

Characterization and Control of Interfaces in Emulsified Incompatible Polymer Blends

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Information on the interfacial region in incompatible polymer mixtures can be gathered using various techniques including electron microscopy, thermal transition analysis, and more sophisticated methods such as nonradiative energy transfer (NRET). Selected examples are reported here to illustrate the exciting potentialities offered by diblock copolymer emulsifiers in controlling interfacial adhesion and devising high performance polymer blends.

INTRODUCTION

The coming of age of polymer melt-blending has certainly provided the easiest and often the most efficient way to generate new higher performance organic materials, starting from largely available monomers and polymers. In spite of the great interest of homogeneous blends (e.g., Noryl), more desirable (1) would be a nonmiscible system, i.e., a heterophase mixture wherein each of the partners retains its own properties, which then sum up in a final product that in addition may also display some new features triggered by the particular phase morphology.

In such systems, however, a satisfactory overall physico-mechanical behavior will critically depend on two demanding structural parameters: a proper interfacial tension leading to a phase size small enough to allow the material be considered as macroscopically "homogeneous," and an interphase "adhesion" strong enough to assimilate stresses and strains without disruption of the established morphology. Unfortunately, that is not the case for most immiscible polymer blends.

That situation has been traditionally alleviated by creating a practically irreversible morphology in the polymerization process itself, as illustrated by the classical examples of high-impact polystyrene and acrylonitrile-butadiene-styrene (ABS) resins. Blending the same rigid and elastomeric polymers would, however, represent a more versatile approach, since it would allow the production of a continuum of different compositions by simply processing various proportions of the base polymers. In order to promote the lacking proper interfacial adhesion, diblock copolymers of tailored structure and molecular weight have been used (2-8), leading to excellent properties of the corresponding fi-

nal materials even when used in rather low proportions (ca., 1 to 2 weight percent).

This paper presents a few illustrative examples that explore that interface situation: its development, behavior, and influence on the final properties, along with some preliminary approaches for a finer characterization of the molecular arrangements in the interface itself, since such basic knowledge would, of course, provide a very useful tool for devising ever more performant materials.

MICROSCOPIC OBSERVATION OF THE "EMULSIFIER" DIBLOCK COPOLYMER

Considering the determinant effect of block copolymers on immiscible blends properties, it was an obvious step to ascribe that beneficial influence to their presence at the interface and to attempt their direct visualization, as already proposed for solution blending (9). That was done in two rather different cases, worth discussing comparatively.

It has been previously demonstrated that blends of polystyrene (PS) and low density polyethylene (LDPE) could be optimized into very interesting materials (2-6) by using emulsifiers prepared from styrene and butadiene block copolymerization followed by diene block hydrogenation (P(S-b-HBD)). Since that hydrogenation process previously described by Falk (10) can be run under conditions where polyisoprene is not reactive, a triblock copolymer poly(styrene-b-isoprene-b-butadiene) was synthesized in which the relatively short (15,000) isoprene sequence (PI) remained unsaturated upon further hydrogenation and could be stained with OsO₄ for direct observation by transmission electron microscopy (TEM). The micrographs of PS/LDPE/P(S-b-I-b-HBD) blends clearly show (Fig. 1) that most of the copolymer is nicely

located at the interface in 80 PE/20 PS as well as in 80 PS/20 PE blends. In this latter material, in fact a high-impact good aging PS, a "salami-type" secondary inclusion structure can even be observed as in classical HIPS, although it is difficult to assess whether these inclusions consist of pure diblock copolymer particles or also contain homopolystyrene. Such an overall situation obviously explains the excellent properties of these materials, which keep their finely dispersed (and sometimes co-continuous) morphology (ca., 0.5 μm) even under drastic processing conditions such as injection molding.

A rough estimation of the interface coverage (continuous and ca. 10 nm thick close to the calculated unperturbed end-to-end chain length of such a PI leads to a surface occupation per molecule of more than 26 nm (11).

For comparison purposes, a blend of 85 PVC/15 SEBS Kraton G was emulsified by a P(HBD-b-MMA) copolymer, since the molecular miscibility of syndiotactic PMMA (s-PMMA) in PVC has been definitively demonstrated in that range of molecular weight (ca., 40,000) by NRET experiments (12). Although that procedure results in the usual phase size decrease down to ca. 1 μm and a definite improvement of the mechanical properties (leading to a very

high impact strength material), transmission micrographs (where the PMMA block has been labelled by consecutive hydrazine and OsO₄ treatments) clearly show that a major part of the copolymer is dispersed in the PVC phase instead of concentrated preferentially at the interface (Fig. 2a); therefore a definitely higher concentration (ca., 5 percent) of block copolymer is needed in order to reach interesting sets of properties. Similar situations are observed in the case of 80 PS/20 PVC blends with 5 percent of a P(S-b-MMA) copolymer (Fig. 2b). That very different behavior dramatically illustrates the prime importance of the interaction parameters balance, to favor selective migration of the emulsifier at the interface. No doubt a properly tailored decrease in interaction of the methacrylate block with PVC (i.e., by controlling microstructure, molecular weight, and composition) would restore a more favorable situation but again at the cost of a long optimization process.

