Molecular Design of Multicomponent Polymer Systems. IV. Comparative Behavior of Poly(styrene-b-ϵ-Caprolactone) and Poly(styrene-b-Methylmethacrylate) Diblock Copolymers in Blends of Polystyrene with Polyvinyl Chloride

Investigations are currently underway in our laboratory with the aim to better understand and control emulsification of incompatible polymer blends by block copolymers in melt processing. In previous papers, complementing partial results published in this field by Paul [1, 2] and Heikens,[3-5] we have reported the highly beneficial effect of poly(hydrogenated butadiene-b-styrene) copolymers on the morphology and mechanical behavior of blends of low-density or high-density polyethylene and polystyrene.[6-8] With the prospect of broadening the applicability of the concept of polymeric emulsifiers for melt processing, other model blends are now being studied. Particular interest has been paid to blends containing polymers such as polyvinyl chloride (PVC).

Several studies have demonstrated that PVC forms compatible mixtures with poly-ϵ-caprolactone (PCL).[9-11] Well-defined PCL block copolymers have been synthesized in our laboratory using a new anionic coordination method based on the ring opening polymerization of lactones by μ-oxo-alkoxy bimetallic catalyst end-capping a preformed polymer chain.[12,13] The role of these copolymers as additives for PVC-containing blends has accordingly been evaluated and the results have been partially published elsewhere.[12, 14, 15] Furthermore, it is known that strong interactions also occur between PVC and syndiotactic polymethyl methacrylate (PMMA), leading to homogeneous mixtures over a broad composition range.[16-19] Therefore, block copolymers based on PMMA can also act as emulsifiers for the PVC-containing blends.

It was obviously of interest to compare the emulsifying effect of the two types of copolymers in model mixtures of polystyrene (PS) and PVC. We report here a preliminary evaluation of the behavior of a PS-b-PCL copolymer [SCL-2, M_n(PS) = 110,000, M_n(PCL) = 90,000] and a PS-b-PMMA copolymer [SM-3, M_n(PS) = 140,000, M_n(PMMA) = 140,000] in blends of a general purpose polystyrene 158K from BASF(M_n = 100,000) with a rigid PVC Solvic RD 258 from Solvay Co. (M_n = 40,000). PS-b-PCL copolymer was prepared as described in Ref. 13. The PS-b-PMMA sample was synthesized by a two-step anionic process (BuLi initiation in tetrahydrofurane at −78°C) according to a procedure described elsewhere.[20]

RESULTS AND DISCUSSION

Binary blends of PS and PVC and added with 9% of SCL-2 or SM-3 copolymer were prepared on a laboratory two roll mill at 185°C for 5 min. They were thereafter compression molded at the same temperature and 2500 psi pressure for 3 min.

Differences are to be expected in the interfacial activity of the two additives, due to differences in the miscibility characteristics of PVC (solubility parameter $\delta = 9.5$) with PCL ($\delta = 9.7$) and PMMA ($\delta = 9.1$) block. Examination of the PVC/PS blends by optical microscopy clearly evidences the emulsifying efficiency of both copolymers. The addition to the blends of 9% of either SCL-2 or SM-3 strongly reduces the particle size as illustrated in Figure 1, and a similar situation is observed at every composition. A very fine dispersion of PVC particles in a PS matrix is observed is PS-rich blends. The size of these particles is far smaller than 1 μm, as deduced from the observation of room temperature fracture surfaces by scanning electron microscopy [Fig. 2(b) and 2(c)]. Furthermore, the electron micrographs put in evidence a reinforced adhesion between the phases in the modified blends [compare Fig. 2(a) to 2(b) and 2(c)]. The emulsifying effect of SCL-2 and SM-3 in PVC/PS blends appears therefore unambiguous and rather similar.

