Molecular Design of Multicomponent Polymer Systems. X. Emulsifying Effect of Poly (styrene-b-methyl methacrylate) in Poly (Vinylidene fluoride)/Noryl Blends.

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Synopsis

The emulsifying activity of block copolymers is investigated in blends of incompatible engineering polymers such as polyvinyldene fluoride (PVF_2) and Noryl (high impact polystyrene-poly-2,6-dimethyl-1,4-phenylene oxide mixture). When the blends are modified by a poly(styrene-b-methyl methacrylate) copolymer, (PS-PMMA) each block of which being selectively miscible with Noryl and PVF_2 respectively, phase dispersion, interfacial adhesion and ultimate mechanical properties are significantly improved; major effect is observed upon addition of 12 percent copolymer, resulting in intermingled and firmly adherent phases and a rough additivity of both tensile strength and elongation at break. All these features clearly demonstrate the important emulsifying effect of PS-PMMA in these very attractive PVF_2/Noryl blends.

INTRODUCTION

As outlined in previous papers,[1-6] much effort is presently being devoted to modification of existing organic materials. Since the production of new polymers exhibiting desirable properties is often cost-prohibitive, the best way of supplying needed specialty materials is the working up of known polymers and particularly their combination in commercially significant blends. Miscible polymer blends have recently reached an attractive position in polymer science and technology: examples are the production of rubber-reinforced polystyrene (HIPS)-poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) (Noryl from General Electric Co) blends, elastomer blends, polyelectrolyte complexes, and high molecular weight plasticizers for poly(vinyl chloride). As mentioned by Olabisi et al., miscibility is not per se a criterion of utility:[7] most commercial multicomponent polymer systems are two-phase blends that display specific advantages over those expected for a single-phase system. The impact strength improvement of brittle, glassy polymers is a convincing example.

It is well-known that the ultimate mechanical properties of phase-separated blends is critically governed by adhesion between individual phases. Thus, the modification of polymer blends with well-chosen block polymers, providing control over interfacial adhesion, can generate heterophase materials with optimum performance. The "emulsifying" activity of block polymers in immiscible polymer blends is the focus of extensive research in our

laboratory, and the beneficial effect of polymeric emulsifiers in binary blends of classic thermoplastics, i.e., polyethylene, polystyrene, and poly(vinyl chloride), has already been reported.[4-6]

These investigations have been extended to engineering polymers such as poly(vinylidene fluoride) (PVF_2), and the "compatibility" of PVF_2 and poly(α-methylstyrene) has been increased by including a poly(α-methylstyrene-b-methyl methacrylate) (PαMS-PMMA) as a bridging material between the phases.[9] This note reports the modification of PVF_2/Noryl blends (in fact, multicomponent blends where the two base components of Noryl [polystyrene (PS) and PPO] are miscible but incompatible with PVF_2), by poly(styrene-b-methyl methacrylate), each sequence of which is selectively miscible with Noryl and PVF_2, respectively

RESULTS AND DISCUSSION

Blends of PVF_2 (SOLEF® 1012 from Solvay; melt flow index (MFI): 3–5 g/10 min at 230°C under 10 kg) and a rubber reinforced PS/PPO mixture (Noryl 731-701 from General Electric Co, believed to contain approximately 50 wt% poly(2,6-dimethyl-1,4-phenylene oxide),[7] were performed on a two-roll mill at 220°C for 5 min and compression-molded at the same temperature. A poly(styrene-b-methyl methacrylate) was prepared by sequential anionic polymerization of styrene and methyl methacrylate according to a procedure described elsewhere.[10] The block polymer contained practically 50 wt% of each block, and its molecular weight was 125,000.

