

Structural Effects of Compatibilizer Localization and Effectivity in Thermoplastic Polyurethane–Polyolefin Blends

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ABSTRACT: A study was performed with blends of thermoplastic polyurethanes and polyolefins to determine the structural requirements for a compatibilizer to be located at the interface. It was demonstrated that during the addition of an incompatible polymeric additive (i.e., incompatible with both blend constituents) to a polyurethane–polyolefin blend, the additive migrated to the interface. This interfacial phenomenon was proven to be virtually independent of compatibilizer viscosity or surface activity. Only when the compatibilizer was quite comparable to one of the phases did small differences in polarity govern whether the compatibilizer remained at the interface or formed micelles. This effect was demonstrated with a series of styrene–(ethylene–butylene)–styrene block copolymer compatibilizers. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2901–2905, 2002; DOI 10.1002/app.10285

Key words: polyurethane–polyolefin blends; compatibilizer; morphology; electron microscopy

INTRODUCTION

It is generally accepted that compatibilizers serve as polymeric surfactants for immiscible blends by migrating to the interface and thereby lowering the interfacial tension.¹ Block copolymer compatibilizers containing segments identical or similar to the blend constituents have proven to be highly effective.² In addition to block copolymers, other materials, such as graft and statistical copolymers and ionomers, have yielded positive results.^{3–6}

However, little is known about the structural requirements for a compatibilizer to remain at

the interface instead of forming micelles in one of the phases. Because the synthesis of appropriate block copolymers is often arduous and time-consuming, a study was performed to determine the necessary structural requirements for maintaining interfacial locality. Blends of thermoplastic polyurethane (PUR) and polypropylene (PP) were prepared with a series of polymeric additives serving as compatibilizers. Their effectivity as compatibilizers was determined after an analysis of the blend morphology and particle size.

The blend system of PUR and PP was immiscible and incompatible. The interfacial tension between the soft segments of PUR and PP was 8.2 mN/m for the polyester-based soft segment and 5.7 mN/m for the polyether-based soft segment.^{7–9} The hard segments of PUR had an interfacial tension of 13.9 mN/m in the presence of PP.

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Therefore, the soft segments of PUR were assumed to segregate at the interface when exposed to a nonpolar partner such as PP. This level of interfacial tension indicated a high degree of incompatibility between PUR and PP.

EXPERIMENTAL

Materials and Blend Preparation

Commercial products were used as raw materials. The PURs consisted of either Elastollan® 1195A or Elastollan® C 64D (Elastogran GmbH, Lemförde, Germany), and the PP was Novolen® 1127 (BASF AG, Ludwigshafen, Germany). Elastollan® 1195A is a poly(ether urethane) based on poly(tetramethylene glycol), 4,4'-diphenylmethanediisocyanate, and butanediol with a durometer hardness of 95 Shore A; Elastollan® C 64D is a corresponding poly(ester urethane) with a durometer hardness of 64 Shore D. The compatibilizers are specified in the text.

Blends with Elastollan® 1195A and Elastollan® C 64D were prepared with a twin-screw extruder (ZSK 30, Werner & Pfleiderer, Stuttgart, Germany) at 200 and 230°C, respectively, depending on the melting range, at a screw speed of 150 rpm and a throughput of 10 kg/h. Various blends were also compounded in a Brabender Plasticorder PL 30 (Brabender OHG, Duisburg, Germany) for 15 min at 60 rpm at temperatures comparable to those used in the ZSK. All blends consisted of 80 wt % PUR and 20 wt % PP. The former component formed the matrix, and the latter consisted of dispersed spherical inclusions.

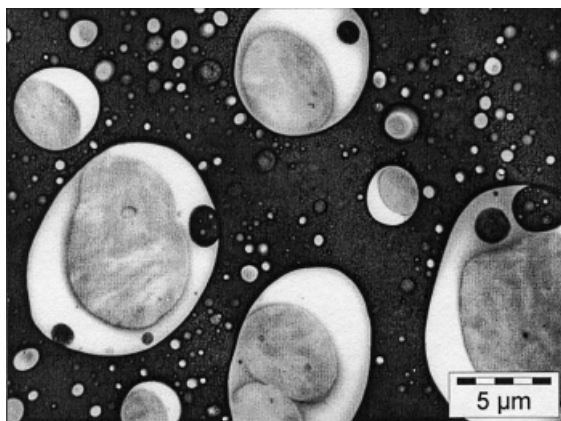


Figure 1 Distribution of a statistical E-AA copolymer (20% AA) compatibilizer (15 wt %) in a PUR-PP blend (80/20/15).

