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Enhancement of Interfacial Adhesion by Means of Surface Segregation in the Interface between Polycarbonate and SAN Blends

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The adhesion between immiscible polymers is of practical importance in numerous industrial applications. The adhesive strength of the bond between such immiscible components depends upon their chemical composition. In particular, the strength of the bond between styrene-*co*-acrylonitrile (SAN) and polycarbonate (PC) has been shown[1,2] to depend upon the acrylonitrile (AN) content of the SAN with a maximum at 24 wt % AN. On the other hand, the tensile strength of SAN also depends upon its AN content.[2] To maximize the tensile strength in a practical product, it is desirable to have a greater AN content than that which provides maximum adhesive strength. Both of these objectives can be achieved by realizing that the surface composition of an SAN blend may differ from its bulk composition. It has been shown that when mixing SAN's with differing AN content, the component having lower AN migrates to the surface.[3] This suggests the strategy of adding a small amount of a lower AN content SAN to a polymer having a higher AN component. In this way one can maintain the desired tensile properties while at the same time obtain the greater adhesive strength arising from the lower AN component which migrates to the surface.

The polymers used in this work were obtained from the Monsanto Chemicals/Bayer Co. The SAN copolymers contained AN contents of 17%, 24%, 26%, 29%, and 31% and had molecular weights of 172K, 160K, 142K, 85K and 93.2 K, respectively.[1] The polycarbonate was of the usual sort based on bisphenol A and had a weight average molecular weight of 32 000. The molecular weights of both the PC and SAN polymers were chosen such that they would be significantly larger than their respective entanglement molecular weights.[4]

It has been shown,[4] that the presence of the usually occurring oligomer in SAN can have a detrimental effect on adhesion. This is believed to occur because of the diffusion of the oligomer to the surface where it reduces the entanglement density and plasticizes the polymer so as to facilitate chain pullout. To avoid this problem, oligomer was removed from the polymer by making an approximately 5% solution in chloroform and then precipitating the SAN by slowly adding the polymer while stirring in a solution of 90% methanol and 10% distilled water. The precipitated polymer was recovered by vacuum filtration and dried by heating at 45 °C for several days in an Ar atmosphere to minimize oxidation. The PC was used as received. All dried polymers were compression molded in a press at 160 °C at 2000 psi between polished, Kevlar-covered, stainless steel molds. The resulting samples were bar shaped and of dimensions 5.0 cm × 1.0 cm × 0.2 cm.

Table 1. SAN Blends Studied[a]

17/24	17/26*
17/29*	17/31*
24/26	24/31
26/29	26/31

[a] Blends marked with an asterisk are partially miscible. See ref 8.

Copolymer blends were prepared by mixing equal amount of powders of SAN having different AN content and molding them. Thus 50/50 blends were used in all cases. The combinations studied are listed in Table 1. Previous studies have shown that blends of molecular weight approximately 10^5 are completely miscible if they do not differ by at most 7% in AN content.[8] Consequently, some of the blends (marked with an asterisk in Table 1) are only partially miscible.

The molded SAN blend samples were first annealed in air at 160 °C for 4 h to allow segregation of the lower energy AN component to the free surface. Laminates of the SAN and PC samples were then prepared by sandwiching the samples together in their respective molds for 1 h at 160 °C and 2000 psi. The sandwiched samples were allowed to cool in the mold to minimize the formation of thermal stresses. As we will show later, the lower AN content component segregates to the PC interface as well, and hence the sandwiching step does not change the original AN content at the interface. The samples were then glued with epoxy to an aluminum plate.

The interfacial strength was measured using the asymmetric double cantilever technique. The asymmetric geometry was chosen in order to prevent the crack from propagating toward the more compliant material, in this case the SAN blends.[9] The asymmetry was achieved as discussed in ref 6 by the attachment (gluing) of the SAN side of the laminate to a rigid 2 mm thick aluminum plate. A single edged razor blade was inserted into the interface between the PC and SAN layers at a constant rate of 100 μm/s using a computer controlled stepping motor. The length of the resulting crack, which propagated along the interface, was measured using an optical microscope with a precision of 0.1 mm. The average of eight measurements were obtained per point and the typical error bars are in Figure 1.

When one layer is attached to a rigid substrate, Kanninen[10] has shown that the fracture toughness (G_c) can be calculated from the following equation:

$$G_c = \frac{3u^2ED^3}{8\,a^4\,(1 + 0.64\,(D/a))^4}\ (\mathrm{J/m^2})$$

where E (= 3.66 GPa) and D (= 2 mm) are the Young's modulus and thickness of the top, unattached layer (the PC), a is the crack length, and u is the wedge thickness.[1] This equation involves the assumption that all of the energy is dissipated in a very small region ahead of the crack tip. It was also assumed that released energy only comes from the bending of the beam. For this reason,

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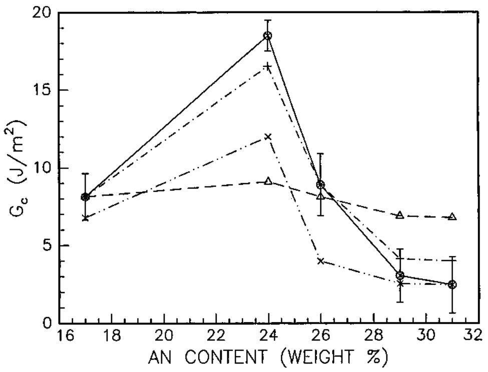

Figure 1. G_c value vs AN content for (—) pure SAN, (- - -) SAN blends with AN 17%, (-•-) SAN blends with AN 26%, (-••-) SAN blends with AN 31%.

it was necessary that the blade be inserted sufficiently slowly so that the crack length achieved its equilibrium value.

