Compatibilizing Effect of Diglycidyl Ether of Bisphenol-A in Polymer Blend System: Nylon 6 Combined with Poly(butyl acrylate) Core and Poly(methyl methacrylate) Shell Particles

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ABSTRACT: A polymeric blend system of nylon 6 and a core–shell impact modifier was studied. The modifier had a poly(butyl acrylate) core and a poly(methyl methacrylate) (PMMA) shell compatibilized with an epoxy resin, diglycidyl ether of bisphenol-A (DGEBA). The compatibilization of DGEBA is achieved by the reaction of its glycidyl group with the amine groups of nylon 6, and hydrogen bonds may be generated between the hydroxyl groups and the carbonyl groups on PMMA. The effect of compatibilization was verified by the dramatic increase in impact strength and the finer dispersing of the core–shell particles in the nylon 6 matrix. The effects of compatibilization on other properties of the blend, such as the tensile and rheological properties, were also investigated. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 24–29, 2000

Key words: nylon 6; core–shell impact modifier; toughening; compatibilization

INTRODUCTION

Nylon 6 is an important engineering plastic with wide applications; however, it is brittle, especially when flaws are present. A large number of efforts were made to improve its toughness; blending it with various elastomers constitutes the majority of the work. However, elastomers are usually incompatible with nylon 6; the impact strengths of the nylon 6 and elastomer blends are barely higher than that of pure nylon 6. For this reason the compatibilization between nylon 6 and the elastomer components becomes a key in the toughening of nylon 6.[1] For example, blends of nylon 6 with styrene–ethylene–butadiene–styrene block copolymer (SEBS) are incompatible and phase separation usually takes place.[2,3] However, when a graft copolymer [SEBS grafted with maleic anhydride (SEBS-*g*-MA)] was added to the blends of nylon 6 and SEBS, its impact strength was remarkably increased.[4–10] In this system the compatibilizing effect originates from the reaction of maleic anhydride with the amine groups of nylon 6. Another key factor in the toughening of nylon 6 is the average particle size of the elastomer in the matrix. It was reported that the optimal particle size of the elastomer in the nylon 6 matrix is in the range of 0.2–0.3 μm.[11–16] In order to ensure that the elastomer is dispersed at the optimum size, impact modifiers in the form of core–shell particles were developed in which the elastomer cores was encapsulated with a hard shell. Acrylonitrile–butadiene–styrene copolymer is one example of such a core–shell particle impact modifier.[17–22] However, when a core–shell impact modifier was used, the problem of compatibility between the matrix and the shell polymer arose. Only when the shell was compatible with the matrix was the core–shell particle well dispersed. Otherwise, the particles existed as lumps

instead of individual particles, which resulted in poor mechanical properties.[23,24] These problems were dealt with by some researchers.[25,26]

In this work a novel system of nylon 6 blends was studied. A core–shell impact modifier, which consists of a rubbery core of poly(butyl acrylate) (PBA) and a glassy shell of poly(methyl methacrylate) (PMMA), was employed as the impact modifier. Because PMMA and nylon 6 are not compatible, an epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), was employed as a compatibilizer of the two components. The impact strength, tensile properties, rheological properties and the morphology of the fracture surface of the blends were investigatevd. The emphasis was focused on the compatibilizing effect of the epoxy resin DGEBA.

EXPERIMENTAL

Materials

Nylon 6 (1013B) with a number average molecular weight of 25,000 was supplied by UCB Chemical Co., Ltd. (Japan). Particles with a PBA core and a PMMA shell (EXL2330) were supplied by Rohm & Haas Co., Ltd. The average diameter of the particles was between 0.2 and 0.3 μm. The epoxy resin DGEBA (LER-2050, epoxy equivalent weight of 1000) was purchased from LG Chemical Co., Ltd. (Korea).

Preparation of Blends

Nylon 6 was dried for 12 h and saved in an airtight aluminum and polyethylene package before use. Blends of various components were mixed with a WP 35-mm twin-screw extruder (*L/D* = 35). All the ingredients were tumble blended and fed through the throat of the extruder. The barrel and die temperature was set at 205–240°C, and the rotation speed of screw was set to 180 rpm. The blends passed through a cooling water bath and were pelletized. All the extrusion parameters were changed as little as possible from one formulation to another.

