

# Molecular Design of Multicomponent Polymer Systems. XIV. Control of the Mechanical Properties of Polyethylene–Polystyrene Blends by Block Copolymers

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## Synopsis

The present investigation deals with the tensile mechanical properties of the melt-blended polyethylene/polystyrene pair as controlled by poly(hydrogenated butadiene-*b*-styrene) copolymers. It is clearly demonstrated that moderate amounts of these copolymers (2–10%) significantly increase both the ultimate strength and elongation at break of blends of polystyrene with various types of polyethylene (low-density, high-density, linear low-density, and hydrogenated polybutadiene) and synergistic effects may result. The mechanical performance is strikingly dependent on the molecular characteristics of the copolymers. Over a broad range of molecular weights (60,000–270,000), diblocks are more effective than graft, triblock, or star-shaped copolymers. It is also demonstrated that using polymeric emulsifiers under usual processing conditions in the melt state is a powerful technique for preparing valuable polymer alloys.

## INTRODUCTION

Multiphase polymeric materials are now of great interest for affording efficient means of improving some deficient properties of traditional polymers and promoting new technological developments.

This opportunity results from the additivity of the main properties of the polymeric partners, whereas only an average value is provided by homogenous multicomponent materials. Block and graft copolymerization is the best route toward tailor-made multiphase materials, providing good control of the phase morphology and related mechanical properties. The chemical bond between immiscible components is the key-point in promoting high interfacial adhesion and a barrier against gross phase separation. Despite high performance, the cost of block and graft copolymers generally prevents them from being used on a large scale. Melt-blending of immiscible polymers is a more direct and less expensive way of producing multiphase systems. This advantage is however counterbalanced by weak interfacial adhesion and poor stability of the phase dispersion.

A compromise can however be found in the interfacial activity that suitable block copolymers exhibit in immiscible polymer blends. That behavior and its favorable effect on the morphology and mechanical properties of multiphase blends are now well supported.<sup>1–10</sup> In our laboratory, extensive research has

focused on the emulsifying activity of block copolymers in multiphase blends. In order to evidence and especially to control the surface activity of block copolymers in melt-blended immiscible polymers, polyethylene and polystyrene (PE/PS) blends have been studied as models and modified by poly(hydrogenated butadiene-*b*-styrene) diblock copolymers (HPB-*b*-PS).<sup>1-6</sup> HPB-*b*-PS copolymers are model emulsifiers, since they can be prepared by living anionic copolymerization of styrene and butadiene and efficient hydrogenation of the polybutadiene blocks. A previous paper dealt with the morphology of PE/PS blends as controlled by HPB-*b*-PS copolymers.<sup>6</sup> The interfacial activity of these copolymers was unambiguously evidenced in blends of polystyrene with various types of polyethylene low-density (LDPE), linear low-density (LLDPE), and high-density polyethylene (HDPE), and hydrogenated polybutadiene (HPB). In all cases, the copolymer was present at least partly at the interface, and as a consequence the phase size was significantly reduced, the interfacial adhesion was dramatically increased, and the phase dispersion was firmly stabilized against coalescence during subsequent thermal processing. Interestingly, only small amounts (1–2 wt%) of copolymers were required to obtain homogeneous, stable dispersions of the phases. Furthermore, the activity of HPB-*b*-PS copolymers was effective over a very large range of molecular weights. In other words, the apparent “block length rule” that limits the utilization of block copolymers in solution-cast mixtures<sup>8</sup> appeared to be less critical in melt-blending processes. Our morphological investigations demonstrated that melt blending of immiscible polymers with small amounts of a suitable diblock copolymer is a powerful technique to prepare polymer alloys. That conclusion has to be assessed by the extent to which the mechanical behavior of blends can be improved by the addition of block copolymers. This paper aims at reporting the beneficial effect that the HPB-*b*-PS copolymers can have on the ultimate mechanical properties of PS blended with various types of PE.

## EXPERIMENTAL

### Homopolymers and Block Copolymers

Most homopolymers and copolymers used in this study were the same as those previously investigated.<sup>6</sup> Table I summarizes the main molecular and rheological characteristics of PS and PE samples.

Pure and tapered poly(butadiene-*b*-styrene) copolymers were synthesized by well-known anionic copolymerization processes (*sec*-BuLi initiation in toluene). Details about synthesis, molecular characterization, and hydrogenation of block copolymers were reported elsewhere.<sup>6</sup>

Molecular characteristics of the samples are reported in Table II.

### Blending Conditions and Characterization of the Blends

Sample of different weight compositions were melt blended with a CAMIL laboratory two-roll mill at 200–210°C for 5 min (roll speed = 30 rpm). The copolymer was melt-milled together with the minor component of the PE/PS blend before addition of the major component. As a rule, the weight percentage of the added copolymer was defined with respect to the total weight of the

TABLE I  
Characterization of PE and PS Homopolymers

Polymer	Trade name	Reference	$\bar{M}_n$ ( $\times 10^{-3}$ )	$\bar{M}_w/\bar{M}_n$	Density (g/cm <sup>3</sup> )	MFI <sup>a</sup>
Low-density polyethylene	Alkathene 15033 (ICI)	LDPE-1	40	> 10	0.922	0.3
Linear LDPE	RS453 (Solvay)	LLDPE-1	—	—	0.93	1.9
High-density polyethylene	Eltex B4002 (Solvay)	HDPE-2	6	37	0.952	0.3
	Eltex B2008 (Solvay)	HDPE-3	15	11	0.958	0.7
Hydrogenated polybutadiene	—	HPB	75	1.1	—	0.58
Polystyrene	Polystyrol 158K (BASF)	PS-1	100	2.5	1.05	0.39
	Anionically prepared	PS-2	80	1.1	—	12

<sup>a</sup>MFI: melt flow index (g/10 min) measured at 190°C, under 2,160 kg.

TABLE II  
Characterization of HPB-*b*-PS Copolymers

Reference	Molecular structure	Wt% of PS	$\bar{M}_n$ total ( $\times 10^{-3}$ )	$\bar{M}_n$ PS ( $\times 10^{-3}$ )	$\bar{M}_n$ HPB ( $\times 10^{-3}$ )	MFI
SE-1	Pure diblock	43	58	25	33	3.77 <sup>a</sup>
SE-2	Pure diblock	49	155	75	80	0 <sup>b</sup>
SE-3	Pure diblock	47	275	130	145	0 <sup>b</sup>
SE-4	Tapered diblock	33	80	26	32	3.13 <sup>a</sup>
SE-5	Pure diblock	50	80	40	40	0.23 <sup>a</sup>
SE-6 <sup>c</sup>	Tapered diblock	32	62	22	25	0.37 <sup>b</sup>

Note: Melt flow index (g/10 min) determined with the Ceast melt indexer.

<sup>a</sup>210°C; 17,185 kg.

<sup>b</sup>190°C; 2,160 kg.

<sup>c</sup>Results from hydrogenation of Solprene 410 (from Phillips).

PE/PS blend. After mixing, the samples were compression molded into sheets with a Fontijn hydraulic press at 200–210°C and 2500 psi pressure for 5 min and allowed to cool to room temperature. Tensile and impact test specimens were machined from the molded sheets.

Stress-strain measurements were performed at room temperature using DIN 53448 specimens and an Instron tester at a cross-head speed of 2 cm min<sup>-1</sup>. The Charpy impact strength of some blends was also determined at room temperature with a CEAST Fractroscope using notched specimens DIN 53453 (0.3 mm notch).

Each tensile or impact value reported is the average of from four to six tests.

