

Morphology and Properties of Polydimethylsiloxane-Modified Epoxy Resin

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ABSTRACT: The morphology and fracture toughness of epoxy resins modified with amino-terminated polydimethylsiloxane (ATPDMS), differing in their molecular weight, and the degree of the preliminary reaction in the melt state were investigated. Tetramethyl biphenol diglycidyl ether (TMBPDGE) was used as the base epoxy resin. The degree of preliminary reaction between epoxy and polysiloxane increased with the decrease of the molecular weight of polysiloxane in the melt state. When the low molecular weight polysiloxane (AT900) was mixed with high molecular weight polysiloxane in the preliminary reaction, the low molecular weight polysiloxane enhanced the compatibility between the epoxy resin and the high molecular weight polysiloxane and produced smaller size and narrow distribution of polysiloxane particles. The small and highly concentrated polysiloxane particles, as determined by scanning electron microscopy improved the fracture toughness of the epoxy resin. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 941–955, 1997

Key words: tetramethyl biphenol diglycidyl ether; polydimethylsiloxane; morphological parameter; fracture toughness; bimodal distribution

INTRODUCTION

Epoxy resins are widely utilized as packaging and insulating materials and adhesives in the fields of electric and electronic industries because of their excellent heat, moisture, solvent, and chemical resistance; superior electrical and mechanical properties; and good adhesion to many substrates. But it is known that when epoxy resins are cured, they can contract and develop internal stresses.^{1,2} The shrinkage and internal stress cause reduced durability, such as in the moisture and heat-cycle resistance of electric and electronic parts.

Recently, tetramethyl biphenol diglycidyl ether (TMBPDGE) has been commonly used as a base material for the encapsulation of microelectronic devices because TMBPDGE has high rubbery modulus, low glassy modulus, and low internal stress compared with bisphenol-A type epoxy resin.³ The characteristic properties of the biphenol type resin are explained as follows.

1. The mobility of biphenyl unit is lower than that of bisphenol-A unit; thus, the motion of the network segment is restricted, and the modulus in the rubbery region is increased.
2. The motion of the network is frozen in a larger free volume state with the decrease in the mobility of network segments; thus,

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the elastic modulus in the glassy region decreases.

3. The reduction of the internal stress is due to the decrease of the modulus in the glassy region with the introduction of biphenyl structure.

However, it is known that epoxy resins, including the biphenol type resin, are relatively brittle polymers with poor resistance to crack growth.

To improve the fracture toughness of epoxy resins, several methods have been proposed. One of the traditional methods involves the addition of a suitable rubber to the uncured epoxy resin and controlling the polymerization reactions in order to induce the phase separation. Liquid acrylonitrile-butadiene copolymers with carboxyl or amine end groups (CTBN, ATBN) have been widely used to modify the resins. When CTBN modifiers are incorporated into resin compositions, a two-phase morphology consisting of relatively small rubber particles ($\sim 0.1\text{--}5\ \mu\text{m}$) dispersed in the epoxy matrix is generated, which toughens epoxy resins.^{4,5} However, phase separation depends upon the formulation, processing, and curing conditions.^{6,7} Incomplete phase separation can result in a significant lowering of the glass transition temperature (T_g). The differences in the morphology and volume fraction of the separated phase affect the mechanical performance of the product. To minimize these problems, the preformation of a stable dispersion of rubbery particles in the uncured epoxy resin via preliminary reaction of epoxy resin using functionalized polysiloxanes has been investigated.

Organosiloxane polymers are known for their excellent thermal and thermooxidative stabilities, very low glass transition temperature ($T_g = -123^\circ\text{C}$), high moisture resistance, good electrical properties, and low stress.⁸ However, the solubility parameter of polydimethylsiloxane, 7.4–7.8, is much lower than that of the epoxy resin, which is about 10.9.⁹ Polydimethylsiloxane is therefore not compatible with epoxy resin unless it has functional groups that react with epoxy groups. Not many studies have been reported on this topic, although Riffle et al.¹⁰ reported that when epoxy was made to react with various piperidine-terminated polysiloxanes and solubilized, and the resultant material blended with epoxy resin, fracture toughness (K_{IC}) increased. Kasemura et al.¹¹ showed that when silicone rubber was dispersed in epoxy resin by using a compatibilizer,

the impact fracture energy of modified epoxy resin increased greatly in proportion to the rubber content.

In this article, the effect of the modification of TMBPDGE with amino-terminated polydimethylsiloxane (ATPDMS) on fracture toughness (K_{IC}) is systematically examined and discussed from the view point of the particle size and particle size distribution of the dispersed polysiloxane. The particle size and particle size distribution of the dispersed phases are known to be important parameters affecting the fracture toughness of rubber-modified epoxies. Kunz-Douglas et al.¹² have reported that large, 40 μm particles are not as efficient in providing an increase in fracture toughness as smaller, 1 μm particles. Pearson and Yee¹³ have also reported that relatively large particles provide only a modest increase in fracture toughness by a particle bridging/crack deflection mechanism, and smaller particles provide a significant increase in toughness by cavitation-induced shear banding. No synergistic effect on the toughness of bimodal rubber-particle distributed epoxy system was observed. At present, the optimal rubber particle size for toughened epoxies appears to be in the 0.1–5.0 μm range, and there is no rationale for this particle size effect.

The overall objective of this study is to investigate the influence of particle size and particle size distribution on toughness of cured epoxy systems in relation to the compositions of ATPDMS differing in molecular weight and the degree of the preliminary reaction conditions in the melt state. Modification of the epoxy by polysiloxane dispersions seems to be promising since in this case both the mean particle size and the particle size distribution can easily be tailored.

EXPERIMENTAL

Materials

TMBPDGE (YX-4000, Yuka Shell Co., 184 epoxy equivalent weight) was used as the epoxy resin (Fig. 1). 4,4'-Diamino diphenylmethane (DDM) was used as curing agent. ATPDMS and the hydride-terminated polydimethylsiloxanes (HTPDMS) were from Shin-Etsu Chemical Co., and their structure and molecular weight are shown in Table I.

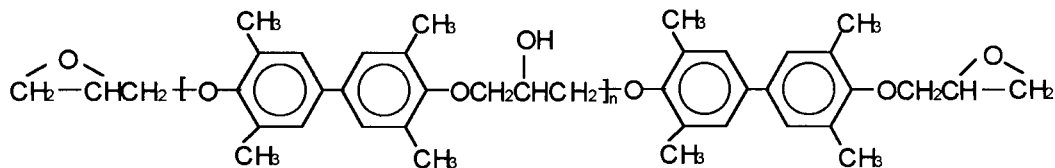


Figure 1 Molecular structure of TMBPDGE.

Preparation of ATPDMS-Modified Epoxy Resin

The modified TMBPDGE was prepared by reacting TMBPDGE with ATPDMS in the melt state at 135°C. Into a four-neck round-bottom flask, equipped with a heating mantle, mechanical stirrer, thermocouple, TMBPDGE was charged, heated to 135°C, and then vigorously stirred under dry nitrogen atmosphere. ATPDMS was then added dropwise while maintaining the reaction temperature at 135°C.

