# Effect of a Tie Layer on the Delamination Toughness of Polypropylene and Polyamide-66 Microlayers

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ABSTRACT: The effect of a thin tie layer on the adhesion of polypropylene (PP) and polyamide-66 (PA) was studied by delamination of microlayers. The microlayers consisted of many alternating layers of PP and PA separated by a thin layer of a maleated PP. The peel toughness and delamination failure mode were determined using the T-peel test. Without a tie layer, there was no adhesion between PP and PA. A tie layer with 0.2% MA provided some adhesion; however, delamination occurred by interfacial failure. Increasing the maleic anhydride (MA) content of the tie layer increased the interfacial toughness. With 0.5% MA, the interfacial toughness exceeded the craze condition of PP, and a transition from interfacial delamination to craze delamination occurred. Crazing ahead of the crack tip effectively reduced the stress concentration at the interface and dramatically increased the delamination toughness. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1461–1467, 1999

**Key words:** polypropylene; polyamide-66; microlayers; compatibilization; delamination toughness

## **INTRODUCTION**

Blends of immiscible polymers typically exhibit a coarse, unstable phase morphology and poor interfacial adhesion that result in poor mechanical properties. A common approach to improved polymer blends involves manipulation of the interface by addition of a third component, which is typically a block copolymer or a functionalized polymer that reacts in situ to form a block copolymer. The compatibilizer acts as an emulsifier to decrease the interfacial tension and to reduce the tendency of the dispersed particles to coalesce during processing. In the solid state, the graft copolymer promotes adhesion between the phases. The benefits of compatibilization to mechanical properties, such as higher tensile strength, tensile elongation, and impact strength, are specifically attributed to finer phase dispersion and improved interfacial adhesion.

Measurements of particle size in the solid state reveal how well a compatibilizer improves dispersion and, in combination with measurements of mechanical properties, are useful for comparing different compatibilization strategies. However, a fundamental understanding of the interfacial phenomena responsible for improved dispersion and adhesion is difficult to achieve from experiments on conventional melt-blended materials. where it is uncertain how much of the compatibilizer is actually at the interface. Specifically, the extent to which a compatibilizer enhances interfacial adhesion cannot be measured directly in melt blends. Although it is generally assumed that adhesion should be maximized, it has also been pointed out that controlled interfacial failure may be desirable.<sup>1</sup> This would imply an optimum interfacial adhesion level. In order to acer-

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Figure 1 Peel curves of PP/PA and PP/PP-g-MA/PA microlayers. Arrows indicate the onset of crack propagation.

tain minimal or optimal conditions, methods for accurately measuring adhesion between the components of polymer blends are needed.

Continuous layer-multiplying coextrusion is a method by which 2 or more dissimilar polymers are combined as many alternating layers with individual layer thicknesses in the micro- or nanoscale.<sup>2,3</sup> The high surface-to-volume ratio attainable with microlayers makes them ideal for studying interfacial phenomena related to polymer blends, as was demonstrated with measurements of interfacial adhesion of polycarbonate and poly(styrene-*co*-acrylonitrile).<sup>4-6</sup> With the versatility of the microlayer technology expanded to add a thin tie layer at each interface,<sup>7</sup> it is now possible to construct a two-dimensional model of the compatibilized blend interface.

In the present study, polypropylene (PP) and polyamide-66 (PA) were microlayered with a compatibilizer as the tie layer. Blends of PP and PA are of commercial importance because they combine the high ductility of PP with the relatively high yield strength of PA. However, because PP and PA are incompatible, the blends require a compatibilizer.<sup>8-13</sup> This is typically a maleated polypropylene (PP-g-MA), which forms a chemical linkage through the reaction of anhydride groups with the PA end groups. Therefore maleated polypropylenes with varying maleic anhydride (MA) content were microlayered with PP and PA. The interfacial strength was measured by the T-peel test and the failure mode was correlated with the graft level of the PP-g-MA.

### **EXPERIMENTAL**

Microlayer sheets were coextruded using the three-component layer multiplying process described previously.<sup>7</sup> Sheets about 1 mm thick and 70 mm wide consisted of alternating layers of PP and PA separated by a tie layer of maleated polypropylene (PP-g-MA). The extrusion was performed with four layer-multiplying dies, which produced a microlayer of 65 layers with PA surface layers (16 PP layers and 17 PA layers separated by 32 tie layers). The melt temperatures were chosen on the basis of melt indices to match viscosities as closely as possible when the melts entered the feed block. These were 226 (PP), 274 (PA), and 217°C (PP-g-MA). The composition taken from the extruder feed ratios was 76:5:19(PP to PP-g-MA to PA), and the average layer thicknesses calculated from the composition and sheet thickness were 60  $\mu$ m (PP), 15  $\mu$ m (PA), and 2 µm (PP-g-MA). A microlayer of PP and PA without a tie layer was obtained by shutting off the extruder with the PP-g-MA; this microlayer had 33 layers with a composition 80 : 20 (PP to PA).



