Toughness of SMI-Modified ABS Alloys and the Associated Deformation Behavior

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ABSTRACT: The mechanical toughness of modified ABS (acrylonitrile-butadiene-styrene) alloys was evaluated using Izod impact, tensile, and compact tension tests. The modified ABS alloys contain 20 wt % of styrene-N-phenylmaleimide (SMI) that is added to enhance the thermal resistance of the ABS. In this study, the effects of matrix composition, rubber/ matrix adhesion, and rubber particle structure on the alloy toughness were investigated. Results from the tensile test and Izod impact test ranked the alloys in an order that is different from that given by K_{Ii} (stress intensity factor for crack initiation), measured from compact tension specimens. This is due to the difference in energy-absorption characteristics for crack initiation and crack growth. The conclusion is supported by optical micrographs on the deformation zone size. The microdeformation behavior of the alloys was examined using transmission electron microscopy (TEM), which revealed different rubbertoughening mechanisms between Izod and tensile specimens. The former contains numerous extensive crazes, while the latter, only a very few short crazes, except in regions within a few micrometers from the fracture surface. The dominant matrix deformation mechanism for the tensile specimens is believed to be shear deformation. Another interesting observation from the study is rubber particle cavitation, commonly observed in tensile specimens and Izod specimens with solid rubber particles; it did not occur in the Izod specimens containing salami-type rubber particles. This is attributed to the salami structure that increased the straining rate for the rubber phase, leading to ductile-brittle transition of the rubber. The transition to brittle deformation of the rubber phase prevented rubber particle cavitation. The microscopic examination indicated that toughening mechanisms by the rubber particles can be very different among the mechanical tests, which should be taken into account for the rubber toughening of polymers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1543-1553, 1999

Key words: ABS; polymer; blends; deformation; toughness

INTRODUCTION

Mechanical toughness, being one of the major properties for polymer characterization, can now be evaluated using many different methods. These include compact tension and singleedge-notched bending tests for $K_{\rm Ii}$ (stress intensity factor for crack initiation), $G_{\rm Ii}$ (strain energy release rate for crack initiation), and $J_{\rm IC}$ (critical energy for *J*-integral), Izod and Charpy impact tests for fracture energy, and the dropweight impact test for input energy for fracture. In certain cases, tensile properties, such as stress-strain curves, are also used for the

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Figure 1 Chemical structure of SMI, which is a random copolymer of styrene, *N*-phenylmaleimide, and maleic anhydride, with a weight ratio of 45 : 53 : 2. Monomer ratio of x : y : z is 57 : 40 : 3.

toughness comparison, especially among polymers of the same family.

It has long been known that the above testing methods can yield quite inconsistent results for toughness. In most cases, the inconsistency was attributed to notch sensitivity of the materials, sample geometry, loading modes, or strain rates selected for the testing.^{1,2} From the materials point of view, it has been shown that these factors may cause various deformation mechanisms that lead to ductile-brittle transition.³ Therefore, toughness characterization for polymers needs to incorporate several different methods to ensure that the polymers are evaluated under all possible deformation conditions.

In this work, toughness for styrene–N-phenylmaleimide (SMI)-modified acrylonitrile-butadiene-styrene (modified ABS) alloy was characterized. The parameters used in the study include matrix toughness, adhesion between rubber particles and matrix, and rubber particle size and structure. The work is part of a much larger study on toughness enhancement for a modified ABS alloy. The modified ABS is a conventional ABS blended with SMI and styrene-co-acrylonitrile (SAN). The SMI is a newly developed, high thermal-resistant copolymer with a glass transition temperature $(T_{\rm g})$ of 196°C.4 Figure 1 shows the chemical structure of SMI, which is a random copolymer of three monomers: styrene (St), Nphenylmaleimide (PMI), and maleic anhydride (MAH). The SMI was converted from styrene-comaleic anhydride through a postimidization process⁵ that transfers most of the MAH units into PMI units. The postimidization process reduces the production costs for SMI, leading to great availability of SMI to many existing polymers for property modification. In the case associated with this study, the SMI is added to ABS for enhancement of its thermal resistance. As the SMI forms a miscible blend with SAN in a wide range of acrylonitrile content, modifying ABS by the addition of SMI increases the thermal resistance for the ABS. DENKA showed⁶ that by adding 20 wt % SMI, the T_g of the ABS alloy increases more than 10°C. Currently, the modified ABS is being used for applications such as interior car fittings and car audio stereo systems that require good thermal resistance to prevent any shape distortion due to heat. As SMI is brittle, with a $K_{\rm IC}$ of only around 0.5 MPa m^{0.5},⁷ it is perceived that the addition of SMI to ABS may lower the toughness for the ABS. Therefore, the major aim for the whole study was to search for methods that can enhance toughness for the modified ABS alloys.

