

Molecular Design of Multicomponent Polymer Systems. XV. Morphology and Mechanical Behavior of Blends of Low Density Polyethylene With Acrylonitrile-Butadiene-Styrene (ABS), Emulsified by a Poly(Hydrogenated Butadiene-*b*- Methyl Methacrylate) Copolymer

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The emulsifying activity of a poly(hydrogenated butadiene-*b*-methyl methacrylate) (HPB-*b*-PMMA) copolymer is investigated in incompatible blends of a low density polyethylene and poly(styrene-co-acrylonitrile) resins (mainly ABS) prepared in the melt state on a two-roll mill. Optical and scanning electron microscopy observations clearly demonstrate that a moderate amount of copolymer (5 wt %) very significantly decreases the particle size and enhances interfacial adhesion. The block copolymer is also responsible for a strong improvement in both the ductility and Charpy impact resistance of PE/ABS blends.

INTRODUCTION

The use of polymeric emulsifiers is becoming an important tool for controlling the morphology and mechanical performances of highly incompatible polymer blends (1–6). Research undertaken in this laboratory has demonstrated the applicability of that concept in numerous incompatible polymer mixtures including common thermoplastics as well as engineering polymers (6). In particular, we have illustrated the efficiency of hydrogenated polybutadiene-polystyrene diblock copolymers (HPB-*b*-PS) in blends of various types of polyethylene (PE) with polystyrene (PS) (7–10). Similarly, diblock copolymers having a syndiotactic poly(methyl methacrylate) (PMMA) block were found to be very efficient for blends containing poly(vinyl chloride) (PVC) (11), styrene-co-acrylonitrile (SAN) (12) or poly(vinylidene fluoride) (PVF₂) (13–15) resins. These results have encouraged further extension of our research to a wider range of polymer mixtures not only of fundamental importance but also of technological and economic interest. In that prospect, particular attention has been paid to blends of polyolefins with various polar polymers. We have already reported the emulsification of PE/PVF₂ mixtures using a HPB-*b*-PMMA diblock copolymer (15). That approach is now extended to the blending of PE with ABS (or SAN) resins (themselves heterophase blends) using a similar diblock copolymer. The purpose of this investigation is not only to broaden the

field of application of this type of emulsifier but also to examine, from a basic as well as technological view-point, to what extent the morphology and impact performances of ABS might be modified in blends with PE in comparison with SAN/thermoplastic elastomers (SBS) blends (12).

On the other hand, PE and ABS have widespread applications which could be even more broadened by suitable combinations leading to improved materials, with respect to weatherability, adhesion, paintability, and other properties.

EXPERIMENTAL

The poly(hydrogenated butadiene-*b*-methylmethacrylate) diblock copolymer (HPB-*b*-PMMA, ref. H101, Mn = 200,000, 50 wt % PMMA) was synthesized by a sequential anionic copolymerization of butadiene and methylmethacrylate in equal weight amounts. Butadiene was polymerized first in a benzene/toluene mixture (1:1) at 40°C for 12 h using *s*-BuLi as initiator. THF was then added to the medium (THF/hydrocarbon = 2:1). In order to decrease the reactivity of the terminal anion towards the ester groups of MMA, the polybutadienyl anion was end-capped by a few vinyl-4-pyridine units (~1 wt %) before the addition of the MMA monomer (16). The polymerization of the MMA was allowed to proceed at -78°C for 2 h. A practically pure diblock copolymer (93%) was recovered by this procedure. Further hy-

drogenation of the PB chains (containing about 90% 1–4 units) was achieved with a Ziegler-type catalyst according to the Falk method (17).

The blended polymers were a ABS Cicolac GSM resin from Borg Warner, (about 30% rubber phase), and a low density polyethylene, Alkathene XDG33 from ICI. SAN resins containing 22% and 28% AN respectively (supplied by LABOFINA) were also used for comparative evaluations. Pure blends (PE/ABS or PE/SAN) and blends modified with 5 wt % copolymer H101 (amount added to 100 wt % of the binary PE/ABS or PE/SAN blends) were prepared in the melt state over the whole composition range on a laboratory two roll mill at 200°C for 5 min. The mixtures were thereafter compression molded into plaques at 200°C for 3 min under 2500 psi 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 a Adamel-Lhomargy tensile tester at a crosshead speed of 2 cm/min. Charpy impact strength was measured at room temperature on a CEAST instrumented fracture scope.