The morphology of the Noryl rich (80%) blends seems already rather homogeneous when observed by optical microscopy (Fig. 1A) and the effect of the block polymer is therefore hardly appreciable (Fig. 1B and C). However, scanning electron microscopy (SEM) of fracture surfaces prepared at liquid-nitrogen temperature shows a lack of interfacial adhesion in these blends (Fig. 2A). Dispersed PVF_2 particles appear unattached to the continuous Noryl matrix and leave clearly apparent holes upon cryofracture. Modified by 2% block polymer, the blends exhibit a more regular and finer phase dispersion (Fig. 2B), but no significant improvement of the interfacial adhesion can be evidenced. The situation evolves drastically when 12% block polymer are used as modifier of the 20% PVF_2 blend (Fig. 2C); cryofracture shows "treads of stairs" constituted by small (ca. 3000 Å) and firmly adherent particles. Cryofracture surfaces of unmodified Noryl (Fig. 3) show a network of bead strings similar to the patterns in Figure 2 C but quite different from those observed in Figure 2A. Thus the cryofracture mechanism of Noryl is not deeply influenced by the mixing of 20% PVF_2 when a sufficient amount of block polymer is used as a "compatibilizing" agent.

The dispersion of 20% Noryl in PVF_2 is very coarse and irregular (Fig. 4A) compared with that of 20% PVF_2 in Noryl (Fig. 1A). The addition of 2% block polymer is sufficient to produce a dramatic modification of the morphology (Fig. 4B), whereas a still finer and highly homogeneous dispersion results from the mixing of 12% block polymer (Fig. 4C). Thus the beneficial effect of the block polymer on the blending of PVF_2 and Noryl is clearly evidenced by optical microscopy in the PVF_2 rich blends.

The SEM of cryofracture surfaces of blends containing 80% PVF_2 confirms the results of optical microscopy. The unmodified blend exhibits very
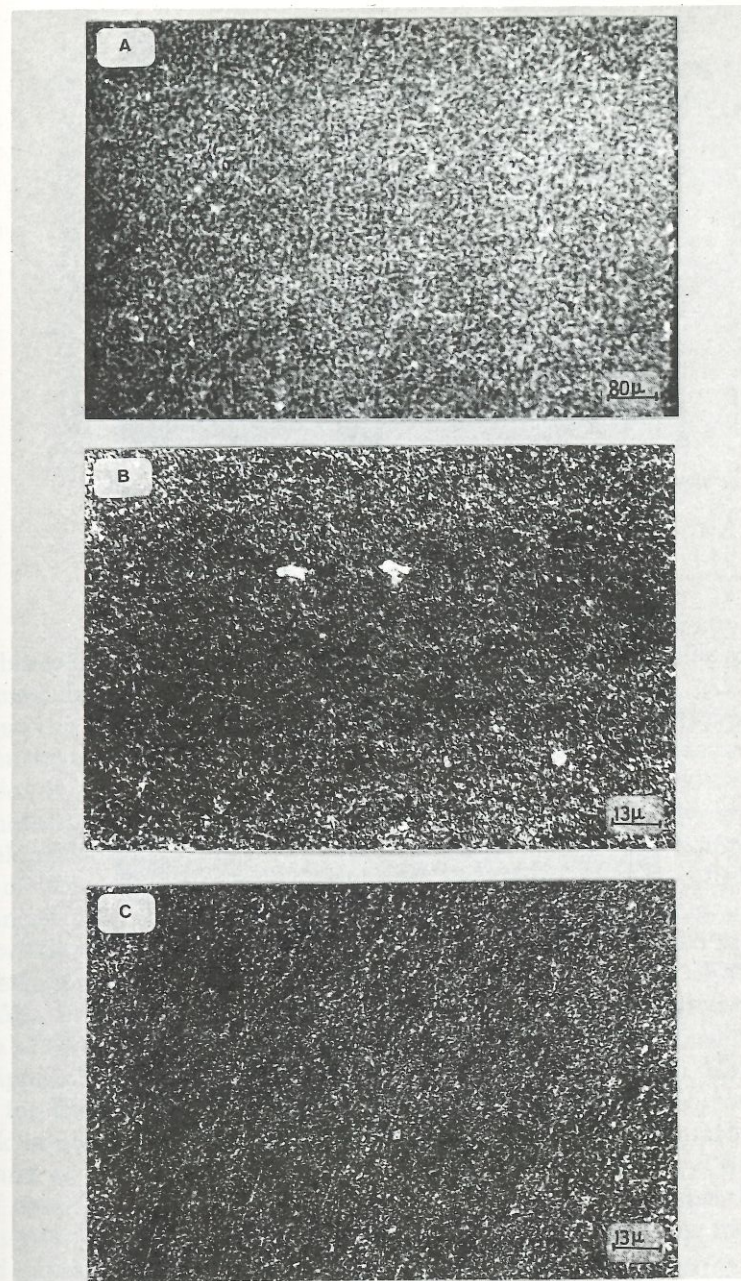
Fig. 1. Optical micrographs of 20/80 PVF_2/Noryl blends: A; without block polymer; B; 2% block polymer added; C; 12% block polymer added.