The degree of the reaction was monitored by titrating tertiary amine with bromphenol blue indicator solution in the reaction mixture. Epoxy equivalent weights of ATPDMS-modified epoxy resins were determined by the titration method with cresol-red indicator solution. All polysiloxane modified epoxies contain 10 phr polydimethylsiloxane.

Specimen Preparation

The epoxy resin was degassed at 105°C under reduced pressure while stirring. Then a stoichiometric amount of curing agent (DDM) was added, assuming that one epoxy group corresponds to one active hydrogen of the amino group. As the curing agent was in the solid state at room temperature, this agent was melted in an oven and then added

to the epoxy resin. The mixture was stirred at 105°C until the curing agent was dissolved completely in the epoxy resin and was then poured into the mold. This resin system was cured at 130°C for 2 h and then at 180°C for 6 h to obtain a cured specimen.

Dynamic Mechanical Thermal Analysis

The dynamic mechanical properties were determined using a dynamic mechanical thermal analyzer (DMTA, Polymer Laboratory). The dimension of the specimen was $20L \times 8B \times 2W$ mm. The specimen was tested in a single cantilever mode and scanned at a frequency of 10 Hz from -150 to 250°C with a heating rate of $3^\circ\text{C}/\text{min}$.

Microstructural Characterization

The mean particle size and the particle size distribution of the polysiloxane particles were determined by Phillips 535M scanning electron microscopy (SEM) on the fractured surfaces of cured ATPDMS-modified samples which were vacuum-coated with gold.

The magnification was chosen to provide a region containing about 100 particles of the dispersed domains. The size distribution was deter-

Table I Polydimethylsiloxane Used for the Modification of TMBPDGE

| Polysiloxane | Structural Formula | Molecular Weight |
|--------------|--|------------------|
| AT900 | $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{R}-\text{Si}-\text{O}-(\text{Si}-\text{O})_n-\text{Si}-\text{R} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ | 900 |
| AT1680 | | 1680 |
| AT3000 | | 3000 |
| AT3880 | | 3880 |
| AT7000 | | 7000 |
| AT12000 | R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ | 12000 |
| HT900 | R = H | 900 |
| HT3000 | | 3000 |

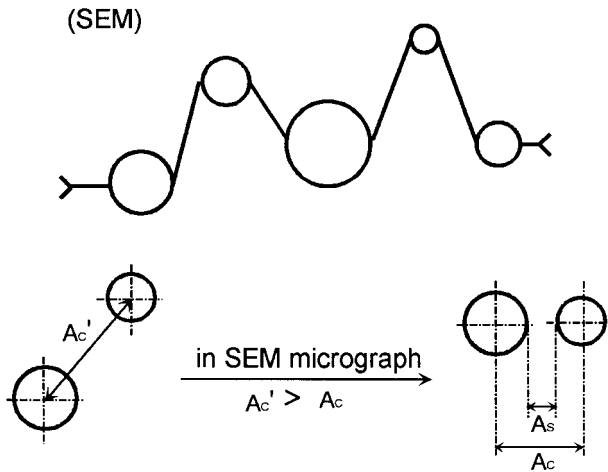


Figure 2 Possible crack trajectory on equatorial planes.

mined by measuring individual particles. From this information, the following parameters were calculated.¹⁴

1. Number-average diameter:

$$\overline{Dn} = \frac{\sum nD}{\sum n} \quad (1)$$

where n is the number of particles having a diameter D .

2. Volume-average diameter:

$$\overline{Dv} = \left[\frac{\sum nD^3}{\sum n} \right]^{1/3} \quad (2)$$

3. Volume fraction of dispersed phase:

$$V = \frac{(\pi/4) \sum nD^2}{A_T} \quad (3)$$

where A_T is the area of the micrograph region under analysis.

4. Concentration of dispersed phase particles:

$$P = \frac{V}{[(\pi/6)\overline{Dv}^3]} \quad (4)$$

Equation (3) assumes that the volume fraction is an isotropic property; hence, values measured on the fracture plane are the same as in the bulk. This volume fraction is regarded as an effective value because it is measured in the plane where the crack propagation has taken place. Figure 2 shows the crack trajectory going through the

equatorial planes of particles that is observed in SEM micrographs. This leads to an estimation of different volume fractions and concentrations of dispersed phase particles that are actually present.

Mechanical Property Measurements

Mechanical properties of cured resins were measured with an Instron Model 420 universal testing machine. Flexural strength and modulus were obtained at a crosshead speed of 1.7 mm/min according to ASTM D790M-86. A three-point loading system was chosen, and the rectangular bar specimens ($80L \times 10B \times 4W$ mm) were made by direct casting.

The fracture toughness K_{IC} was determined by using a single-edge notched (SEN) type specimen ($60L \times 5B \times 10W$ mm) in a three-point bending geometry.¹⁵ These specimens were precracked by placing a 3 mm notch into the center of the 5 mm side. A razor blade was placed into the notch and tapped lightly to initiate a sharp precrack. Crosshead speed was 1 mm/min. K_{IC} values were calculated according to eq. (5), as follows:

$$K_{IC} = \frac{6P}{BW^{1/2}Y} \quad (5)$$

where P is load, B is width, W is thickness, and Y is a sample geometry factor that is defined as

$$Y = 1.93R^{1/2} - 3.07R^{2/3} + 14.53R^{5/2} - 25.11R^{7/2} + 25.80R^{9/2}$$

where $R = a/W$, and a is the length of the precrack.

RESULTS AND DISCUSSION

Preliminary Reaction

TMBPDGE was reacted with ATPDMS. The resulting ATPDMS-modified TMBPDGE contained 10 phr of ATPDMS. The degree of the preliminary reaction was determined by titrating primary, secondary, and tertiary amine. Tertiary amine was the final form of the amino group reacted with epoxy group of TMBPDGE in the reaction mixture. A high concentration of tertiary amine

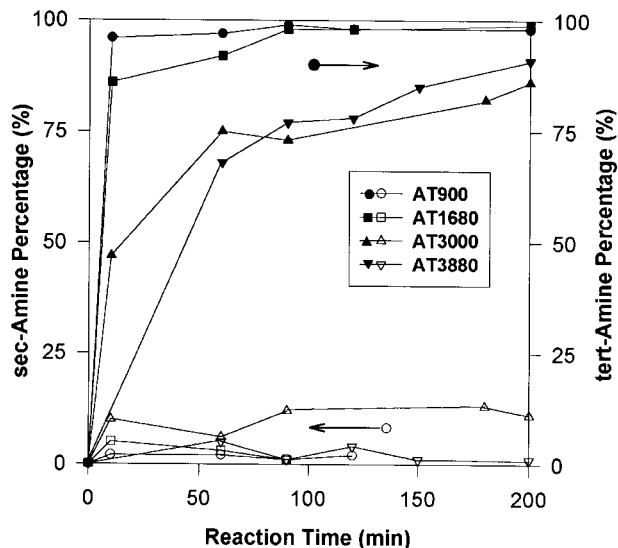


Figure 3 The degree of the preliminary reaction versus reaction time.

was observed in the reaction of amino groups of ATPDMS with epoxy groups of TMBPDGE. The percentage of primary amine in the reaction mixture decreased with the increase of the tertiary amine, but a small amount of secondary amine existed during the entire reaction time (Fig. 3). These results indicated that the preliminary reaction in the melt state occurred in the interfacial region of the ATPDMS particle and the epoxy matrix. The primary amines that existed on the surface of the polysiloxane particles reacted with the epoxy groups of TMBPDGE, and this initial reaction product increased the compatibility of the polysiloxanes with TMBPDGE. Consequently, the secondary amines produced from this initial reaction reacted rapidly with epoxy groups of TMBPDGE. Therefore, the lifetime of the secondary amine was short. In contrast, the primary amines, which existed in the inside of polysiloxane particle, should diffuse out of the polysiloxane particle to the surface.

