

Structure and Properties of Epoxy Resins Modified with Acrylic Particles

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ABSTRACT: The morphology and material properties of dicyandiamide (DICY)-cured epoxy resins modified with acrylic particles consisting of a PBA (polybutyl acrylate) core and a PMMA (polymethyl methacrylate) shell and epoxy resins modified with acrylic rubber (PBA) particles alone were studied. It was found that the epoxy system modified with core/shell acrylic particles showed higher fracture toughness, indicating that the modification had a larger effect on improving the material properties of the epoxy resin. A characteristic shown by the core/shell acrylic particles is that they swell along with the epoxy resin under exposure to heat and gel before the latter cures. In this process, the epoxy resin penetrates the surface of the shell layer and a bond is formed between the epoxy matrix and the core/shell acrylic particles. This suggests that the epoxy matrix around the core/shell acrylic particles has the effect of increasing the level of energy absorption due to plastic deformation of the matrix. This is thought to explain why the epoxy resin modified with core/shell acrylic particles showed higher fracture toughness. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2955–2962, 1999

Key words: epoxy resin; core/shell acrylic particles; acrylic rubber particles; adhesion; fracture toughness

INTRODUCTION

Epoxy resins are widely used as adhesives and as the matrix resins of composites because of their good adhesion and mechanical properties as well as their excellent chemical and electrical resistance. In recent years, they have also been used in the automotive industry as structural adhesives for assembling car bodies. The automotive indus-

try, in particular, has adopted an adhesive bonding method whereby an adhesive is coated on body panels and preheated to form a gel that temporarily holds the panels in place.

We have developed two types of epoxy resin adhesives that are now being used with this method. One type of adhesive has acrylic particles of a uniform structure dispersed in the epoxy resin, and the other type has core/shell acrylic particles dispersed in the epoxy resin.^{1–3}

When the epoxy resin dispersed with core/shell acrylic particles is heated, the epoxy resin and the acrylic particles swell and gel, making it possible

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to bond parts temporarily. Further heating cures the epoxy resin and the effect of the acrylic rubber core of the acrylic particles dispersed in the epoxy resin results in strong adhesion.

Liquid rubber has also been used traditionally to modify epoxy resins for the purpose of improving toughness. An example of this type is the CTBN (carboxyl-terminated butadiene-acrylonitrile copolymer)-modified epoxy and the toughening mechanism has been the subject of considerable research.⁴⁻⁸

When the CTBN-modified epoxy resin cures, phase separation occurs, causing domains to be produced. Some of the rubber components melt into the phase of the matrix epoxy resin, thereby lowering the glass transition temperature, which degrades the thermal resistance of the cured resin as a result. This type of problem does not occur with epoxy resins dispersed with acrylic rubber particles because the particles are dispersed in the epoxy in advance. The modification of epoxy resins through the dispersion of acrylic rubber particles seems to be a suitable approach to improving resin toughness. There are several reports in the literature concerning the toughening mechanism of core/shell rubber-modified epoxy systems.⁹⁻¹²

The purpose of this research was to make clear the toughening effect obtained by dispersing in an epoxy resin the core/shell acrylic particles developed by the authors. A comparison was made with an epoxy resin modified with an acrylic rubber made of PBA that forms the core of the core/shell acrylic particles. Observations of the two types of resins focused in particular on the phase structure, and results worthy of interest were obtained.

EXPERIMENTAL

Materials

The epoxy resin used was a bisphenol A epoxy resin [Epikote #828 (Ep-828), Yuka Shell Epoxy Co., Ltd., Japan] and dicyandiamide (DICY) was used as a heat-activated curing agent (EH3636AS, Asahi Denka Kogyo Co., Ltd., Japan). The core/shell acrylic particles used had a crosslinked polybutyl acrylate (PBA) core and an ion-crosslinked polymethyl methacrylate (PMMA) shell. The weight ratio of the core to the shell was 1/1.2. The glass transition temperature (T_g) of the particles was 123.8°C as determined by dif-

ferential thermal analysis. The ion-crosslinked PMMA shell was prepared by continuously adding small amounts of methacrylic acid at the later stage of MMA polymerization and treating the latex obtained with a potassium hydroxide aqueous solution (1 wt %) after polymerization.