The rubber toughening of polymer alloys has long been studied. Macroscopically, the toughness of the alloys is affected by the matrix toughness,⁸ rubber content (especially for a type of low molecular weight polybutadiene),⁹ rubber particle size and particle/matrix adhesion,8 and matrix ligament thickness (matrix thickness between neighboring rubber particles).¹⁰ For SAN under tension, crazing is a well-known deformation mechanism,¹¹ but in ABS, the matrix may have localized shear deformation due to the cavitation of the rubber particles.¹² Nevertheless, crazing is still deemed the dominant deformation mechanism for the ABS. Increase in the number of crazes is a well-accepted means to increase toughness for the alloy.¹³

In this study, increase of the matrix toughness was through increase of the acrylonitrile content in SAN, which has been shown to be an important factor for toughness enhancement of ABS.¹⁴ Increase of the interface adhesion was through increase of the entanglement strength between the grafted SAN and matrix polymers, via increasing the molecular weight for the grafted SAN and grafting ratio (defined as the percentage of SAN in the ABS that is grafted to the butadiene rubber). It was expected that the strong adhesion transfers sufficient force from the matrix to the rubber particles, thus encouraging the rubber particle deformation. As the rubber particles with grafted SAN of high molecular weight are also large in size (with diameters increased to $0.5 \ \mu m$, compared to 0.1 μ m) and contain SAN occlusions to form a salami-type structure, the measured toughness increase may not be solely due to the increase of interface adhesion. Through microscopic examination on the deformation behavior, however, effects of these factors can be distinguished. It should be noted that the size of the rubber particles used in the study should be much smaller than the critical size at which, as suggested by Wu,¹⁵ a sharp tough-brittle transition

Composition		Alloy 1	Alloy 2	Alloy 3
Blend composition (wt %)	SMI SAN _{add} ABS	SMI55 (20%) SAN28 (44%) ABS-g1 (36%) 50 : 50 (Bd : SAN)	SMI55 (20%) SAN25 (44%) ABS-g1 (36%) 50 : 50 (Bd : SAN)	SMI55 (20%) SAN28 (35%) ABS-g2 (45%) 40 : 60 (Bd : SAN)
M_w	${ m SMI} \ { m SAN}_{ m add} \ { m SAN}_{ m ABS}$	171,000 120,000 89,000	171,000 114,000 89,000	171,000 120,000 129,000
Monomer composition (wt %)	PMI MAH styrene AN Bd	$ 10.6 \\ 0.4 \\ 54.6 \\ 16.4 \\ 18 $	$ 10.6 \\ 0.4 \\ 55.9 \\ 15.1 \\ 18 $	$10.6 \\ 0.4 \\ 54.5 \\ 16.5 \\ 18$
ABS	Particle size Grafting %	0.1 μm 35	$\begin{array}{c} 0.1 \ \mu \mathrm{m} \\ 35 \end{array}$	0.5 μm 66

Table I Material Information for the Alloys Used in This Study

is expected to occur. This is based on the observation that, as to be shown here, the lowest toughness for the ABS is still much higher than the toughness of the SMI/SAN blend matrix.

Toughness for the modified ABS alloys was evaluated using tensile, Izod impact, and compact tension tests. As to be shown in the Results, the three tests did not provide consistent toughness ranking for the alloys. Explanations for the inconsistency, in terms of physical meaning of the measured toughness values and deformation mechanisms involved in the specimens, are provided here.