Figure 4 shows SEM micrographs of the cured epoxy resins modified with ATPDMS as a function of preliminary reaction time. It is worth noting that gelation and aggregation took place in the case of the longer reaction time (Fig. 4). This gelation results from the rapid growth of the localized cross-link network formation at the surface of the polysiloxane particles because the reaction was carried out only at the restrictive region of polysiloxane and epoxy resin interface. The gelation particles migrate to the upper region of the re-

acting mixture because of their low density and form aggregates by their high concentration in the upper region. Gelation and aggregation take place earlier when the molecular weight of polysiloxane is high. Table II shows the percentage of primary, secondary, and tertiary amines in a comparatively homogeneously dispersed state of polysiloxane particles before aggregation takes place. The preliminary reaction was stopped when the mixture reached homogeneously dispersed state before forming aggregation, and the reaction time is listed in Table II.

The degree of the preliminary reaction in the melt state increases as the molecular weight of the polysiloxanes decreases since the low molecular weight polysiloxane forms smaller particles due to better compatibility and the interfacial area is increased (Fig. 3). Figure 4 shows the comparatively small amount of polysiloxane particles in the AT900 modified epoxy resin. These results also confirm that the compatibility of polysiloxanes with TMBPDGE affects the reaction.

The high molecular weight ATPDMS (above 4000) had poor solubility in the epoxy resin and could not be blended well because macroscale phase separation was observed, and the preliminary reaction at the interface did not have an effective compatibilizing role. In order to improve the compatibility of the high molecular weight ATPDMS with epoxy resin, the low molecular weight ATPDMS (AT900) was mixed. AT900 enhances the interfacial reaction of the high molecular weight ATPDMS and helps the dispersion of polysiloxane particles.

Dynamic Mechanical Analysis

The dynamic mechanical properties of the cured epoxy resins are summarized in Table III. Except for AT900, $\log E'$ (25°C) is only slightly affected by the polysiloxane molecular weight. The $\tan \delta$ curves for the epoxy network exhibit two major relaxations: at about 194°C for α transition corresponding to the major T_g of the cured epoxy resin; and the broad peak at about -40°C for β transition, which is attributed predominantly to the motion of the hydroxyether group of the epoxy. In addition to the epoxy α and β peaks, the curves show an additional markedly smaller peak from -120 to -100°C corresponding to the T_g of the polysiloxane phase. This small peak further supports the multiphase separation.

It is interesting to note that the major peak

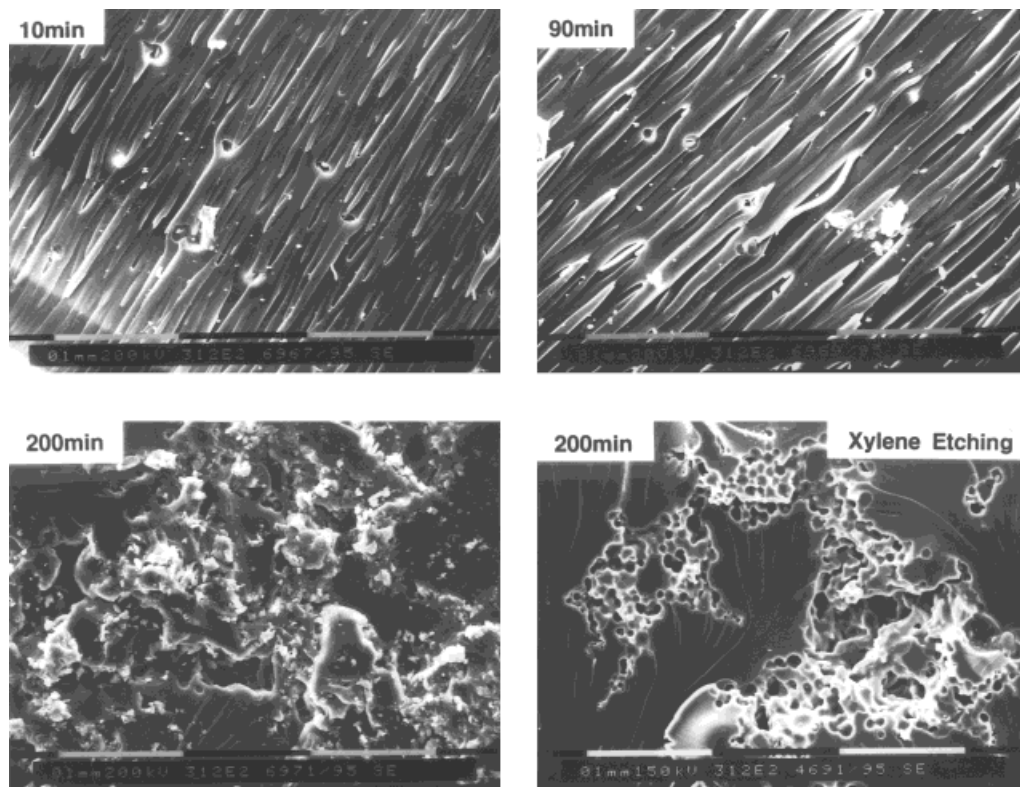


Figure 4 Morphology of the fracture surfaces of cured epoxy resins modified with AT900 (10 phr) versus preliminary reaction time.

position of the AT900-modified resin is shifted, and the T_g of the polysiloxane phase does not appear in the AT900-modified resin system (Fig. 5). This result indicates incomplete phase separation of polysiloxane and/or a small amount of polysi-

loxane dispersed in the epoxy resin. The solubility of polydimethylsiloxane in epoxy resin increases when the molecular weight of the polydimethylsiloxane becomes smaller.

The volume fraction of polydimethylsiloxane

Table II Percentage of Primary, Secondary, Tertiary Amine of the ATPDMS-modified Epoxy Systems Comparatively Homogeneous Dispersed State of Polysiloxane Particles (ATPDMS Content: 10 phr)

| Composition | Reaction Time (min) ^a | <i>pri</i> -Amine (%) | <i>sec</i> -Amine (%) | <i>tert</i> -Amine (%) |
|-----------------------|----------------------------------|-----------------------|-----------------------|------------------------|
| AT900 | 60 | 1 | 2 | 97 |
| AT1680 | 60 | 5 | 3 | 92 |
| AT3000 | 90 | 15 | 12 | 73 |
| AT3880 | 120 | 18 | 4 | 78 |
| AT900/AT1680 (1 : 1) | 60 | 1 | 2 | 97 |
| AT900/AT3000 (1 : 1) | 90 | 1 | 7 | 92 |
| AT900/AT3880 (1 : 1) | 120 | 2 | — | 98 |
| AT900/AT7000 (1 : 1) | 250 | 2 | 3 | 95 |
| AT900/AT12000 (1 : 1) | 400 | 1 | 1 | 98 |

^a Preliminary reaction time when the polysiloxane particles are homogeneously dispersed before aggregation takes place (amine percentage was determined at this time).