## RESULTS AND DISCUSSION

### General Behavior

It is well known that PE/PS blends display very poor ultimate mechanical properties, since they combine over a broad composition range the low

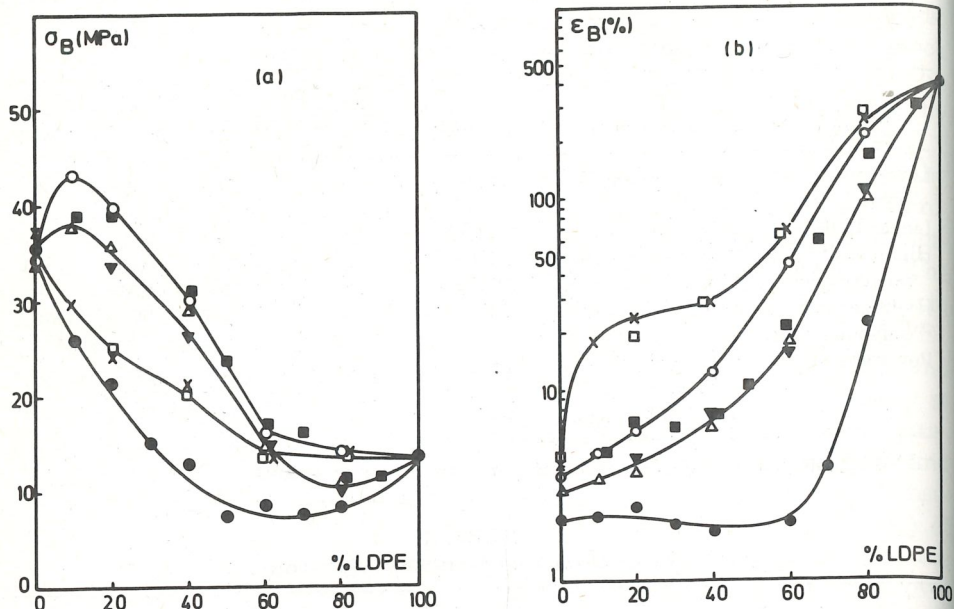


Fig. 1. (a) Ultimate tensile strength  $\sigma_B$  and (b) elongation at break  $\epsilon_B$  of LDPE-1/PS-1 blends: without copolymer (●), and added respectively with 10% SE-1 (Δ), SE-2 (×), SE-3 (□), SE-4 (○), SE-5 (▼) and SE-6 (■).

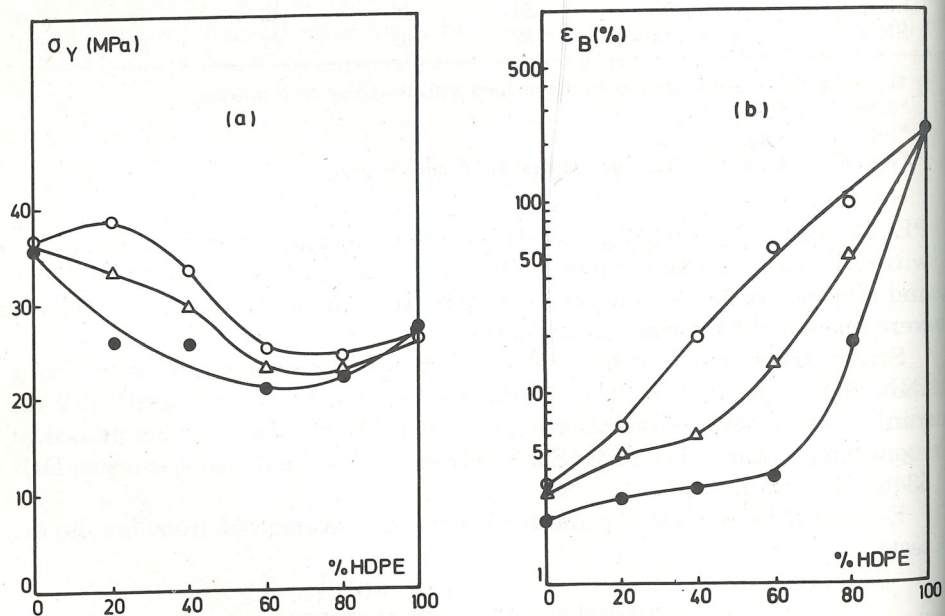


Fig. 2. (a) Yield stress  $\sigma_Y$  and (b) elongation at break  $\epsilon_B$  of HDPE-3/PS-1 blends: without copolymer (●), added with 10% SE-6 (Δ), and added with 10% SE-2 (○).



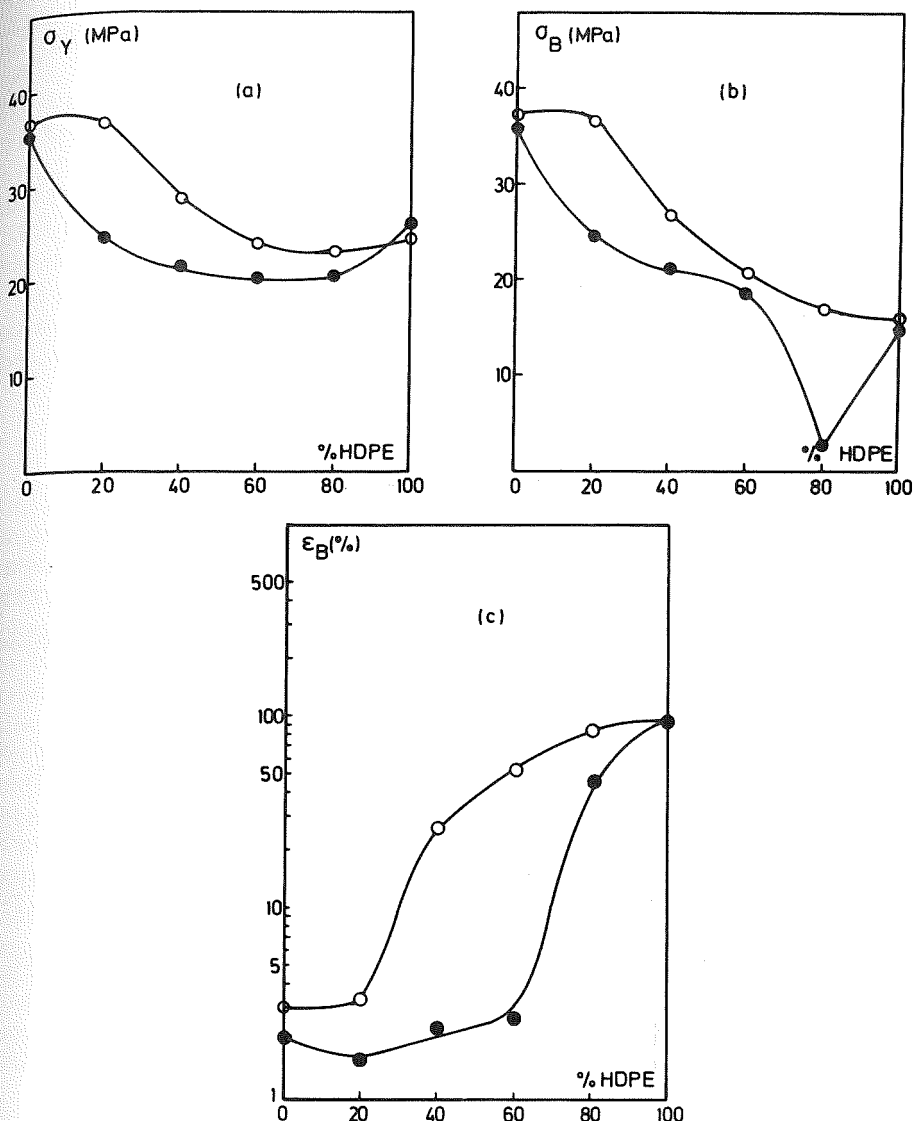


Fig. 3. (a) Yield stress  $\sigma_Y$  and (b) ultimate tensile strength  $\sigma_B$  and (c) elongation at break  $\epsilon_B$  of HDPE-2/PS-1 blends: without copolymer (●), added with 10% SE-2 (○).

strength ( $\sigma_B$ ) of PE and the brittleness (low  $\epsilon_B$ ) of PS.<sup>1,2,7</sup> Furthermore, the dependence of both strength and ductility on blend composition commonly exhibits a minimum value smaller than that of either pure component (Figs. 1-3). This deleterious weakness results from many defects and early failure promoted by poor interphase adhesion, as observed by microscopy.<sup>6</sup> The addition of HPB-*b*-PS copolymers to LDPE-1/PS-1 blends significantly enhances both the ultimate strength and the elongation at break (Fig. 1).