By weight, the epoxy system consisted of 100 parts of epoxy, 4 parts of DICY, 3 parts of SiO₂ powder (Aerosil 200, Aerosil Nippon Co., Ltd., Japan), and 50 parts of core/shell acrylic particles. The constituents were mixed in a mixer and defoamed to obtain the epoxy system. The epoxy resin dispersed with acrylic rubber particles was prepared with the following method. After polymerization of the acrylic rubber (PBA) was completed, the emulsion was removed and its density was adjusted so that the PBA content of Ep-828 would correspond to the PBA content of the other type of epoxy when the latter was mixed with 50 parts of core/shell acrylic particles. The emulsion was then added to Ep-828 and heated at 70°C under low pressure to remove the water. The specified amounts of DICY and SiO₂ powder were then added to the acrylic rubber-dispersed epoxy resin thus obtained. The constituents were mixed in a mixer and defoamed to obtain the epoxy system. The epoxy system consisted of 100 parts of epoxy, 4 parts of DICY, 3 parts of SiO₂ powder (Aerosil 200, Aerosil Nippon Co., Ltd., Japan), and 22.7 parts of acrylic rubber particles. The particles and acrylic emulsion were produced by Nippon Zeon Co., Ltd., of Japan. For the purpose of comparison, an epoxy system consisting only of Ep-828, DICY, and SiO₂ powder was also prepared.

Measurements

The curing behavior of the epoxy resins was observed by torsional braid analysis (TBA; RD1100, Rhesca Co., Ltd., Japan). Specimens were prepared by impregnating a glass braid with neat resin and measurements were performed at a frequency of approximately 3 Hz over a temperature range from 50 to 230°C, with the temperature increased at a rate of 1°C/min.

The fracture toughness of the modified epoxy resins was measured according to the ASTM E399-1981 procedure. The tests were performed using an Autograph DSS2000 (Shimadzu Co., Ltd., Japan) test machine equipped with a 2000-kg load cell. The crosshead rate was 1 mm/min. Measurements were repeated on a minimum of five specimens to ensure accuracy.

The specimens for measuring the dynamic mechanical properties were prepared by spreading the resin mixture onto a Teflon sheet to a thickness of about 1 mm and heating it at 180°C for 1 h, and then cutting the sheet into pieces. Dynamic mechanical properties were measured with a dynamic mechanical thermal analyzer (DMTA, Polymer Laboratories Co., Ltd.) at 3 Hz over a temperature range of -100 to 200°C (See Fig. 1).

Lap shear strength and T-peel strength were measured in accordance with ASTM D1002-72 and ASTM D1876-72. Cold-rolled carbon steel degreased with acetone was used as the adherent. The specimen thickness was 1.6 mm for the lap shear strength measurements and 0.8 mm for the T-peel strength measurements. The overlap length of the lap shear joint was 12.5 mm. The adhesive joints were cured at 180°C for 1 h. The respective crosshead speeds were 5 and 200 mm/min.

Conditions of Morphology Observations

A field emission scanning electron microscope (Hitachi S-4700) was used to observe the phase structure of cured specimens. Prior to examination, specimens were stained with a 5% RuO₄ aqueous solution.

RESULTS AND DISCUSSION

Gelation Behavior of Epoxy Modified with Core/Shell Acrylic Particles

The cured epoxy specimens containing 50 parts by weight of core/shell acrylic particles dispersed in Ep-828 gelled in a short period of time upon heating at temperatures above 120°C. This behavior is primarily attributed to the swelling and gelling of Ep-828 and PMMA in the shell layer of the core/shell acrylic particles. It indicates that the epoxy resin penetrated the shell layer of the acrylic particles. The curing process of the epoxy resin modified with core/shell acrylic particles is shown schematically in Figure 2.

