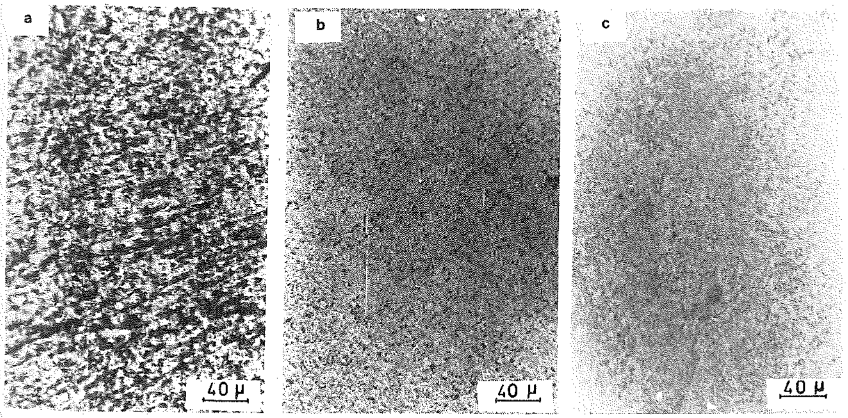

Fig. 1. Optical micrographs of 80 HDPE/20 PS blends: (a) no copolymer, (b) with 9% H-7, (c) with 9% SE-7. PS phases are dark area.

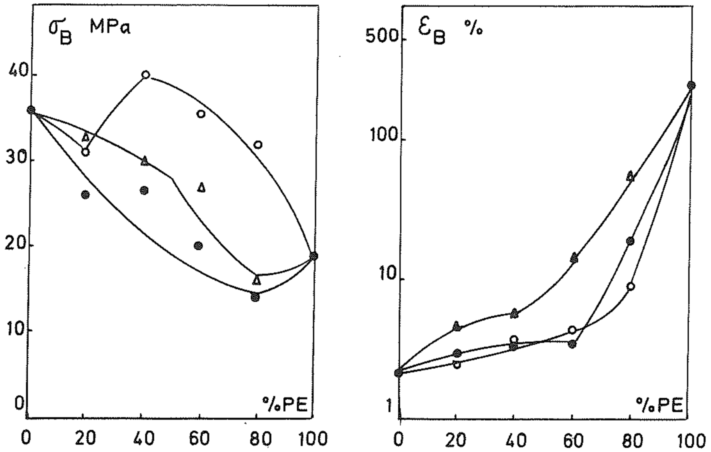

Fig. 2. Ultimate tensile strength (σ_B) and elongation at break (ϵ_B) of HDPE/PS blends: (●) no copolymer, (○) with 9% H-7, (△) with 9% SE-7.

Fig. 3(b) or 3(c)]. This situation is consistent with a strong anchoring of the two phases provided by both copolymers. However, the fracture surfaces of the so emulsified blends appear to be rather different depending on the choice of H-7 or SE-7. PE and PS phases are essentially intermingled in the SE-7 modified blend [Fig. 4(a)] whereas the H-7 modified sample exhibits well separated PS particles in the PE matrix [Fig. 4(b)].

Additional studies are needed to fully explain these different morphologies and to correlate them with the mechanical response of the two types of blends. However, it is obvious that their different behavior must result in part from the different characteristics of the HPB blocks. In copolymer SE-7, that block is a poly (ethylene–co–butene) chain with a low crystalline content ($\simeq$ 10%) exhibiting an elastomeric behavior and linked to PS through a tapered block (soft). Hence, it should form at the blend interface a more or less extended soft zone having a lower modulus than that of the HDPE component.

This situation could be responsible for the more ductile response of the material to applied stress. In particular this morphology would allow the sample to yield at a moderate stress level (even lower than that of pure HDPE) and further to stretch up to a high extent (50%). On the contrary, the linear HPB block of the H-7 copolymer has the main characteristics of a HDPE, the interactions of which with the HDPE component must therefore be much better than in the former case. The expected cocrystallization of that block with the HDPE homopolymer at the blend interface would provide for a stronger anchoring of the phases than with the SE-7 copolymer. The so-modified and rigid interface region could be responsible for the higher strength but low ductility of the sample.

However, this latter interpretation has obvious limitations, since one has also to consider the short PS block length in H-7 (due to β-elimination transfer reactions in styrene polymerization by η^3-allyl nickel complexes). It is indeed too short ($\overline{M}_n$ = 10,400) to provide efficient anchoring through entanglements with homo-PS (critical entanglement length for PS being

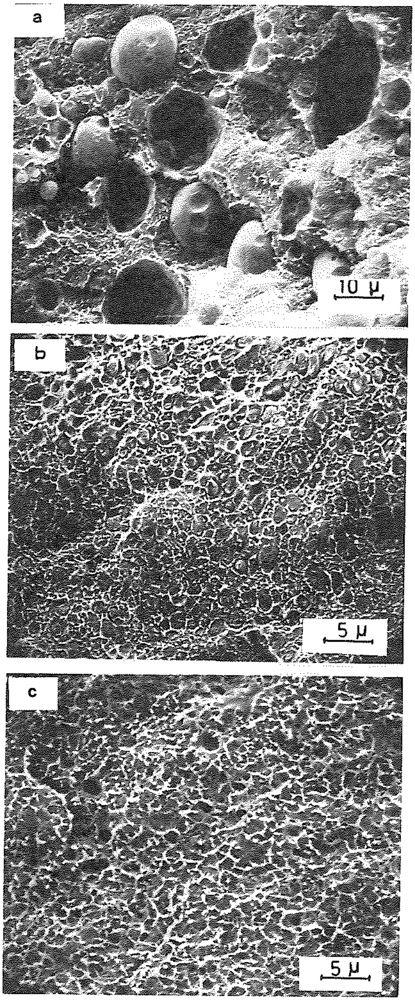

Fig. 3. Scanning electron micrographs of cryofracture surfaces of 80 HDPE/20 PS blends: (a) no copolymer, (b) with 9% H-7, (c) with 9% SE-7.

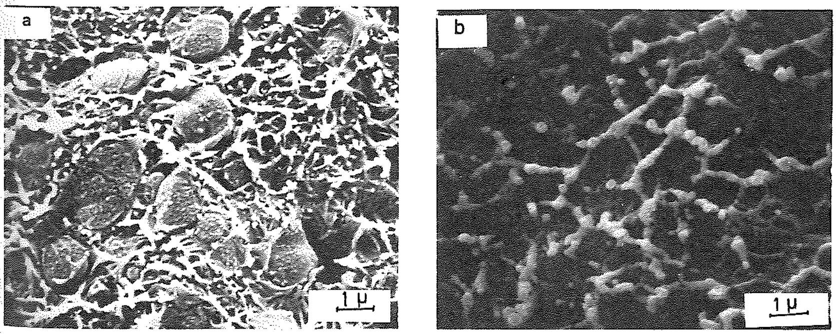

Fig. 4. (a) Detail of fig. 3(b), (b) detail of fig. 3(c).

ca. 20,000), and might accordingly be less effective than SE-7 block in improving small-scale dispersion and ductility.

In conclusion, additional investigations are certainly in order to confirm these interpretations, and hopefully improve further the properties of these materials. Nevertheless, the present observations put again in evidence the unexpected sensitivity of the macroscopic blend properties to rather minute variations in the molecular structure of the copolymer additive (see also Ref. 5).

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