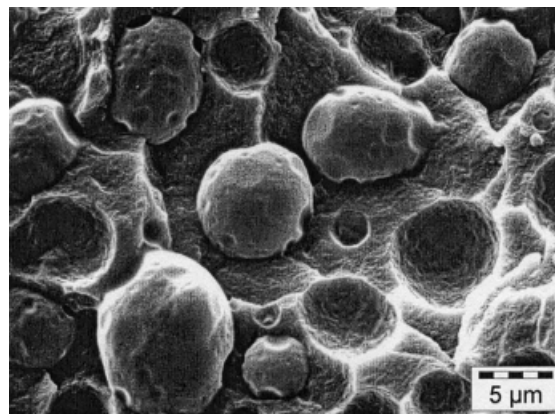


Figure 2 Cryofractured surface of a PUR-PP blend with a polyisobutylene compatibilizer illustrating the polyisobutylene-covered surface of the PP particles.

The compatibilizers were blended simultaneously with PUR and PP. The micrographs represent the polyester PUR. Blends containing poly(ether urethane) yielded similar results.

Transmission Electron Microscopy (TEM) Investigations

The samples for TEM were cryomicrotomed at -140°C with thicknesses ranging from 50 to 100 nm. Microtomed sections were subsequently stained with either OsO_4 or RuO_4 to optimize the contrast between phases. The TEM instrument used was a Hitachi H 7100 (Hitachi, Ltd., Tokyo, Japan) set at an acceleration voltage of 100 kV.

Scanning Electron Microscopy (SEM) Investigations

SEM was carried out with a Hitachi S 4000FE at an acceleration voltage of 10 kV. Cryofractures were prepared with liquid nitrogen. Fracture surfaces were sputtered with gold to avoid electrostatic charging.

RESULTS AND DISCUSSION

Ethylene-acrylic acid (E-AA) copolymers were initially evaluated as compatibilizers. Figure 1 shows a representative electron micrograph of a blend containing the polyester PUR, PP, and 15 wt % of an ethylene copolymer compatibilizer with 20% acrylic acid (Luwx® ES 9656, BASF). This blend was prepared in the twin-screw extruder. Ultrathin, microtomed sections were stained with RuO_4 . In this figure, PP particles

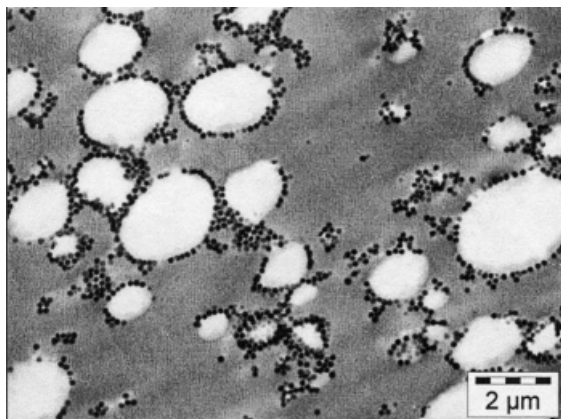


Figure 3 Insertion of an impact modifier with a PB-PMMA core-shell structure into the interface of a PUR-PP blend (80/20 + 10 wt % modifier).

appear gray, the compatibilizer appears white, and the surrounding PUR matrix appears dark.

Although the compatibilizer was different from the two phases, it was always located at the interface and covered the PP particles. However, its distribution was not uniform; the layer around PP showed various thicknesses, as also reported in ref. 10. This trend is similar to that of PE-PP blends with ethylene-propylene-rubber as the compatibilizer, as reported in ref. 11. The high compatibilizer content also caused some inclusions of PUR in Luwax.

