less than 15 MPa and decreased to a constant value of about 0.2 mm by increasing the holding pressure to 40 MPa. This tendency was closely associated with the relation between the WELD strength and the injection pressure, shown in *Figure 4*. After all, the weld strength is largely influenced by the poor bonding range D_w, of 0.2–0.3 mm, rather than by the fine V-notch on the surface, because the poor bonding range is in a "precrack" state and may act like a real V-notch (see *Fig. 9*).

CONCLUSIONS

The conclusions derived from the experimental results on the weld line of polystyrene injection moldings are summarized as follows:

1. The V-notch was not readily observed by SEM studies of the fracture surface, but the V-notch effect could be confirmed by tensile tests.

2. The depth of a V-notch could be determined by tensile tests using samples from which the skin layers were removed to different levels of depth. It was defined as the "depth of weld."

3. The depth of weld, dependent on molding conditions, was about 0.2 mm at filling and holding pressures of 41.9 and 41.9 MPa, respectively.

4. The V-notch effect is caused by a poorly bonded layer near the weld surface, rather than by the V-notch on the surface. The depth of weld could be measured.

5. The relationship among the depth of weld, molding conditions, and the weld strength have been studied.

6. The higher the filling pressure, the higher was the strength of the weld line. The strength was improved by raising the holding pressure, even when the filling pressure was low.

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Molecular Design of Multicomponent Polymer Systems. XVIII: Emulsification of High-Impact Polystyrene and Low Density Polyethylene Blends Into High-Impact Alloys

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The interfacial activity of a hydrogenated polybutadiene-polystyrene tapered diblock copolymer, (HPB-b-PS) is investigated in blends of a low density polyethylene (LDPE) with a high impact polystyrene (HIPS) prepared in the melt state on a two-roll mill. Optical and scanning electron microscopy examinations of smoothed or fracture surfaces and also surfaces obtained after THF-extraction of PS phases demonstrate that the copolymer promotes the dispersion and interfacial adhesion of the components, whatever the composition and is able to create and stabilize particular dispersions of the rubber particles in these blends. Tensile and Charpy impact properties are also very significantly improved. All these features demonstrate that the ductility and toughness of PS and LDPE/PS blends can be closely controlled by adequate combinations of rubber particles and a HPB-b-PS copolymer.

INTRODUCTION

Thanks to the use of tailored polymeric emulsifiers, blends of highly incompatible polymers can be converted into real alloys displaying controlled morphologies and often largely improved mechanical properties (1–5). Research undertaken in this laboratory has firmly established that potentiality for numerous incompatible polymer pairs emulsified in the melt state by well-chosen block copolymers (4, 5). In that respect, it has been demonstrated that the morphology and tensile mechanical properties of blends of polystyrene (PS) with various types of commercial polyethylene (PE) are closely controlled by poly(hydrogenated butadiene-b-styrene) diblock copolymers (HPB-b-PS) (6–10). Indeed, these emulsifiers are responsible for a significant decrease of the particle size and an improved interfacial adhesion at every composition; they also stabilize co-continuous two-phase structures displayed by PS-rich blends (80% PS) by preventing the coalescence of the PE domains into discrete particles (6). Both the strength and elongation at break, which have low values for pure blends are significantly increased upon addition of moderate amounts (5%) of HPB-b-PS copolymers and a synergy in the strength may result (6, 10). On the other hand, a high impact resistance is not obtained for PS-rich blends displaying co-continuous structures. In other words, a network of PE fibers would not be suitable for imparting a high toughness. Similar limitations were also observed by addition of

small amounts of LDPE (10–20%) to other brittle materials such as SAN and PVC, although their emulsification was achieved by efficient block copolymers (11, 12). These emulsified blends also displayed co-continuous two-phase structures.

The evaluation of HPB-b-PS copolymers has now been extended to blends of a low density polyethylene (LDPE) with a commercial high-impact polystyrene (HIPS). The purpose is to investigate the particular morphology of the ternary blend (LDPE, PS, and rubber particles) as modified by the block copolymer and to put in evidence the resulting modifications on the tensile and impact properties, in comparison with those of emulsified binary LDPE/PS blends.

EXPERIMENTAL PART

The homopolymers used for this study were a low density polyethylene Alkathene XDG33 (from ICI) and a high impact polystyrene Finastyr 615-PO (from Labofina) containing about 9% rubber.

The melt flow index of LDPE and HIPS is 0.96 g/10 min (190°C, 50 N) and 4 g/10 min (200°C, 50 N), respectively.