EXPERIMENTAL

Materials

Three modified ABS alloys were selected for the study. For convenience, the three alloys are named #1, #2, and #3 in the rest of the article. All the alloys contain 20 wt % SMI55 that has monomer composition of 45:53:2 for styrene : phenylmaleimide : maleic anhydride (St : PMI : MAH). Alloy #1 acted as the control material, consisting of ABS-g1, SMI55, and SAN28. Details of the mixing ratio and monomer composition of the constituents are given in Table I. SAN28 is a random copolymer of St and AN (acrylonitrile) at a ratio of 72 : 28. ABS-g1 is an ABS that has 50 wt % rubber (butadiene or Bd) particles with a mean diameter of 0.1 μ m. The grafting ratio for ABS-g1 is 35%.

Instead of SAN28, alloy #2 used SAN25 as the SAN_{ABS} (SAN existing in the original ABS, as

shown in Table I). The SAN25 has a monomer ratio of 75: 25 for St: AN. Other constituents for alloy #2 are the same as those for alloy #1. Alloy #3 is different from alloy #1 in the original ABS used for blending, that is, ABS-g2 instead of ABSg1. ABS-g2 contains 40 wt % of rubber, instead of 50 wt % in ABS-g1, and has a grafting ratio of 66%, instead of 35% for ABS-g1. Other differences between ABS-g1 and ABS-g2 are (i) the molecular weight for the SAN: The former is 89,000, while the latter 129,000; (ii) rubber particle size: The former has a mean diameter of 0.1 μ m, while the latter 0.5 μ m; and (iii) rubber particle structure: The former appears to be uniform in the micrograph, but the latter has salami-type structure with SAN occlusions. Both ABSs contain SAN of 23 wt % acrylonitrile content.

The mixing ratio for alloy #3 is 20:35:45 for SMI: SAN: ABS, which is different from that for alloys #1 and #2 (20:44:36 for SMI: SAN: ABS). This is to maintain the same monomer ratio (PMI, MAH, St, AN, and Bd) among the three alloys. Therefore, the main differences between alloys #1 and #3 are (i) rubber particle size, (ii) grafting ratio of the ABS, (iii) molecular weight for the SAN_{ABS}, and (iv) rubber particle structure. It should be noted that all the above factors are in favor of making alloy #3 tougher than alloy #1.

Figure 2 shows the blend morphology of the alloys. Figure 2(a) represents the typical morphology observed in alloys #1 and #2, in which rubber particles were uniformly stained by osmium tetraoxide (OsO₄). Figure 2(b) represents the morphology for alloy #3, which contains rub-



Figure 2 Blend morphology of the modified ABS alloys: (a) for alloys #1 and #2; (b) for alloy #3.

ber particles of a salami structure with SAN occlusions. Both micrographs show well-dispersed rubber particles surrounded by a homogeneous matrix.

Matrices of the alloys consist of three constituent polymers: SMI, SAN_{ABS} , and SAN_{add} . SAN_{ABS}, as mentioned above, is SAN in the original ABS, while SAN_{add} is the SAN blended in the alloy during the mixing process. Since the SMI55 is miscible with both SANs,⁷ the three polymers form a homogeneous matrix with a single glass transition temperature.

Test Specimens

SMI55, SAN_{ABS}, and SAN_{add} were first blended together using a twin-screw extruder that had barrel temperature set at 280°C. Due to the high shear rate introduced by the twin screws, the

resin temperature reached approximately 300°C during the blending. The extruded pellets were then injection-molded to form dumbbell specimens 65 mm long in the gauge section, rectangular bars of a 6 \times 12.7 mm² cross section, and rectangular plates 3 mm in thickness. The barrel temperature for the injection molding was 260°C, which resulted in the resin temperature of 275°C. The mold temperature for injection molding the above specimens was kept at 60°C. After the injection molding, a notch was machined in the bars and plates to make Izod specimens and compact tension specimens. The compact tension specimens were $50 \times 50 \text{ mm}^2$ in length and height, with the machined notch of 18 mm in length. The dimensions followed the recommendations described in ASTM D256 and E399 for Izod and compact tension specimens, respectively.