The morphology of the blends was examined by optical microscopy: 5 μm-thick sections were observed by the phase contrast technique. Fracture surfaces prepared either at liquid nitrogen (cryofracture) or room temperature were examined by scanning electron microscopy (Philips 501). Selective extractions of ABS phases by chloroform or THF were also performed on ABS-rich blends in order to define unambiguously the nature of the continuous phase.

RESULTS AND DISCUSSION

As expected, blends containing no copolymer exhibit coarse and heterogeneous dispersions of the phases as illustrated in *Figs. 1a* and *2a*. It is to be noted that, whereas PE-rich blends exhibit dispersion of ABS particles in a LDPE matrix, a more or

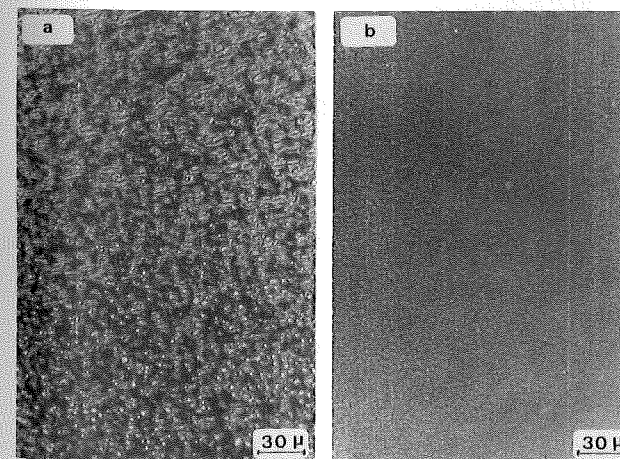


Fig. 1. Phase contrast microscopy of 80 LDPE Alk XDG33/20 ABS Cicolac blends. (a) no copolymer, (b): with 5% copolymer H101.

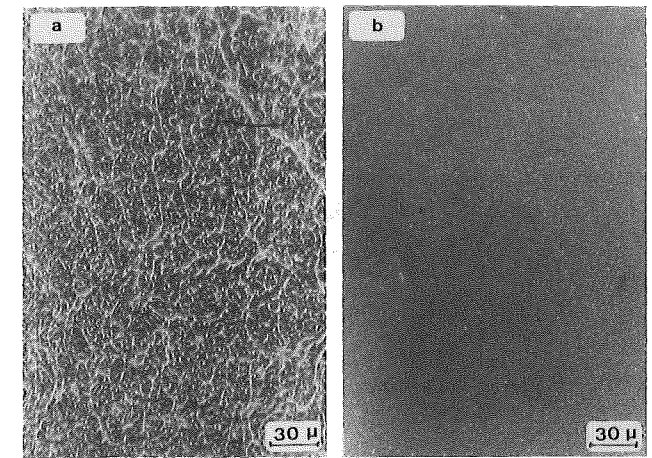


Fig. 2. Phase contrast microscopy of 20 LDPE Alk XDG33/80 ABS Cicolac blends. (a) no copolymer, (b) with 5% copolymer H101.

less co-continuous two-phase structure is observed in ABS-rich blends (10–20% PE) (*Fig. 2a*). That particular morphology was confirmed by selective extraction of ABS (SAN) phases with chloroform leaving a self-supporting PE network as evidenced by scanning electron microscopy (*Fig. 3a*). A similar situation was already reported for binary PE/PS blends (7, 9) but was only observed before compression molding of the samples. In ABS-rich blends, this particular structure persists even after compression molding, indicating that the coalescence, which provoked the disruption of the PE-network and allowed the formation of discrete PE particles in unmodified PE/PS blends, does not occur, at least to the same extent, in this case.