Secondary ion mass spectrometry and atomic force microscopy were used to characterize interfacial segregation. SAN blend films, approximately 700 Å thick (the exact thickness was determined by ellipsometry) were spun cast directly on silicon wafers from chloroform solution. Some of the films were covered by a 700 Å thick PC overlayer spun cast on glass and floated from the water surface. Annealing was performed in an oil trapped vacuum oven at 10^{-4} Torr and 160 °C. The sample surfaces were examined with a Digital Nanoscope III AFM in the contact mode with Si_3N_4 tip. SIMS sputtering was performed with a 2 keV Ar ion beam rastered at 30° incidence. The intensity of negative ions (CN, C, CH, O, etc.) was detected as a function of sputtering time. Volume fraction as a function of distance was obtained using the procedure outlined in ref 5.

The techniques were first tested by measuring G_c for the interface between PC and single component SAN samples of differing AN content. The results, shown as a solid line in Figure 1, are in quantitative agreement with the previously reported data, and show that the maximum G_c occurs at about 24 wt % AN content. Results for G_c measurements for the interface of PC with various SAN blends are also shown in Figure 1 together with those of the pure SAN/PC samples. From the figure we can see that the strength of the interface for a 50%/50% blend of 24% and 26% SAN is over twice that for the pure 26% SAN and comparable to the G_c of the samples of pure 24% SAN. This is believed to result from the 24% component enriching the interfacial layer, leading to stronger adhesion than that obtained for a pure 26% sample. Enhancement is obtained for all other systems as well where the 24% AN represents the fraction with the lowest AN content. In the blends with 17% AN content no increase in G_c is observed, since the 24% AN fraction is the higher AN content and not expected to segregate to the interface.

In order to test the effect on G_c at the PC interface of possible phase segregation within the SAN blend samples, the G_c between slabs of 24% SAN with 17% SAN or 31% SAN were measured. The values obtained for both samples were 120 J/M^2 (comparable to the pure materials) and crazing at the fractured interface was observed. This indicates that at the annealing temperatures studied, the interfacial width between the respective phases is very broad, and the interface is very strong. The much reduced fracture toughness measured between laminates of the blends and PC is entirely due to the PC and SAN blend interfacial properties. This interface, known[4] to be very narrow (approximately 40 Å), is due to the large degree of immiscibility between SAN and PC.[5] Even when enhanced adhesion is observed, examination of the fractured surfaces shows no crazing and indicates that chain pullout is the predominant mechanism. Consequently we believe that the G_c shown even for the immiscible blends in Figure 1 is dominated by the SAN component present at the PC interface, rather than failure within the SAN blend sample. This effect can be demonstrated in Figure 1 by comparing the G_c curves of the 17% and 31% series. It should be noted that blends differing in AN content by more than 7% are partially miscible, the degree of miscibility being a function of AN content difference. Consequently, some of the blend samples in both series are only partially miscible (Table 1). It can be seen in Figure 1 that the G_c at the PC interface is enhanced in the 24/31 sample and no enhancement is observed in the 17/24 sample even though the two sets of blends have comparable degrees of immiscibility. In fact, very little variation in G_c is seen in the 17% curve for all blends, consistent with the 17% component always having the lowest AN content and segregating to the PC interface.

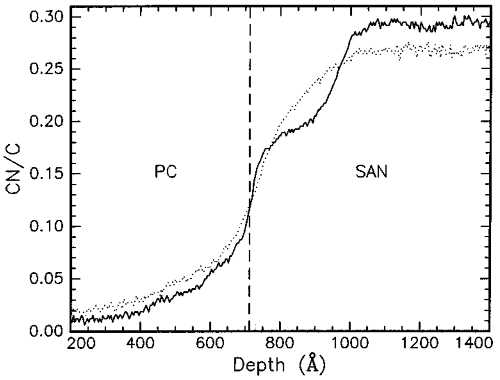

Figure 2. Secondary ion mass spectrometry (SIMS) concentration profile of the AN content in a bilayer sample of PC/17%−31% SAN blend. The dotted line corresponds to the unannealed bilayer sample while the solid line corresponds to the bilayer sample annealed at $T = 160$ °C for 24 h. The vertical line marks the original interface.

In order to determine the composition profile of the SAN blends, and verify that the component with the lower AN content segregates to the PC as well as the vacuum interface, dynamic SIMS was performed on thin-film bilayer samples. The layer adjacent to the Si substrate was a 50%/50% mixture of 17% and 31% SAN copolymers and a PC layer was floated on top at the air interface. Since no deuterated SAN samples were available, the CN ions were used to profile the SAN blend layer. The 17% and 31% mixture was chosen since they provided the largest scattering contrast. The results are shown in Figure 2 where we plot the volume fraction of AN content in the bilayer film as a function of depth. The dashed line indicates the bilayer interface. The dotted trace corresponds to the unannealed samples. The solid line corresponds to the same sample after annealing for 24 h at 160 °C. From the figure we can see that the SAN film, which is initially of uniform composition, separates after annealing into two layers, one containing only the 17% component, and the other only 31% component. The 17% component wets the PC interface, as expected. The small amount of SAN observed in the PC phase is probably due to remaining oligomer in the SAN film that can diffuse into the PC layer. It is important to note that the separation of the SAN blend into two layers exactly corresponding to the two original component indicates that the 17% SAN layer at the PC interface is laterally homogenous. This type of homogenous layering has been previously observed in many other blends where one of the components is preferentially segregated to an interface.[7]

In conclusion we have shown that it is possible to enhance adhesion between a homopolymer and a blend through the enrichment at the interface of the component which provides the strongest adhesion. This provides a means by which it is possible to optimize both the mechanical properties of a polymer and its adhesion to another polymer.

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