Mechanical Properties Test

The tensile properties were measured with an Instron Universal Testing Machine (model 1130) according to ASTM D638 at room temperature. The notched Izod impact strength was measured with a Sumitomo impact tester according to
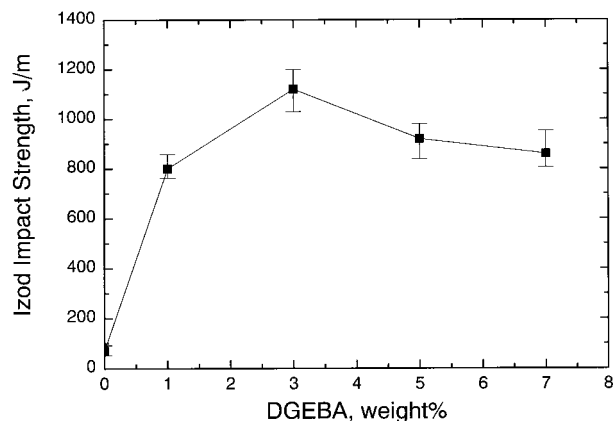

Figure 1 The notched Izod impact strength of the blends.

ASTM D256 at −25 to 25°C. The thickness of the Izod impact specimens was 1/8 in., and the impact energy was 4 J. Five measurements were done for each data point in all mechanical property testings.

Rheological Properties Measurement

The melt flow index was measured according to ASTM D1238 at 250°C with a 2160-g weight. The mixing torque of the blend samples was measured with a Brabender mixer (Plasti-Corder model PLE 330) at 240°C for 15 min, and the torque was recorded as a function of time. The apparent viscosities at various shear rates were measured with a capillary rheometer (Toyoseiki mode 1B) at 240°C with a capillary with an *L/D* ratio of 43/1.

Scanning Electron Microscopy (SEM)

The sample bars were fractured in liquid nitrogen. The fractured surface was etched with boiled toluene for 2 h, coated with an Au/Pd alloy, and subsequently observed under SEM (Cambridge S250). The SEM photomicrographs were analyzed with an image analyzer (IBAS 1/2).

RESULTS AND DISCUSSION

Impact Strength

Figure 1 shows the impact strengths of nylon 6 and core–shell particles blends against the content of the compatibilizer DGEBA. In this study the weight ratio of nylon 6 to the core–shell particles was always 80/20 (w/w), which was chosen

because it was extensively reported that maximum toughening can be achieved at this weight ratio.[11–22] When the compatibilizer was zero, the impact strength was only 70 J/m. Because the impact strength of pure nylon 6 was 47 J/m (measured in this study), the improvement by blending with core–shell particles alone was moderate. This suggested that the compatibility between nylon 6 and PMMA was poor. However, after the compatibilizer DGEBA was introduced, the impact strength of the blend increased sharply and exhibited a maximum (~1100 J/m) when the DGEBA content was 3 wt % of the blend, which was about 15 times higher than that of the uncompatibilized blend. The compatibilization can be attributed to the bridging effect of the epoxy resin. The epoxy group of DGEBA may react with the amine groups of nylon 6 in the following manner:
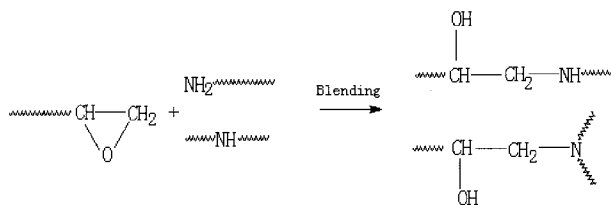
And hydrogen bonds may be readily generated between the hydroxyl groups on the DGEBA and the carbonyl groups on the PMMA as in the following structure:
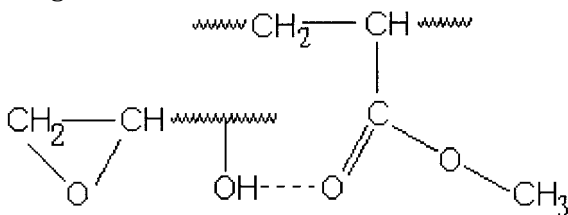
The more H bonds there are, the better the combination between the nylon 6 and the PMMA shell. However, DGEBA itself is a rigid component; introduction of it improved the interfacial bonding between nylon 6 and PMMA on the one hand, but on the other hand it increased the rigidity (brittleness) of the system. A proper amount of DGEBA would markedly improve the toughness of the system; too much DGEBA, however, would increase the brittleness. As seen in Figure 1, when the content of DGEBA was higher than 3 wt %, the impact strength decreased.