The emulsifying effect of the HPB-*b*-PMMA copolymer is exemplified in *Fig. 1b* and *2b*. A marked decrease in the particle size is indeed observed upon the addition of 5% copolymer. It also preserves and stabilizes the co-continuous two-phase structure of the ABS-rich blends, as illustrated in *Fig. 3b*. Scanning electron microscopy (SEM) examination of fracture surfaces prepared either at room or at liquid nitrogen temperature (cryofracture) confirms the optical observations. They further indicate a very poor interfacial adhesion in the unmodified ABS-rich blends (*Fig. 4a*). The benefit of the block copolymer at this level is quite obvious, as observed in *Figs. 4b* and *4c*; the phases are so intermingled that it becomes very difficult to distinguish the components. A similar effect, although less pronounced, is observed in PE-rich blends, (*Figs. 5a, b*). It is, however, to be noted that fracture in a 20 ABS/80 PE blend containing no copolymer often occurs within both phases, without decohesion between them (*Fig. 5a*). This situation is believed to result from the difference in the thermal expansion coefficients of the two components ($\alpha_{\text{ABS}} = 9\text{--}10 \cdot 10^{-5} \text{ K}^{-1}$ and $\alpha_{\text{LDPE}} = 16\text{--}18 \cdot 10^{-5} \text{ K}^{-1}$). Since LDPE retracts more than ABS upon cooling the compression molded sample, ABS particles remain firmly "encapsulated" in the PE matrix and a

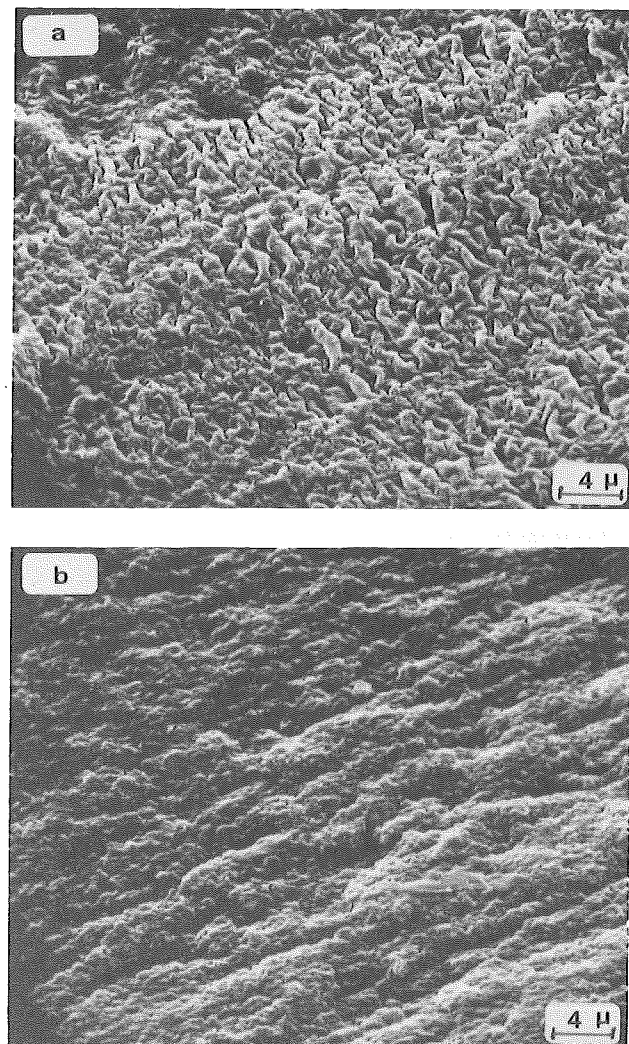


Fig. 3. SEM of 20 LDPE Alk XDG33/80 ABS Cyclocac blends after extraction of ABS phases with chloroform (a) no copolymer; (b) with 5% copolymer H101.

strong mechanical "interaction" between the phases results. Nevertheless, these morphological features do not lead to good mechanical properties. In fact, the tensile behavior of the unmodified blends remains poor over the whole range of composition (Fig. 6a, b). A minimum appears in the strength, σ_B , as well as in the ductility, ϵ_B , curves and is particularly significant for this latter. That situation demonstrates again the prime importance of interfacial adhesion (either through entanglements or dipolar interactions of the corresponding block with its own phase) in the control of the mechanical performances of incompatible polymer blends.