Table III Dynamic Mechanical Properties of Cured Epoxy Resin Systems

| Composition | PDMS T_g (°C) | Epoxy T_g^β (°C) | Epoxy T_g^α (°C) | Log E' (25°C) (Pa) |
|-----------------------|--------------------|---------------------------|----------------------------|-------------------------|
| Control | — | -39 | 194 | 9.33 |
| AT900 | — | -39 | 174 | 8.90 |
| AT1680 | -110 | -39 | 194 | 9.26 |
| AT3000 | -106 | -39 | 194 | 9.25 |
| AT3880 | -107 | -39 | 194 | 9.25 |
| AT900/AT1680 (1 : 1) | — | -39 | 186 | 9.20 |
| AT900/AT3000 (1 : 1) | -106 | -43 | 190 | 9.28 |
| AT900/AT3880 (1 : 1) | -107 | -43 | 190 | 9.27 |
| AT900/AT7000 (1 : 1) | -105 | -43 | 190 | 9.28 |
| AT900/AT12000 (1 : 1) | -105 | -44 | 192 | 9.29 |

All ATPDMS-modified epoxy systems contain 10 phr ATPDMS.

dissolved in the matrix, Φ^C , may be estimated from the decrease in the T_g of the matrix, ${}_{\text{Epoxy}}T_g$, when compared with the neat system, ${}_{\text{Epoxy}}T_{g,\text{pure}}$. Assuming the validity of the Fox Equation,¹⁶ then

$$\frac{1}{{}_{\text{Epoxy}}T_g} = (1 - W^C)/{}_{\text{Epoxy}}T_{g,\text{pure}} - W^C/{}_{\text{PDMS}}T_{g,\text{pure}} \quad (6)$$

where W^C is the mass fraction of polydimethylsiloxane dissolved in the matrix, related to the volume fraction Φ^C by

$$\Phi^C = [W^C/\rho_{\text{PDMS}}]/[W^C/\rho_{\text{PDMS}} + (1 - W^C)/\rho_{\text{Epoxy}}] \quad (7)$$

The T_g of the matrix without polysiloxane is ${}_{\text{Epoxy}}T_{g,\text{pure}} = 194^\circ\text{C}$, and ${}_{\text{PDMS}}T_{g,\text{pure}}$ for the pure polydimethylsiloxane is -123°C . ρ_{Epoxy} and ρ_{PDMS} are, respectively, the density of epoxy and polydimethylsiloxane. The volume fraction of dissolved polydimethylsiloxane is shown in Table IV. This shows again that the use of low molecular weight polydimethylsiloxane, which is more miscible with the matrix, leads to an incomplete phase separation associated with a significant decrease of the matrix T_g .

Microstructural Details

The size distributions of the polysiloxane particles, as evaluated from SEM micrographs (Figs.

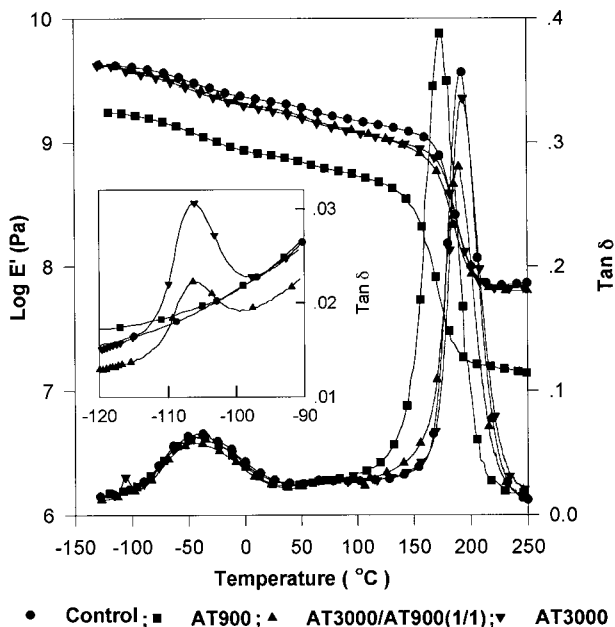


Figure 5 Dynamic mechanical properties of various ATPDMS-modified epoxy resins (10 Hz).

Table IV Volume Percentage of Dissolved Polydimethylsiloxane to the Initial Volume of Polydimethylsiloxane Calculated from Fox Equation

| Composition | Volume Percentage of Dissolved Polydimethylsiloxane (%) |
|----------------------|---|
| AT900 | 33 |
| AT900/AT1680 (1 : 1) | 13 |

All ATPDMS-modified epoxy systems contain 10 phr ATPDMS.

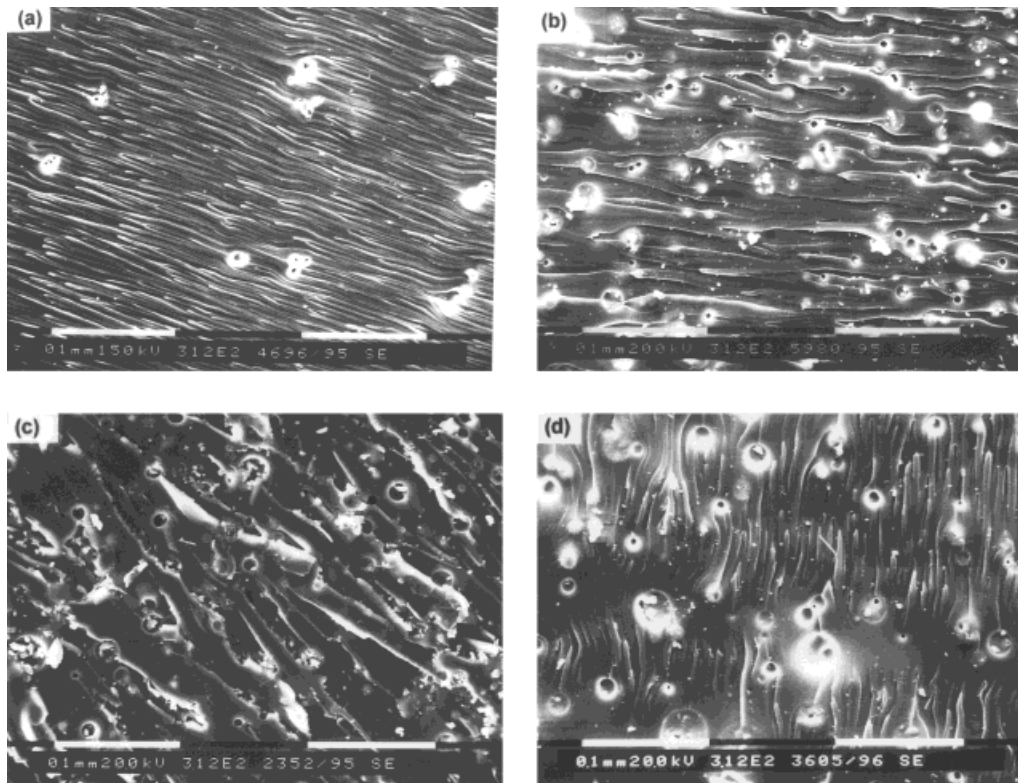


Figure 6 Morphology of the fracture surfaces of cured epoxy resins modified with various ATPDMSs (10 phr): (a) AT900, (b) AT1680, (c) AT3000, and (d) AT3880.