The emulsifier was a poly(hydrogenated butadiene-b-styrene) tapered diblock copolymer (*Ref. SE-4*, $\bar{M}n$ = 80,000) already used in LDPE/PS blends (8, 10). It was prepared by anionically polymerizing a mixture of equal weight amounts of butadiene and styrene in toluene (sec-BuLi initiation) and further hydrogenation of PB chains (containing about 10% vinyl units) by Ziegler-type catalysts. In this tapered structure, a

more or less random copolymer forms a transition zone between pure PB and PS blocks. This zone is assumed to contain equimolar amounts of butadiene and styrene. Then, the copolymer can be described by the sequence of partial molecular weights 32,000-22,000-26,000 for PB-b-P (B-co-S)-b-PS (8).

Simple blends of LDPE and HIPS and blends modified with 5 parts copolymer SE-4 (amount added to 100% pure LDPE/HIPS blends) were prepared in the melt state over the whole composition range by using a laboratory two-roll mill at 200°C. Pure LDPE/HIPS blends were mixed for 5 min after homogenization of the molten components on the rolls. In a general manner, the block copolymer was first incorporated to the minor component on the roll-mill before addition of the major component (although the order of addition should not change significantly final properties as already observed for PE/PS blends) and the mixture was roll-milled for 5 min after homogenization. The resulting blends were thereafter compression molded into plaques at 200°C for 3 min under 17.5 MPa pressure and allowed to cool to room temperature.

Tensile specimens DIN 53448 and notched impact specimens DIN 53453 (0.3 mm notch) were machined from the plaques. Stress-strain measurements were performed on an Adamel-Lhomargy tensile tester at a cross-head speed of 20 mm·min⁻¹. Charpy impact strength was measured at room temperature on a Ceast instrumented fractoscope.

The morphology of the blends was investigated by various methods: 5 μm-thick sections were observed by optical microscopy after selectively staining the PS-phases in deep-violet according to a method devised in this laboratory (13). Fracture surfaces prepared either at liquid nitrogen temperature or at room temperature (from tensile or impact tests) and further surfaces smoothed with a microtome were examined by scanning electron microscopy (SEM, Philips 501). Selective extractions of free PS by THF (3 successive extractions at room temperature for 24 h) were also performed on HIPS-rich blends in order to define the nature of the continuous phase and to gain morphological information on the rubber phase.

RESULTS AND DISCUSSION

Morphology of the Blends

The morphology of polymer blends is primarily affected by two factors: interfacial tension and rheological properties (14). Particle size increases as the interfacial tension increases and as the viscosity ratio deviates from unity. In the present case, the melt indices of the two polymers suggest that LDPE is much more viscous than HIPS; furthermore, interfacial tension between PE and PS is reported to be high: 5.1 mN/m at 180°C (14). As a result, coarse phase dispersions are observed in the studied LDPE/HIPS blends at every composition, a situation which is quite similar to that already reported for other LDPE/PS mixtures (9).

Optical micrographs obtained after staining the HIPS phases clearly depict this dramatic situation for 80/20 and 20/80 compositions (Fig. 1a and 1c). SEM micrographs of surfaces smoothed with a microtome also put in evidence that these coarsely dispersed phases display no adhesion with the matrix. Interfacial failures occur upon cutting the sample with the glass knife of the microtome (Fig. 2a–d).