The curing behavior data measured by torsional braid analysis for this resin are plotted in Figure 3. Point a in the figure indicates the onset of swelling and gelling by the acrylic particles and the epoxy resin, and point b indicates the completion of gelling. As the temperature is raised further, the shear modulus G_r becomes more or less constant; however, during this period, it is

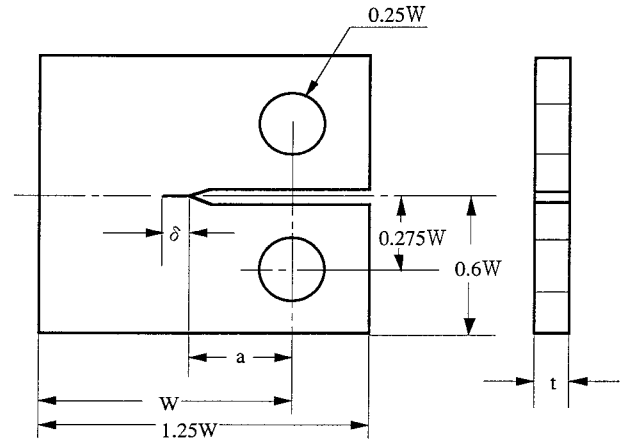


Figure 1 Compact tension specimen used for fracture toughness experiment. $W = 40$ mm, $a = 15$ mm, precrack = δ , $t = 4$ mm.

thought that the shell of the acrylic particles continues to swell. When the temperature reaches 164°C (point c), the shear modulus begins to rise, indicating that the epoxy resin is starting to cure because of the action of DICY. Following the onset of curing, the PBA component of the acrylic rubber core disperses in the epoxy matrix and the curing of the epoxy resin is then completed.

Fracture Toughness and Observation of Fracture Surfaces

Polybutyl acrylate is the principal constituent of the acrylic rubber contained in both the epoxy resin modified with core/shell acrylic particles and the epoxy resin modified with acrylic rubber particles. Acrylic rubber was added to each resin such that both resins would contain the same amount. Nonetheless, the epoxy resin modified with core/shell acrylic particles showed higher fracture toughness than the epoxy resin modified with acrylic rubber particles. The mean fracture toughness measured for the cured resins is shown in Figure 4, where the error bars indicate the maximum and minimum values. A large difference is seen in fracture toughness even though the quantity and molecular structure of the acrylic rubber in each epoxy resin were the same.

The fracture condition of the compact tension specimens used in the measurements also differed considerably between the two epoxy resins. Figures 5 and 6 show the fractured surface of specimens made of each type of resin. In order to examine the state near the onset of fracture in more detail, the original ultrafine polish treat-

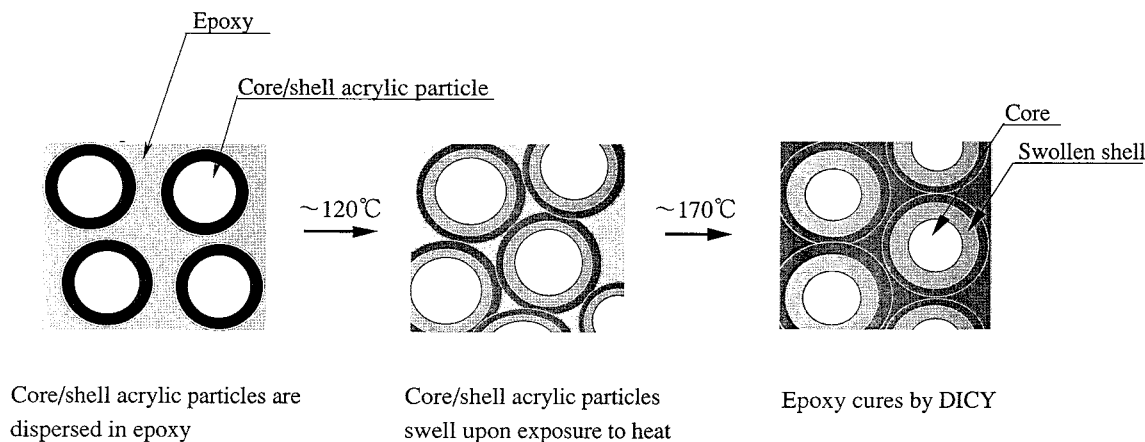


Figure 2 Curing process of epoxy resin modified with core/shell acrylic particles.