If the block copolymer is preferentially located at interface between the PVC and the PS, the mechanical characteristics of this region must be quite different when a PCL or a PMMA block is used. The plasticizing effect of the former in PVC would indeed soften the critical interface region, whereas a stiffening effect is expected with the latter. The mechanical response of the

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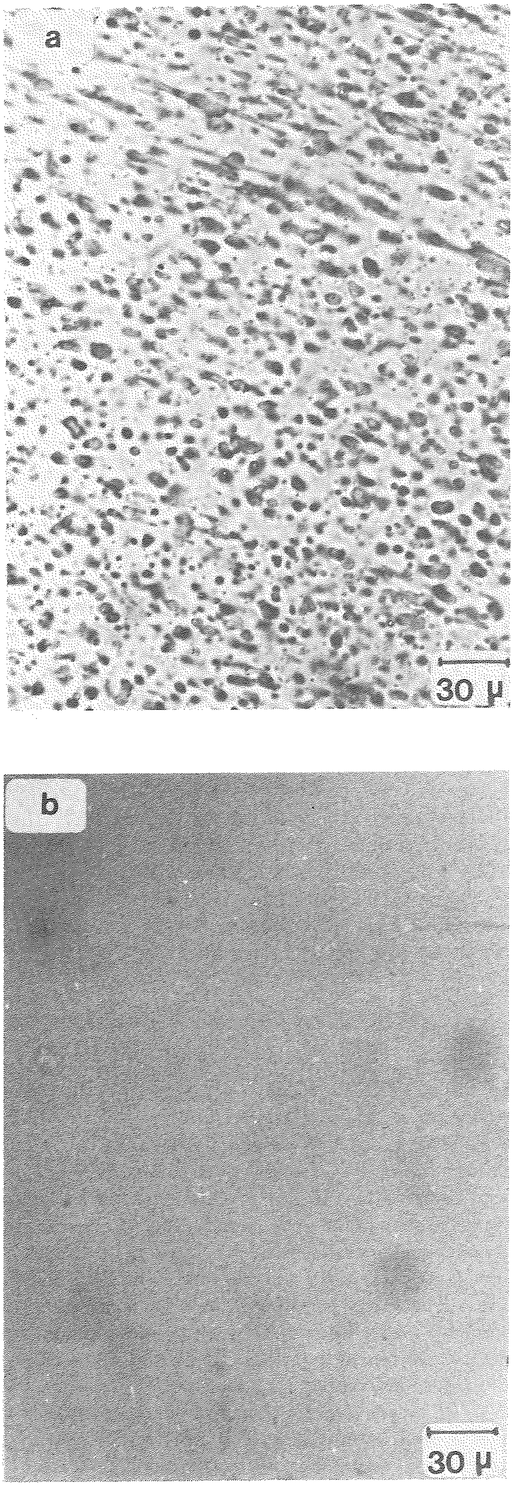

Fig. 1. Optical micrographs of a 20 PVC/80 PS blend: (a) without copolymer, (b) with 9% SCL-2, (c) with 9% SM-3. Five micrometer thick sections were observed under natural light. PVC phases (dark area) were selectively stained in red according to a method devised in our laboratory.[21]

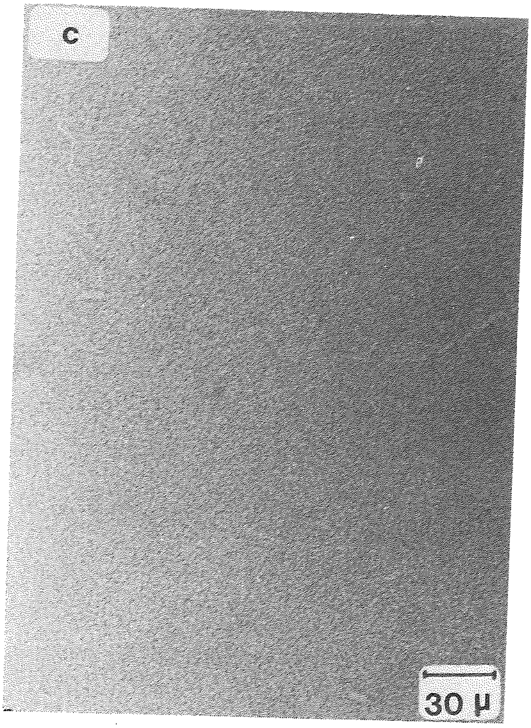

Fig. 1. (*Continued from the previous page.*)