Upon addition of the block copolymer (5 parts), emulsification of LDPE and HIPS takes place leading to a much finer dispersion of phases (Fig. 1b and 1d). It is to be noted that the rubber content of HIPS is about 9% but the rubber particles contain typically a similar amount of hard PS inclusions (15). This structure is characteristic of material that has gone through a phase inversion during polymerization; a so-called "salami-type" structure is thus observed when sections are examined by electron microscopy (15). Most of this substantial amount of PS phase associated with the rubber is chemically grafted. Considering this PS content, the volume of the rubber phase in the present HIPS sample should be close to
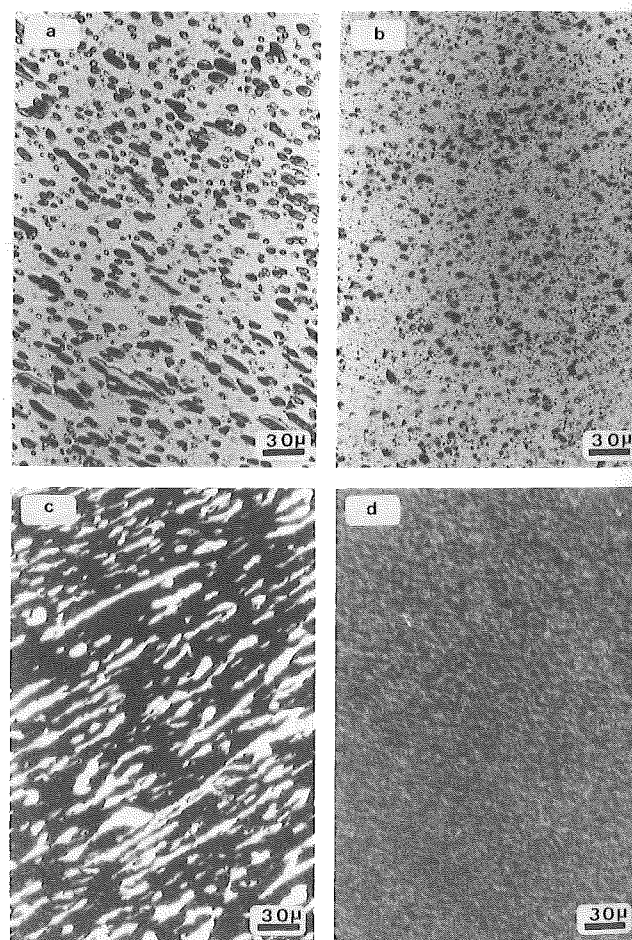

Fig. 1. Optical microscopy of LDPE/HIPS blends after selective staining of PS phases (a): 80PE/20HIPS without copolymer; (b): the same with 5 phr HPB-b-PS copolymer; (c): 20PE/80HIPS without copolymer; and (d): the same with 5 phr HPB-b-PS copolymer.

18%, with a mean particle diameter of about 5 μm (15). These rubber particles remain thus unchanged in the emulsified blend (as, for instance, observed in Fig. 1b) and are dispersed either in LDPE or in PS phases depending on the composition. Micrographs obtained by SEM of smoothed surfaces depict fairly well this particular morphology displayed by the emulsified LDPE/HIPS blends (Fig. 3a–d). They also put in evidence that the copolymer is responsible for a better interfacial adhesion. Whereas abundant interfacial failures occur in the unmodified blends, sectioning the emulsified samples both in the PE matrix and the rubber particles does not promote any apparent decohesion, as clearly illustrated in Fig. 3a for the blend containing 80% LDPE.

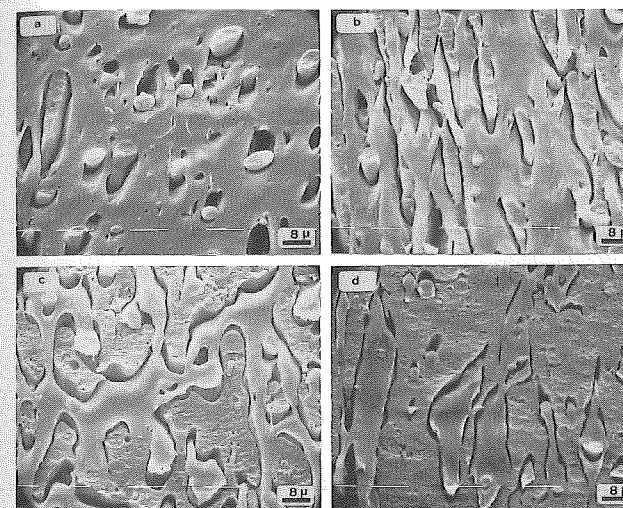It is also to be noted that smoothing is performed

Fig. 2. SEM of LDPE/HIPS blends (smoothed surfaces) (a): 80PE/20HIPS; (b): 60PE/40HIPS; (c): 40PE/60HIPS; and (d): 20PE/80HIPS.
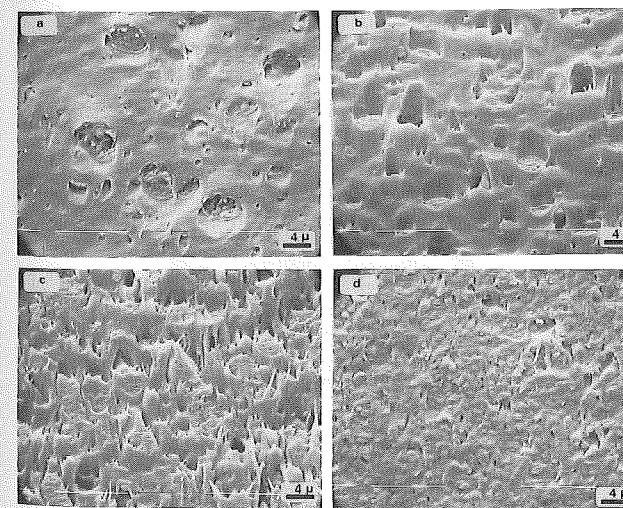