large domains of Noryl (5–10 μm) with poor adhesion to the PVF_2 matrix (Fig. 5A). A 2% block polymer makes the dispersion of Noryl easier (mean size of Noryl phases ±2 μm) without significantly improving the interfacial adhesion (Fig. 5B). As in the case of Noryl-rich blends (Fig. 2A–C), the addition of 12% block polymer to blends containing 80% PVF_2 is responsible for a deep modification of the morphology (Fig. 5A and C); it is then im-
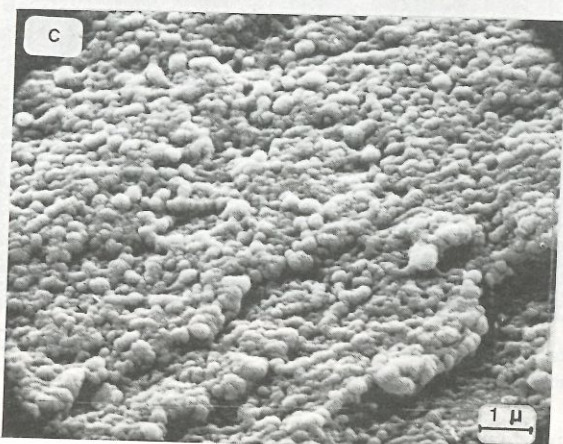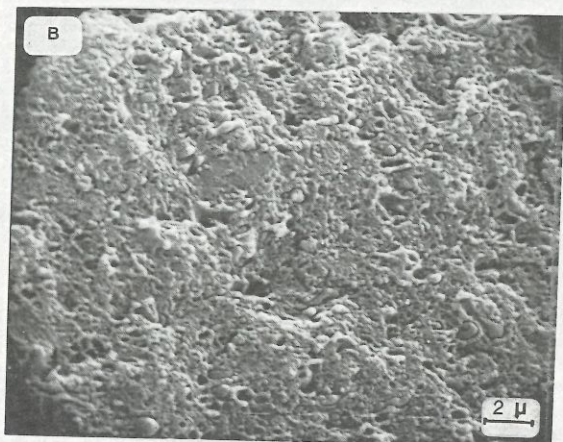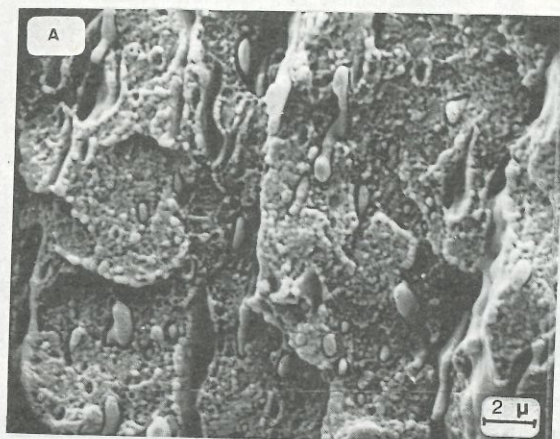
Fig. 2.   Scanning electron micrographs of 20/80 PVF$_2$/Noryl blends: A; without block polymer; B; 2% block polymer added; C; 12% block polymer added.
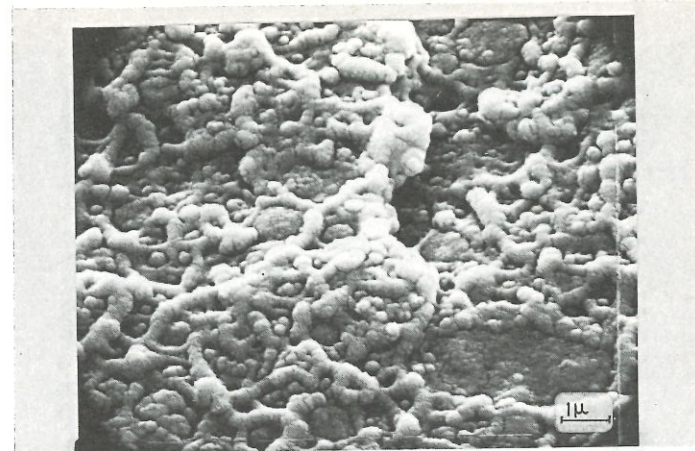