Mechanical Tests

Tensile tests were conducted using an Instron 4505 universal testing machine at a crosshead speed of 5 mm/min. An extensometer with an initial gauge length of 50 mm was used to measure strain in the elastic region. Because of the long extension before fracture, the extensometer could not measure the fracture strain. Therefore, only total elongation is reported.

Most of the Izod tests were conducted using a conventional pendulum-type Izod impact tester. Some of the Izod specimens were tested for measurement of force and energy as a function of specimen deflection, using a Radmana ITR2000 instrumented impact tester at an impact speed of 3.5 m/s. The compact tension tests were conducted using a Shimazu universal testing machine (Model DDS-5000) at a crosshead speed of 1 mm/min.

Examination of Fracture Behavior

The fracture behavior was analyzed using optical microscopy and transmission electron microscopy (TEM). The former was for bulk deformation, while the latter, for deformation at the micrometer level. Transmission optical micrographs were taken in a pseudo-dark-field mode using diffused reflected light transmitting through specimens. The pseudo-dark-field imaging enhances the contrast between regions with different light transmittance. In this case, the contrast is between the deformed, whitening region and the undeformed region. As to be shown in the next section, the deformed, whitening region appears to be dark, in



Figure 3 Tensile test results for the three alloys, including tensile strength, Young's modulus, elongation at the tensile strength point, and elongation at fracture.

contrast to the undeformed region that appears to be bright. Specimens for the pseudo-dark-field imaging had a thickness of around 3 mm, which is the original thickness for tensile and compact tension specimens and half the thickness for the Izod specimens.

Microdeformation behavior was characterized using ultramicrotomed specimens. The specimens were first "trimmed" using a glass knife to a trapezoidal shape that has a size of less than 0.3 mm in base length and then stained in the vapor of an OsO_4 solution of 2 wt % for 48 h before being microtomed using a Diatech diamond knife. Some specimens were mounted to grids that had been coated with holely carbon film. The carbon film stabilized the specimens under the electron beam, especially when imaging was near the edge of the specimens, which was needed for observing deformation immediately beneath the fracture surface. When the grids with the holely carbon film were used, an image of the holely carbon film is visible on the micrographs, but the feature is easily distinguishable from the material deformation behavior.

Two TEMs were used for the study, a JOEL 2000EX and a Hitach H7100, operated at 200 and 100 keV, respectively. There was no special reason for selecting the TEMs, rather, mainly due to the availability of the machines at the time when examination was needed.

Deduction of K_{li}

 $K_{\rm Ii}$ (stress intensity factor for crack initiation) was calculated from the compact tension test results, following the method described in ASTM E399. A force, named $P_{5\%}$, was determined from a point on the force-displacement curve, which is the intersection of the curve with a straight line plotted from the origin with 5% offset from the initial slope. In this study, the $P_{5\%}$ was found to be about 60% of the maximum force value. Using $P_{5\%}$, $K_{\rm Ii}$ was calculated using the following equation:

$$K_{\rm Ii} = (P_{5\%}/BW^{0.5}) \times f(a/W) \tag{1}$$

where W is specimen width, a crack length, B the specimen thickness, and

$$f(a/W) = [(2 + a/W)(0.886 + 4.64 a/W) - 13.32 a^2/W^2 + 14.72 a^3/W^3 - 5.6 a^4/W^4]/(1 - a/W)^{3/2}$$
(2)

It should be noted that due to significant plastic deformation at the crack tip the K_{Ii} values might not satisfy the plain strain condition. Nevertheless, the values are useful in a toughness comparison among the alloys.

RESULTS AND DISCUSSION

Mechanical Tests

The tensile strength, Young's modulus, elongation at the tensile strength point, and elongation at fracture are shown in Figure 3. The three alloys showed nearly the same modulus and elongation at the point for tensile strength point, but the tensile strength is in the order of #2 = #1 > #3(49, 49, and 41 MPa, respectively) and elongation



Figure 4 Izod impact test results, obtained from a conventional pendulum-type Izod impact tester.

at fracture $\#2 < \#1 \ll \#3$ (4.9, 7.5, and 22.3 mm, respectively, out of a gauge length of 65 mm). Total energy absorption in terms of the area under the force-displacement curve is in the order of $\#2 < \#1 \ll \#3$.