ment to the cross section of the sample was performed in the following manner (named the N-ARC method by Nissan Arc Co., Ltd., Japan).¹³ A cross section of a part that was cut off from the sample was at first grinded with the abrasive paper disc (No. cc120 ~ 1000, Sankyo Rigaku Co., Ltd., Japan). Next, the cross section was polished cautiously using Al₂O₃ fine powder as an abrasive in the polishing cloth. This treatment enabled the observation of the core/shell acrylic particle aggregation structure in the cross section. The optics-microphotographs in Figures 7 and 8 show enlarged views of the origin of fracture in each

epoxy resin. In Figure 7, it is observed that aggregates of core/shell acrylic particles ranging in size from several tens of microns to several hundreds of microns formed and were dispersed throughout the matrix of the epoxy resin modified with these particles. The fractured surface run through the aggregates of core/shell acrylic particles is also observed. By contrast, the photograph in Figure 8 shows that aggregates of rubber particles around several microns in size were nonuniformly dispersed in the epoxy resin modified with acrylic rubber particles. In the vicinity of the fractured surface, in particular, the epoxy resin matrix shows an uneven surface compared with the epoxy resin modified with the core/shell acrylic particles. This appearance is indicative of a brittle fractured surface. These observations revealed

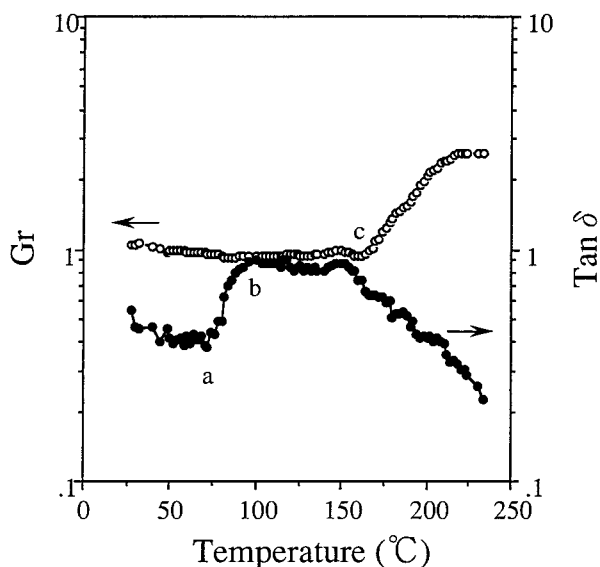


Figure 3 TBA data of epoxy resin modified with core/shell acrylic particles (50 phr). (○) G_r , relative rigidity, (●) $\tan \delta$.

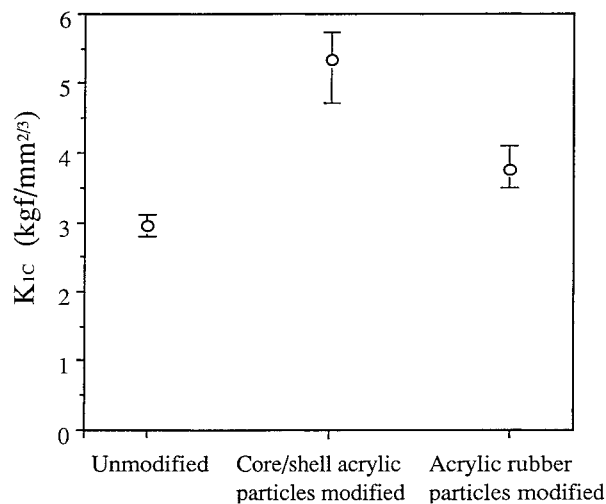


Figure 4 Fracture toughness of cured epoxy resins.

