Molecular Design of Multicomponent Polymer Systems, XI, Emulsifying Effect of Poly(hydrogenated Diene-b-Methyl Methacrylate) in Poly(vinylidene Fluoride)/Polyolefins Blends

The mixing of block polymers in immiscible polymer blends has become a valuable method to control the phase separation process, i.e., to avoid the usually detrimental effects of the components immiscibility on the morphology and the mechanical properties of their blends.[1-5] That procedure provides the compounders with an efficient tool in the difficult task of combining on an economical basis dissimilar materials to form a composite with optimum performances.

Research undertaken in this laboratory shows evidence that the mixing of only a few percent of well-chosen block polymers can significantly alter the properties of blends of classical thermoplastics such as polyethylene, poly(vinyl chloride), and polystyrene.[2-5] Similarly, block polymers of methyl methacrylate behave as efficient modifiers of blends containing poly(vinylidene fluoride) (PVF$_2$), a very attractive engineering polymer. Poly(methyl methacrylate-b-α-methylstyrene) and poly(methyl methacrylate-b-styrene) have been successfully used in the melt-blending of PVF$_2$ with poly(α-methylstyrene) and Noryl, respectively.[6,7] That approach is now extended to the blending of PVF$_2$ with polyolefins, and more especially with polyethylene (PE) and polypropylene (PP), which is a difficult challenge, considering the extreme incompatibility of the polymeric components. This is not obvious from analysis of the solubility parameters [δ (cal/cm^3)$^{1/2}$] of each polymer which are 7.7–8.4, 8.2–9.2, and 7.75 (calculated) for PE, PP, and PVF$_2$, respectively.[8] In spite of the slight difference in δ for the PE/PVF$_2$ pair, the melt-blending of these polymers results in a gross phase separation ($\geq 10^4 \mu$m).

RESULTS AND DISCUSSION

PVF$_2$ (SOLEF 1012 from Solvay) was melt-blended with isotactic polypropylene (ELTEX P HS 200 from Solvay), low density polyethylene (ALKATHENE XDG-33 from ICI) and high density polyethylene (ELTEX B-3925 from Solvay). The blends were prepared on a two roll-mill at 200°C for 5 min and compression molded at the same temperature for 3 min.

As already mentioned, the immiscibility of PVF$_2$ and polyolefins was so extreme that the two polymers separated into macrophases during the melt blending process [Figs. 1(a), 2(a), 3(a)]. After thorough milling and molding, the blends were quite heterogeneous and exhibited coarsely layered and noncohesive structure. In order to limit the demixing of the polymeric partners and the loss of mechanical strength, suitable block polymers were prepared and evaluated as "compatibilizing agents." For that purpose, a synthesis of copolymers containing both a poly(methyl methacrylate) block miscible with PVF$_2$ and a polyolefin block was devised: The sequential anionic polymerization of a diene (butadiene or isoprene) and methyl methacrylate was first performed as described elsewhere,[9] and the unsaturated block was then hydrogenated into a polyolefin one with a Ziegler-type catalyst.[10] The diblock polymers contained approximately 50 wt% of each block and the molecular weight of poly(hydrogenated butadiene-b-methyl methacrylate) (HPB-b-PMMA) and poly(hydrogenated isoprene-b-methyl methacrylate) (HPI-b-PMMA) was 10^5 and 8×10^4, respectively. The 1,4 unit content of the polydiene blocks was high (ca. 90%) and their hydrogenation led either to polyethylene containing a small amount of 1,2-butene (from polybutadiene) or to an alternating ethylene–propylene copolymer (from polyisoprene). The PVF$_2$/polyethylene and PVF$_2$ polypropylene blends were modified by both HPB-b-PMMA and HPI-b-PMMA.

When the PVF$_2$/polyolefin blends are modified with 10% block polymer, the macrophase separation is no longer observed either during their melt blending or after their compression molding. The block polymer behaves as an efficient processing aid and also as a compatibilizing agent. Indeed the melt blending of PVF$_2$ and polyolefins becomes quite easy and leads now to a melt homogeneous to the naked eye.