COPOLYMER BEHAVIOR AT INTERFACE FROM NONRADIATIVE ENERGY TRANSFER (NRET) MEASUREMENTS

The application of NRET measurements to synthetic polymers, as pioneered by Morawetz

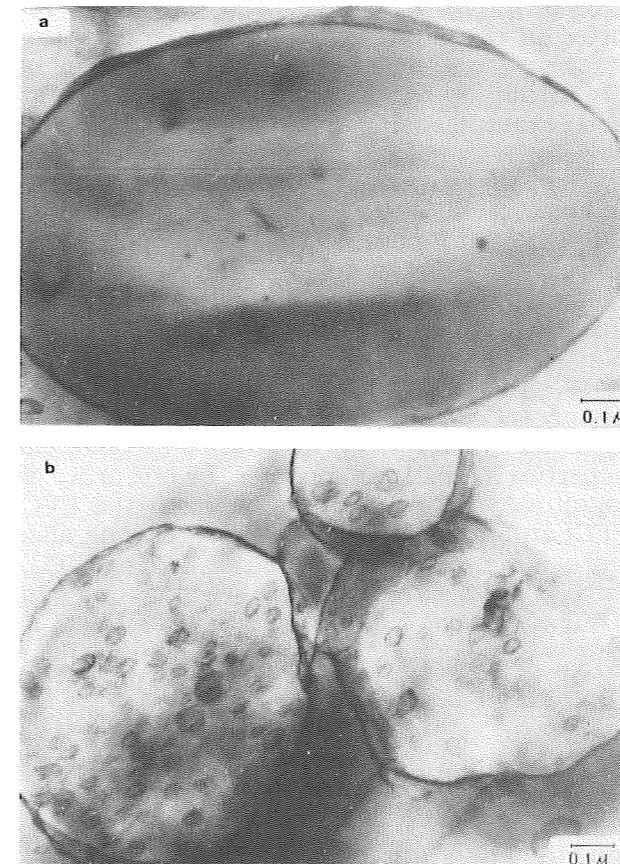


Fig. 1. Transmission electron micrographs of LDPE/PS blends (roll-milled and compression molded) with 10 weight percent P(S-b-I-b-HBD) copolymer added: (a) 80 weight percent LDPE/20 weight percent PS; (b) 20 weight percent LDPE/80 weight percent PS (Reproduced with permission (11) of *J. Polym. Sci.*).

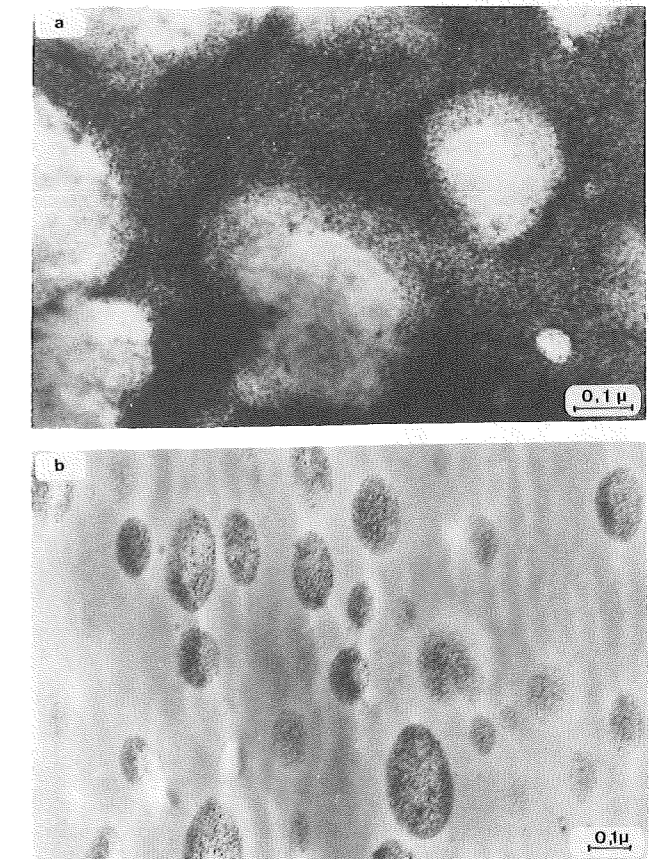


Fig. 2. Transmission electron micrographs of roll milled and compression molded blends: (a) 80 weight percent PVC/15 weight percent Kraton G/5 weight percent P(HBD-b-MMA) copolymer; (b) 20 weight percent PVC/80 weight percent PS with 10 weight percent P(S-b-MMA) copolymer added. PMMA was selectively stained by consecutive hydrazine and OsO₄ treatment.