Results of the Izod impact strength are shown in Figure 4 in which toughness for the three alloys is ranked in the order of #2 < #1 < #3 (11, 17.2 and 20.3 kg cm/cm, respectively), which is in the same order as that given by the energy absorbed in the tensile specimens, although different in the scale of toughness difference. Results from the instrumented impact tests are shown in Figure 5 in which force and energy absorption were measured as a function of specimen deflection. The results suggest that the energy absorption among the three alloys remained almost the same until the point of maximum force, after which the energy-absorption curves diverted, resulting in total energy absorbed for fracture to be in the order of #2 < #1 < #3.

As the crack growth in the Izod impact test started most likely at the point of maximum force, the energy-absorption curves in Figure 5 indicate that the difference in impact strength is due mainly to the energy absorption for crack growth across the specimen, rather than for crack initiation from the notch.

The K_{Ii} from the compact tension tests showed a completely different trend in toughness, which ranked the three alloys in a slightly decreasing order of #1, #2 and #3 (3.3, 3.1, and 2.9 MPa m^{1/2}, respectively, as shown in Fig. 6). Since the K_{Ii} was calculated from values at the point of $P_{5\%}$, which is very close to the initiation of crack growth, the toughness trend indicated by the $K_{\rm Ii}$ should be more closely related to the toughness for crack initiation rather than to crack growth. Therefore, even though the Izod impact test and compact tension test have very different testing condi-



Figure 5 Instrumented Izod impact test results: (a) force versus deflection; (b) absorbed energy versus deflection.



Figure 6 K_{Ii} from compact tension tests.

tions, the toughness values presented in Figures 4 and 6 are not contradictory to each other, at least in terms of the toughness ranking, as both showed that the three alloys require similar energy for crack initiation. The difference in the Izod impact strength is due to the energy for crack growth across the specimen.

The above conclusion can also be applied to the tensile test results. As shown in Figure 3, the three alloys required similar energy for deformation up to the point of maximum stress, but very different energy at the point of fracture. This is an indication of the similar energy for crack initiation, but the different for fracture.

To further verify that the compact tension specimens and the Izod specimens showed the same ranking for total energy required for crack growth among the three alloys, the size of the whitening zone in the two types of specimens was compared using optical microscopy. As shown in the micrographs of Figures 7 and 8, the size of the whitening zone (dark regions in the micrographs) is in the same order of #2 < #1 < #3.

Microdeformation Behavior

Characterization of the microdeformation was conducted on tensile specimens and Izod specimens. The two types of specimens were selected because of their extremely different straining rates, of at least 4 orders of difference in magnitude.¹⁶ The straining rate for the compact tension specimens is expected to be within the two extremes.

TEM micrographs for the tensile specimens are shown in Figure 9. The micrographs were taken in regions just beneath the fracture surface with arrows indicating where the fracture surface is on the micrographs. Figure 9(a) represents the typical deformation behavior for alloys #1 and #2, while Figure 9(b), for alloy #3. Although rubber particle deformation in Figure 9(b) is much more extensive than that in Figure 9(a), both micrographs show that only in regions within a few micrometers from the fracture surface is the matrix crazing extensive. Further away from the fracture surface, the crazes are barely visible. On the other hand, cavitation is prevalent among the rubber particles.

Micrographs for tensile specimens of alloy #3 in regions of approximately 30 μ m and 3 mm away from the fracture surface are presented in Figure 10. Again, rubber particle cavitation can be seen



Figure 7 Optical micrographs of fractured Izod specimens: (a) from alloy #1; (b) from alloy #2; (c) from alloy #3.



Figure 8 Optical micrographs of fractured compact tension specimens: (a) from alloy #1; (b) from alloy #2; (c) from alloy #3.

more often than long crazes, despite the extensive elongation of the specimens. This suggests that the crazing is not a popular deformation mechanism for these specimens. The stress whitening was possibly due to rubber particle cavitation. It should be noted that the same conclusion was drawn from the TEM examination on alloy #2. However, as alloy #2 did not have the same extensive deformation as that for alloy #3, the former did not show a high density of rubber particle cavitation as that shown in Figure 10.