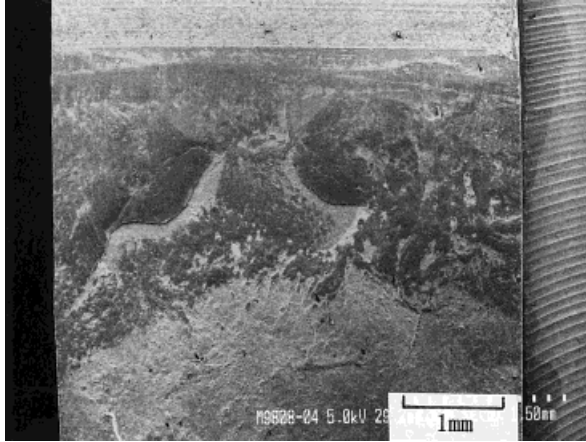


Figure 5 Fractured surface of epoxy resin modified with core/shell acrylic particles.

that the macro phase structures of the two types of modified epoxy resins differed considerably, which corresponded to the difference in their fracture toughness.

Phase Structure of Cured Epoxy Resins

Figure 9 presents the dynamic mechanical properties measured for the two types of cured epoxy resins. The glass transition temperature (T_g) of the epoxy resin modified with core/shell acrylic particles was higher than that of the epoxy resin modified with acrylic rubber particles. The shell layer of core/shell acrylic particles showed a T_g of 123.8°C by DSC measuring. The rubber plateau moduli of the two systems are clearly different. This fact suggests that swelling between acrylic

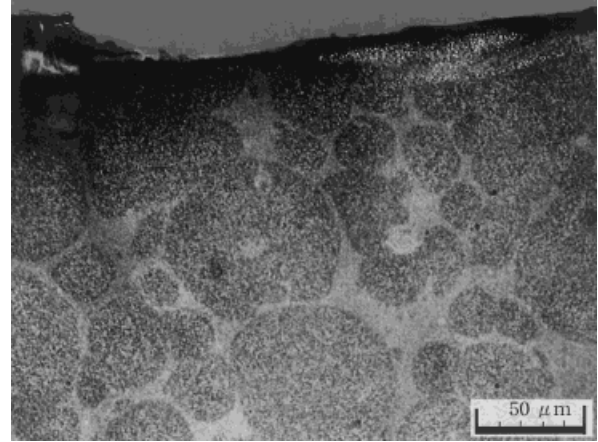


Figure 7 Fractured cross section of epoxy resin modified with core/shell acrylic particles.

rubber particles and the epoxy resin, without any chemical reactions, reduces the T_g of the acrylic rubber-modified epoxy. On the other hand, the core/shell acrylic particle is made of both a PBA core and an ion-crosslinked PMMA shell. Considering the structure of the particle, the shell swells easily with the epoxy matrix. On the contrary, the core swells with the matrix only with great difficulty. It is thought that swelling of the core with the matrix lowers the T_g of the system slightly. Consequently, the core/shell acrylic particle-modified epoxy has a higher T_g than that of the acrylic rubber particle system. However, the dynamic mechanical properties of the two types of resins show virtually the same overall patterns.

The structure of the fractured surface of the epoxy resin specimens used in the fracture tough-

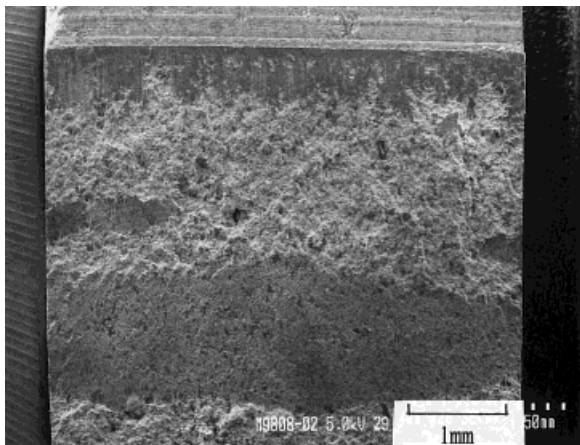


Figure 6 Fractured surface of epoxy resin modified with acrylic rubber particles.