6 and 7) are depicted in Figure 8. When the epoxy resin is modified with single ATPDMS modifier, a rather broad distribution is observed. The polysiloxane particle size increases as the molecular weight of ATPDMS increases. The shape of these polysiloxane particles is almost spherical.

In the cases of mixing AT900 and other high molecular weight ATPDMS in 1 : 1 ratio, narrow distribution of polysiloxane particles and relatively small particle size are observed (Fig. 8). The optical microscopic observations of the uncured epoxy in Figure 9 show that AT900 reduces the particle size and that HT900 increases the particle size. AT900 is more reactive than the higher molecular weight polydimethylsiloxane (Fig. 3) and partially miscible with the epoxy resin (Table IV). AT900 reacted with the epoxy resin at the early state of preliminary reaction compatibilizes the epoxy resin and the high molecular weight polydimethylsiloxane. However, since HT900 is not reactive and increases the immiscible portion of the polydimethylsiloxane, larger particles of polysiloxane are formed. Therefore, the partial miscibility of low molecular weight

polysiloxane does not help to decrease the particle size of high molecular weight polydimethylsiloxanes.

Table V shows morphological parameters obtained from SEM micrographs. The number-average particle diameter of epoxy modified with AT3000 alone is $10.2 \mu\text{m}$, and the particle size is reduced to $3.0 \mu\text{m}$ when AT900 is mixed with AT3000. Decreasing the polysiloxane particle size leads to an increase in the concentration of dispersed particles, and the concentration increases from 7.6×10^7 to $98.2 \times 10^7 \text{ cm}^{-3}$ when AT900 is added. It is also shown that the distance between polysiloxane particles decreases as the concentration of polysiloxane particles increases (Fig. 10).

Interparticle distance (A) can be calculated from the known particle diameter and volume fraction with eq. (8),

$$A = (\sqrt[3]{\pi/6V - 1}) \times D \quad (8)$$

where V is the particle volume fraction, and D is the particle diameter.¹⁷

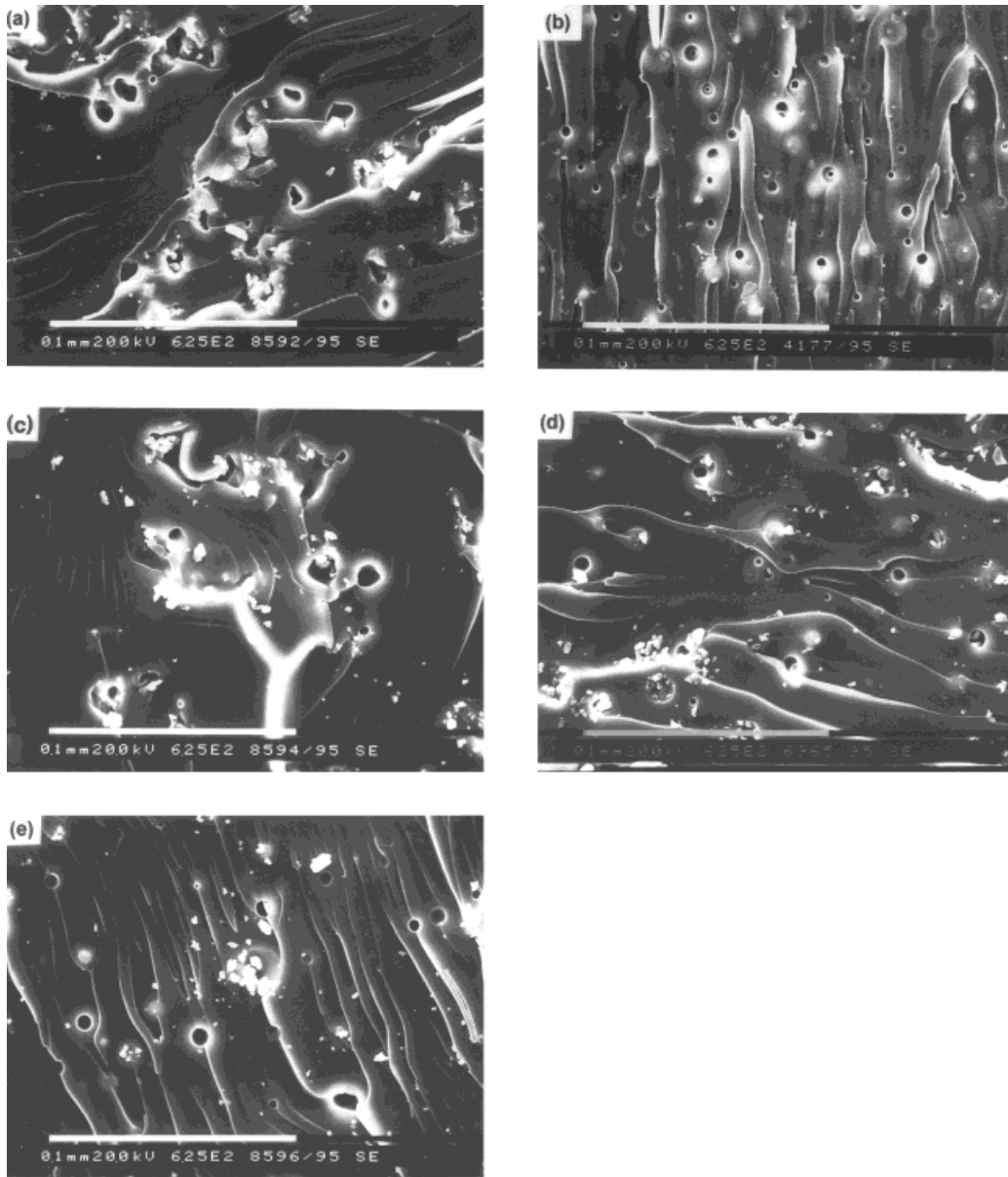


Figure 7 Morphology of the fracture surfaces of ATPDMS-modified epoxy resins in the case of mixing AT900 with high molecular weight ATPDMS: (a) AT900/AT1680, (b) AT900/AT3000, (c) AT900/AT3880, (d) AT900/AT7000, and (e) AT900/AT12000 (all 1 : 1 ratio and 10 phr concentration to epoxy).