The block copolymer H101 greatly improves the elongation of the blends at every composition, leading to ϵ_B values always much higher (up to a decade) than that of pure ABS. However, the improvement in strength, σ_B , remains rather limited. It is to be noted that the strength of the same ABS modified only by 5% copolymer is also somewhat lower than that of pure ABS, whereas elongation is significantly in-

creased. That situation is believed to result from the increase in the soft phase content of ABS. In other words, the σ_B curve would mainly reflect the influence of the soft PE (continuous) phase.

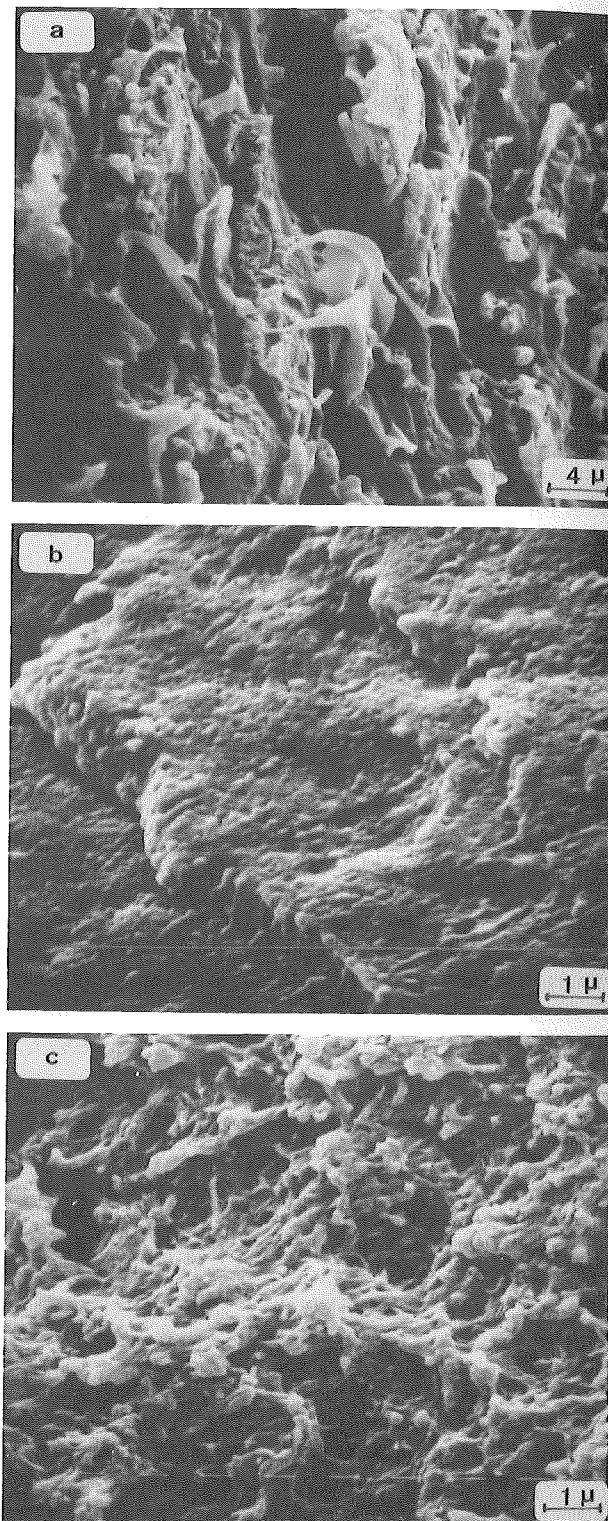


Fig. 4. SEM of LDPE Alk X DG33/80 ABS Cyclocac blends (a) 20 PE/80 ABS blend without copolymer (cryofracture); (b) same with 5% H101 (cryofracture); (c) 10 PE/90 ABS blend added with 5% H101 (room temperature fracture surface from a Charpy impact test).