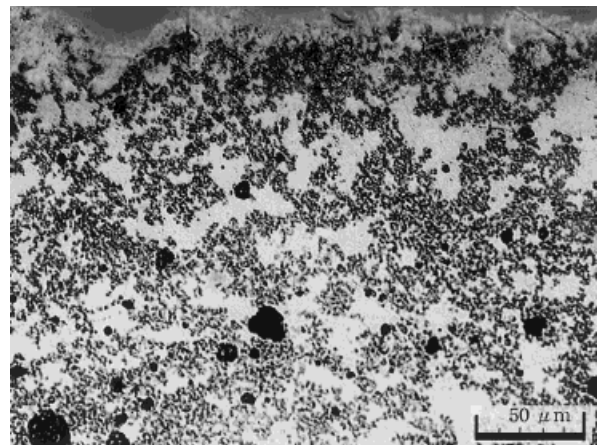


Figure 8 Fractured cross section of epoxy resin modified with acrylic rubber particles.

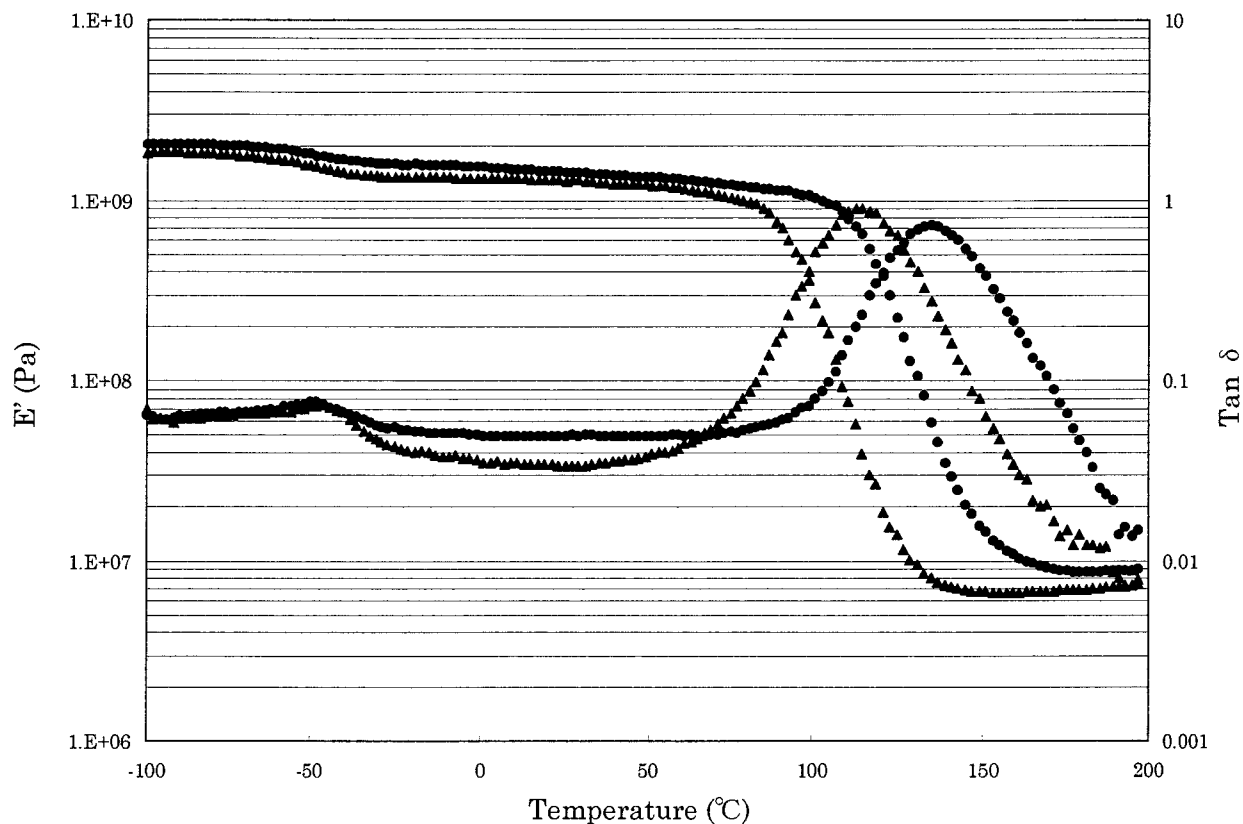


Figure 9 Dynamic mechanical properties of epoxy resin modified with acrylic particles. ●, modified with core/shell acrylic particles; ▲, modified with acrylic rubber particles.