It is worth noting that some block copolymers are effective in eliminating the minimum in the ultimate strength dependence on blend composition (Fig.

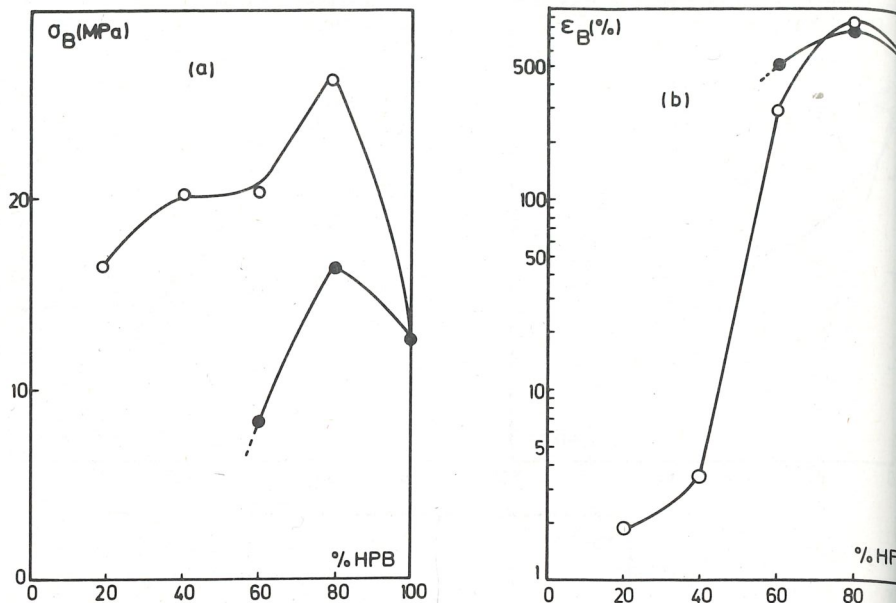


Fig. 4. (a) Ultimate tensile strength  $\sigma_B$  and (b) elongation at break  $\epsilon_B$  of HPB/PS-2 blends without copolymer (●), added with 10% SE-2 (O).

1). Figures 2 and 3 show the improvement in the mechanical behavior of HDPE-2/PS-1 and HDPE-3/PS-1 blends when they are added with HPB-PS copolymers. Unmodified blends containing less than 80 wt% HDPE-2 or HDPE-3 are brittle and break at the yield stress. Modified by a HPB-*b*-PS copolymer, these blends exhibit yielding and subsequent neck formation. Further details on the reinforcement of HDPE/PS blends by HPB-*b*-PS copolymers have been reported elsewhere.<sup>2</sup>

Model blends of PE(HPB) and PS(PS-2) have also been investigated (Fig. 4). In that case, the original blends containing more than 50% PS are too weak and brittle to be characterized by stress-strain measurement. The beneficial effect of the block copolymers is obvious since blends containing up to 80% PS-2 can be evaluated by that technique.

### Synergism

Still more interesting is the synergism in strength that PS-rich blends display when they involve either LDPE or HDPE (Figs. 1 and 2). In this composition range, a particular co-continuous two-phase morphology is observed and probably has much to do with the improved mechanical properties. When each phase is continuously connected throughout the blend, the stress does not have to be transferred across the interface area, and high interphase adhesion is no longer required to achieve good mechanical properties.

This is supported by the high level of ductility and strength exhibited by IPNs and semi-IPNs, i.e., materials consisting of two chemically different extended interpenetrating networks.<sup>11</sup> Synergism in PE/PS blends is only observed when a suitable block copolymer is used. This means that a favorable phase topology combined with phase stability and improved interfacial

Adhesion can account for the observed maximum in tensile strength. In model PB/PS-2 blends (Fig. 4), synergism in ultimate elongation is observed for the PB rich blends, whereas the ultimate strength behaves similarly within the whole accessible composition range. Examples of synergism are also provided by other polymer blends such as LDPE/ethylene-propylene elastomers (EPR) and PS/poly(phenylene oxide) systems.<sup>12,13</sup> In the former case, the ability of EPR to crystallize is controlling, whereas the latter example refers to miscible blends of wholly amorphous components.

It turns out that the origins of the synergism in the three reported examples must be different and that several routes should be possible to promote behavior of high practical interest.

### Effect of Copolymer Structure

It is widely recognized that the surface activity of the usual detergents is related to the intramolecular repulsion of hydrophobic segments, which prefer to associate with oil and water, respectively. Similarly block copolymers, each sequence of which is selectively miscible with a polymer phase, are expected to locate at the interface provided their propensity to segregate into separate phases is pronounced. This ideal situation could be challenged by a tendency of the copolymer to disperse in either of the homopolymer domains. The relative importance of the two tendencies depends on the copolymer properties, i.e., segmental interactions, molecular weight, molecular structure, and composition, which are key criteria in the activity of polymeric emulsifiers. In order to balance properly segmental interactions, copolymers with blocks of comparable molecular weight have been synthesized and evaluated.

When the copolymer architecture is considered, a block copolymer is preferred to a graft structure which should suffer from more drastic conformational restraints at the interface. That expectation is proved by the performances of LDPE-1/PS-1 blends added with graft and block copolymers, respectively (Table III). Grafts enhance the tensile strength of blends but have a detrimental effect on the elongation at break. The efficiency of block copolymers depends, among other things, on the number and arrangement of

TABLE III  
Maximum Improvement in Tensile Strength ( $\Delta\sigma_B$ ) and Elongation ( $\Delta\epsilon_B$ ) for LDPE/PS Blends Added with 6% of Graft<sup>a</sup> and 10% of Various Block Copolymers

Copolymer structure	20 LDPE/80 PS		80 LDPE/20 PS	
	$\Delta\sigma_B$ (%)	$\Delta\epsilon_B$ (%)	$\Delta\sigma_B$ (%)	$\Delta\epsilon_B$ (%)
Graft	55	0	75	0
Block	20	0	30	40
Staton G 1651 (Shell)				
Star-shaped				
Hydrogenated Solprene	20	0	10	130
5 (Phillips)				
Blocks				
Pure SE-2	25	900	60	1000
Tapered SE-4	100	100	60	1000

<sup>a</sup>Data for graft are taken from figures in reference 7.