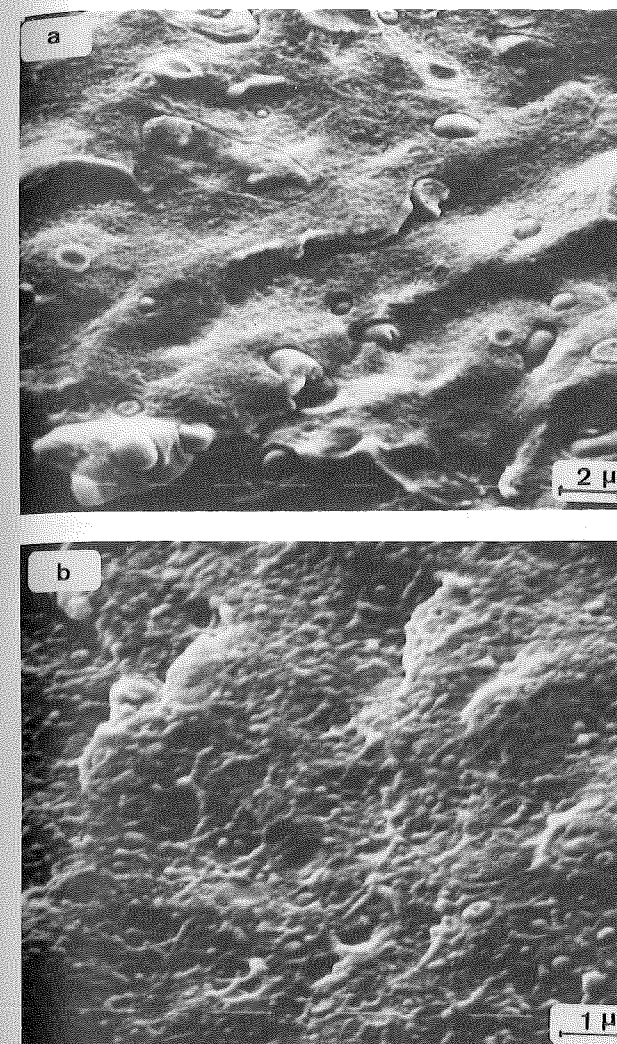


Fig. 5. SEM of 80 LDPE Alk XDG33/20 ABS Cyclocac blends (cryofractures) (a) no copolymer, (b) with 5% copolymer H101.

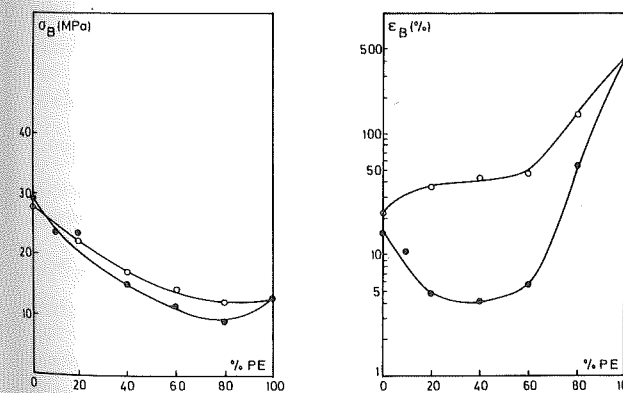


Fig. 6. Strength at break (σ_B) and elongation at break (ϵ_B) of LDPE Alk XDG33/ABS Cyclocac blends. (●) without copolymer, (○) with 5% copolymer H101.

For comparison purposes, yield strength σ_Y , ultimate strength σ_B , and ϵ_B values for some blends based on SAN resins instead of ABS are gathered in Table 1. The efficiency of the block copolymer H101 in

Table 1. Tensile Behavior of LDPE/SAN Blends.