(13), has provided scientists with a method for the evaluation of different macromolecule interpenetration at the molecular level, giving rise to many applications with respect to polymer chain dynamics and interactions. Thus, it was of great interest to apply that method to an immiscible blend situation, thanks to the post-labeling methods recently developed in our laboratories (12).

In particular, they allowed us to compare a blend of PVC and s-PMMA to an exactly corresponding situation (in terms of composition and molecular weights where the homopolymer was replaced by a P(S-b-MMA) diblock. The PMMA was labelled with 1.5 mol percent anthracene (acceptor), whereas the PVC was grafted with 1 mol percent naphthalene (donor). The NRET from donor to acceptor chromophores depends on the extent to which the chains of the different polymers are able to interpenetrate. The efficiency of the energy transfer is measured by the ratio of the emission intensity of the naphthyl and anthryl labels (I_D/I_A), which is, therefore, a sensitive indicator of polymer miscibility on a scale of a few nm. The fluorescence behavior of these systems is illustrated in Fig. 3 where it appears that compared to a blank giving an I_D/I_A value of 0.18 (value for a homogeneous system), lower molecular weight (4×10^4) PMMA is practically miscible with PVC on a molecular scale (ca., 2 nm) up to a molar fraction of 0.8; while an increasing molecular weight (15×10^4) results in a somewhat lower solubility (note however, that total phase separation should theoretically give a I_D/I_A value of 13.2). More unexpectedly (12), the labelled PMMA sequence in the block copolymer behaves exactly as free PMMA homopolymer with maximum intermixing, although the PS block is obviously insoluble in PVC and forms its own segregated domains. In other words, a reduction of the interface at the expense of interactions between the s-PMMA block and PVC is an unfavorable proc-

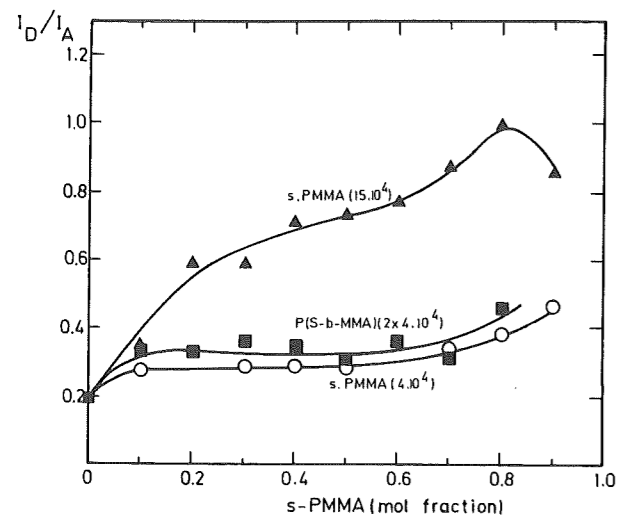


Fig. 3. Emission intensity ratio (I_D/I_A) as a function of molar fraction of syndiotactic PMMA in PVC/s-PMMA and PVC/P(S-b-MMA) blends.

ess, at least in that range (4×10^4) of molecular weights.

These results certainly support the validity of our approach using tailored polymer emulsifiers P(A-b-C) to bridge the incompatibility gap between polymers, A and B, provided C is miscible with B. They also represent a first exploratory demonstration of a general method to investigate in depth the situation of block copolymers at interfaces, by labelling in turn the different partners in the blend and systematically modifying their structural parameters. Although qualitative, the results can be put on a relative scale indicating existing trends, and thus represent an additional and sensitive key for tailoring these situations.

THERMAL TRANSITIONS AS A PROBE FOR INTERFACES

Certainly of less general application, thermal transitions may however represent, in spite of their indirect indications, an interesting probe for the existence and nature of interfacial regions, particularly for unstable ones. For example, differential scanning calorimetry (DSC) and thermally stimulated depolarization currents (TSDC) have been used to seek thermal transitions indicative of special interphase situations, even transient ones. In particular, three different T_g 's have been repeatedly reported in reorganizing two-component heterophase systems, being either block copolymers (14-16) or ion-containing polymers (17). Another example using a dynamic method will henceforth be used to these potentialities.

When measuring the isochronous torsion modulus of 80 PVC/20 PS blends combined with different amounts of a block copolymer P (caprolactone-b-styrene), P (CL-b-S) acting as an emulsifier since polycaprolactone is miscible with PVC (18, 19), one observes the usual features characteristic of such materials: heterophase situation (practically unchanged homopolymers T_g 's), decreased phase size, and improvement (see Fig. 4) in physico-mechanical properties (i.e., strong increase, by one order of magnitude, of the modulus between the PVC (80°C) and PS (100°C) T_g 's). However, one also clearly observes a third transition around 50°C, which counter experiments have shown not to be due to PCL crystallinity; in all probability, it expresses the presence of a crown of PVC "plasticized" by PCL blocks around the PS domains. Moreover, its position is slightly dependent on the amount of copolymer added (10 and 20 percent), and allows one to calculate the possible composition of that mixed interface (in this case 11 to 15 weight percent of PCL respectively), using the Fox-Flory relation (19).