Fracture Failure Mode

The fracture surface of the unmodified epoxy resin in SEM studies exhibits a very smooth appearance, with only a few ribs parallel to the crack growth direction (Fig. 11). These ribs are formed by a lateral coalescence of slightly different crack plateaus. The more these fractures are

formed, the greater the crack growth resistance should be.¹⁸

Figures 6 and 7 show a very rough fracture surface on which a great number of debonded, globular-shaped polysiloxane particles can be seen. The rather unusual roughness of the fracture surface is, in this case, a result of an easy debonding of the polysiloxane particles due to

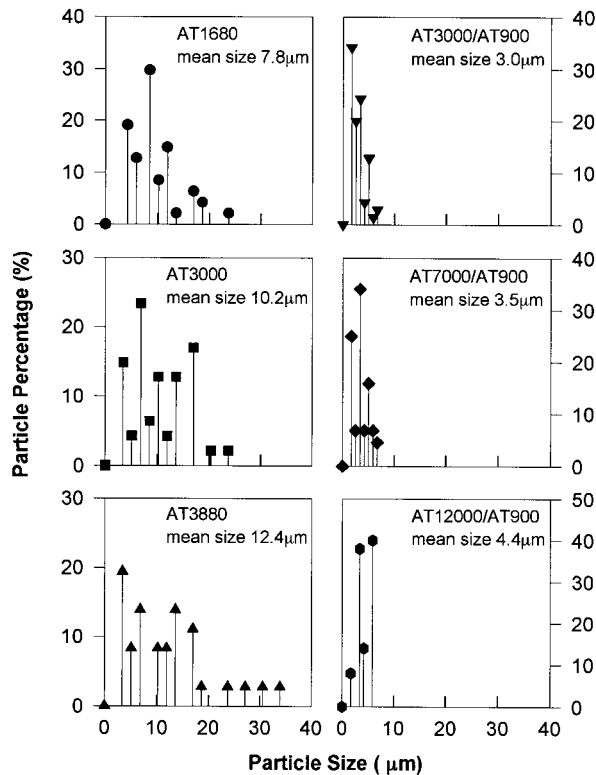


Figure 8 Particle size distributions for ATPDMS-modified epoxy resins.

a lack of chemical links to the epoxy matrix. Thus, the coarse polysiloxane particles show rather smooth (bare) surfaces after their separation from the matrix. In addition, the stress field in front of the crack tip is perturbed by the polysiloxane particles because the polysiloxane particle has elastic constants, i.e., Young's modulus and Poisson's ratio, different from those of the epoxy matrix. Both effects alter the crack growth angle from the original direction, and bifurcate the crack into two cracks. These phenomena would both create new fracture surfaces. Consequently, more ribs and curved ribs are formed.

Mechanical Properties

Table VI shows the flexural properties and the fracture toughness of various ATPDMS-modified epoxy resins. The results show that the flexural strength and the modulus decrease as the polysiloxane particle size increases. When the low molecular weight AT900 is mixed with high molecular weight ATPDMS, the reduction is less.

Figure 12 shows the dependence of the fracture toughness on the polysiloxane particle size. The smaller the polysiloxane particles, the higher the K_{IC} values. There is 15–20% enhancement of fracture toughness due to the small particle size and high concentration of polysiloxane particles in the cases of mixing AT900 and other high molecular weight ATPDMS. Small particles are generally more efficient in producing a toughening effect than large particles. The origin of this particle size dependence arises from the role played by the particle, which is governed by the size of the formal plastic zone proposed by Irwin.¹⁹ Irwin stated that the formal plastic zone size may be estimated for the plane strain case by

$$r_p = 1/6\pi(K_{IC}/\sigma_y)^2 \quad (9)$$

where r_p is the radius of the plastic zone, and σ_y is the yield stress. The yield stress of the neat epoxy matrix is 51.8 MPa. For DDM-cured epoxy, the resultant plastic zone size would be approximately 10 μm . If this rationale is correct, then smaller particles than 10 μm , which lie in the plastic zone, are forced to promote shear yielding, which provides an increase in fracture toughness. Large particles lying outside the plastic zone are only able to act as bridging particles.²⁰ However, due to the lack of chemical links to the epoxy matrix, the interfacial adhesion between the polysiloxane particle and the matrix is not strong. Thus, the amount of toughening induced by the bridging particles is not sufficient to increase the fracture toughness in this epoxy system.

The effects of the concentration of polysiloxane particles and the distance between particles were also investigated. Michler²¹ insisted that maximum fracture toughness is observed only if the average interparticle distance is between the critical minimum interparticle distance and the critical maximum interparticle distance. With less than the critical minimum interparticle distance, a viscoelastic smearing of the stress concentration prevents shear deformation; and with larger than the critical interparticle distance, shear deformation cannot occur, since stress concentration is low because of the lack of stress-field superposition. From our results, the critical interparticle distance may be about 11 μm (Fig. 13). It is very interesting to note that this value coincides with the plastic zone size of 10 μm . However, in this limited study, it is difficult to determine both the minimum and maximum interparticle distance.

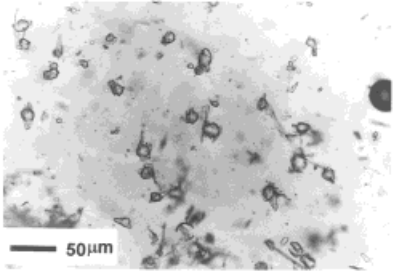
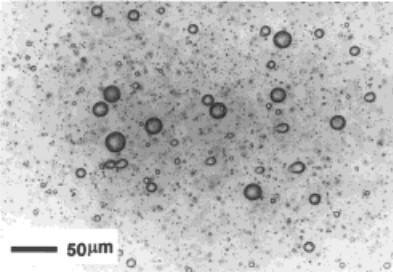
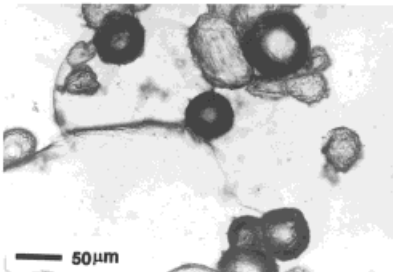
| Composition | Optical Photograph |
|--------------------------------|--|
| AT 900 : 5phr AT3000 : 5phr |  |
| AT 900 : 5phr HT3000 : 5phr |  |
| HT 900 : 5phr AT3000 : 5phr |  |

Figure 9 Optical micrographs of the uncured polysiloxane-modified epoxies in the melt state (all polysiloxane-modified epoxies contain 10 phr polysiloxane).

In spite of the lower particle size and the higher particle concentration in the polysiloxane composition for AT900/AT12000 mixed system, the K_{IC} value is low (Figs. 12 and 13). The number of reactive functional groups that can link to the epoxy matrix on the surface of a polysiloxane particle decreases as the molecular weight of polysiloxane increases. Therefore, a small number of interfacial links between polysiloxane and epoxy are responsible for the reduction of energy dissipation

by debonding of the polysiloxane particles from epoxy matrix.