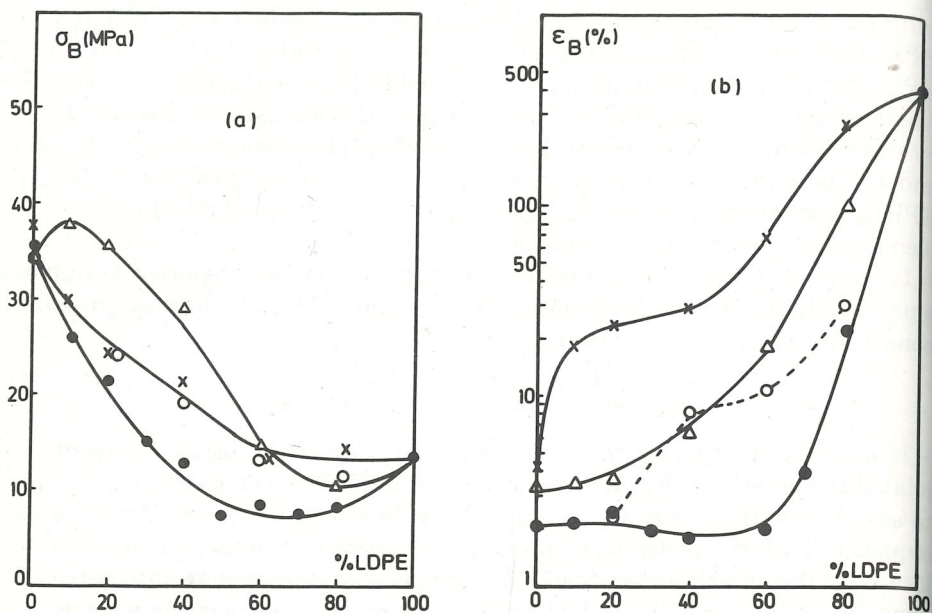


Fig. 5. (a) Ultimate tensile strength  $\sigma_B$  and (b) elongation at break  $\epsilon_B$  of LDPE-1/PS-1 blends: without copolymer (●), and added with 10% SE-2 (×), 10% SE-1 (△), and 10% triblock Kraton G 1651 (○).

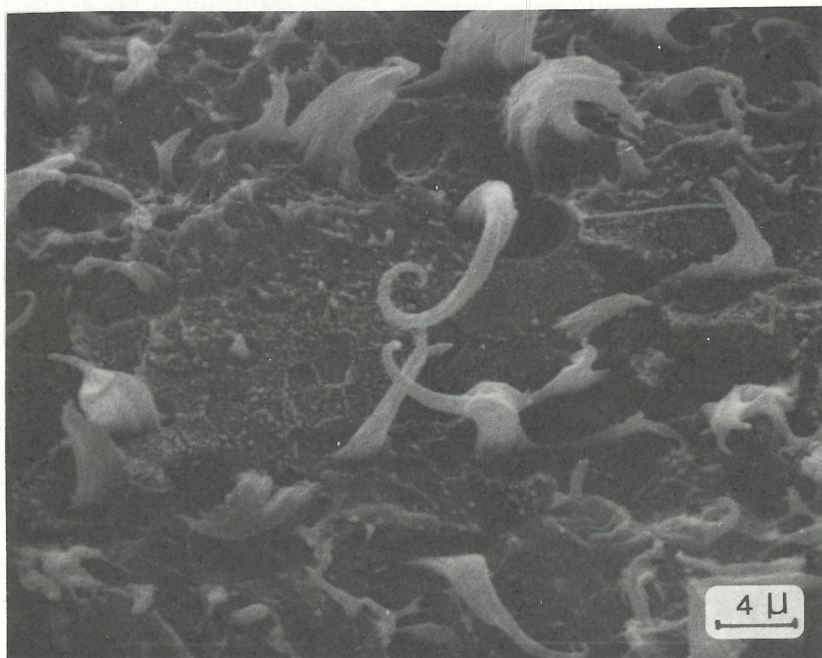


Fig. 6. Scanning electron micrograph of 20 LDPE-1/80 PS-1 blend added with 10% Kraton G 1651. Room temperature fracture surface.



the constituent blocks. For instance, the opportunity for individual blocks to penetrate the corresponding homopolymer phase is likely to be higher for diblock copolymers than for triblock, multiblock, or star-shaped copolymers. That situation is supported by results listed in Table III, where the efficiency of a triblock copolymer (Kraton G1651 from Shell) and of a four-arm star-shaped copolymer (HPB-*b*-PS)<sub>4</sub> (hydrogenated Solprene 415 from Phillips) is compared with that of diblock copolymers. Furthermore, Figure 5 demonstrates that the improvement in the mechanical properties ( $\sigma_B$  and  $\epsilon_B$ ) upon the addition of the triblock is limited and generally lower than that provided by the less-efficient diblock copolymer. Morphological observations also support the poor emulsifying activity of the triblock copolymer. Figure 6 shows that the interfacial adhesion is very weak and that a major part of the copolymer is dispersed in the individual phases rather than at the blend interface. The results reported in Table III illustrate the effect of the molecular architecture on the efficiency of block copolymers in the emulsification of PE/PS blends.

The superiority of block copolymers and especially of diblocks is clear, as indicated by the improvement of ductility.

This conclusion agrees with a previous study by Riess et al.<sup>8</sup> on ternary blends of AB block copolymers with A and B homopolymers.

#### Effect of Molecular Features of Diblock Copolymers

When HPB-*b*-PS copolymers are used, their molecular weight and structure (pure or tapered diblocks) play an important role in terms of reduction of phase size, phase stability, adhesion, and ultimate mechanical behavior. Therefore, major emphasis has to be placed on these parameters, which control the emulsification of the melt-blended PE/PS pair. Since the molecular weight of the copolymer determines the amount required to fill up the interface, the economic advantages of low-molecular-weight copolymers is obvious. Nevertheless the block length must be sufficient to impart a pronounced segmental repulsion between the individual sequences and to anchor them firmly into the phases they penetrate. Early studies focusing on solutions of immiscible polymers and solvent-cast blends concluded that block copolymers act as efficient emulsifiers only when the molecular weight of the sequences is comparable to or higher than the molecular weight of the corresponding homopolymer.<sup>8</sup> This experimental rule may be a limitation in the use of block copolymers as polymer-in-polymer emulsifiers. Fortunately, the results reported here provide evidence that this requirement on molecular weight is less stringent in melt-blending processes than in systems that allow the equilibrium state to be approached.

As long as the LDPE-1/PS-1 blends are concerned, the PS block of all the available copolymers is shorter than the homo PS used, except for SE-3. Furthermore, SE-1, SE-4, and SE-6 have a PE block the  $M_n$  of which is smaller than that of LDPE-1. According to the rule mentioned above, only SE-3 should meet the requirements of an efficient polymer-in-polymer emulsifier. It is however obvious that all the diblock copolymers reported in Table II play unambiguous interfacial activity to an extent depending on their molecular characteristics.

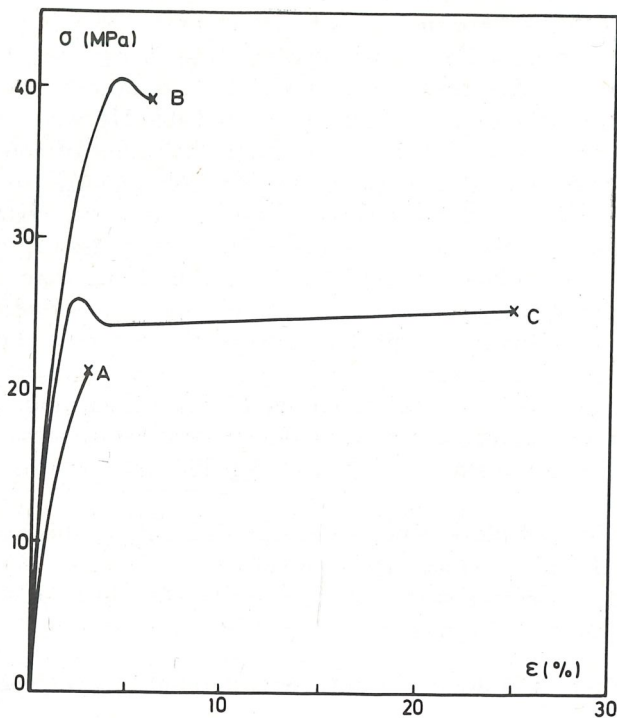


Fig. 7. Stress-strain curves of 20 LDPE-1/80 PS-1 blends: (A) without copolymer, (B) added with 10% SE-4, and (C) added with 10% SE-2.