Fig. 3. SEM of LDPE/HIPS blends modified with 5 phr HPB-b-PS copolymer (smoothed surfaces) (a): 80PE/20HIPS; (b): 60PE/40HIPS; (c): 40PE/60HIPS; and (d): 20PE/80HIPS.

at room temperature; it creates lots of yielding in the emulsified blends only, but not in the pure blends (compare Fig. 2 to Fig. 3). Yielding is thus to be related to the presence of the emulsifier.

When HIPS is melt blended with LDPE alone (without emulsifier), the rubber particles tend to remain in the PS phases and little rubber-LDPE interface is formed since PS grafted on the rubber promotes the adhesion of the particle to the free PS content of the HIPS. Thus, in a PE-rich blend, HIPS is mainly dispersed in the PE matrix as rubber particles surrounded by free homo-PS (see Fig. 4a). The emulsifying effect of the HPB-b-PS copolymer will then consist in removing the surrounding free PS and dispersing it as fine and stabilized particles in the PE matrix. As a result, a LDPE matrix/rubber particles interface is generated. Thanks to interactions between the PS block of the emulsifier and PS grafted at the rubber surface, the block copolymer is indeed able to locate at this LDPE/rubber interface, and ensure mutual adhesion. Two types of dispersions are so obtained as illustrated in Fig. 4b and micrographs 1b and 3a.

When the PE content of the blend decreases, co-continuous structures are formed even in mixtures containing only 20 wt% of PE, as already reported for LDPE/PS blends (9). Co-continuous phases are
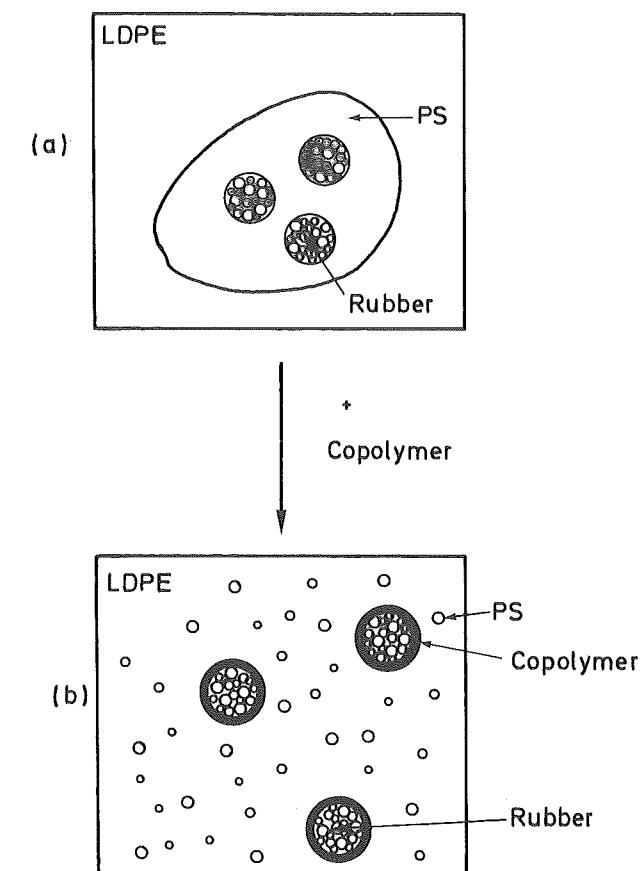

Fig. 4. Effect of the HPB-b-PS copolymer on the dispersion of HIPS in a PE matrix.

well evidenced for blends containing 60% and 40% LDPE (see *Fig. 2b* and *c*). On the other hand, the co-continuous structure displayed by blends containing only 20% PE is quite unstable, in the absence of emulsifier; coalescence of the PE domains takes place upon compression molding the roll-milled samples, destroying completely or partly the continuous PE phase, as illustrated in *Fig. 1c* and *2d*. The HPB-b-PS copolymer is expected to prevent this coalescence phenomenon and to stabilize thus finely interpenetrated PE and PS phases.