Blends Composition				Tensile Properties		
% LDPE Alk XDG 33	% SAN	% Co-polymer		σ_Y MPa	σ_B MPa	ϵ_B %
—	100 (22% AN)	—		—	49.5	3.1
20	80 "	—		—	20	2.1
20	80 "	5 H101		—	43.3	4.1
80	20 "	—		9.9	8.6	76
80	20 "	5 H101		12.5	12.1	104
—	100 (28% AN)	—		—	63.7	3.7
20	80 "	—		—	13.5	1.8
20	80 "	5 H101		—	42.8	5.2
80	20 "	—		9.4	8.5	70
80	20 "	5 H101		13.2	11.7	108

improving both the strength and elongation of these blends is quite obvious, and noticeable whatever the AN content (22 and 28%) of the SAN resin. Of further importance is the striking improvement in the σ_B of the SAN-rich blends (up to a factor 3.2 for the blend containing 80% SAN (28% AN) in Table 1) in comparison with the limited improvement recorded for the corresponding ABS-rich blends (Fig. 6a). A more completed discussion of the behavior of these PE/SAN model blends will be presented elsewhere. Considering now the impact behavior of the ABS-rich blends (Fig. 7), it is seen that when no block copolymer is added, the Charpy impact strength of ABS drops dramatically upon addition of LDPE leading to a negligible resistance for the 20 PE/80 ABS sample. This low toughness, which confirms the poor tensile behavior of these blends, is assumed to result from the lack of adhesion between the phases. Indeed, modification of ABS by 5% of H101 copolymer increases significantly its impact strength. However, the addition of PE to this binary mixture leads again to a drop of the impact resistance, although final values are much higher than those recorded in pure PE/ABS blends.

Thus, it is clear that the block copolymer improves significantly the impact strength of the ABS/PE blends and induces ductile fractures as illustrated in Fig. 4c. Nevertheless, one might expect an increase instead of a decrease in the impact resistance as the PE content of the blend increases. Furthermore, we have observed that substituting a part of the ABS in the blends by pure SAN resin, in order to maintain the total amount of soft phase close to that of pure ABS (about 30% rubber phase), lowers again the impact strength despite the fine morphology also displayed by these materials. For instance, a blend containing 30% ABS, 50% SAN (28% AN), and 20% LDPE to which was added 5% copolymer H101 has an impact strength of 15 kJ/m² whereas the corresponding blend containing no SAN (thus 20 PE/80 ABS + 5% copolymer) displays a value of 27 kJ/m². It is to be noted that the impact value for same blends containing no copolymer is 3.3 and 4.3 kJ/m², respectively. The efficiency of the copolymer remains

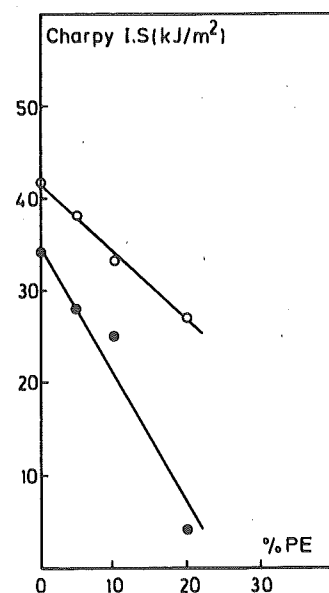


Fig. 7. Charpy impact strength of LDPE Alk XDG33/ABS Cyclac blends (●) without copolymer, (○) with 5% copolymer H 101.

therefore quite obvious. All these results might, of course, indicate that LDPE is not an appropriate soft phase for the preparation of very high impact ABS. However, we believe that another main limitation comes from the particular morphology displayed by the ABS (or SAN)-rich blends. In other words, the formation of a co-continuous two phase structure, or at least of PE long fibrils in these blends, would not be suitable to generate high impact performances. That situation was also reported in previously studied LDPE/PS blends (10). We indeed observed that a high impact strength was obtained in PS-rich blends only when we could control (by adjusting the characteristics of the HPB-b-PS copolymer) the formation of LDPE droplets in a PS matrix, and therefore generate a two-phase structure close to that of a classical HIPS. On the contrary, PS-rich blends exhibiting a co-continuous two phase morphology or containing PE fibrils displayed unexpected high tensile strength but poor impact resistance. A similar situation could also be invoked in the present case.

Nevertheless, despite these present and unexpected limitations, we can conclude that, thanks to the use of an efficient emulsifier added in moderate amounts (5%), it is possible to modify a classical ABS resin with moderate amounts of LDPE (ca. 10%) while keeping most of the impact resistance of the pure resin, as demonstrated in Fig. 7. That blending could lead to an improved material with respect to its weatherability and resistance to polar solvents, thanks to the possible formation of a PE surface layer as already reported for PP/ABS blends (18). It was similarly reported that a minor proportion of ABS in PP may improve adhesion and platability of the ma-

terial (18). Interesting applications could, therefore, result from the design of PE/ABS blends, and additional experiments in that prospect are envisioned.