Added into PS-rich blends, the low-molecular-weight block copolymers (SE-1, SE-4, SE-5, and SE-6) are remarkable in promoting a synergism in strength, whereas the high-molecular-weight copolymers (SE-2, SE-3) display a comparatively greater improvement in the ultimate elongation (Figs. 1 and 7). The values of energy to break (Fig. 8) and impact strength (Table IV) show that the largest improvement in ductility is finally afforded by the high-molecular-weight copolymers. Modified by these copolymers (SE-2 or SE-3), the PS-rich blends suffer from a decrease in tensile strength but enjoy a great improvement in elongation, in such a way that behavior typical of a toughened PS is reported. Results in Table IV indeed show that only the 20PE/80PS blend modified with SE-3 exhibits an impact resistance close to that of a commercial HIPS; the other blends emulsified with SE-4 display poor toughness.

Whatever their molecular features, diblock copolymers are observed to stabilize a cocontinuous two-phase structure. However, some morphological differences are observed by SEM in the continuous PE network which consists of either long ribbons when low-molecular-weight copolymers are used (Fig. 9a) or more or less spherical particles tied together in the presence of the SE-2 and SE-3 copolymers (Fig. 9b). At this stage it cannot be determined whether the differences in the morphology result from a change in the interfacial activity of the block copolymers or from modifications in the microrheology of the emulsified blends. Young's modulus should reflect these morphological differences in PS-rich blends (80% PS) and should also give useful information

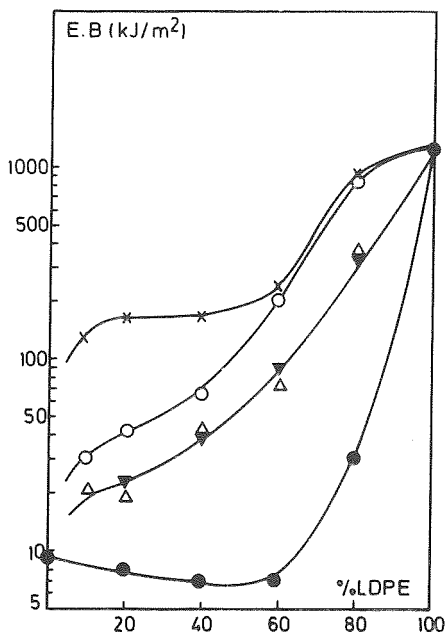


Fig. 8. Energy to break (area under the stress-strain curve at break) of LDPE-1/PS-1 blends: without copolymer (●), and added with 10% SE-1 (▼), 10% SE-2 (×), 10% SE-4 (○), and 10% SE-5 (△).

on the distribution of the copolymer in the blend. Also it is of interest to calculate the modulus assuming either cocontinuous phases or particulate dispersions for comparison with experimental data. Modulus values evaluated from the slope of the stress-strain curves for LDPE-1/PS-1 blends have already been reported.<sup>1</sup> Such results are however not accurate enough (rather large scatter) for useful discussion. This will be the subject of a future paper based mainly on dynamic mechanical measurements.

Scanning electron microscopy of fracture surfaces of blends (Fig. 10a and b) show that the interfacial adhesion is quite high whatever the molecular weight of the copolymers (SE-2 or SE-5) added into the LDPE-1 (20 wt%)/PS-1 blend. Nevertheless, the adhesion between the phases seems to be

TABLE IV  
Impact Strength of Some LDPE/PS Blends

Percent PS-1	Percent LDPE-1	Percent copolymer <sup>a</sup>	Charpy impact strength (kJ/m <sup>2</sup> )
80	20	0	2.3
80	20	2 SE-4	5
80	20	5 SE-4	3.4
80	20	10 SE-4	4.2
90	10	10 SE-4	3.5
80	20	10 SE-3	11.4
PS Styron 461 (Dow)			11.2

<sup>a</sup>Added to 100% of the binary PE/PS blend.



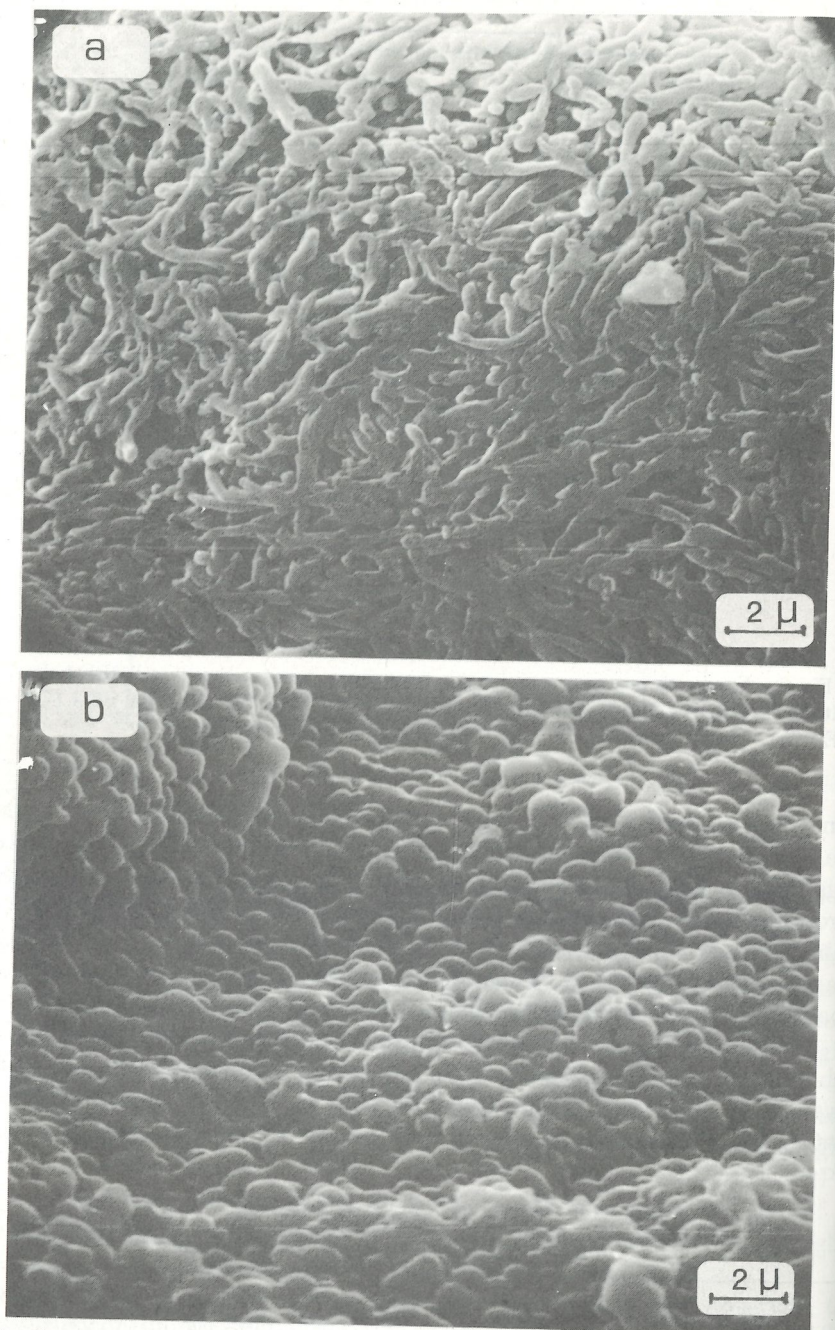


Fig. 9. Scanning electron micrographs of 20 LDPE-1/80 PS-1 blends after THF extraction of PS phases: (a) added with 10% SE-1 and (b) added with 10% SE-2.