INTERFACIAL ADHESION AS SEEN BY SCANNING ELECTRON MICROSCOPY (SEM)

Although the methods discussed above can certainly lead to a better view of the molecular

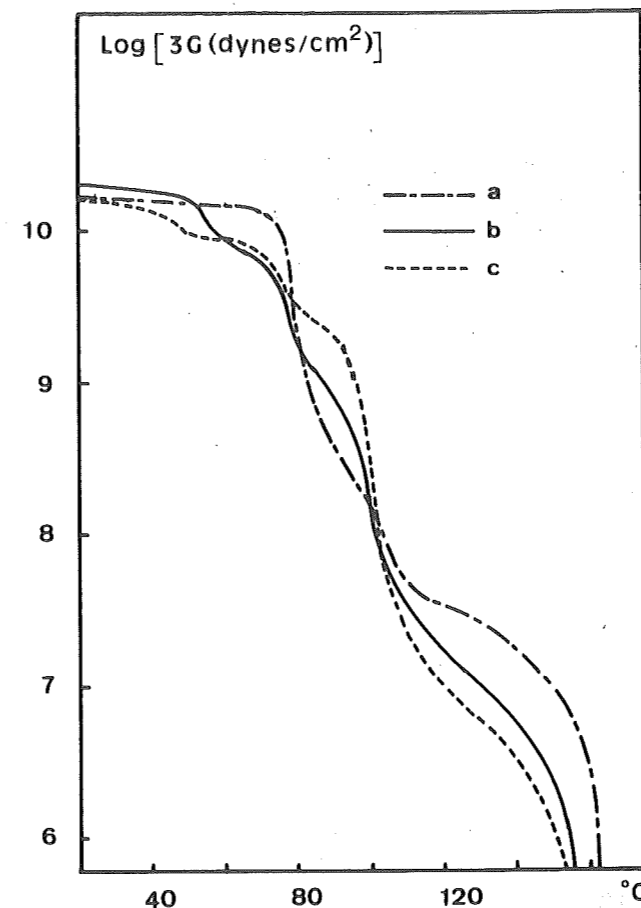


Fig. 4. Torsion modulus versus temperature for PVC/PS blends (roll-milled and compression molded): (a) 80 weight percent PVC/20 weight percent PS; (b) 72 weight percent PVC/18 weight percent PS/10 weight percent P(CL-b-S) copolymer; (c) 64 weight percent PVC/16 weight percent PS/20 weight percent P(CL-b-S) copolymer.

situation at interfaces, they do not provide a clear handle on the essential feature, that is, interphase adhesion under constraint. While physico-mechanical properties do convey that characteristic, it is in a very partial and indirect manner. In spite of the fact that SEM can scarcely locate the emulsifier in interfacial regions (except for a few still questionable cases as illustrated in Fig. 5a), it probably represents one of the more direct and illustrative methods for evaluation of that adhesion, when fracture surfaces of different blends are systematically compared. A number of illustrative cases are presented below.

PS-PE blends may represent interesting materials, especially as substitutes for HIPS, displaying excellent weathering characteristics. In the presence of optimized P(S-b-HBD) emulsifiers mentioned earlier, fracture micrographs show indeed an excellent adhesion between finely dispersed phases, interconnected by fibrils of a few dozen nms in diameter, (Fig. 5b). In some cases, they also give indication of co-continuous situations from which homo-PS, even if dominant, can be extracted without disrupting the general shape of the sample (2, 5) (Fig. 5c).