The blend morphology observed after milling and compression molding confirms that the block polymer favors and stabilizes a fine dispersion of phases. Optical microscopy [Figs. 1(b), 2(b) and 3(b)] evidences semicontinuous phases, the width of which is in the range of a few microns for low density polyethylene (LDPE) and of 10 μm for polypropylene. Stabilization by the block polymer
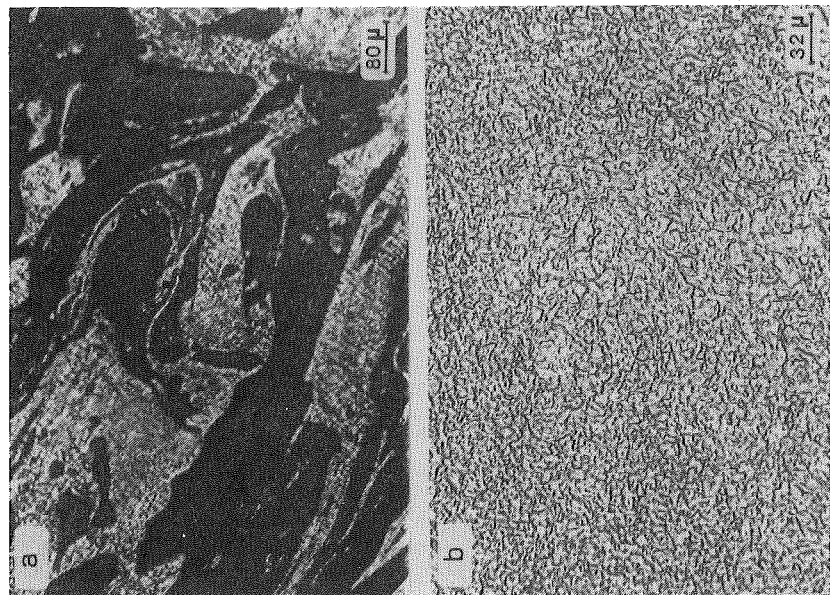
Fig. 1. Optical microscopy of PVF$_2$/LDPE blends: (a) 60 wt % PVF$_2$/40 wt % LDPE; (b) 60 wt % PVF$_2$/30 wt % LDPE/10 wt % HPB-b-PMMA copolymer.