stronger when a high-molecular-weight copolymer is used. The high-molecular-weight copolymers (SE-2, SE-3) are again more efficient in improving the ductility of the blends rich in LDPE-1 (Fig. 1). The minimum in tensile strength has completely disappeared to reach the value of pure LDPE-1. It is noteworthy that when the molecular weight of the block copolymers is



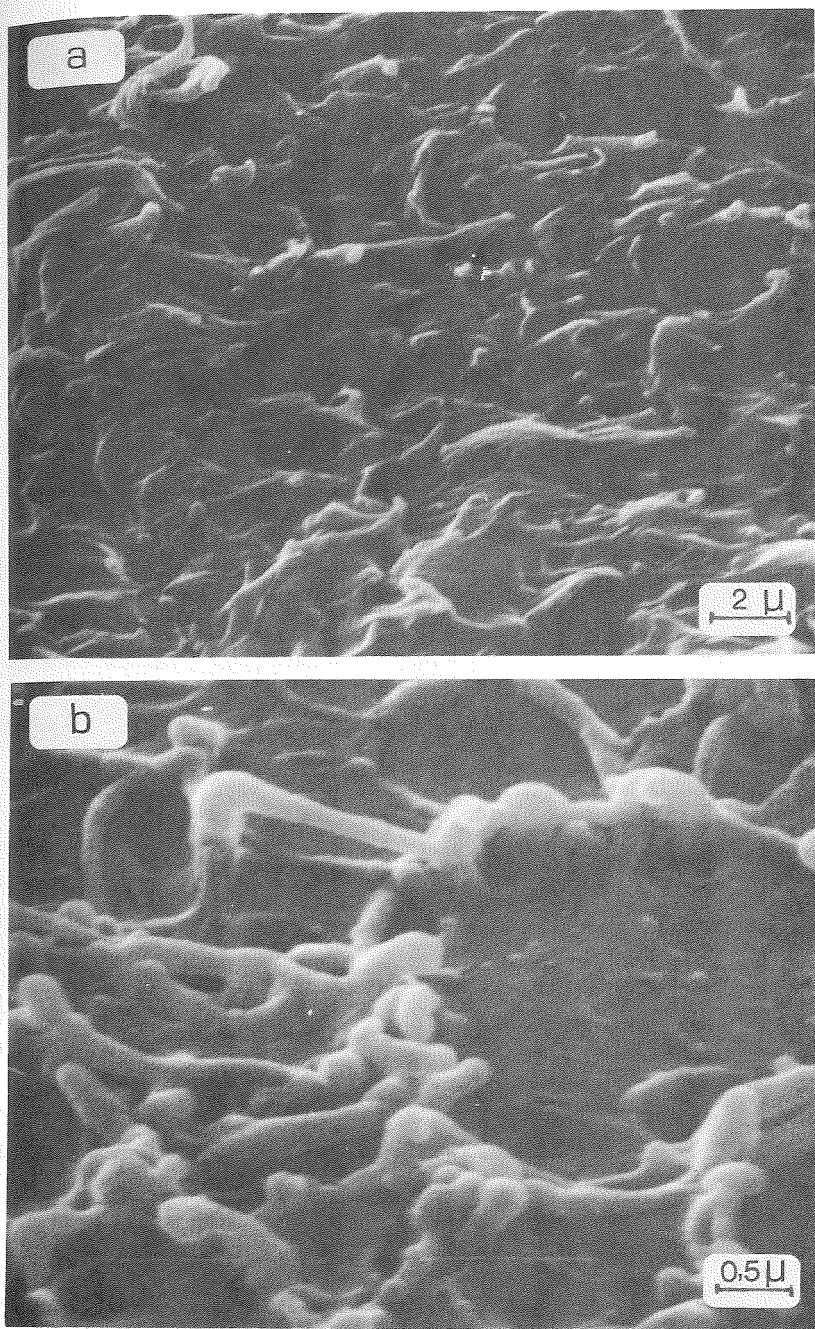


Fig. 10. Scanning electron micrographs of 20 LDPE-1/80 PS-1 blends: (a) added with 10% SE-2 and (b) added with 10% SE-5. Room temperature fracture surfaces.

sufficiently high, the elongation at break is higher than the weight-average value over the whole composition range. Similarly, the size of the dispersed PS-1 particles is more effectively reduced by SE-2 than by SE-5.<sup>6</sup>

Although the block copolymers reported in Table II exert obvious interfacial activity, their beneficial effect on the mechanical properties of LDPE/PS

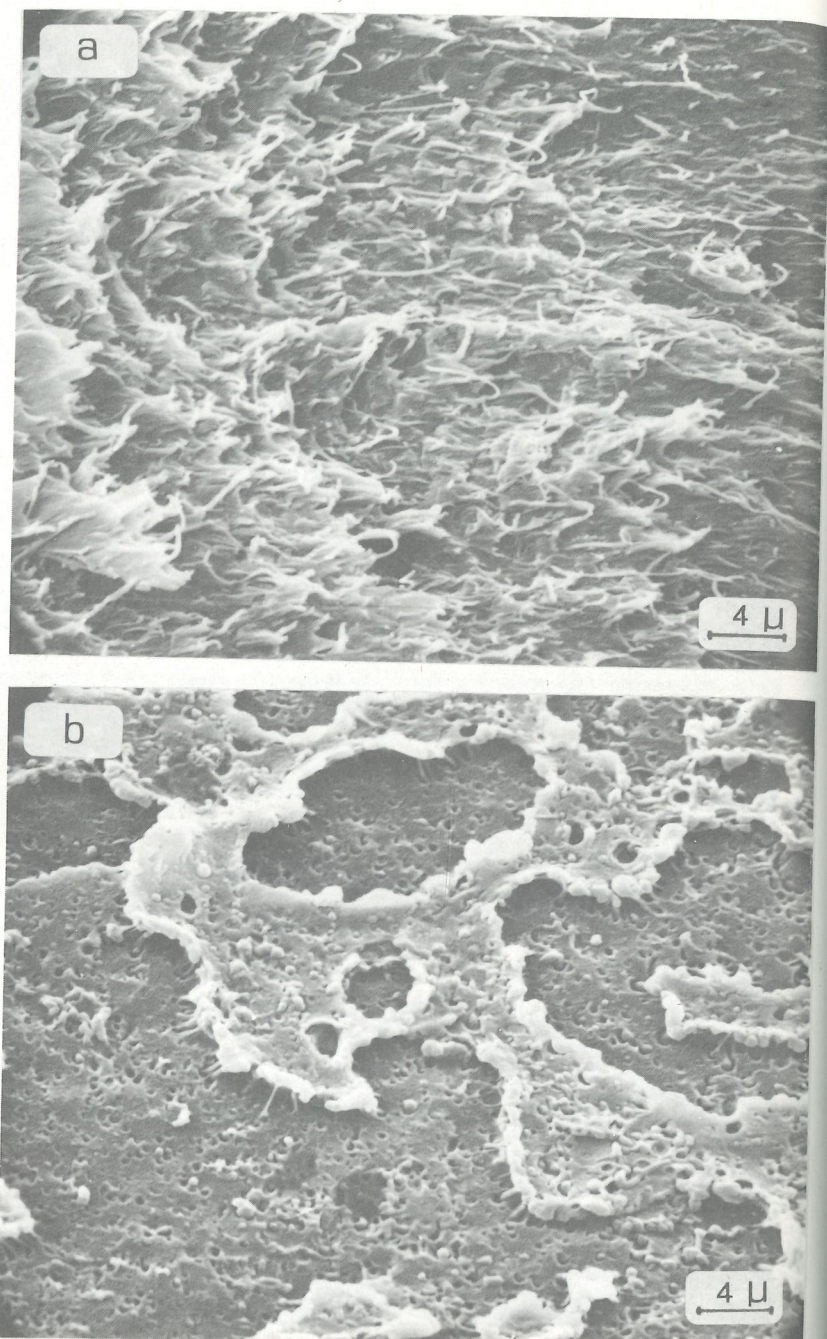


Fig. 11. Scanning electron micrographs of 20 LDPE-1/80 PS-1 blends: (a) added with 10% SE-4 and (b) added with 10% SE-5. Room temperature fracture surfaces.