Further experiments revealed that the polar carboxylic groups were not necessary for driving the compatibilizer to the interface. Similar results were also obtained with ethylene-acrylic ester copolymers, PP-AA graft copolymers, and

polyisobutylene. This is shown in Figure 2 for a cryofractured surface of an 80/20 blend with 2 wt % polyisobutylene (Oppanol® B 15, BASF) that was prepared in the Brabender mixer. Because the primary objective here was to study the localization of the compatibilizer, the different methods of blend preparation and compatibilizer contents were not important.

It is obvious that the PP particles were coated with polyisobutylene, similar to the E-AA compatibilizer. This observation is quite intriguing because polyisobutylene is neither surface-active nor compatible with either phase.

This outcome is not dependent on the viscosity of the compatibilizer, as shown in Figure 3, in which 10 wt % of an impact modifier with crosslinked particles consisting of a poly(butadiene) (PB) core and a poly(methyl methacrylate) (PMMA) shell was added (Paraloid® EXL 3600, ROHM & HAAS, Louisville, KY). The PB core portion of the modifier was stained with OsO₄. Likewise, this additive was again localized at the interface, although it was neither compatible nor surface-active and had infinite viscosity.

Very subtle structure effects were only visible when the compatibilizer was extremely similar to one of the two blend constituents. This was particularly evident with the styrene-(ethylene-butylene)-styrene (SEBS) block copolymers. These were prepared by hydrogenation of the inner PB block of styrene-(butadiene)-styrene block copolymers, which was transformed into an ethylene-butylene structure. Because these polymers are commercially attractive on account of their high compatibilizing activity, a comparison was per-

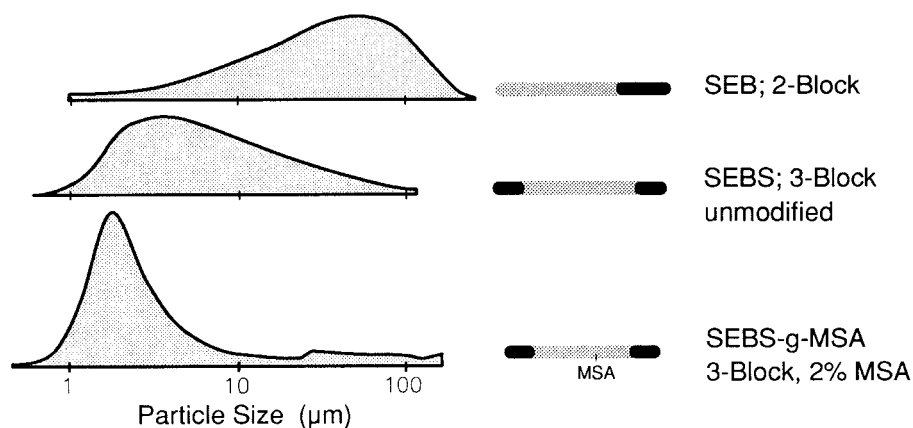


Figure 4 PP particle size distributions of PUR-PP blends with an SEB block copolymer compatibilizer (80/20 + 3 wt %) obtained by light scattering (Malvern Master Sizer) with DMF solutions.

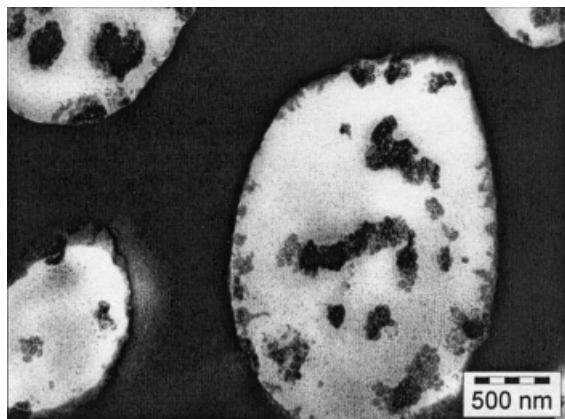


Figure 5 Distribution of an SEB two-block copolymer compatibilizer in a PUR-PP blend (80/20 + 3 wt %).

formed with unmodified two-block and three-block copolymers (Kraton® G 1701 and G 1652, Shell Centre, London, UK) and maleic anhydride (MSA)-grafted SEBS (Kraton® G 1901). All the polymers were similar in styrene content and differed only in the block structure and MSA grafting.