ness measurement was observed by SEM and the micrographs taken are shown in Figures 10 and 11. Although it is difficult to discern differences in the structure of the specimens from these micrographs, close examination reveals that the epoxy

resin modified with acrylic rubber particles shows a brittle fractured surface. It is seen that some of the acrylic rubber particles were dislodged from the epoxy matrix. This suggests that, in the places where the acrylic rubber particles aggre-

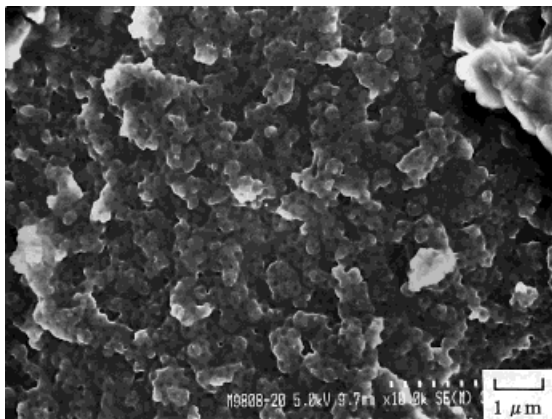


Figure 10 SEM micrograph of the fractures surface of epoxy resin modified with core/shell acrylic particles.

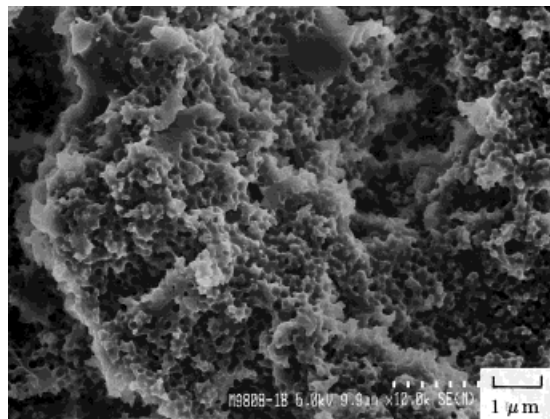


Figure 11 SEM micrograph of the fractures surface of epoxy resin modified with acrylic rubber particles.



Figure 12 SEM micrograph of the etched surface of epoxy resin modified with core/shell acrylic particles.

gated, fracture occurred mainly at the interface between the rubber particles and the epoxy matrix.

An investigation was then made of the adhesion between the acrylic particles and the epoxy matrix. Cured specimens of both types of epoxy resins were etched in an osmium tetroxide aqueous solution in an attempt to remove the epoxy resin layer from the surface. Figures 12 and 13 present SEM micrographs of the etched surface of the two resins. In these micrographs, the epoxy resin has been dissolved from the surface and minuscule acrylic particles of from 100 to 200 nm are seen in relief. In Figure 12 for the epoxy resin modified with core/shell acrylic particles, it is seen that resin matrix components adhered to the particle surface. This indicates the result of the strong bond that occurs between the core/shell acrylic particles and the epoxy resin during heat curing when the particles and the resin swell and the latter penetrates the shell layer. In other words, the swelling of the core/shell acrylic particles and the epoxy resin lowers the crosslink density of the resin matrix in the vicinity of the particle surface. This is thought to result in a structure conducive to plastic deformation of the matrix between the particles under stress loading.

By contrast, in Figure 13 for the epoxy resin modified with acrylic rubber particles, globular particles are observed that might be attributable to the relatively weak interaction between the acrylic particles and the matrix. The form is clearly different from that observed for the epoxy resin modified with core/shell acrylic particles. In other words, adhesion between the acrylic rubber

particles and the epoxy matrix was weaker than that between the core/shell acrylic particles and the matrix. The fracture toughness of epoxy resins containing elastomers is greatly influenced by energy absorption due to plastic deformation of the matrix. Because adhesion between the acrylic rubber particles and the epoxy matrix was weaker, the epoxy resin modified with acrylic rubber particles was inferior to the other epoxy resin with respect to energy absorption resulting from plastic deformation of the matrix between the acrylic rubber particles. That is thought to explain why its fracture toughness was lower than that of the epoxy resin modified with core/shell acrylic particles.