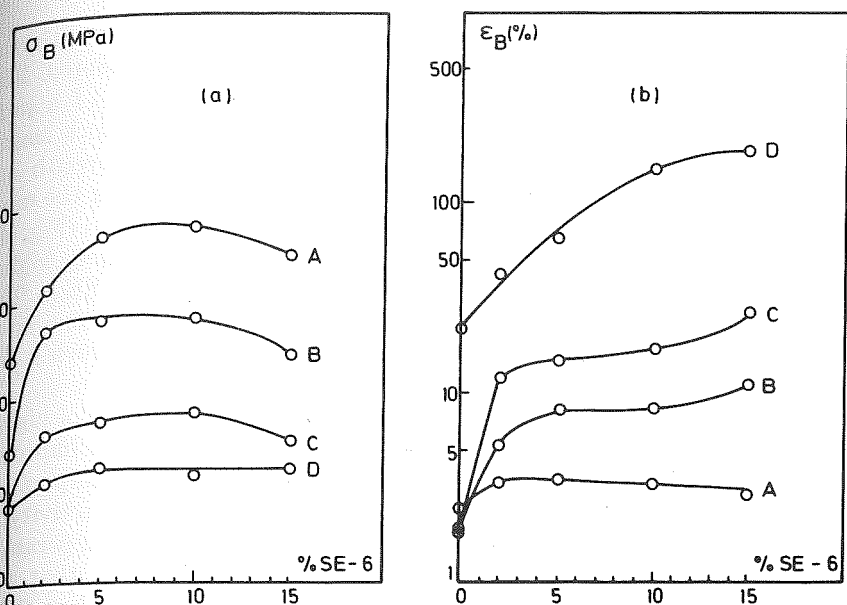


Fig. 12. (a) Ultimate tensile strength  $\sigma_B$  and (b) elongation at break  $\epsilon_B$  of LDPE-1/PS-1 blends as a function of amount of copolymer SE-6 added: (A) 20 LDPE/80 PS, (B) 40 LDPE/60 PS, (C) 60 LDPE/40 PS, and (D) 80 LDPE/20 PS.

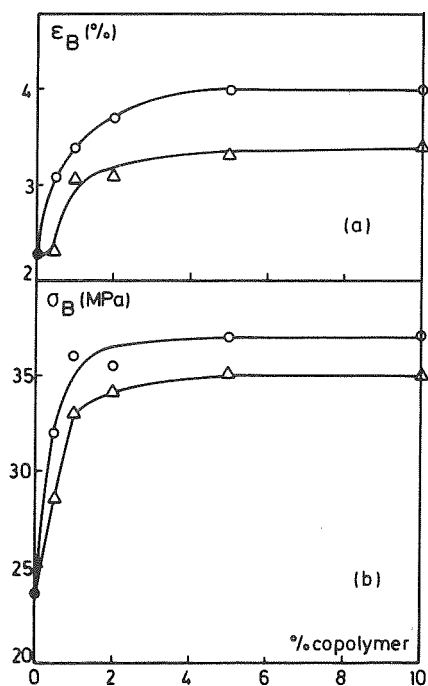


Fig. 13. (a) Elongation at break  $\epsilon_B$  and (b) ultimate tensile strength  $\sigma_B$  of 20 LLDPE-1/80 blends as a function of the amount of copolymer added, SE-4 (O) or SE-5 ( $\Delta$ ).



blends seems to increase with molecular weight. Beside the chain length, the internal structure of the diblock copolymers has also been considered. The effect of a tapered diblock SE-4 has been compared with that of a pure diblock of either the same molecular weight (SE-5) or the same block length (SE-1). The tapered diblock confers the highest tensile strength on LDPE/PS-1 blends, whatever their composition; it is responsible for the most pronounced synergism in strength reported at 20 wt% LDPE-1 (Fig. 1). Moreover,  $\epsilon_B$  and chiefly the energy to break (Fig. 8) are definitely higher when the blends are modified by SE-4 rather than by SE-1 or SE-5. The efficiency of a low-molecular-weight tapered diblock (SE-4) is quite similar to that of high-molecular-weight pure diblocks (SE-2, SE-3) in improving the ultimate mechanical properties of blends rich in LDPE-1 (Fig. 1).

The superiority of a tapered copolymer (SE-6) over a pure diblock of higher molecular weight and block length (SE-5) is illustrated by the higher improvement in both ultimate strength and elongation (Fig. 1). The phase morphology of LDPE-1 (80 wt%)/PS-1 blends agrees with the higher interfacial activity of SE-4 compared with SE-5.<sup>6</sup> SEM examinations of the room-temperature fracture surfaces of LDPE-1 (20 wt%)/PS-1 blend clearly show that the tapered copolymer (SE-4) promotes stronger interfacial adhesion than SE-5 and stabilizes a finer interlocked structure preventing PE from coalescing into discrete and less adherent particles as observed in the presence of SE-5 (Fig. 11a and b). Defects in the interfacial region when SE-5 is substituted for SE-4 could account for the earlier rupture of the blend.

### Effect of Amount of Copolymer Added

The above results clearly point out that "emulsification" is highly effective in improving the performance of immiscible polymer blends. The interest of that approach on a cost-benefit basis is however dependent on the minimum amount of block copolymer that can be used. In that respect, the mechanical properties of LDPE-1/PS-1 blends have been investigated in relation to the percentage of the added SE-6 copolymer. Figure 12 shows that about 2% copolymer is generally enough to reach the maximum improvement in  $\sigma_B$  and  $\epsilon_B$ . That conclusion is assessed by the mechanical behavior of the LDPE-1 (20%)/PS-1 when modified by 0.5, 1, 2, 5, and 10%, respectively, of either the tapered diblock (SE-6) or the pure diblock (SE-5) copolymer (Fig. 13). It must be stressed that the blend morphology changes when the block copolymer percentage increases up to about 5%,<sup>6</sup> i.e., a percentage for which the ultimate mechanical properties have reached the optimum value. That observation is of prime interest for the use of block copolymers as polymer-in-polymer emulsifiers and the need for further investigations of the underlying morphology-mechanical property relationships.