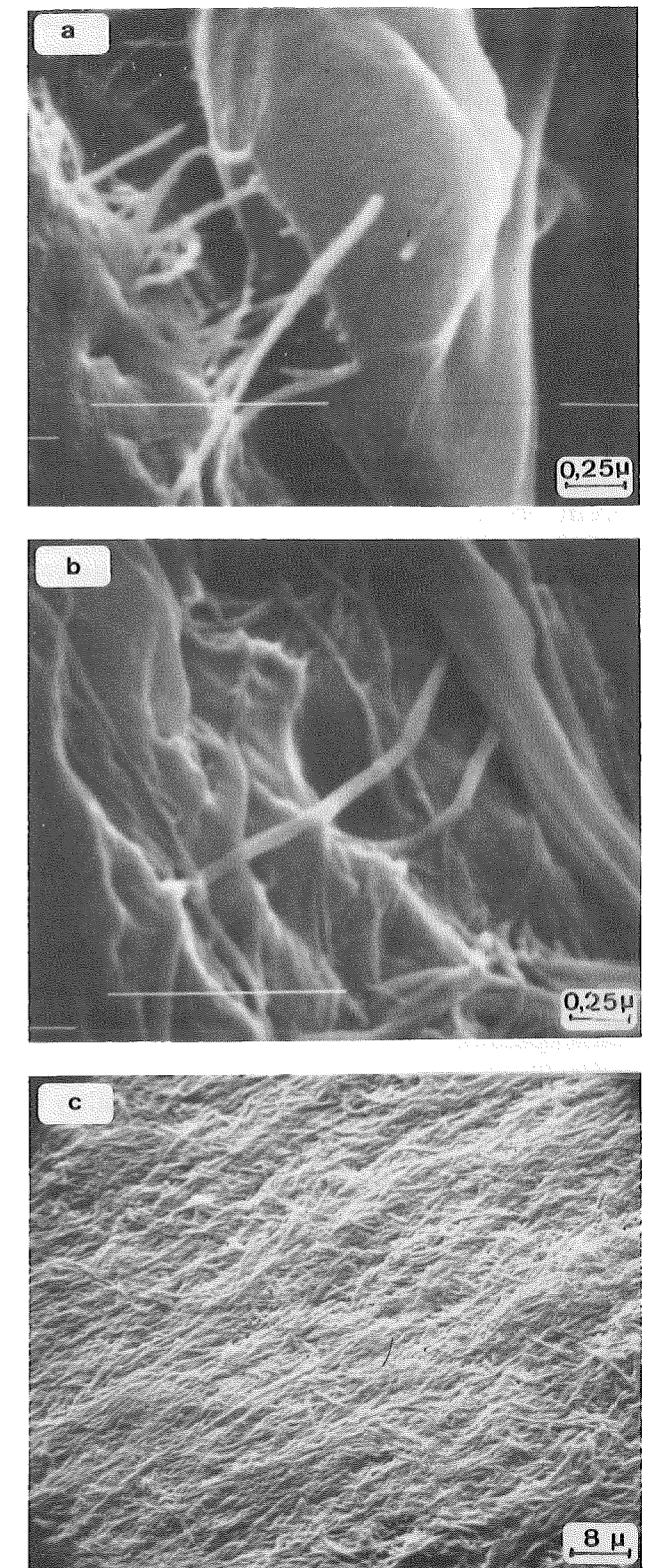


Fig. 5. Scanning electron micrographs of PE/PS blends (roll milled and compression molded): (a) and (b) room temperature fracture surface of 20 weight percent HDPE/80 weight percent PS with 10 weight percent P(S-b-HBD) copolymer added; (c) remaining LDPE phase after THF-extraction of PS in 20 weight percent LDPE/80 weight percent PS with 10 weight percent P(S-b-HBD) copolymer added.

SAN-diene rubber blends are interesting materials similar to ABS, although different from them to some extent. Again, scanning micro-

graphs give an interesting clue to the adhesion situation in such blends: compared to weak heterogeneous materials when no copolymer is used, superbly intermixed products are obtained when a P(BD-b-MMA) copolymer is added, wherein the syndiotactic PMMA sequence strongly interacts with SAN. The excellent adhesion, even better than that of a typical industrial ABS, is evidenced in room-temperature fracture micrographs (Fig. 6) leading to higher impact resistance values and better fractograms (load-time) profiles than ABS itself (7). It is worth stressing that in this case, microscopy even provides for a possible relative evaluation of the resulting material performances.

PS-Nylon-6 blends are another attractive combination of two materials offering very different properties. Despite their extremely different solubility parameters, very fine dispersions of these two polymers can be achieved, wherein one can clearly see the "gluing" of the dispersed phase to the matrix (Fig. 7) thanks to a suitable copolymer; this latter can be any block copolymer of polystyrene and of another polymer ensuring strong interactions with the polyamide including Nylon-6 itself (20).

A final example pertains to an engineering plastic, namely polyvinylidene fluoride, PVF₂, the very attractive properties of which are unfortunately limited by its high price and some adverse characteristics. Thus it would be of prime interest to fill it with cheaper polymers (or inorganics), thus yielding more economical materials while still retaining the essential PVF₂ properties (i.e., as the matrix continuous phase) plus potential slight improvements promoted by the filler. Again, s-PMMA block copolymers were chosen, based on the miscibility of that polymer with PVF₂. One variation on that theme is illustrated in the micrographs of Figure 8, demonstrating how a very coarse and

weak blend of 80 PVF₂/20 Noryl (itself a blend of HIPS and polyphenylene oxide) is progressively converted, upon addition of increasing amounts of P(S-b-MMA), into an extremely fine dispersion of perfectly adhering phases, up to a point where they become practically indistinguishable. Needless to say, a parallel improvement of the physico-mechanical properties of the corresponding materials is recorded (8).