**Figure 2** Scanning electron micrographs of peel fracture surfaces: (a) PA surface of PP/PA, (b) matching PP surface, and (c) PA surface of PP/0.5 MA/PA; (d) matching PP surface.

The PA was Zytel 42 (DuPont) and the PP was Profax 6323 (Himont) with a melt flow index of 12. Maleated polypropylenes were Polybond 3002, 3150, and 3200 (Uniroyal) with 0.2, 0.5, and 1.0% MA by weight and molecular weights of 440,000, 330,000 and 110,000, respectively. The 4 microlayers studied are identified by the MA content of the tie layer as follows: PP/PA (no tie layer), PP/0.2 MA/PA, PP/0.5 MA/PA and PP/1.0 MA/PA.

Delamination was carried out with the T-peel test (ASTM D1876). Specimens 15 to 25 mm wide were notched by pushing a fresh razor blade into the midplane of the sheet. The notch was examined in the optical microscope to ensure that the crack started along a single layer. Specimens were loaded at a rate of 2.0 mm/min.

Some tests were interrupted, and the crack tip region was sectioned perpendicular to the plane of the crack with a low-speed diamond saw (Isomet, Buehler Ltd.). The sections were polished on a metallurgical wheel with wet sandpaper and alumina oxide aqueous suspensions. A polished section was mounted on a scanning electron microscope (SEM) stage that had been modified to hold a stretched specimen and was coated with 90 Å of gold either before or after it was stretched to open the crack tip. The peel fracture surfaces were also coated and examined in the JEOL JSM 840A SEM.

#### **RESULTS AND DISCUSSION**

The PP/PA microlayer without a tie layer delaminated before a measurable load was applied to the beam arms. In contrast, the arms of the PP/0.2 MA/PA microlayer bent into the T-peel configuration as the load was applied (Fig. 1), and the crack



**Figure 3** Peel crack tip of PP/0.5 MA/PA: (a) low magnification with arrows indicating the PA layer; (b) higher magnification.

then propagated in a stable manner at a relatively constant load,  $P_{\rm cr}$ , from which the delamination toughness,  $G = 2P_{\rm cr}/W$ , was obtained for a specimen of width W. After the specimen was unloaded, the beam arms returned to their original position, indicating little or no plastic deformation of the beam arms. This microlayer had a low but measurable peel toughness of  $7 \pm 2$  J/m<sup>2</sup>.

Infrared (IR) analysis of the peel fracture surfaces from both PP/PA and PP/0.2 MA/PA microlayers revealed only polyamide peaks on one surface (PA surface) and only polypropylene peaks on the other (PP surface). This indicated interfacial crack propagation between PA and PP (PP/PA) or between PA and the tie layer (PP/0.2 MA/PA). Matching peel fracture surfaces of PP/PA and PP/0.2 MA/PA are compared in Figure 2. Both PA surfaces [Fig. 2(a) and (c)] exhibited a spherulitic topology and lamellar morphology with no evidence of plastic deformation. The only feature that differentiated the surfaces was occasional holes at the spherulite boundaries on the PA surface of PA/0.2 MA/PP. The PP surface of PP/PA [Fig. 2(b)] showed numerous voids that probably formed when the layers contracted during crystallization and pulled apart. These voids did not appear on the PP surface of PP/0.2 MA/PA [Fig. 2(d)]; this surface closely mirrored the matching PA surface with depressions that were imprints of the PA spherulites. Occasionally, fibers extended from the ridges that defined the edges of the spherulite imprints. The PP fibers matched holes on the PA surface.

During solidification of the microlayers, the PA crystallized first while the PP was still in the melt. If there was no interaction between the layers, the PP subsequently crystallized essentially independently of the PA layer. The layers contracted as they solidified, and the integrity of the PP/PA interface was lost. In contrast, the tie layer in PP/0.2 MA/PA created enough block copolymer to hold the PP and PA layers in contact during crystallization. As a result, the PP layer assumed the surface topology of the PA layer. Fibers on the PP surface and holes on the PA surface provided evidence that some PP was pulled into the interspherulitic regions as PA crystallized. Mechanical interlocking contributed to the peel toughness. However, the tie layer did not impart sufficient adhesion to prevent adhesive failure of the interface.

The peel toughness of PP/0.5 MA/PA and PP/1.0 MA/PA was much higher (Fig. 1). Increasing the MA content of the tie layer from 0.2 to 0.5% increased the measured toughness by two orders of magnitude, from 7 to 970  $\pm$  170 J/m<sup>2</sup>. Increasing the MA content further from 0.5 to 1.0% produced a toughness of 770  $\pm$  150 J/m<sup>2</sup>, which was not a significant change. For both microlayers, the beam arms were permanently bent after the peel test, which indicated that the measured toughness included a contribution from plastic deformation.