These compatibilizers exhibited large differences in effectiveness when blended into the PUR-PP system. These differences are noticeable in the particle size distributions illustrated in Figure 4. The particle size distributions were obtained by light scattering (Malvern Master Sizer, Malvern Instruments Inc., Southborough, MA) with dimethylformamide (DMF) solutions of the blends because PP remained insoluble. It is evident from Figure 4 that the styrene-(ethylene-butylene) (SEB) two-block copolymer was completely ineffective. The three-block system showed only weak compatibilizing activity. In contrast, the corresponding MSA-grafted system displayed high compatibilizing activity. The reason for this striking differences becomes clear from the electron micrographs given in Figures 5–7 (the PS block and the PUR matrix were stained with RuO_4). As shown in Figure 5, only a minor amount of the total 3 wt % SEB two-block system was located at the interface between the PP particles and the surrounding PUR matrix. Most of the compatibilizer was distributed inside the PP particles, forming fine micelles or clusters.

Figure 6 is a TEM image of a PP-PUR blend containing the SEBS three-block copolymer. In this case, 10% compatibilizer were added for better visualization. Because only the localization of the compatibilizer was of interest, comparisons did not need to be done on an equal basis. More of

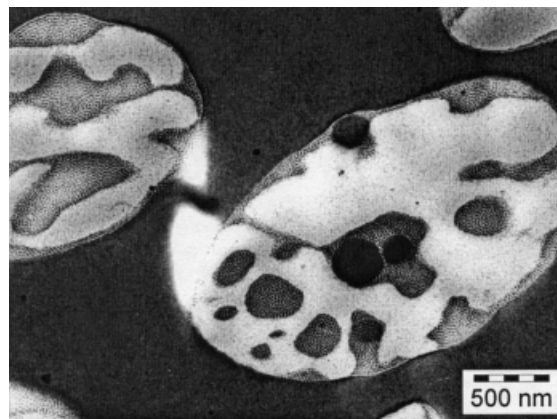


Figure 6 Distribution of an unmodified SEBS three-block copolymer compatibilizer in a PUR-PP blend (80/20 + 10 wt %).

the PP surface was covered with compatibilizer, and the compatibilizer formed large inclusions in the PP. In some instances, the compatibilizer formed distinct channels from the surface into the PP particles. This type of structure may be indicative of a cocontinuous network between PP and the compatibilizer. This observation is particularly interesting because such behavior has yet to be reported in the literature.

For the unmodified SEBS three-block system, the balance between the interfacial forces and compatibilization led to a mixed structure with compatibilizer existing both at the interface and inside the PP. If the polarity of the SEBS three-block system was slightly enhanced with MSA as with Kraton® G 1901, the compatibility with PP was further reduced. The compatibilizer re-

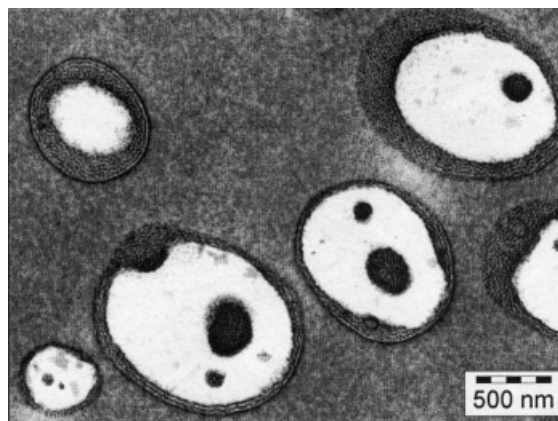


Figure 7 Insertion of an MSA-grafted SEBS three-block copolymer compatibilizer into the interface of a PUR-PP blend (80/20 + 10 wt %).

mained almost completely at the interface between PP and PUR. This change was caused solely by changes in polarity because no reactive coupling between the anhydride groups of the compatibilizer and PUR occurred, as demonstrated in ref. 7.

In summary, these data indicate that for the incompatible blend system PUR-PP, dissimilar compatibilizers (i.e., incompatible with either blend constituent) or polymeric additives always migrated to the interface. Micelle-like structures only occurred when the compatibilizer was partially or completely compatible with one of the phases.

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