CONCLUSIONS

The selected but certainly nonexhaustive examples discussed here clearly illustrate the exciting potentialities offered by diblock copolymer emulsifiers, in devising high performance polymer blends. It has to be stressed, however, that optimization of their structural and size characteristics is an extremely critical key process, often implying painstaking feedback cycles between synthesis and evaluation, an imperative requirement due to narrow structural "windows" within which the high performance properties develop.

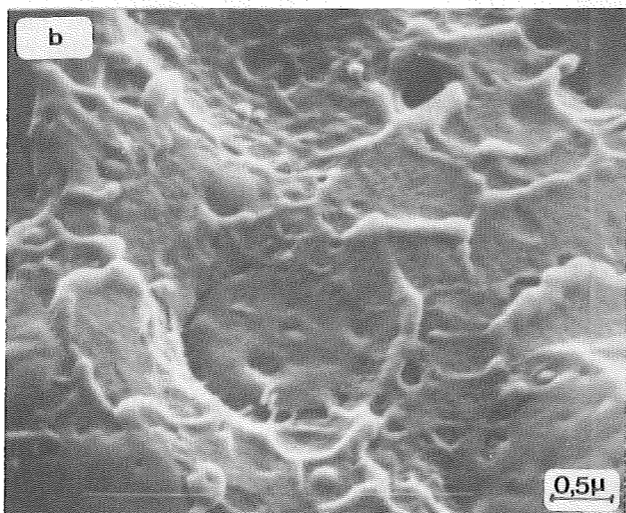
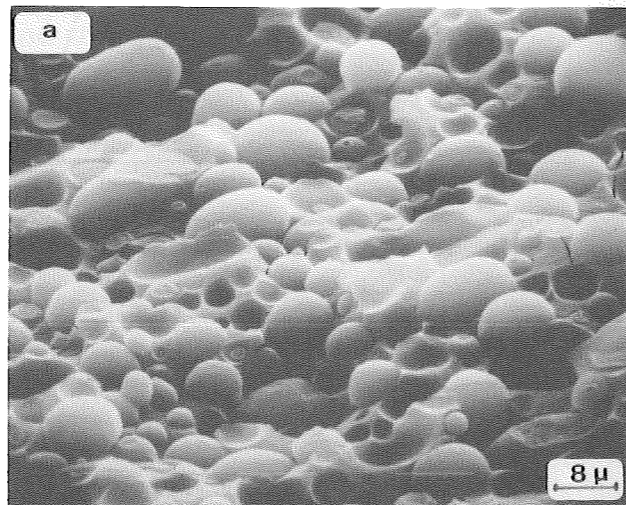


Fig. 7. Scanning electron micrographs of room temperature fracture surface of 50 weight percent PS/50 weight percent Nylon-6 blends (roll-milled and compression molded): (a) without copolymer; (b) with 5 weight percent copolymer added.

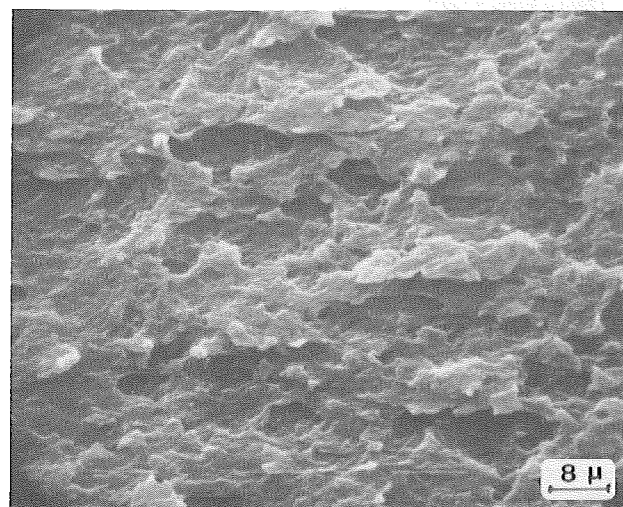


Fig. 6. Scanning electron micrograph of fracture surface (from a Charpy impact test) of 66.5 weight percent SAN/23.5 weight percent Solprene 411, SB thermoplastic elastomer/10 weight percent P(BD-b-MMA) copolymer (roll-milled and compression molded blends).