Adhesion Properties

The difference in the toughening effect seen for the two types of modified epoxy resins also appeared in their measured adhesion properties. Figures 14 and 15 show the measured lap shear strength and the T-peel strength of the epoxy resins. Both figures present mean values, with the error bars indicating the maximum and minimum values. The epoxy resin modified with core/shell acrylic particles showed higher lap shear strength and T-peel strength than the epoxy resin modified with acrylic rubber particles. The toughening effect on the epoxy resins is especially evident in the T-peel strength results, which is related to the fact that the stress load applied during the peel test concentrates in lines running across the width of a specimen. Consequently, higher T-peel strength is measured in proportion to increasing toughness of the adhesive.



Figure 13 SEM micrograph of the etched surface of epoxy resin modified with acrylic rubber particles.

CONCLUSIONS

Two types of dicyandiamide-cured epoxy resins were fabricated and observations were made of their fracture toughness and phase structure. One type had a dispersion of particles consisting of a PBA core and a PMMA acrylic resin shell, and the other type had a dispersion of PBA acrylic rubber particles only. An examination of the toughening mechanism of the epoxy resins modified in this manner made clear the following points.

1. The epoxy resin modified with core/shell acrylic particles showed higher fracture toughness and adhesion strength than the resin modified with acrylic rubber particles, indicating that the former modification had a larger effect on improving the toughness of the epoxy resin.
2. The reason for this difference can be understood as follows. The core/shell acrylic particles swell together with the epoxy resin under exposure to heat and gel before the resin cures. In this process, the epoxy resin penetrates the surface layer of the shell and a bond is formed between the epoxy matrix and the acrylic core/shell particles. This suggests that the epoxy matrix around the core/shell acrylic particles has the effect of increasing the level of energy absorption due to plastic deformation of

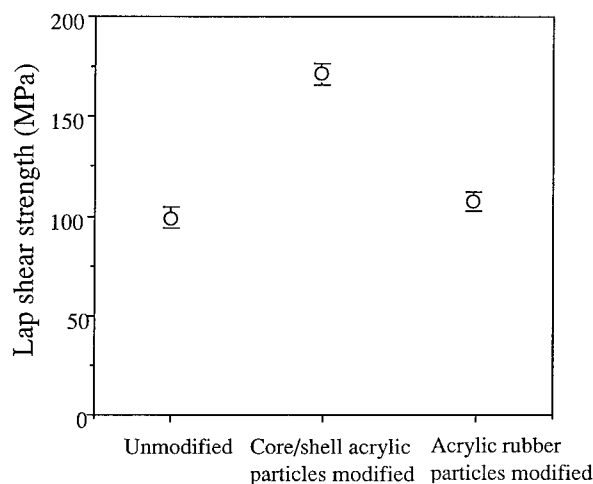


Figure 14 Lap shear strength of epoxy resins.

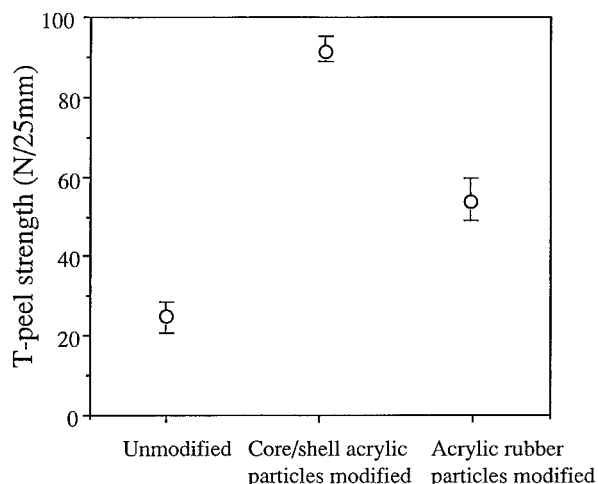


Figure 15 T-peel strength of epoxy resins.

the matrix compared with that of the resin modified with acrylic rubber particles. As a result, the epoxy resin modified with core/shell acrylic particles shows higher fracture toughness.

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