blends should thus be sensitive to this situation. The ultimate tensile strength σ_B and the elongation at break ϵ_B of the pure and modified blends are shown in Figure 3. The pure PVC/PS blends exhibit poor mechanical properties over the entire composition range. They are brittle and their tensile strength σ_B continuously decreases as the PS content increases. As a result, σ_B values lower than that of the pure components are recorded over the whole range of composition. This behavior is obviously related to the lack of adhesion between the phases as observed by scanning electron microscopy [Fig. 2(a)]. The addition of the diblock copolymer SCL-2 or SM-3 induces significant but also rather unexpected modifications in the mechanical behavior of these blends. Both copolymers have a positive effect on σ_B of the PVC-rich blends. However, the superiority of the PS-b-PMMA copolymer over the PS-b-PCL one is obvious. The highest σ_B values are recorded when SM-3 is used; they are close to the yield stress of pure PVC ($\sigma_Y = 66$ MPa). The superiority of SM-3 is again apparent when the elongation at break of PVC-rich blends is considered (logarithmic scale). In this range, no positive effect of the PS-b-PCL copolymer is observed.

The improvement in ϵ_B when SM-3 is used is however rather limited and the blends so modified remain brittle. This situation is not surprising since tough or ductile materials are not expected to be obtained from a mixture of two brittle thermoplastics.

On the other hand, the behavior of the PS-rich blends modified with one or the other copolymer is intriguing. While the improvement in ϵ_B is negligible (especially with the SM-3 emulsifier), a depression of σ_B is observed. The variation of σ_B shows a transition near the 50/50 composition (see in particular, the σ_B curve of the SCL-2 modified blends). Furthermore, this embrittlement of the PS-rich blends is enhanced when the SM-3 copolymer is used. It must be assumed that this situation results from the effective interfacial activity of the PS-b-PMMA copolymer. The adhesion of finely dispersed PVC particles to PS matrix combined with the stiffening effect of the PMMA block promotes earlier rupture of the PS matrix. A similar

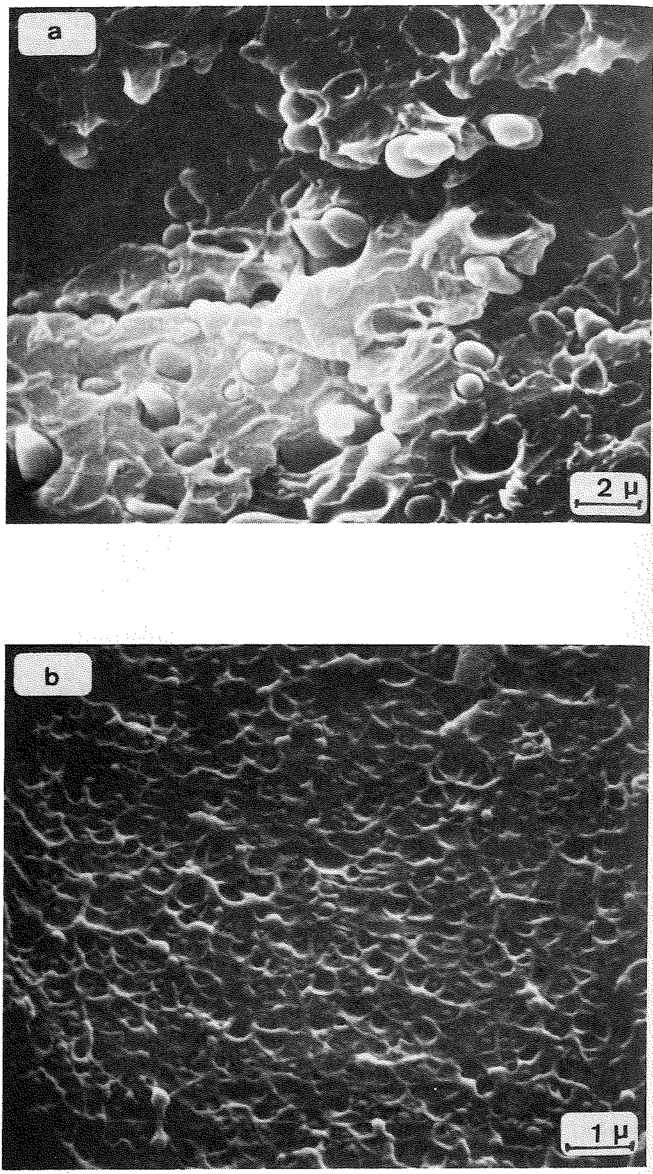

Fig. 2. Scanning electron micrographs of a 20 PVC/80 PS blend: (a) without copolymer, (b) with 9% SCL-2, (c) with 9% SM-3.