For Izod specimens, TEM micrographs taken from regions immediately beneath the fracture surface are shown in Figure 11. Again, the fracture surface is indicated by arrows on the micrographs. Compared with Figure 9, the micrographs in Figure 11 contain much extensive craze deformation. It was also found that the rubber particle cavitation rarely occurred beneath the fracture surface for the Izod specimens of alloy #3, although it occurred extensively in alloys #1 and #2 in the same region.

The TEM examination reveals that different deformation mechanisms were involved in the Izod and tensile specimens. The latter had little crazing, but contained extensive rubber particle cavitation and also rubber particle elongation for alloy #3. The extensive rubber particle elongation is believed to occur only if the following conditions are satisfied: (1) sufficient adhesion between rubber particle and matrix, and (2) the matrix undergoing extensive deformation. Without crazing, shear deformation is believed to dominate the matrix deformation.

Shear deformation in ABS was previously reported by Haaf et al.¹⁷ who examined microtomed samples of deformed ABS using TEM and de-



Figure 9 TEM micrographs of specimens near the fracture surface of tensile specimens: (a) the behavior observed in alloys #1 and #2; (b) the behavior in alloy #3.



Figure 10 TEM micrographs of alloy #3 after tensile test: (a) from a region 30 μ m away from the fracture surface; (b) from a region 3 mm away from the fracture surface.

formed bulk specimens using light scattering. Their results suggested that in a system with only small rubber particles (about 70 nm in diameter) deformation of the ABS is through rubber particle cavitation and shear deformation of the matrix. Stress whitening was attributed to the rubber particle cavitation, instead of crazing. The results were later supported by Donald and Kramer¹² who conducted a TEM study on the solution-cast ABS thin films and concluded that the crazes do not readily grow in ABS that contains small rubber particles. It is worth mentioning that in Donald and Kramer's study the diameter of the



Figure 11 TEM micrographs of specimens near the fracture surface of Izod specimens: (a) the behavior observed in alloys #1 and #2; (b) the behavior in alloy #3 (copper grids with holely carbon film was used).

rubber particles was in a similar range as that used in this study.

Breuer et al.,¹⁸ through the study on pure SAN, suggested that under a high straining rate, such as that introduced in the Izod impact test, chain scission is encouraged, making craze the favorite deformation mechanism. This is consistent with our observation that matrix crazing is more extensive in Izod specimens than in the tensile specimens.

DISCUSSION

The toughness difference between alloys #1 and #2 is believed due to the intrinsic toughness difference in the matrix. This is because the toughness for SAN25 is lower than that for SAN28, owing to the higher acrylonitrile content of SAN28. Since the tensile specimens and Izod specimens ranked the two alloys in the same order, for which the deformation mechanisms were dominated by shear deformation and crazing, respectively, it is also believed that in both deformation mechanisms the matrix for alloy #3 is tougher than that for alloy #1.

The matrix toughness alone, however, could not provide a satisfactory explanation for the significantly different ductility between alloys #1 and #3 in the tensile tests. The matrices in the two alloys are mainly different in molecular weight for 30 wt % SAN: 89,000 for alloy #1 and 129,000 for alloy #3. Such a difference in molecular weight is not expected to cause a significant difference in the ductility between the two alloys. Other factors, such as rubber particle size, adhesion between rubber particles and matrix, and rubber particle structure, should have contributed to the toughness difference between the two alloys. Effects of these factors on the toughness depend on the deformation mechanisms involved in the fracture process, as to be explained in the following paragraphs.