K_{IC} of the epoxy resin is improved up to 1.2 times by polysiloxane addition (10 phr), and the large particle appears not to be as efficient in providing an increase in fracture toughness. Kim et al.¹⁷ showed that K_{IC} of core-shell rubber modified epoxy/DDM resins increased up to 1.3 times that of neat resin with increasing core-shell rubber content up to 30 phr. They insisted that shear

Table V Morphological Parameters Determined by SEM

| Composition | Number-Average Diameter, \bar{D}_n (μm) | Concentration of Polysiloxane Particles, P ($\times 10^7 \text{ cm}^{-3}$) | Interparticle Distance, A (μm) |
|-----------------------|--|--|---|
| AT1680 | 7.8 | 13.0 | 12.8 |
| AT3000 | 10.2 | 7.6 | 18.2 |
| AT3880 | 12.4 | 3.0 | 23.5 |
| AT900/AT3000 (1 : 1) | 3.0 | 98.2 | 8.3 |
| AT900/AT7000 (1 : 1) | 3.5 | 44.3 | 11.1 |
| AT900/AT12000 (1 : 1) | 4.4 | 33.1 | 13.4 |

All ATPDMS-modified epoxy systems contain 10 phr ATPDMS.

deformation can be restricted because of high cross-link density. Karger-Kocsis and Friedrich²² also reported that K_{IC} of the epoxy practically is unaffected by incorporation of the polysiloxane dispersion when tests were performed at low crosshead speed (1 mm/min). It needs further investigation.

In this investigation, comparing polysiloxanes having different molecular weights or mixing a low molecular weight polysiloxane with a high molecular weight polysiloxane, the small particle size and narrow distribution and high particle concentration enhance the fracture toughness of ATPDMS-modified epoxy resins. The smaller the particle, the more particles per volume exist.

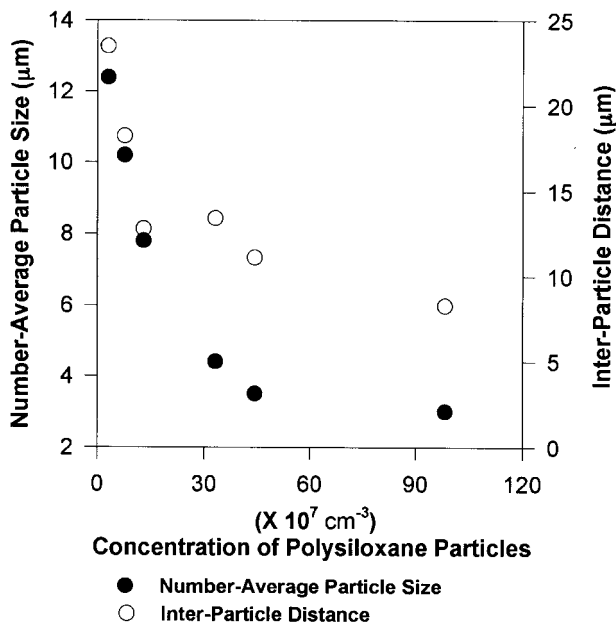


Figure 10 The relationship between morphological parameters.

Therefore, since small-size particles have higher probability of inducing and terminating sliver cracks, a large fracture energy is consumed. In addition, the small particles have larger surface area; thus, they have better interaction between the particle and the matrix. As a result, low reduction in flexural strength and highly enhanced fracture toughness are observed. When the low molecular weight polysiloxane is mixed with high molecular weight polysiloxane, smaller rubber particle size and narrower distribution are obtained.

To investigate the fracture toughness behavior of toughened epoxy resin with bimodal polysiloxane particle size distribution, we attempted to mix large and small molecular weight polysiloxanes while keeping the total polysiloxane content constant. Polysiloxane-modified epoxy resins were fabricated with the polysiloxanes in constant total content of 10 phr, but with varied weight ratios. The weight ratios for AT900/AT12000 were 1 : 1, 1 : 2, 1 : 3, and 1 : 5, respectively.

The result shows that the concentration of poly-

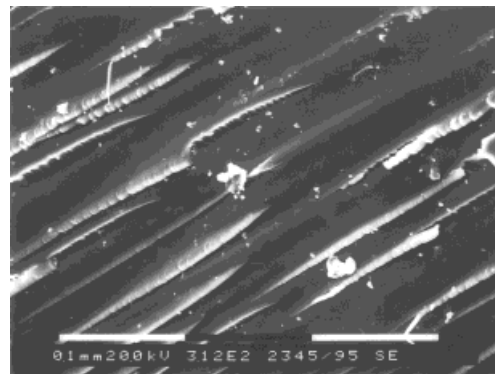


Figure 11 Fracture surface of the neat cured epoxy system.

Table VI Flexural Properties and Fracture Toughness of Cured Epoxy Resins Modified with Various ATPDMSs

| Composition | Flexural Strength (kg _f /mm ²) | Flexural Modulus (kg _f /mm ²) | Fracture Toughness (K_{IC}) (MPa m ^{1/2}) |
|-----------------------|---|--|---|
| Control | 10.27 (0.48) | 219.58 (11.95) | 0.71 (0.06) |
| AT900 | 9.41 (0.24) | 215.03 (15.55) | 0.69 (0.05) |
| AT1680 | 6.57 (0.13) | 181.91 (6.74) | 0.79 (0.08) |
| AT3000 | 7.30 (0.23) | 185.98 (10.53) | 0.73 (0.03) |
| AT3880 | 4.81 (1.11) | 152.40 (9.44) | 0.63 (0.03) |
| AT900/AT1680 (1 : 1) | 9.43 (0.46) | 214.90 (7.92) | 0.73 (0.04) |
| AT900/AT3000 (1 : 1) | 8.08 (0.41) | 193.70 (13.04) | 0.84 (0.05) |
| AT900/AT3880 (1 : 1) | 6.88 (0.37) | 192.29 (8.84) | 0.79 (0.07) |
| AT900/AT7000 (1 : 1) | 9.46 (0.25) | 188.72 (7.00) | 0.84 (0.05) |
| AT900/AT12000 (1 : 1) | 8.57 (0.28) | 200.84 (15.52) | 0.07 (0.02) |

All ATPDMS-modified epoxy systems contain 10 phr ATPDMS. Values in parentheses indicate a deviation.

siloxane particles decreases and the interparticle distance increases as the amount of AT12000 increases. However, K_{IC} values increased somewhat (Table VII). SEM analysis represents that the bimodal rubber particle size distributions appear as the ratio of AT12000 increases (Fig. 14). This result shows the possibility that a bimodal polysiloxane particle size distribution can result in enhancement in fracture toughness of polysiloxane-modified epoxy systems. However, there is no evidence of interactions between large particles and small particles to give a synergistic toughening effect. This will be the subject of a future study.

