

INTERFACE MODIFICATION IN POLYMER BLENDS

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I. INTRODUCTION

During the last decade, increased attention focused on blends of existing polymers in order to expand the spectrum of properties of known polymeric materials and to meet new technological requirements at low cost. Although homogeneous blends are interesting since they afford a regular variation of some properties upon varying composition, most of the efforts in the field have been centered on multiphase materials. The main reason has to be found in the possible control of the final properties thanks to the additivity of properties of each component together with morphological versatility. It is however well-known that melt blending of immiscible polymer pairs leads to blends with a relatively weak adhesion between coarse phases and, accordingly, with a poor mechanical behavior. This situation can however be alleviated by the two strategies discussed hereafter.

II. BLOCK COPOLYMERS AS INTERFACIAL AGENTS

II.1. Polystyrene-Polyolefin model materials

Several approaches have been proposed in order to tailor an interesting spectrum of properties from blending immiscible polymers. Using block or graft copolymers as interfacial agents is more likely to be the most versatile and successful approach. It has been demonstrated that the addition, even in small amounts, of polystyrene/hydrogenated polybutadiene block or graft copolymers to mixtures of polystyrene (PS) with various polyolefins is very efficient in improving the poor ultimate properties of the original blends. The investigation of these model polyblends has emphasized significant reductions in domain size and increased interfacial adhesion as supported by fracture surfaces (1,2), lap shear adhesion tests (3) and volume dilatation during mechanical stressing (4). Quite interestingly, co-continuous two phase morphology has been observed when PS is the major component, resulting in a dramatic increase of the energy to break (1). Finally, the overall architecture of the additive is important, the diblock copolymer being generally the most efficient interfacial agent (1). Composition, molecular weight and microstructure (pure versus tapered diblocks) of the copolymers are key features in the final control of mechanical properties and phase morphology (1,2).

II.2. Tailoring of commodity polymer blends

Immiscible PA and PB polymer blends can be modified not only by the related diblock copolymers but also by PA-PC diblock in which PC is miscible with homopolymer PB. Situations where PC is syndiotactic polymethylmethacrylate (S-PMMA) deserve interest since this polymer is miscible with a variety of commodity polymers, such as PVC and SAN. A family of diblock copolymers comprising an alkyl methacrylate component can be prepared by appropriate living anionic pathways.

Furthermore this type of block is easily modified into other methacrylic esters or even acid which increases the range of application of the parent copolymers as blending agents.

SAN-polybutadiene (PBD) is an example of immiscible polymers the block copolymerization of which is quite a problem. Nevertheless, SAN has been blended with Kraton-type rubbers in the presence of s-PMMA-PBD diblocks as additives, resulting in ABS-like blends with exceptionally good impact strength (5). Toughness is generally better than that displayed by commercial ABS resins which might be rationalized by the stronger interfacial adhesion promoted by the diblock architecture in contrast to the graft copolymer used in the classical ABS resins.

II.3. Engineering plastics blends

Blending of engineering plastics with lower cost resins or fillers is also of great interest especially from an economic point of view. The challenge is thus to disperse commodity polymers or minerals into high performance expensive materials without deleterious effects on the mechanical properties and hopefully with the broadening of the application range of those engineering products.

Since s-PMMA is also miscible with polyvinylidene fluoride (PVDF), at least in its amorphous region, diblock copolymers comprising this component are very instrumental in loading PVDF with polymers, such as Noryl, poly(α -methylstyrene) (PMS) or even polyolefins, provided PMMA is copolymerized with PS, PMS and hydrogenated PBD, respectively (6).

II.4. Considerations of the role played by diblock copolymers

Undoubtedly, ^{13}C bulk state NMR and fluorescence techniques (Non radiative energy transfer or NRET) are very helpful in the investigation of polymer miscibility, since they allow the polymer mixing to be probed at a few nanometers scale (7,8). NRET has also shown that miscibility of PVC and s-PMMA is not at all affected by the block polymerization of PMMA with PS (8). It means that the immiscible PS block is unable to prevent PMMA to interact with PVC, and this agrees with the beneficial effect that PS-PMMA diblocks have on properties of PS/PVC blends.