Fig. 3.   Scanning electron micrograph of unmodified Noryl.

possible to distinguish PVF$_2$ and Noryl phases, and the interfacial adhesion becomes unquestionable.

The pure PVF$_2$ Noryl blends display very poor *mechanical properties*, as demonstrated by the dependence of their ultimate properties on the composition (Figs. 6 and 7). At compositions ranging from 20 to 80% Noryl, the ultimate tensile strength is lower than that of each homopolymer, whereas the elongation at break is very small (approximately 1%) compared with that of Noryl (17%) and PVF$_2$ (133%), respectively. A 2% block polymer enhances quite significantly the ultimate tensile strength (Fig. 6), whereas the brittleness of the blends is scarcely improved ($\epsilon_B \simeq$ 2–5%; Fig. 7) in agreement with the poor interfacial adhesion evidenced by SEM (Figs. 2B and 5B). Increasing the percentage of the added block polymer (from 2% up to 12%) has no further beneficial effect on the ultimate tensile strength, the approximate additivity of which is still observed (Fig. 6). However (except for the PVF$_2$ richer blend), a rough additivity of the elongation at break is now noted (Fig. 7). Of course, the simultaneous improvement of σ_B and ϵ_B greatly enhances the ductility of the PVF$_2$/Noryl blends. The SEM observations agree with a reinforcement of the interfacial adhesion when 12% block polymer is mixed with these blends, and this modification could explain the very satisfying elongation behavior. However, this situation is different from that in the PVF$_2$-poly(α-methyl-styrene) blends, which remain quite brittle even when they are modified by 12% block polymer PαMS-PMMA, the "compatibilizing" effect of which is nevertheless unequivocally evidenced by SEM.[9]