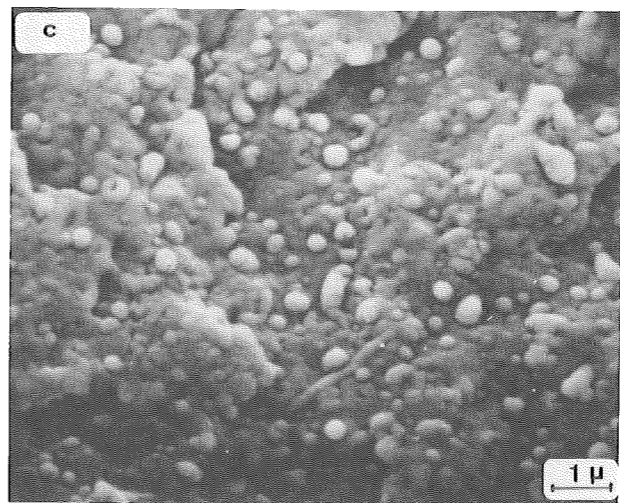
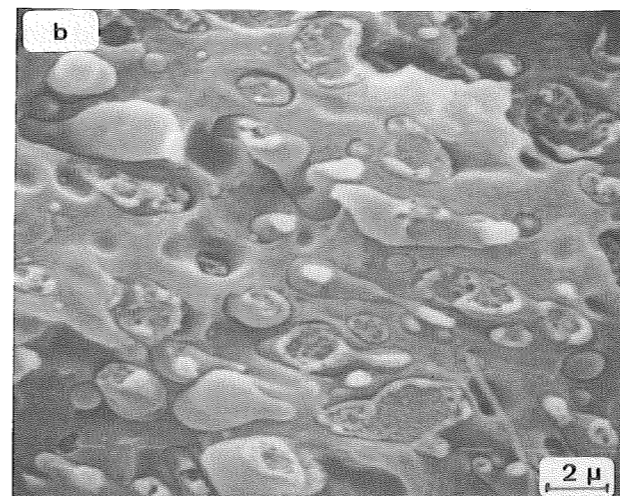
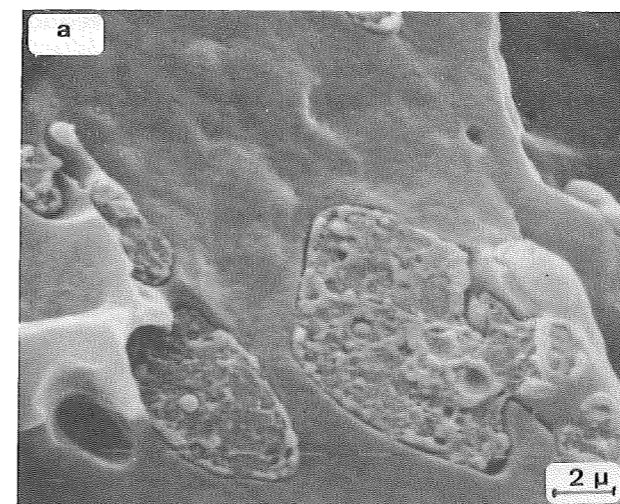


Fig. 8. Scanning electron micrographs of room temperature fracture surfaces of 80 weight percent PVF₂/20 weight percent Noryl blends (roll-milled and compression molded): (a) without copolymer; (b) with 2 weight percent P(S-b-MMA) copolymer; (c) with 12 weight percent P(S-b-MMA) copolymer. Reprinted with permission (8) of *J. Polym. Sci.*

theoretical approaches (such as those of Meier (21) and Noolandi *et al.* (22)), a detailed experimental characterization of the interface situation will be a necessary foundation in this field. Thus it is fortunate that a number of powerful, if delicate, physical techniques are now available for that purpose: electron microscopy (SEM, TEM), solid-state NMR spectroscopy (possibly using D or ¹³C labelled copolymers), scattering techniques using synchrotron radiation (23), and last but not least, the nonradiative energy transfer method will certainly help us to unravel the fascinating behavior of these interfaces and to meet the challenge of using them to fabricate better materials.

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With that respect, deeper understanding of the necessary structural and processing features for further improving that general approach is obviously desirable. Beside valuable

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NOMENCLATURE

LDPE	= low density polyethylene.
HDPE	= high density polyethylene.
PS	= polystyrene.
PMMA	= polymethylmethacrylate.
s-PMMA	= syndiotactic PMMA.
PVC	= polyvinyl chloride.
PCL	= poly- ϵ -caprolactone.
SAN	= styrene-co-acrylonitrile polymer.
PVF ₂	= polyvinylidene fluoride.
HIPS	= high impact polystyrene.
ABS	= acrylonitrile-butadiene-styrene copolymer.
SEBS	= styrene-ethylene butene-styrene triblock copolymer.
P(S-b-I-b-HBD)	= styrene-isoprene-hydrogenated butadiene triblock copolymer.
P(S-b-HBD)	= styrene-hydrogenated butadiene diblock copolymer.
P(BD-b-MMA)	= butadiene-methylmethacrylate diblock copolymer.
P(S-b-MMA)	= styrene-methylmethacrylate diblock copolymer.
P(CL-b-S)	= caprolactone-styrene diblock copolymer.

DISCUSSION

A. P. Plochocki: How did you prepare your blends? Did you mix in a molten state?

Ph. Teyssié: We used different methods and different mixers, but most often a two-roll mill to follow the kinetics of dispersion by microscopy. However, these di-blocks were also used in other classical operations, e.g., extrusion, and they work very well.

