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 (manufactured 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 this 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-poly(ethylene diblock copolymer (HPb-b-PE) 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 polystyrene (PS) and poly(vinyl chloride) (PVC) (11), styrene-co-acrylontri- nitrile (SAN) (12) or polystyrene/poly(vinylidene fluoride) (PVDF) (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 containing several various polymeric blends. We have already reported the emulsification of PE/PVDF mixtures using a HPb-b-PMMa diblock copolymer (15). The present study is now extended to the blending of PE with ABS (or SAN) resins (themselves heterogeneous 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 viewpoint, to what extent the morphology and impact performances of ABS might be modified in blends with PE in comparison with SAN/thermoplastic elastomers (SSEs) 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, printability, and other properties.

EXPERIMENTAL

The poly(hydrogenated butadiene-b-methyl methacrylate) 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 excess groups of MMA, the polybutadienyl anion was end-capped by a few vinyl-4-pyrindine units (−1 wt %) before the addition of the MMA monomer (1.0). The polymerization of the MMA was allowed to proceed at −78°C for 2 h. A practically pure diblock copolymer (80%) was recovered by this procedure. Further py

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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, \( \sigma_t \), as well as in the ductility, \( \delta_t \), 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 \( \delta_t \) values always much higher (up to a decade) than that of pure ABS. However, the improvement in strength, \( \sigma_t \), 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 increased. That situation is believed to result from the increase in the soft phase content of ABS. In other words, the \( \delta_t \) curve would mainly reflect the influence of the soft PE (continuous) phase.

Improving both the strength and elongation of these blends is quite obvious, and noticeable whatever the AN content (22 and 28\%) of the SAN resins. Of further importance is the striking improvement in the \( \delta_t \) 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 complete 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 24 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
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 for 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 not expected 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 HP-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 PS 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. 2. 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 PS 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 pliability of the material (18). Interestingly, 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-acrylonitrile copolymer.
ABS = acrylonitrile-butadiene-styrene polymer.
HP-b-PS = hydrogenated polystyrene-polystyrene diblock copolymer.
HP-b-PMMA = hydrogenated polystyrene-polymethyl methacrylate) (syndiotactic diblock copolymer).
γb = strength at break or tensile strength.
εb = elongation at break.

REFERENCES

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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 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 Infrared analysis, indicated modification of the resin properties in a zone around the glass fibers. Each of the silane coatings provided more stable thermomechanical properties than those obtained with uncouated 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 laminate 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 structural 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 stress transfer. By transmitting stress 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 provide 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 treat 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 interfacial contact. 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, particularly for glass, is organosilanes, which have the form X₃SiR. The R group is resinous, 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 silicate 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