Rubber Particle Size

Toughness for glassy polymers has long been known to depend on their rubber particle size.^{8,19,20} More recently, Wu,¹⁵ using Izod impact testing, provided convincing evidence to suggest that the rubber toughening is dominated by the matrix ligament thickness, not by the rubber particle size. But for SAN that may have crazing as the main fracture mechanism,¹¹ toughness does not always increase with the decrease of matrix ligament thickness. An optimum particle size in the range of 0.1–1 μ m was

reported²¹ to render the highest toughness for ABS. This is because the optimum particle size provides the best combined effect on craze initiation and termination. For the craze termination, the decrease of particle size increases the termination site density, but the efficiency for terminating the crazes decreases.¹⁵ For craze initiation, the large particles induce a sufficient displacement misfit at the particle/matrix interface for craze initiation.²² Small particles, on the other hand, can hardly generate a sufficient displacement misfit between the matrix and rubber particles, thus having little effect on toughness enhancement. This concept suggests that the larger rubber particles in ABS-g2 are more effective on toughness enhancement than are those in ABS-g1.

As crazing is the dominant deformation mechanism in Izod specimens, the above concept can explain why alloy #3 gave a higher Izod impact strength. But it does not satisfactorily explain the excellent ductility shown by alloy #3 in tensile testing, compared to alloy #1, in which crazing is not the dominant deformation mechanism.

Interface Adhesion Between Rubber Particles and Matrix

Past studies^{8,23,24} have suggested that the interfacial adhesion between the rubber particle and the matrix is important for the rubber toughening of glassy polymers. Most of the studies drew the conclusion based on the concept that the rubber particles act as termination points for crazes, as discussed above. For the Izod specimens that have crazing as the dominant deformation mechanism, a strong interfacial adhesion makes the rubber particles effective in stopping the craze growth, thus enhancing the toughness.

Since the dominant deformation mechanisms for the tensile specimens do not include matrix crazing, the effectiveness of rubber particles in terminating craze growth cannot be attributed to high toughness for alloy #3. Rather, it is the suppression of the craze generation, due to strong interfacial adhesion between rubber particles and matrix, that caused alloy #3 to be tougher than the other two alloys. The strong interfacial adhesion of alloy #3, due to the large molecular weight and high grafting ratio of the grafted SAN, enables the matrix to have extensive shear deformation before crazes were initiated for fracture.

Rubber Particle Structure

As mentioned previously, rubber particle cavitation in Izod specimens is more extensive in Figure 11(a), for alloys #1 and #2, than in Figure 11(b), for alloy #3. This is believed to be due to the difference in the rubber particle structure, that is, uniform for alloys #1 and #2 and salami type for alloy #3. The salami structure consists of hard SAN occlusions surrounded by a rubbery phase. Little deformation of the rigid occlusions made the true straining rate of the rubbery phase in the salami-type rubber particles higher than that introduced to the specimens. Under an impact loading that gives an overall straining rate of over 250% s⁻¹,¹⁶ it is possible that the straining rate for the rubbery phase is sufficiently high to cause ductile-brittle transition of the rubber, thus preventing the development of rubber cavitation. Although this is a speculation requiring supporting physical evidence, the small particle size and lack of information on the crosslink density of the rubber may prevent us from obtaining the physical evidence. Nevertheless, it is conceptually possible that the combined high straining rate and salami structure may lead to prevention of the rubber particle cavitation.

CONCLUSIONS

A toughness study for the SMI-modified ABS alloys was carried out using a tensile test, Izod impact test, and compact tension test. Results from the three methods suggest that the energy for crack initiation is similar among the three alloys, but the total energy absorption for fracture is in the order of #2 < #1 < #3. The difference of the fracture toughness is attributed to the difference in molecular weight and acrylonitrile content in the SAN of the matrix, interfacial adhesion between rubber particle and matrix, rubber particle size, and rubber particle structure.

The deformation characterization obtained from TEM suggests that the rubber particle cavitation and matrix shear deformation were the main deformation mechanisms in the tensile specimens. But for the Izod specimens, extensive crazing replaced the shear deformation to be the dominant matrix deformation mechanism. The extent of the toughness difference among the alloys depends on the testing methods used.

Results from the study indicate that the deformation behavior for the modified ABS is similar to that which occurred in a conventional ABS. The addition of SMI did not affect its deformation behavior. Therefore, the approaches used for improving the toughness of ABS should be applicable to the toughness enhancement for the modified ABS.

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