Because of the reactive nature of DGEBA chains, its compatibilizing effect was greatly influenced by temperature. One can conclude from
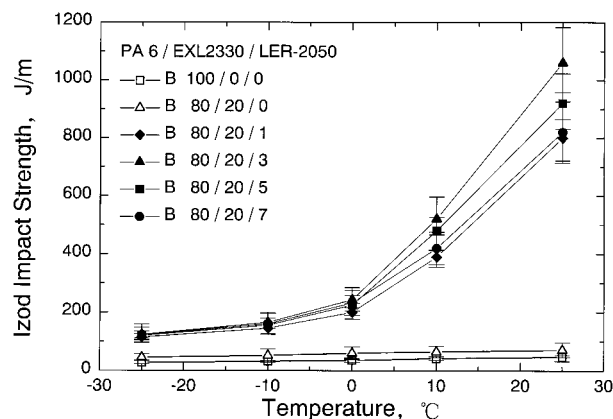

Figure 2 The effect of temperature on the impact strength.

Figure 2 that the higher the temperature, the more effective the compatibilizing effect. At low temperatures (<0°C) the reactivity and mobility of DGEBA was low; it could not bridge nylon 6 and PMMA effectively. However, when the temperature was higher than 0°C, the compatibilizing effect became increasingly stronger. This was because sufficient chemical bonds occurred between the DGEBA and nylon 6, and therefore there were sufficient H bonds between the DGEBA and PMMA.

Tensile Behavior

The stress–strain curves for pure nylon 6 and nylon 6 blend with core–shell particles (80/20 w/w) are shown in Figure 3. It is seen that the blending makes the material softer and weaker. The decrease in tensile strength is partly because of the introduction of the elastomer (PBA core) and partly because of the poor combination of the nylon 6 and the PMMA shell. However, the latter can be improved by compatibilization. As seen in Figure 4, the tensile strength increased almost linearly with the amount of the compatibilizer DGEBA. When the content of DGEBA was higher than 3 wt %, the tensile strength exceeded that of pure nylon. The increase in tensile strength was partly due to the compatibilization partly due to the rigidity of the DGEBA chains. Figure 4 shows that the elongation at break does not increase permanently with the content of the compatibilizer, but it exhibits a maximum at the point where DGEBA is 3 wt %. At too high DGEBA content the rigidity of DGEBA depresses the movement of the segments and elongation at break decreases.
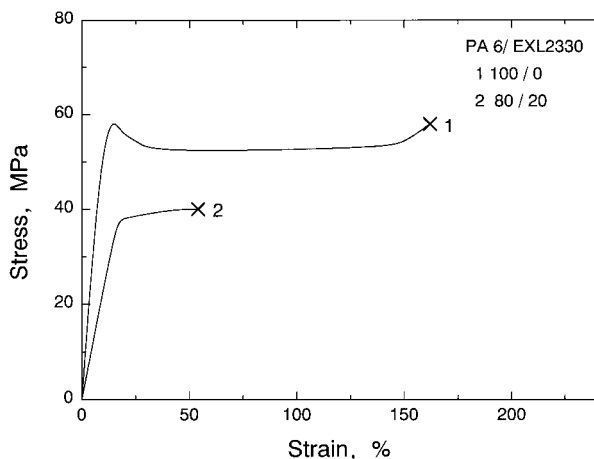
Figure 3 The stress–strain curves of nylon 6 and the uncompatibilized blend.

It is worthwhile to mention that the change in crystallinity of nylon 6 with blending may play a role in tensile strength and elongation at break. Because of the interation between the amine group and DGEBA, the movement of the nylon segment would be inhibited and, as a result, decrease the crystallinity, which may result in the increase in tensile strength and the decrease in the elongation at break to some extent.

Rheology Behaviors

The rheology behaviors of the blends reflect the mobility of the molecular chains and the interaction among the components. Figure 5 contains the plots of the mixing torque of the melt against time for systems with various compositions. Pure nylon 6 had the lowest torque (curve a). The torque
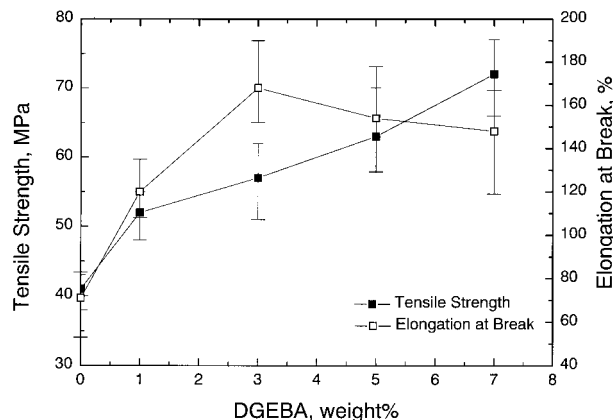