### CONCLUSIONS

Melt blending of immiscible polymers with suitable diblock copolymers is a powerful technique for preparing polymer alloys with enhanced performance. The present investigation clearly demonstrates that moderate amounts of HPB-*b*-PS copolymers significantly increase both the tensile strength and



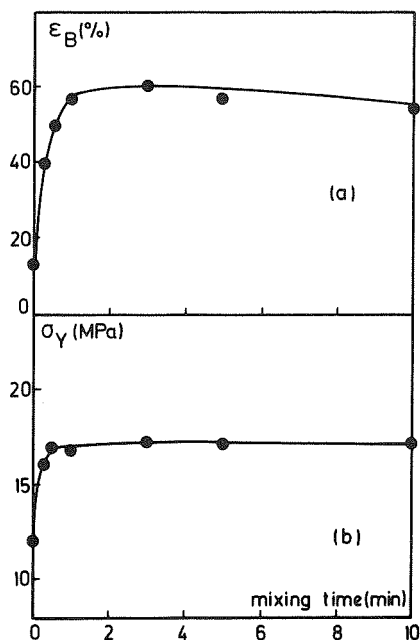


Fig. 14. (a) Elongation at break  $\epsilon_B$  and (b) yield stress  $\sigma_Y$  of 70 LLDPE-1/30 PS-1 blends as a function of mixing time with 10% SE-6.

elongation of blends of PS with various types of PE (low-density, high-density, linear low-density, and hydrogenated polybutadiene). Mechanical performances are strikingly dependent on the molecular characteristics of the HPB-*b*-PS copolymer, which are the key thermodynamic parameters in the control of the emulsification. However, when blending is performed in the melt state, kinetic and rheological factors play a determining role. In order to define the technological interest of the polymer-in-polymer emulsification, that process has to be investigated under processing conditions (extrusion, injection) involving very high shear and low residence times. Although it is outside the scope of this paper to discuss that situation, Figure 14 demonstrates that mixing a preformed PE/PS binary blend with a HPB-*b*-PS copolymer for only 30 sec (PE/PS blended first for 3 min on a two-roll mill) is sufficient to obtain the maximum improvement in  $\sigma_B$ , whereas 1 min of mixing is sufficient for reaching the maximum  $\epsilon_B$  value. This interesting feature is only observed when a suitable block copolymer is used; actually, the viscosity of the block copolymer should not be too much higher than that of the homopolymers.

Furthermore, Figure 15 demonstrates that a very significant reduction of the particle size (a situation quite comparable to that recorded with roll-milled samples) is observed when PE/PS blends are extruded and injection molded in the presence of 10% copolymer SE-6. It is noteworthy that the elongation at break of these blends is improved to an extent which is very close to that observed for roll-milled samples. (Fig. 16).

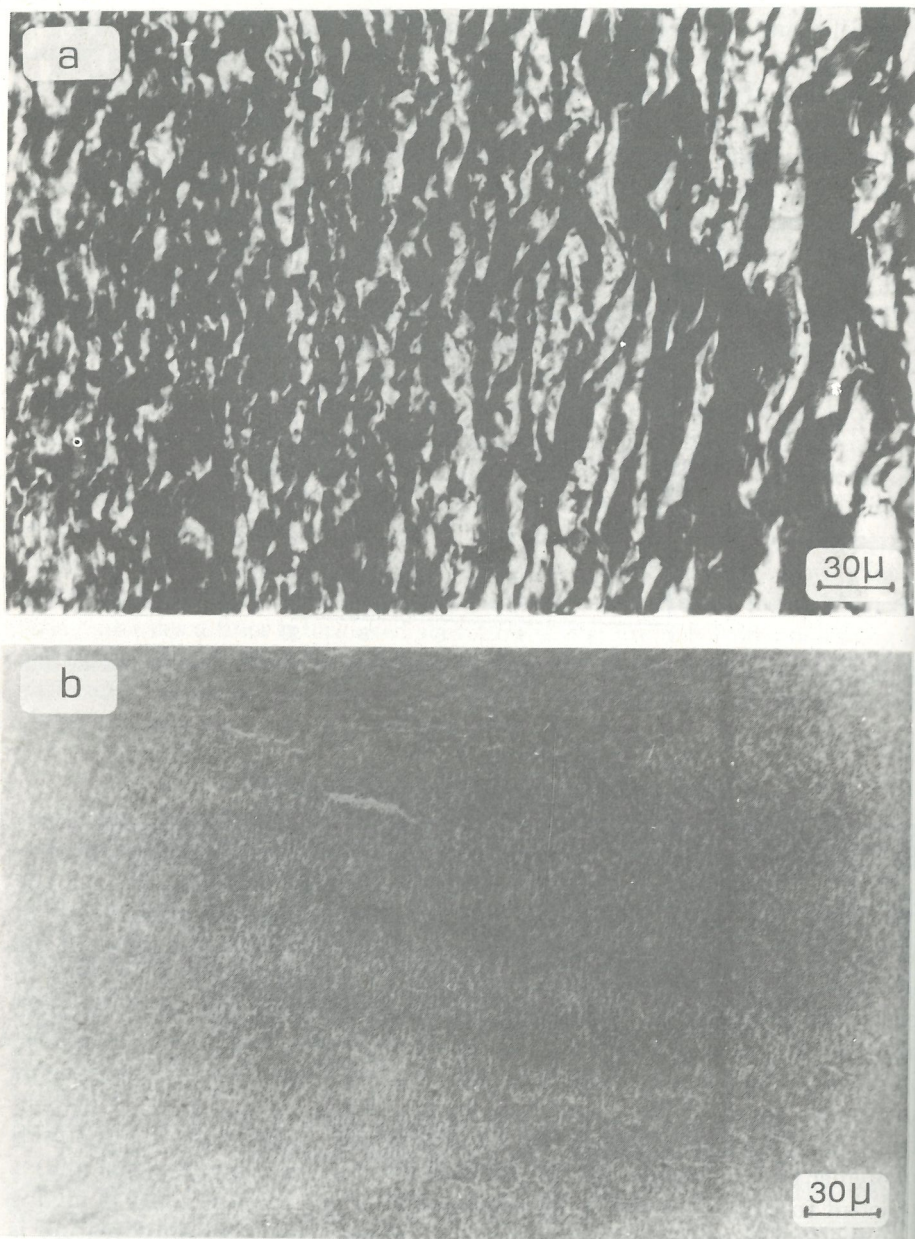


Fig. 15. Optical microscopy of 50 LDPE-1/50 PS-1 injection-molded blends: (a) without copolymer and (b) added with 10% SE-6. PS phases (dark area) were selectively stained in violet according to a method devised in the laboratory.

These preliminary results demonstrate that using polymeric emulsifiers under the usual processing conditions is not a dream and supports an optimistic forecast of the potential offered by the new "plasturgy."

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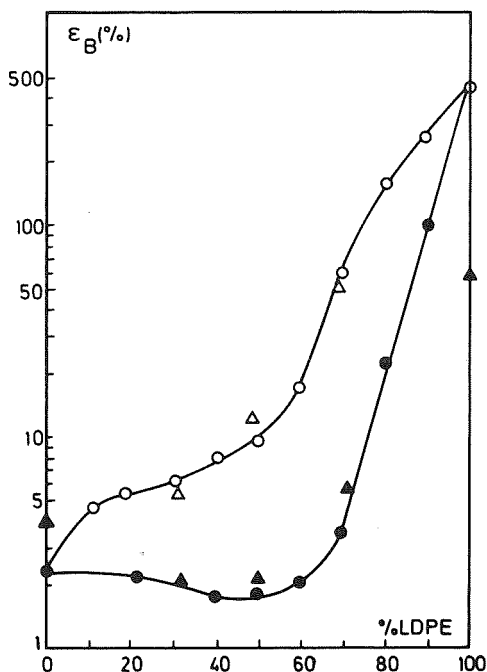


Fig. 16. Elongation at break  $\epsilon_B$  of LDPE-1/PS-1 blends: roll-milled and compression-molded blends without copolymer (●) and added with 10% SE-6 (○); extruded and injection-molded blends without copolymer (▲) and added with 10% SE-6 (△).

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