C. L. Beatty: Did you see any difference in morphology changing the blending method?

Ph. Teyssié: Not really. Of course you have to mill for a few minutes, until equilibrium. If you

have the proper blocks, mixing for 30 seconds may be sufficient.

L. W. Kleiner: Have you determined the equilibrium concentration of compatibilizers in these blends?

Ph. Teyssié: Yes. This will be published very soon. The optimum concentration depends a lot on the optimum structure that you want to develop. If you optimized the copolymer, and that is not an easy process, then one percent is enough; you will reach a plateau in the properties and morphology. If you use too much of it, then you loose. In general, for well tailored block copolymers 1 to 2 percent is enough.

L. A. Utracki: In principle, you are achieving the enhancement of polymer blend properties by treating the two-phase polymeric liquid mixture as an emulsion, stabilizing the system with an emulsifier, called here two-block compatibilizer. You are controlling the dispersion and in general achieving greater reproducibility of properties by modifying the interfacial properties in the molten state. This immediately suggests three questions: (i) did you develop adequate means of characterization of the interfacial properties, e.g., to measure the interfacial tension; (ii) how the solidification in the presence of a difference in the thermal expansion coefficient affects the interfacial behavior; and (iii) is the method suitable only to generate droplet-type morphology or can it be also used efficiently to enhance properties in blends with co-continuous structures?

Ph. Teyssié: Yes, we are trying to optimize the performance of immiscible polymer blends by addition of small amounts of specially designed interfacial agents. As far as the measurement of the interfacial properties are concerned, we are using several approaches which I mentioned during the presentation. Microscopy with or without staining, nonradiative energy transfer (NRET), scattering techniques, or NMR. However, there is a need to develop a simple experimental method to characterize the interface. The most universal at the moment seems to be the NRET, but it requires chemical modification of the system.

Formation of Dispersed Phase in Incompatible Polymer Blends: Interfacial and Rheological Effects

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The formation of dispersed phase in blends of incompatible polymers during melt extrusion with a co-rotating twin screw extruder was studied, using nylon and polyester as the matrix and ethylene-propylene rubbers as the dispersed phase. A master curve is obtained, i.e., $G\eta_m a/\gamma = 4p^{\pm 0.84}$, where G is the shear rate, a the particle diameter, γ the interfacial tension, η_m the matrix viscosity, η_d the dispersed-drop viscosity, and $p = \eta_d/\eta_m$. The plus (+) sign applies for $p > 1$, and the minus (-) sign for $p < 1$. Thus, the dispersed-drop size is directly proportional to the interfacial tension and the ± 0.84 power of viscosity ratio. The dispersed drops are the smaller, when the interfacial tension is the lower and the viscosity ratio is the closer to unity. The interfacial tension is largely controlled by the polarities of the two phases, and can be varied over several orders of magnitude by using appropriate dispersants.

INTRODUCTION

The size and shape of the dispersed phase are important factors that determine the mechanical properties of incompatible polymer blends. In rubber-toughened plastics, two types of behavior have been observed. In blends that dissipate fracture energy mainly by matrix crazing, the toughness is the greatest at an optimum rubber particle size (1). Examples are blends with matrices of polystyrene and poly(methyl methacrylate). On the other hand, in blends that dissipate fracture energy mainly by matrix yielding, a sharp brittle-tough transition occurs at a critical rubber particle size, or when the interparticle distance is at the critical value (1). Examples are blends with matrices of nylon and thermoplastic polyesters.

Melt extrusion is an important process for making polymer blends. During extrusion, the components are melt-blended, and the minor phase is broken up to form the dispersed phase. The size and shape of the dispersed phase are much controlled by the interfacial tension, rheological properties, and the complex strain field of the extruder. In this work, we study the interfacial and rheological effects on the dispersion process during melt extrusion of polymer/rubber blends in a co-rotating twin screw extruder.

EXPERIMENTAL

Materials

Two nylon 66 resins (coded as nylon Z-1 and Z-2) and one poly(ethylene terephthalate) (coded as PET) were used as the matrix phase. Fourteen ethylene-propylene rubbers of essentially the same chemical composition (63 percent ethylene and 37 percent propylene by weight), but of different molecular weights were used as the dispersed rubber phase in the binary polymer/rubber blends. Eight of the 14 rubbers are non-reactive (coded as EP rubbers), i.e., they do not contain any reactive groups that could react with the matrix. On the other hand, the other six rubbers are reactive (coded as EPX rubbers), i.e., they contain less than 1 percent by weight of carboxyl groups. The reactive rubbers can react with the matrix to form graft copolymers, which act as *in situ* formed dispersant. The molecular weights and the code names for all the materials used are listed in Table 1.

All the polymers (nylons and PET) were vacuum-dried at 120°C overnight, and all rubbers at 80°C overnight before use.

Melt Extrusion

Binary polymer/rubber blends were prepared by melt extrusion, using a co-rotating twin