Fig. 2. Optical microscopy of PVF$_2$/HDPE blends: (a) 60 wt % PVF$_2$/40 wt % HDPE; (b) 60 wt % PVFF$_2$/30 wt % HDPE/10 wt% HPB-b-PMMA copolymer.
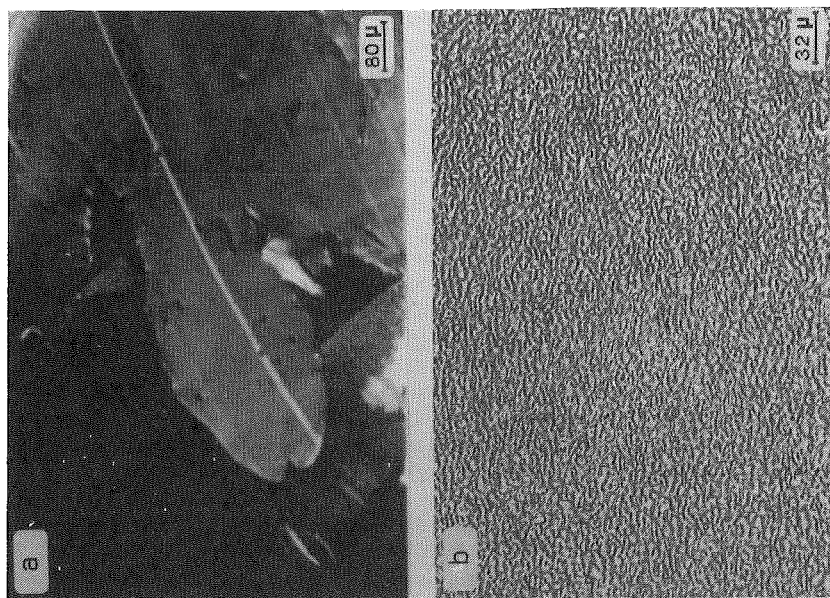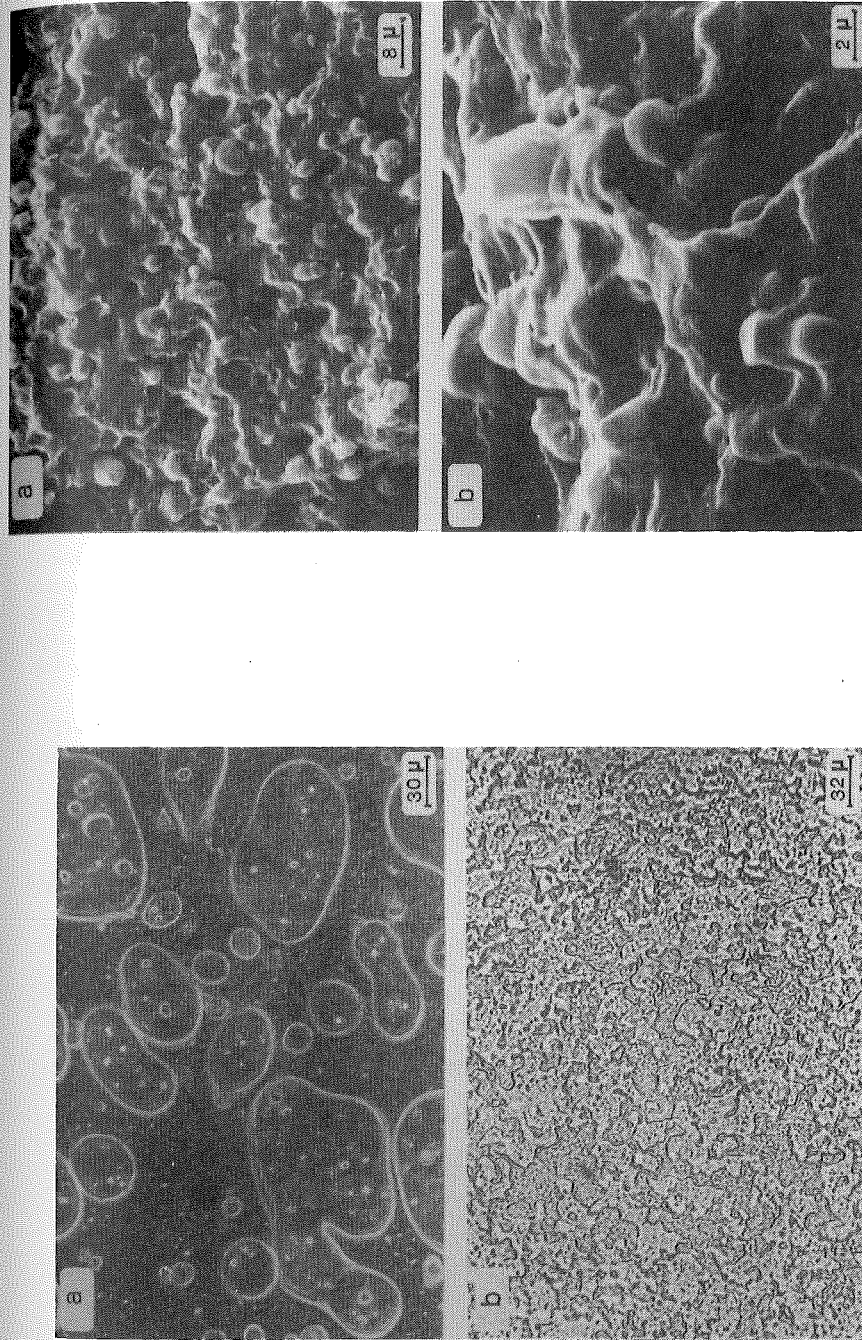
Fig. 3. Optical microscopy of PVF$_2$/PP blends: (a) 60 wt % PVF$_2$/40 wt % PP; (b) 60 wt % PVF$_2$/30 wt% PP/10 wt % HPI-b-PMMA copolymer.