In order to put in evidence the particular morphology of these PS-rich blends and to gain additional information on the situation of the rubber particles before and after emulsification by the block copolymer, the PS phases of 20PE/80HIPS mixtures were selectively extracted by THF. Since most of PS occluded in rubber particles is chemically grafted to rubber, extraction is expected to keep unchanged the shape and size of these rubber particles. *Fig. 5a–d* show various aspects of the remaining PE and rubber components after THF extraction for a 20PE/80 HIPS blend containing no copolymer. Note that, since the total gel content of the HIPS is about 18% as mentioned above, the proportion of PE and rubber after removing free PS should be close to 52/48 wt/wt; which is in accordance with the microscopy observation. Indeed, micrographs *5a–d* show a rather self supporting continuous PE-phase with agglomerates of spherical rubber particles tied together.

The situation is quite different when PS is extracted from a blend added with 5 parts of HPB-b-PS copolymer. *Fig. 6a* shows that PE forms a continuous phase with voids of two types: the smaller voids result from the dissolution of free PS microphases by THF whereas the bigger spherical ones contained each a rubber particle (probably removed during extraction). *Fig. 6b* and *c* show that the remaining rubber particles adhere fairly well to LDPE. The most important feature due to the presence of the copolymer is that
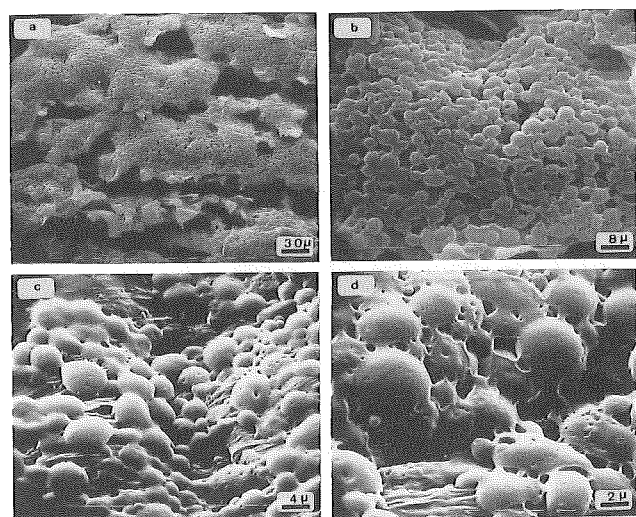

Fig. 5. *SEM of 20LDPE/80HIPS blends after extraction of PS phases with THF.*

no more aggregates of rubber particles are observed but only separate spheres dispersed and anchored in the PE matrix by the block copolymer.

Finally, the beneficial effect of the HPB-b-PS copolymer on the dispersion and interfacial adhesion of PE/HIPS blends is also examplified by the observation of fracture surfaces prepared either at liquid nitrogen or room temperature. SEM micrographs of 20/80 and 80/20 PE/HIPS mixtures containing no copolymer (*Figs. 7a* and *8a*) once again illustrate the poor phase dispersion and adhesion in these blends. In the presence of the copolymer (*Figs. 7b, c* and *8b, c*), the phases are so intermingled that it is very difficult to distinguish them; only the rubber particles are easily observable (see *Fig. 8c*).

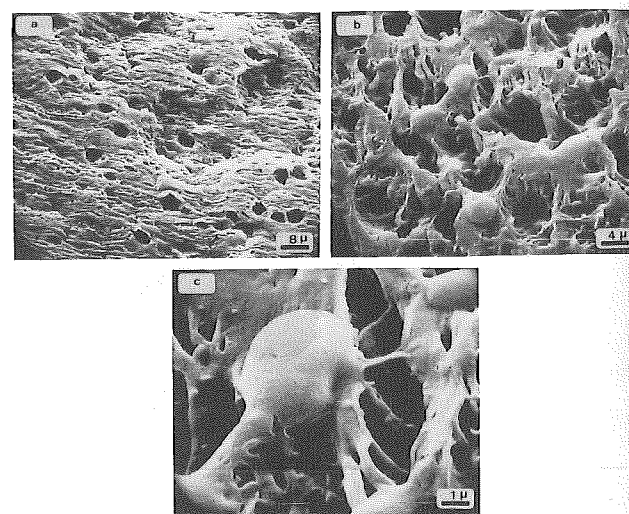Thus, the HPB-b-PS copolymer exerts a highly ben-