The dramatic increase in *G* corresponded to a change in the peel mechanism. A cross section through the crack tip in Figure 3(a) shows a single craze propagating at the interface. The entire thickness of the PA layer is visible in the micrograph together with a portion of the PP/PP-g-MA layers on either side. There is no visible interface between PP and PP-g-MA because these PP-g-MA compositions interpenetrate and cocrystallize with PP.<sup>14</sup> The specimen shown at higher magnification in Figure 3(b) includes a region where the craze fibrils have started to fracture. This specimen was coated before the crack was opened, and, therefore, cracking of the gold coating created some of the



**Figure 4** Scanning electron micrographs of peel fracture surfaces of PP/0.5 MA/PA: (a) PA surface, (b) matching PP surface, and (c) another area of the PA surface; (d) matching PP surface.

surface features. However, the micrograph provides a view into the craze, which reveals that the craze fibrils fractured near the PA interface. The resulting fibrous texture on the PA layer (bottom surface) is also discernable. Fracture near the PA interface could be a consequence of peeling layers of different moduli. Alternatively, the craze grows in width behind the craze tip by drawing material into the fibrils from an uncrazed layer at the craze boundary.<sup>15</sup> This mechanism of craze growth can proceed normally on the PP side of the craze; however, on the PA side, with little or no uncrazed material for craze growth, the fibrils would be expected to thin down and break.

Peel fracture surfaces of PP/0.5 MA/PA and PP/1.0 MA/PA exhibited the same textural features; these are illustrated with matching surfaces of PP/0.5 MA/PA in Figure 4. Typically, the

PA surface contained very dense fine fibrils with no indication of the underlying spherulitic texture [Fig. 4(a)]. Additionally, long strips of material appeared to have been pulled out of a surface layer. The dimensions of the strips and the matching fissures suggested a thickness of about 1  $\mu$ m. The fine fibrils and the thick strips melted at about 160°C when heated on the hot stage in the optical microscope, which confirmed that they were PP. The matching PP surface had a highly porous texture characteristic of fracture through a craze [Fig. 4(b)].

Although most of the fracture surface exhibited the textures illustrated in Figure 4(a) and (b), about 5–20% of the fracture surface exhibited the somewhat different textures illustrated in Figure 4(c) and (d). Spherulite boundaries were visible on the PA surface [Fig. 4(c)], and the matching PP



POLYAMIDE

**Figure 5** Schematic illustration of the fracture path through the crack tip craze that produced the surface features in Figure 4.

surface was quite smooth [Fig. 4(d)]. The surfaces had a superficial resemblance to the interfacial failure surfaces of PP/PA and PP/0.2 MA/PA, although there were significant differences. On the PA surface, the lamellar texture of the spherulites was less distinct than in Figure 2(a) or (c); and on the PP surface spherulite imprints were absent, and occasional cracks revealed underlying cavitation.

The schematic of the fracture path in Figure 5 is inferred from the combined observations of the crack tip craze and the fracture surfaces. In PP/ 0.5 MA/PA and PP/1.0 MA/PA, a craze grows in the PP layer very close to the PA interface. On the PA side of the craze, the craze fibrils emanate from a thin layer of PP that is attached by graft copolymer to the PA surface. Generally, the crack propagates through the craze as the craze fibrils draw out and fracture. The fibrils do not fracture in the center of the craze; instead, they fracture near the craze boundary on the PA side of the craze. This produces different textures on the PA surface and the PP surface, as seen in Figure 4(a)and (b). Occasionally, a strip of the thin PP layer that anchors the craze fibrils on the PA side is pulled loose from the underlying PA layer. Larger areas of interfacial failure are also seen where the crack deviates from the craze to the interface between the thin PP layer and the underlying PA layer. On the PA fracture surface, the undeformed spherulitic texture of PA is exposed, and on the PP fracture surface, the smoother texture of the thin PP layer covers the underlying craze. Even though final separation in PP/0.5 MA/PA sometimes occurs at the interface, the interface is strong enough to support crazing in the PP layer. This is not true for PP/0.2 MA/PA, which fails interfacially before the PP layer crazes.

Conceptually, the transition from interfacial failure to craze fracture when the MA content of

the tie layer increases from 0.2 to 0.5% is analogous to the transition observed in microlayers of polycarbonate and poly(styrene-co-acrylonitrile) as a function of rate, temperature, and acrylonitrile content.<sup>4-6</sup> The transition depends on the relationship between interfacial toughness and the stress required for crazing in one of the layers. As the concentration of MA in the PP-g-MA increases and the amount of copolymer at the interface correspondingly increases, the condition for interfacial failure becomes more severe. A transition occurs when the interfacial toughness exceeds the condition for crazing in the PP layer. Crazing ahead of the crack tip effectively reduces the stress concentration at the interface and dramatically increases the delamination toughness.

The peel tests reveal the dramatic increase in toughness that is achieved when adhesion is strong enough for cohesive damage to initiate in one of the components. By analogy, the results suggest that in order to combine the high yield strength of PA with the high ductility of PP in PP-rich blends, adhesion of the phases should be strong enough to withstand initiation of cohesive damage, and subsequent deformation of the PP phase during yielding, without debonding. However, it can be imagined that the maximum ductility might be achieved if debonding at a higher strain removes constraints imposed by the less ductile component. Possibly, increasing the adhesion above an optimum level for cohesive deformation would not be beneficial and might even be detrimental.

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