Fig. 4. Scanning electron microscopy of 60 wt % PVF$_2$/ 30 wt % LDPE/10 wt % HPB-b-PMMA copolymer. Two different magnifications.
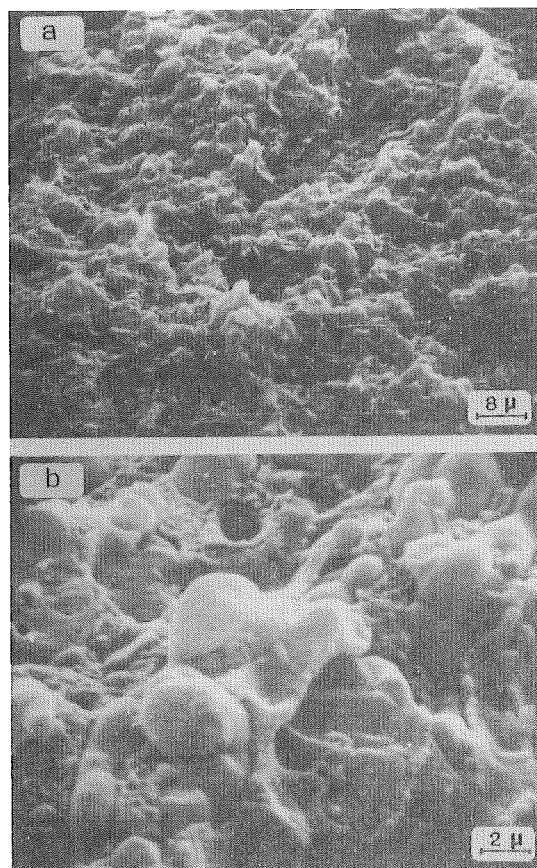
Fig. 5. Scanning electron microscopy of 60 wt % PVF$_2$/ 30 wt % HDPE/10 wt % HPB-b-PMMA copolymer. Two different magnifications.
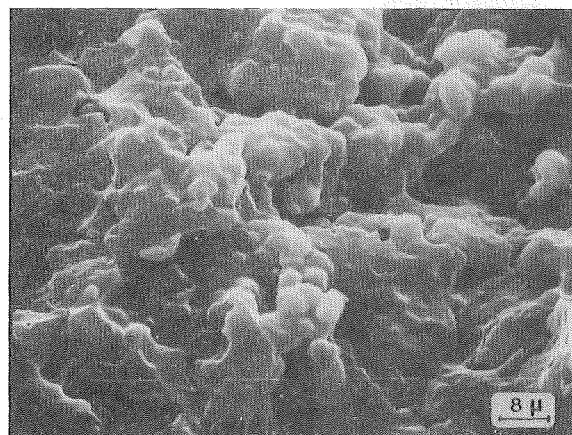

Fig. 6. Scanning electron microscopy of 60 wt % PVF$_2$/30 wt % PP/10wt % HPI-b-PMMA copolymer.

of the dispersed phases may be claimed, as a pronounced coalescence of the phases takes place during the compression molding of the pure blend as reported elsewhere for polyethylene/polystyrene blends.[3,4] The scanning electron microscopy (Phillips 501 apparatus) of cryofractures at liquid nitrogen temperature gives further details about the morphology. When 30% LDPE is mixed with PVF$_2$ (60%) in the presence of HPB-b-PMMA (10%), it seems that cylinders of the minor component cross over the PVF$_2$ matrix; sections of a few microns through the polyolefin "cylinders" are evidenced on Figures 4(a) and 4(b). Sections through dispersed phases ($\simeq 2\mu$m) also clearly appear in the case of the high density polyethylene (HDPE) based blend [Figs. 5(a) and 5(b)]. The adhesion of HDPE to PVF$_2$ is probably rather weak as evidenced by the holes left by the dispersed polymer during the cryofracture. When LDPE is used instead of HDPE, this phenomenon takes also place, but to a less extent. The SEM of the PVF$_2$/polypropylene (PP) blend is difficult to analyze accurately (Fig. 6). The "porous" cryofracture may correspond to the PVF$_2$ matrix from which the minor and dispersed PP has been eliminated during cryofracture. Voids of about 10 μm (or more) are easily observed and suggest that PP is dispersed more coarsely and adheres less strongly to PVF$_2$ than both LDPE and HDPE. This observation is consistant with the nature of the polyolefin block of the copolymers used. Hydrogenation of a polybutadiene block containing about 10–15 mol % of vinyl units leads to a block rather similar to LDPE with approximately 30 ethyl branches per 1000C atoms. The HPB block is therefore expected to be miscible with LDPE and to interact strongly with HDPE. That assumption is quite consistant with the results reported here and elsewhere.[3-5] Hydrogenation of polyisoprene gives rise to an alternating EP copolymer which is expected to be less miscible with PP than HPB is with PE. The degree of miscibility of the hydrogenated polydiene block with the polyolefin component could explain why the efficiency of the block polymers is different in the blending of PVF$_2$ with LDPE, HDPE, and PP, respectively. Further efforts are now devoted to reach an optimum situation and especially to improve the interfacial adhesion between PVF$_2$ and polyolefins.

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