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NOMENCLATURE

LDPE	= low density polyethylene (also referring to PE).
PS	= polystyrene.
SAN	= Styrene-co-acrylonitrile polymer.
ABS	= acrylonitrile-butadiene-styrene polymer.
HPB-b-PS	= hydrogenated polybutadiene-poly-styrene diblock copolymer.
HPB-b-PMMA	= hydrogenated polybutadiene-poly-(methyl methacrylate) (syndiotactic) diblock copolymer.
σ_B	= strength at break or tensile strength.
ϵ_B	= elongation at break.

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Evaluation of Surface Treatments for Glass Fibers in Composite Materials

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The thermomechanical stability of a number of organosilane surface treatments for glass fibers was evaluated for use in a fiber reinforced epoxy resin. All of the silane coatings were found to improve the tensile strength of E-glass filaments, particularly at large gauge lengths. A phenylamino silane and an amino silane were particularly effective in this regard. The fiber/matrix interface was evaluated as a function of temperature and after exposure to boiling water using a single-fiber composite test. All silane coatings transmitted a higher interfacial shear stress than obtained in composites with no coatings, and in all cases the shear stress transmission was considerably higher than would be expected from the yield properties of the resin. Measurements of the glass transition temperature of the epoxy resin, as well as Fourier-Transform Infra-Red analysis, indicated modification of resin properties in a zone around the glass fibers. Each of the silane coatings provided more stable thermomechanical properties than those obtained with uncoated glass, at least until the silanes were irreversibly degraded by boiling water. A phenylamino silane provided the most thermally stable properties. Finally, unidirectional E-glass fiber reinforced laminae were fabricated and the measured values of longitudinal strength were compared favorably to theoretical predictions.

INTRODUCTION

There exists a continued interest in the development of high performance composite materials consisting of high strength fibers, such as glass or carbon, embedded in a polymer matrix. Because of their high strength and stiffness per unit weight they are used in primary and secondary structural applications where high strength, light weight materials are needed. The properties of these materials not only depend on the material properties of the fibers and the polymer matrix, but also on the interfacial region between the two components. Therefore, an understanding of the interface is essential in the study of fiber reinforced composite materials.

The primary function of the composite interface is to transmit stress from the weak polymer matrix to the high strength fibers. The ability to transmit stress depends on the mechanical properties of the matrix, the load bearing ability of the fiber, and the strength of the fiber/matrix interface. The absence of adhesion between the two phases will cause low strength and may enable environmental agents to penetrate and destroy the interface. Degradation caused by water at the interface is a primary concern, particularly for glass fiber reinforced composites. Therefore, in order to obtain high performance composite materials, a strong, chemically stable interface is necessary (1).

The properties of high strength reinforcing fibers, such as carbon or glass, depend strongly on the fiber surface defects obtained during processing and handling. Mixtures of coupling and sizing agents are applied to the brittle fibers during the fiber manufacturing process in order to prevent surface damage and breakage. The primary function of a coupling agent is to promote fiber-matrix adhesion, while a sizing agent is used to protect the fibers against abrasion caused by handling and fiber-fiber interactions. A coupling agent can also act as a protective coating.

A coupling agent interacts either chemically or physically with both the fiber surface and the polymer matrix. The most common type of coupling agents, particularly for glass, is the organosilanes, which have the form X_3SiR . The R group is resinophilic and is varied to optimize reactivity with the polymer matrix being used. The X groups are either methoxy, ethoxy, or chloro. The X groups hydrolyze in the presence of water to form silanols, which can either react with silanols on the glass surface to form siloxane linkages, or react with each other to form a polysiloxane coating on the surface.

Many theories have been proposed to explain the improved composite properties with the use of silane coupling agents. These include the chemical bond theory (1, 2) the interpenetrating network theory (3), the restrained layer theory (4-6), the preferential