Fig. 6. *SEM of 20LDPE/80HIPS blends with 5 phr HPB-b-PS copolymer after extraction of PS phase with THF.*
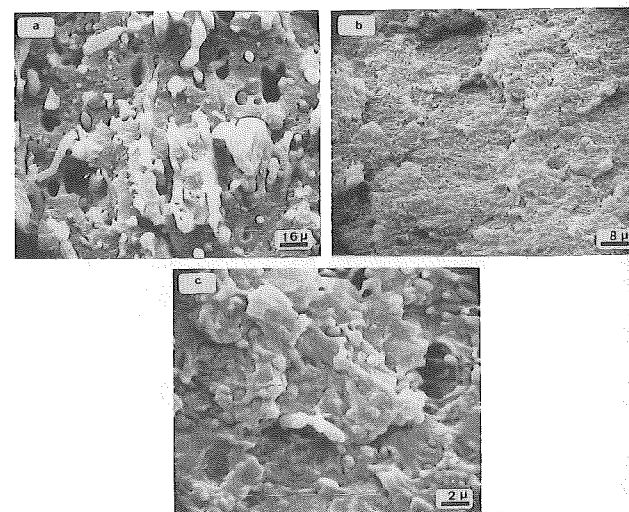

Fig. 7. *SEM of 20LDPE/80HIPS blends (room temperature fracture surfaces from impact tests) (a): no copolymer; (b): with 5 phr HPB-b-PS copolymer; and (c): magnification of (b).*

eficial effect on the morphology of PE/HIPS blends, whatever the composition, and is able to create particular dispersions of the rubber particles in these blends. It is now of interest to investigate the benefit of this emulsifier on the tensile and impact properties of the mixtures.

Mechanical Properties of the Blends

Tensile Behavior

Similarly to LDPE/PS blends previously studied (6, 10), pure LDPE/HIPS blends exhibit poor tensile mechanical properties, although brittleness is less pronounced at certain compositions. Considering the elongation at break, ϵB, the curve in *Fig. 9* indicates that blends containing 10 or 20% LDPE are rather ductile ($\epsilon B > 10\%$) whereas blends richer in PE (40 and 60%) are brittle ($\epsilon B = 3–5\%$). Nevertheless, elongation remains significantly lower than that of pure components and a pronounced minimum in the 40–60 composition range of the ϵB curve is recorded. The
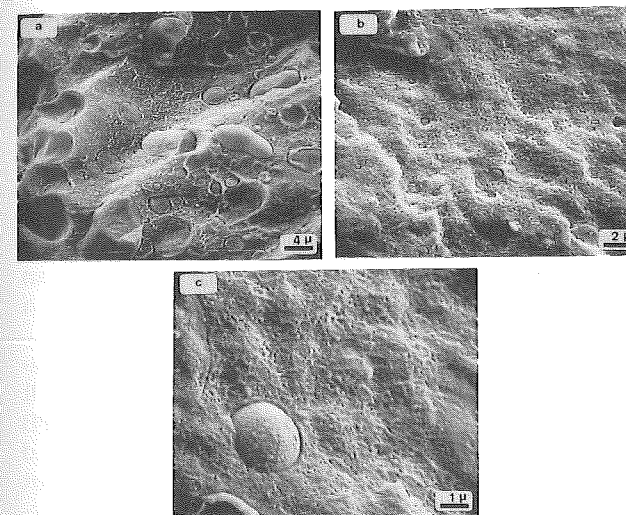

Fig. 8. *SEM of 80LDPE/20HIPS blends (cryofractures) (a): no copolymer; (b): with 5 phr HPB-b-PS copolymer; and (c): magnification of (b).*
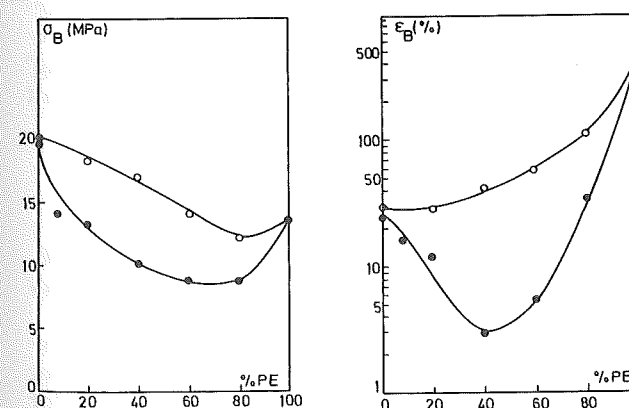