In other words, the beneficial effects of block polymers in immiscible polymer blends are obvious, but the mechanisms that alleviate both the morphology and the mechanical properties of these heterophase systems are not yet fully understood and will require further careful investigation, aiming at a detailed knowledge of the interfacial situation.
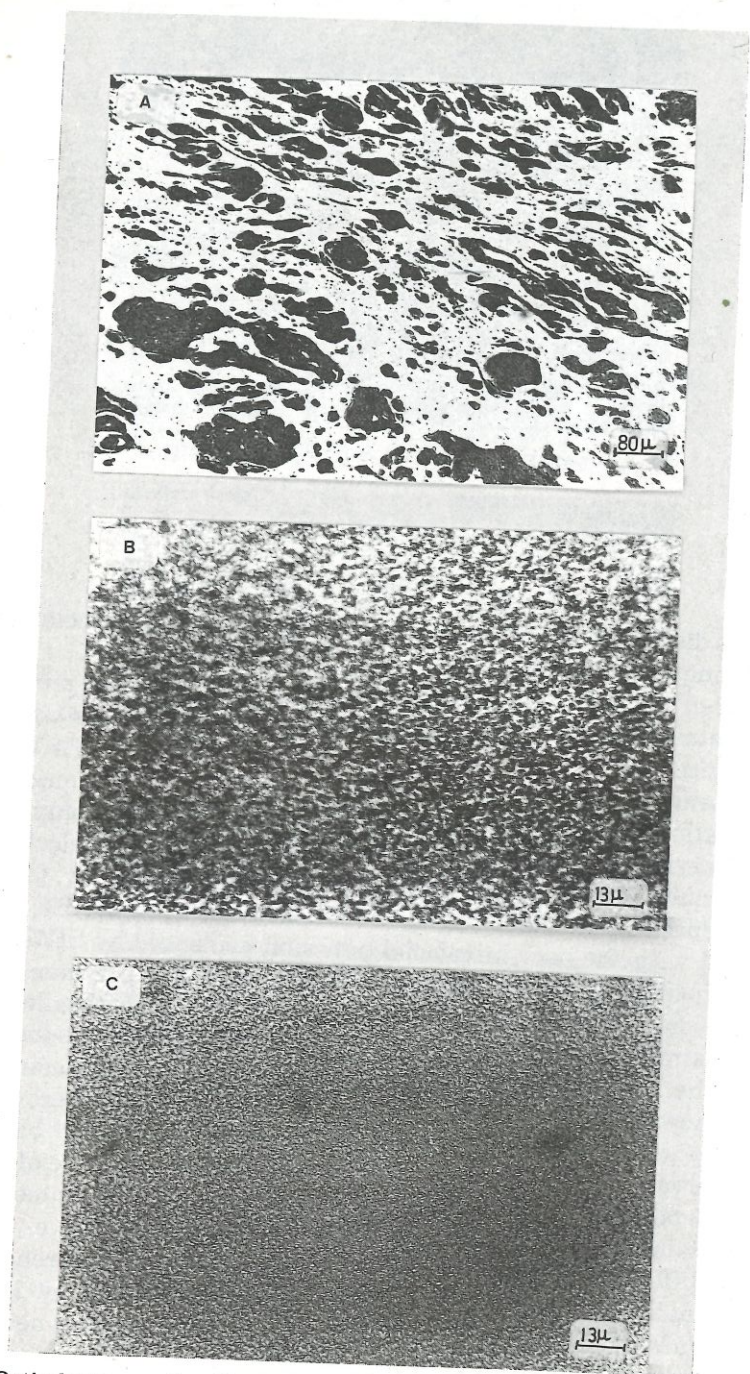
Fig. 4.   Optical micrographs of 80/20 PVF$_2$/Noryl blends: A; without block polymer; B; 2% block polymer added; C; 12% block polymer added.
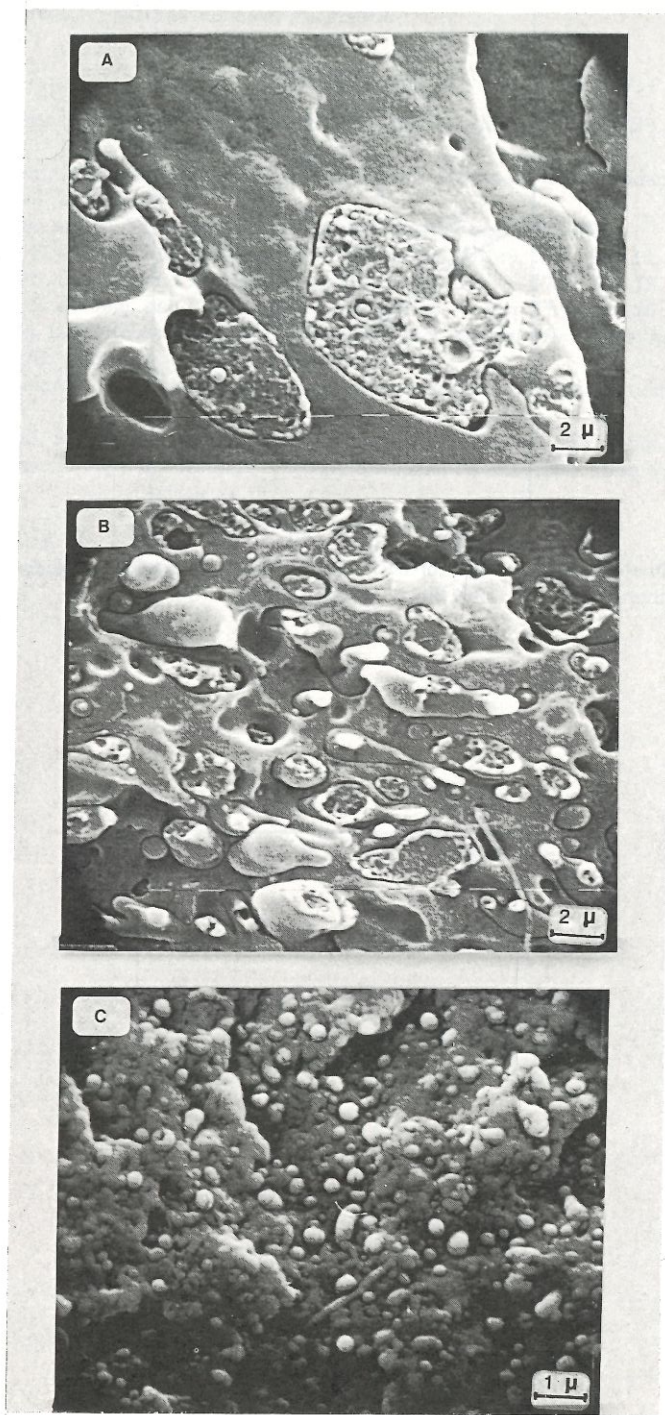