Figure 4 The effect of compatibilizer on the tensile strength and the elongation at break.
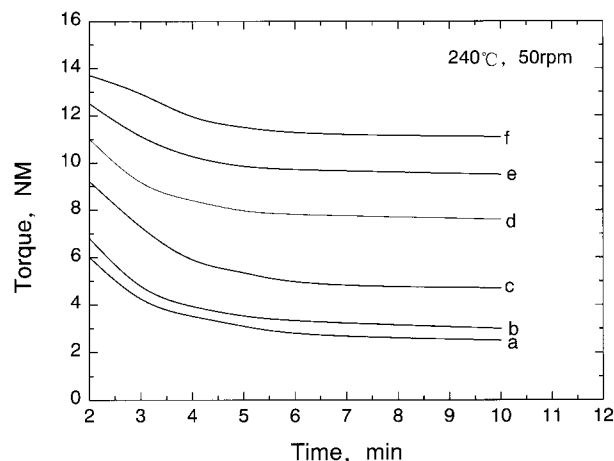

Figure 5 The mixing torque of the blends with various DGEBA contents. Curves a–f are the pure nylon 6, blends of nylon 6, and core–shell particles with the DGEBA content of 0, 1, 3, 5, and 7 wt %, respectively.

of the blend of nylon 6 and core–shell particles (curve b) was a little higher. The torque is a reflection of the melt strength, which depends on several factors, mainly, the molecular weight of the components, the interaction and entanglement among the segments, and the presence of foreign particles. The blending of nylon 6 and the core–shell affected the melt strength in a complicated way. The core–shell particle acted as a foreign particle, which should increase the melt strength considerably; in the meanwhile, its PMMA shell is incompatible with nylon 6 segments, which decrease the torque. The net result of the two effects was that the torque of the blend was only a little higher than that of pure nylon 6. However, when the compatibilizer DGEBA was introduced into the system, the glycidyl groups on the DGEBA may have reacted with the amine groups on the nylon 6 and thus increased its molecular weight. The increase in molecular weight would greatly increase the entanglement and result in a higher melt strength and the torque. As seen in Figure 5, the more DGEBA introduced, the higher the torque was. These effects on melt strength were also reflected in the decrease in the melt flow index and the increase in the apparent viscosity with the increase of the DGEBA content. One may find those changes in Figures 6 and 7, respectively.

Morphology of Fracture Surface of Blends

Figure 8 shows the morphologies of the fracture surface of blend samples after etching with tolu-
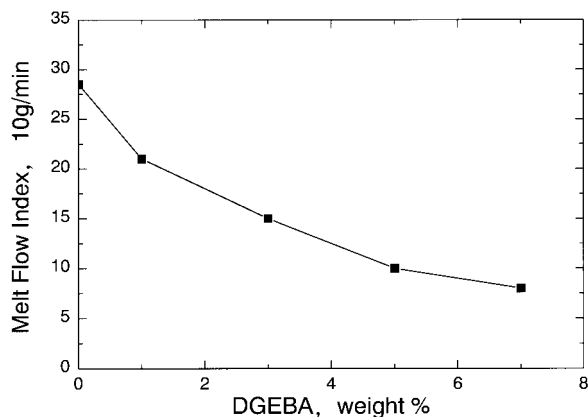
Figure 6 The effect of the compatibilizer on the melt flow index.

(a)

(b)