The substantial improvements observed in the mechanical properties of modified immiscible polymer blends might be attributed to an increase in the interfacial adhesion. Measurements of adhesion have pointed out the propensity of a diblock copolymer to mutually adhere rather well to each of the corresponding homopolymers which display only a poor mutual affinity (3). Since adhesion is known to be related to the possible diffusion of molecules from one substrate to another one, diffusion of homopolymers into block copolymer structures should provide for a relevant piece of information. Purposely diffusion of d-PS and d-PMMA into protonated PS-PMMA diblock copolymers has been studied using elastic recoil detection, at a temperature well above T_g of each block, i.e. 160°C (9). The tracer diffusion coefficients are just over an order of magnitude smaller for diffusion into the copolymer than values measured for the diffusion into the respective homopolymer hosts. This large difference is primarily related to the tortuosity and orientation of the microphase separated domains and not due to interfacial effects. Since diffusion coefficients have been measured in the absence of any mechanical deformations, it may be anticipated that restrictions to diffusion of homopolymers into copolymer systems should be less severe under relatively high shear, i.e. during processing of the immiscible polymer blends.

III. Modification of the interface by strong interactions between the phases

The implementation of strong interactions at the interface is another powerful way to ensure dispersion and interfacial adhesion in multiphase blends. In this regard, random incorporation of specifically interacting groups into otherwise immiscible polymers has been described as a method of promoting miscibility (10). In order to take advantage of this concept while preserving the existence of a multiphase system, blends of immiscible polymers have been modified by ionic interactions via a proton transfer from the acid end groups of one polymer to the tertiary amine end groups of a second polymer. IR spectroscopy shows that proton transfer from carboxylic (or sulfonic) acid endgroups to the dimethylamino end groups actually occurs with the formation of ammonium carboxylate (or sulfonate) ion pairs (11). According to optical microscopy, it is possible to obtain homogeneous mixtures on a scale of ca. 0.2 μm , depending on molecular weight of the immiscible polymers and strength of the ion pairs. Nevertheless, two distinct T_g 's for the acid and tert-amine telechelic polymer mixtures are observed which indicate that these blends are microphase separated and form essentially a multi-block copolymer in the bulk. Small angle X-ray scattering studies of this type of polyblends, and especially of those containing ammonium sulfonate ion pairs, support that they mimic morphologies seen in block copolymers, e.g. the improvement of the microphase separation upon heating above T_g 's, and the observation of an order/disorder transition (12). It is worth noting that in contrast to covalently bonded block copolymers the width of the interface remains sharp in these copolymers formed by ionic associations as the order/disorder transition is approached. Dynamic mechanical measurements support the analogy with block copolymers and show under appropriate conditions two extra relaxations in the temperature range above T_g of each polymeric component. These relaxations should be characteristic of the ion pairs: the lower temperature relaxation has been tentatively attributed to the ion pair aggregates, while the complete dissociation of the ion pairs at higher temperature (ca. 200°C) would be responsible for the second relaxation.

These preliminary results clearly show that functional groups selectively attached at both ends of linear immiscible chains can control the interfacial situation by promoting thermoreversible interactions. This pathway to block copolymer-type materials deserves of course interest for the first strategy discussed in this paper.

Acknowledgment

The authors are very much indebted to the "Services de la Programmation de la Politique Scientifique" for financial support. They would like to thank P.F. Green of the Sandia National Laboratory (New Mexico) for diffusion measurements, T.P. Russell of the IBM Almaden Research Center for SAXS measurements, and L.A. Utracki of the Industrial Materials Research Institute (Qué., Canada) and P. Charlier (author's Lab.) for dynamic mechanical measurements.

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