Fig. 9. *Strength at break (σB) and elongation at break (εB) of LDPE/HIPS blends (●): no copolymer; (○): with 5 phr HPB-b-PS copolymer.*

strength at break, σB, of pure blends is also significantly lower than that of HIPS and LDPE, in the region of 60 to 80% PE composition (*Fig. 9*). This poor tensile behavior is markedly improved in blends modified with 5 parts HPB-b-PS copolymer. Both the strength and elongation are increased at all compositions. The minimum in the ϵB curve completely disappears and it is noteworthy to observe that the improvement in the 50/50 composition region is even better for these PE/HIPS blends than for PE/PS ones when emulsified by the same block copolymer SE-4 (6, 8, 10). For instance, ϵB is increased by a factor of 14 for a 40PE/60HIPS blend, whereas a factor 5 only is obtained for the corresponding 40PE/60PS. It seems, therefore, that a combination of HPB-b-PS copolymer and rubber particles is favorable for controlling the ductility of PE/PS blends. Furthermore, a significant increase of the tensile strength, σB, is also observed at every composition, as reported in *Fig. 9*, the extent of improvement remaining close to that reported for PE/PS blends.

Impact Resistance

Previous results (10) demonstrated that the low impact resistance of PS is not increased by simple addition of small amounts of LDPE (10–20%). Curve A in *Fig. 10* illustrates that situation which results mainly from the poor control of phase dispersion and interfacial adhesion. Furthermore, even when both parameters are closely controlled by addition of an efficient HPB-b-PS copolymer, the impact performances remain low, in comparison with those of a classical HIPS (see curve B in *Fig. 10*). That unexpected situation was related to the co-continuous morphology displayed by the emulsified PE/PS blends containing 10 or 20% PE (10). Nevertheless, quite similar results are also recorded when PS is modified with 10 or 20% of HPB-b-PS copolymer, alone (curve B) although no co-continuous phases are observed in this case. All these features demonstrate therefore that the adequate toughening of PS critically depends on both the nature and structure of the soft phase.

Owing to these considerations, it was thus of particular interest to investigate the impact behavior of HIPS as modified by LDPE and/or the HPB-b-PS copolymer. Curve C in *Fig. 10* shows that the Charpy impact strength of HIPS is significantly lowered upon addition of 5, 10, or 20% LDPE and it continuously decreases as the amount of LDPE increases (at least up to 20%). That stresses the importance of the interfacial adhesion in controlling the impact resistance of PS. In contrast to the situation reported for PS (curve B), addition of HPB-b-PS copolymer to pure HIPS or to LDPE/HIPS blends very significantly increases their impact resistance (curves D, E). The beneficial effect of the copolymer (5 parts added in PE/HIPS blends) is noteworthy when curves C and D are compared. For instance, the impact resistance of a 20LDPE/80HIPS blend is increased from 5.3 kJ/m2 to 16.1 kJ/m2 upon addition of the emulsifier,
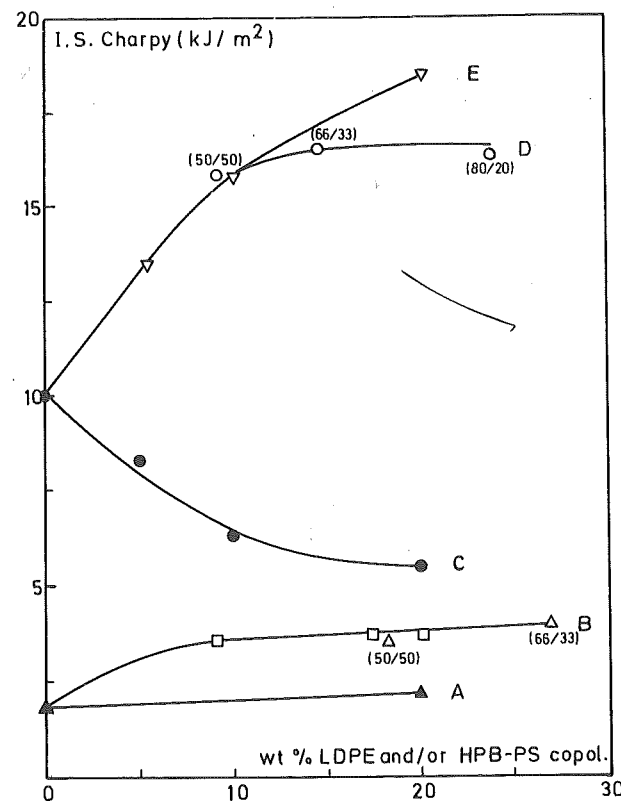
Fig. 10. Charpy impact resistance of HIPS (or PS) blended with LDPE and/or HPB-b-PS copolymer: curve A: PS/LDPE; curve B: PS/HPB-b-PS (□); PS/(LDPE + HPB-b-PS) (△) (10 phr copolymer added to binary PS/PE blends); curve C: HIPS/LDPE; curve D: HIPS/(LDPE + HPB-b-PS) (5 phr copolymer added to binary HIPS/PE blends); and curve E: HIPS/HPB-b-PS. The composition of the LDPE/copolymer soft phase is indicated at corresponding points in curve B and D.
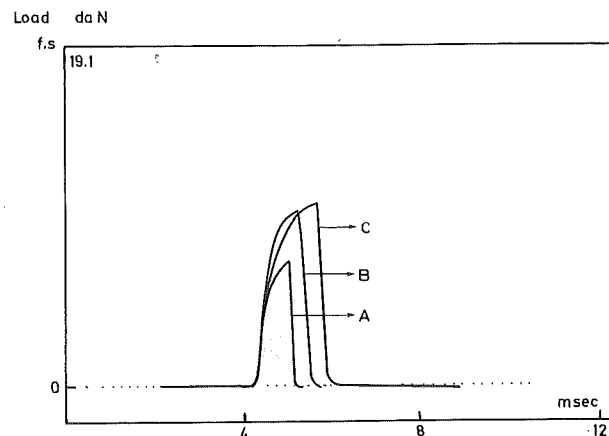