Fig. 5.   Scanning electron micrographs of 80/20 PVF$_2$/Noryl blends: A; without block polymer; B; 2% block polymer added; C; 12% block polymer added.
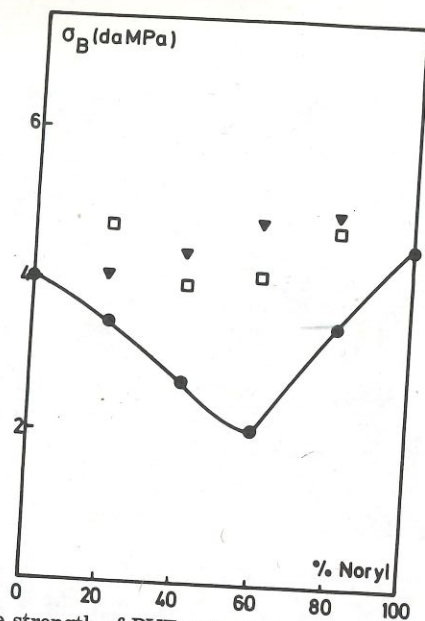
Fig. 6. Ultimate tensile strength of PVF$_2$/Noryl blends: (●); without block polymer; (□); 2% block polymer added; (▼); 12% block polymer added.
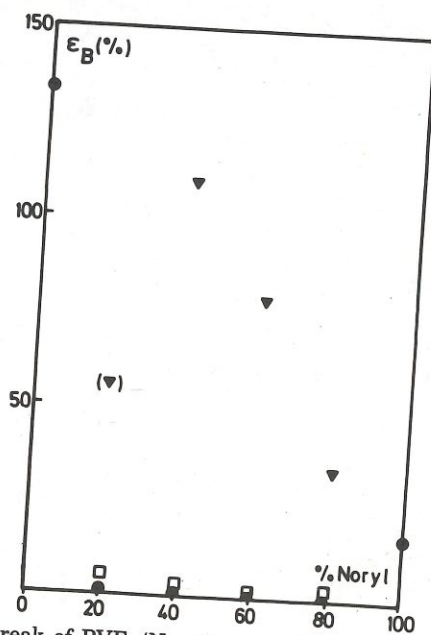

Fig. 7. Elongation at break of PVF$_2$/Noryl blends: (●); without block polymer; (□); 2% block polymer added; (▼); 12% block polymer added.

References

1. D. Heikens, N. Hoen, W. Barentsen, P. Piet, and H. Ladan, *J. Polym. Sci., Polym. Symp.*, **62**, 309 (1978).

2. D. R. Paul, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 2, Chap. 12.

3. R. Jerome and R. Fayt, *Actualité Chimique*, **September** 21, (1980).

4. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 79 (1981).

5. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys. Ed*, **19**, 1269 (1981).

6. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys. Ed*, **20**, 2209 (1982).

7. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.

8. C. B. Bucknall, *Toughened Plastics*, Materials Science Series, Applied Science, London, 1977.

9. T. Ouhadi, R. Fayt, R. Jerome, and Ph. Teyssie, accepted for publication in *Polymer*.

10. Ph. Teyssie, R. Fayt, R. Jerome, T. Ouhadi, European Patent Application N. 76539 (Solvay Cie).