ene. There are holes on the fracture surface. The average size of the holes is listed in Figure 9. From the size of the holes one may know the average diameter of the dispersed phase; from the smoothness of the holes one can judge the interfacial bonding between the nylon 6 and core–shell particles. Figure 8(a) shows that when no DGEBA was introduced the holes were large (1.5–2 μm) and smooth. The smooth surface reflected the poor combination between the matrix and the impact modifier. The average particle size of the core–shell particles is 0.2–0.3 μm, which is much smaller than the size of the holes. As mentioned above, if the compatibility between the matrix and the shell had been not good enough, the impact modifier would not have been dispersed as individual particles, but as lumps. Therefore, the morphology in Figure 8(a) indicates poor compat-
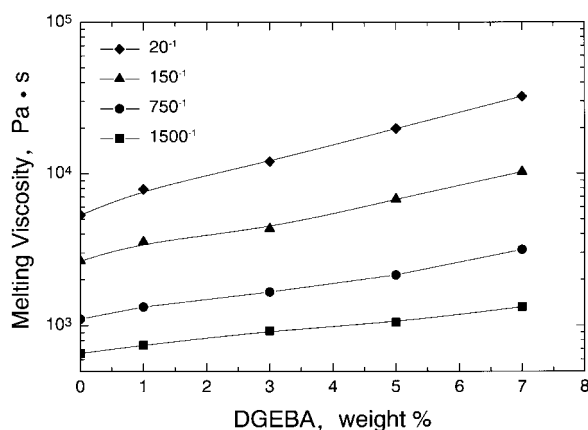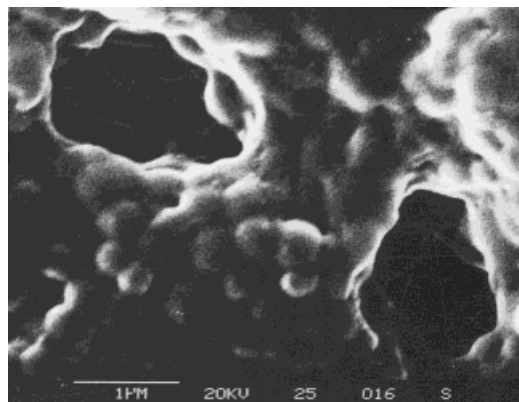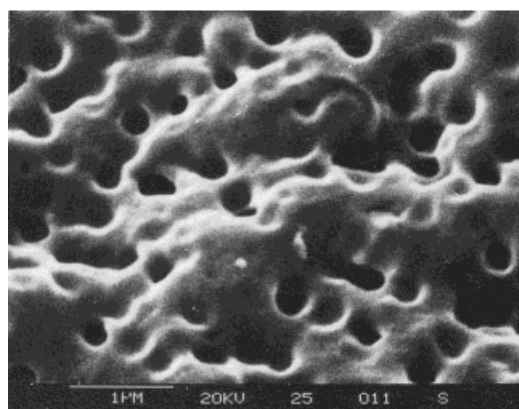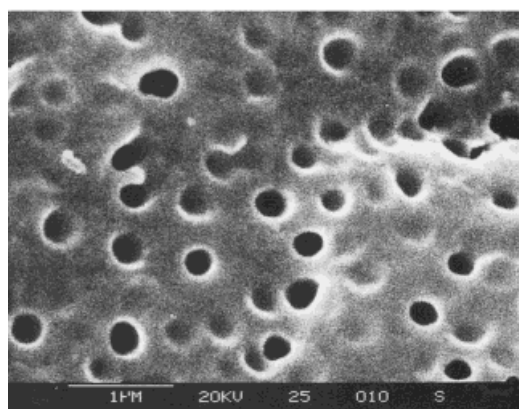

(c)

Figure 8 SEM photomicrographs of the fracture surface of the samples: (a) the uncompatibilized blend, (b) 1 wt % DGEBA content in the blend, and (c) 3 wt % DGEBA content in the blend.
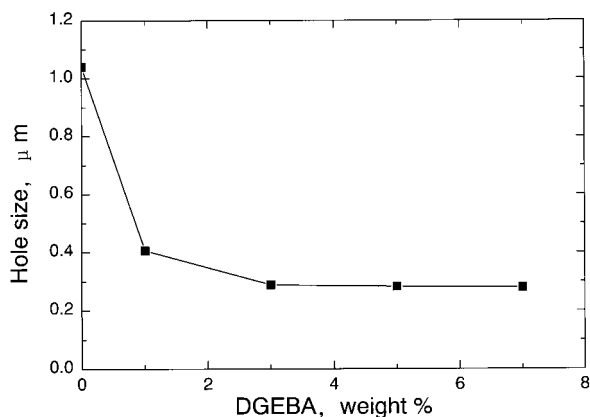

Figure 7 The effect of the compatibilizer on the apparent viscosity.

Figure 9   The average hole size on the fracture surface.

ibility. In Figure 8(b,c) one can see that the holes were much finer and coarser. The coarse surface suggests intimate bonding between components. As shown in Figure 9, the average size of the holes decreased with the content of DGEBA increased. When the DGEBA content was higher than 3 wt %, the average hole size was about 0.3 μm and subsequently leveled off. One may conclude that in the presence of a proper amount of compatibilizers, the core–shell particles were dispersed nearly in the form of individual particles.

CONCLUSION

A blend system of nylon 6 and a core–shell impact modifier with a PBA core and PMMA shell can be well compatibilized with the epoxy resin DGEBA. When the content of DGEBA is 3 wt % of the blend, the impact strength of the system can be about 15 times higher than that of the uncompatibilized system. The tensile strength and apparent viscosity of the blend increase with the increase of the content of the compatibilizer. However, the elongation at break of the blend exhibits a maximum when the DGEBA is 3 wt % of the blend. DGEBA makes the core–shell impact modifier

disperse in the nylon 6 matrix nearly as individual particles.

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