Fig. 11. Fractograms of 10LDPE/90HIPS (curve A); pure HIPS (curve B) and 10LDPE/90HIPS with 5 phr HPB-b-PS copolymer (curve C). Fractogram of a 10HPB-b-PS/90 HIPS blend is similar to curve C.

despite the fact that this emulsified blend exhibits a co-continuous-two phase structure (see Fig. 6). Furthermore, it is interesting to note that the two types of blends (HIPS/copolymer and HIPS/LDPE/copoly-

mer) display the same impact behavior (see curves D and E) when the amount of soft phase added to HIPS does not exceed about 10%, corresponding in fact to 5% LDPE in the emulsified PE/HIPS blend. For higher contents in soft phase, the block copolymer alone is more efficient than LDPE/copolymer combinations in improving the toughness of HIPS. That situation could be related, at least partly, to the formation of a continuous LDPE phase which could be less efficient than discrete particles for controlling the fracture of HIPS. However, additional experiments should be performed to support these considerations.

Finally, fractograms reported in Fig. 11 also show that the fracture mechanism of pure HIPS (curve A) is not affected by the presence of PE and/or copolymer (curves B, C). In all cases, fracture is mainly controlled by crazing; the fractograms have the same shape; only the area representing the total energy to break is increased.

CONCLUSION

The present investigation clearly demonstrates the highly beneficial effect of a HPB-b-PS copolymer on the morphology and mechanical properties of LDPE/HIPS blends. The copolymer promotes the dispersion and interfacial adhesion with LDPE of both PS and rubber particles constituting HIPS. The very significant and simultaneous improvement in both the tensile and impact behavior of the blends indicate that the ductility of LDPE/PS blends can be efficiently controlled to an even better level than in HIPS by an appropriate combination of rubber particles and a suitable diblock copolymer.

Synergistic effects might result from such combinations and that eventuality will be investigated. It is also interesting to mention that replacing the HPB block of a HPB-b-PS copolymer by a hydrogenated polyisoprene one leads to an emulsifier quite efficient for improving very significantly the impact resistance of PS/EPDM blends (5).

All these results emphasize that the interest of diblock copolymers goes beyond their simple interfacial action in incompatible polymer mixtures. Particular morphologies displaying interesting properties can be generated during the emulsification process, with, in addition, the possibility of "freezing" them by an adequate crosslinking (γ post-treatment or other).

ACKNOWLEDGMENT

NOMENCLATURE

LDPE	= low density polyethylene (also referring to PE)
PS	= polystyrene
HIPS	= high impact polystyrene
HPB-b-PS	= hydrogenated polybutadiene-polystyrene diblock copolymer
ϵB	= strength at break
ϵB	= elongation at break

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