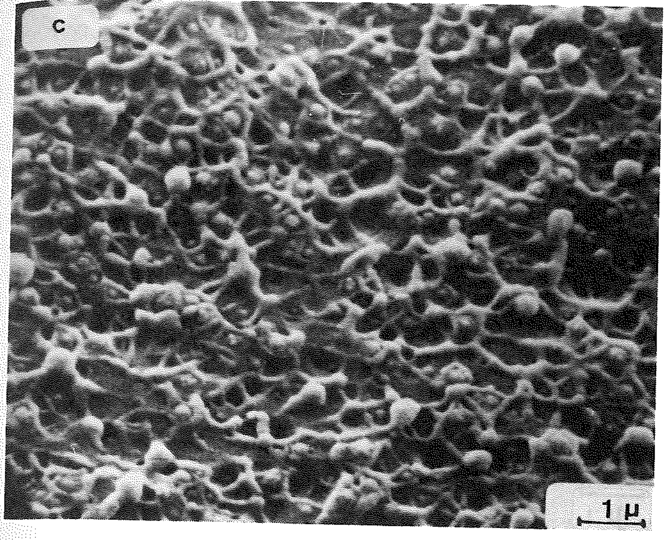

Fig. 2. (*Continued from the previous page.*)

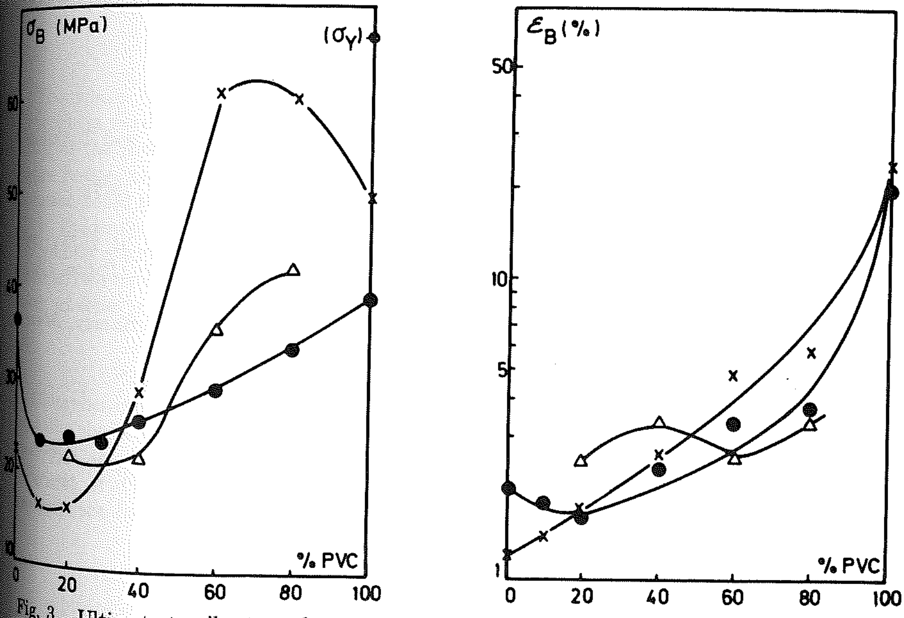

Fig. 3. Ultimate tensile strength (σ_B) and elongation at break (ϵ_B) for PVC/PS blends: (●) without copolymer, (△) with 9% SCL-2, (×) with 9% SM-3. Stress–strain measurements were performed on tensile specimens DIN 53448 at a cross-head speed of 2 cm/min. Each point is the average of 4–6 measurements.

situation should not be expected for the blend modified by the PS-b-PCL copolymer. If this additive is located at the blend interface, a PCL-plasticized PVC layer should envelop the rigid PVC particles. The softened interface region thus generated should induce improved responses of the PS-matrix to the applied stress. This favorable effect should be observed even if part of the copolymer is solubilized in the PVC phase rather than at the blend interface.

Additional investigations are certainly in order to fully explain this situation; in particular, the localization of the copolymer in the blends is of prime importance. Furthermore, dynamic mechanical measurements could provide useful information on the characteristics of the interface region. Also, the possibility of crystallization of PCL in PVC must be considered. Whatever the issue of these further investigations, the present results demonstrate significantly that the emulsifying efficiency of a copolymer does not always lead to good mechanical performances; depressing or "allergic" effects may result as well.

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