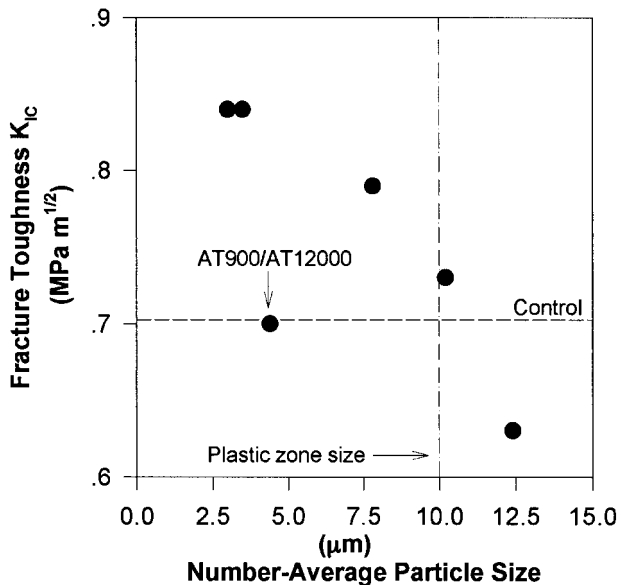


Figure 12 Dependence of fracture toughness on polysiloxane particle size.

CONCLUSION

This study was to investigate the morphology and mechanical properties of cured epoxy systems in relation to the compositions of various amino-terminated polydimethylsiloxanes differing in their

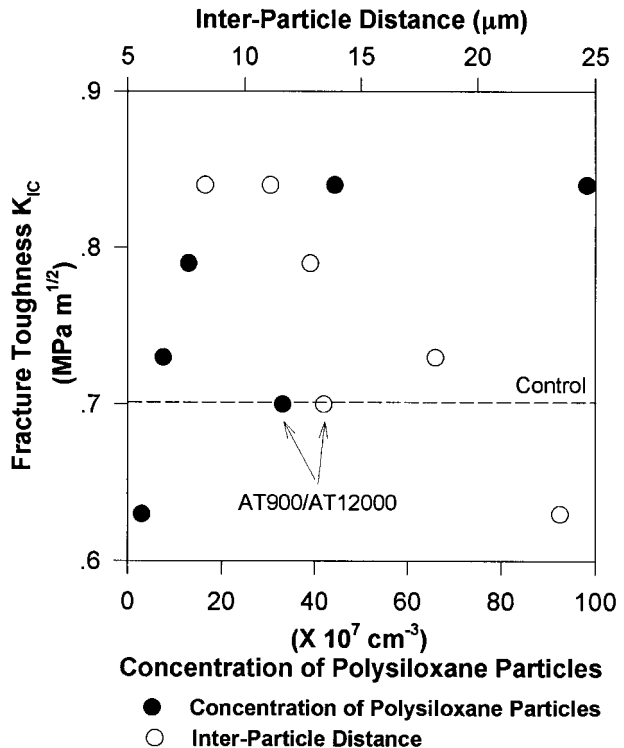


Figure 13 Dependence of fracture toughness on the concentration of polysiloxane particles and the distance between particles.

Table VII Morphological Parameters and Fracture Toughness of AT900/AT12000 Mixed Toughened Epoxy Resin

| Weight Ratio of AT900/AT12000 | Number-Average Diameter, \overline{Dn} (μm) | Concentration of Polysiloxane Particles, P ($\times 10^7 \text{ cm}^{-3}$) | Interparticle Distance A (μm) | Fracture Toughness, K_{IC} ($\text{MPa m}^{1/2}$) |
|-------------------------------|--|--|--|---|
| 1 : 1 | 4.4 | 33.1 | 13.1 | 0.70 |
| 1 : 2 | 6.4 | 7.7 | 14.8 | 0.69 |
| 1 : 3 | 7.5 | 4.7 | 17.5 | 0.72 |
| 1 : 5 | 7.7 | 5.3 | 19.6 | 0.78 |

All ATPDMS-modified epoxy systems contain 10 phr ATPDMS.

molecular weights and the preliminary reaction conditions in the melt state. The main conclusions from this study are as follows.

1. The degree of preliminary reaction between polysiloxane and epoxy resin in the melt state increases as the molecular weight of polysiloxane decreases. The reaction in the melt state is conducted in the
2. restricted interfacial region of polysiloxane and epoxy resin. When the low molecular weight polysiloxane is mixed with high molecular weight polysiloxane, low molecular weight polysiloxane compatibilizes epoxy resin and high molecular weight polysiloxane. It is also noted that smaller particle size and narrower distribution of polysiloxane particles

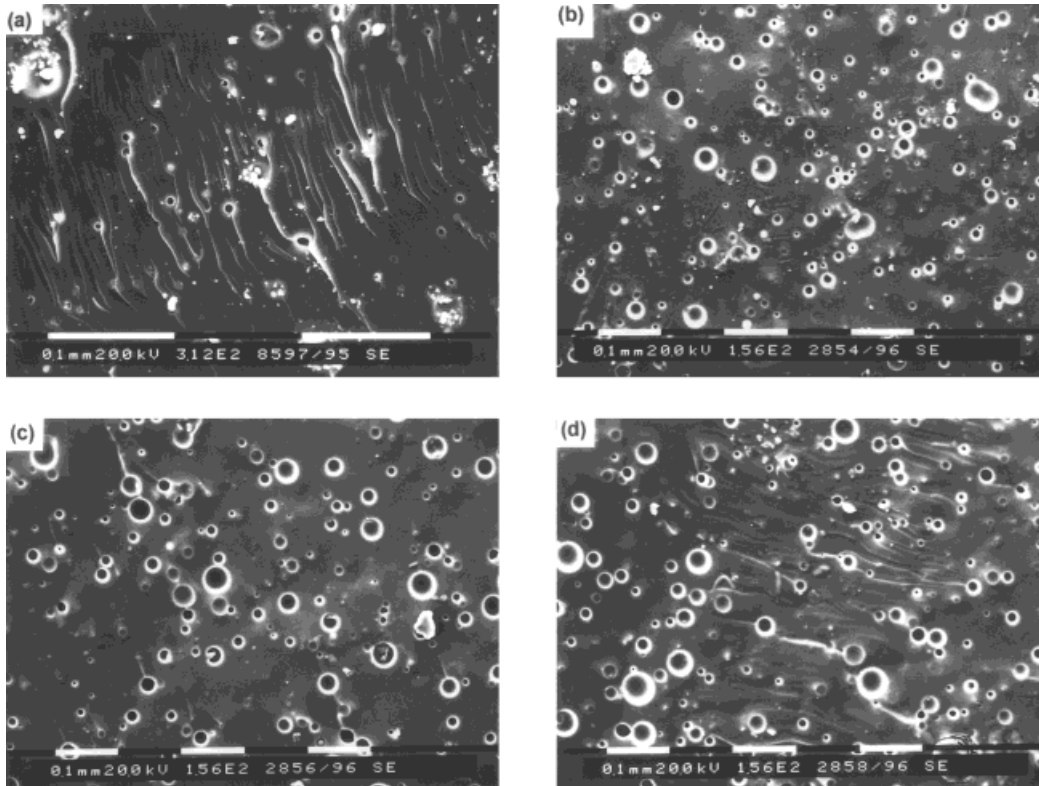


Figure 14 Morphology of the fracture surfaces from AT900 and AT12000 mixed toughened epoxy resins in which the weight ratios of AT900 to AT12000 are (a) 1/1, (b) 1/2, (c) 1/3, and (d) 1/5.

are obtained in the mixed polysiloxane system.

3. The fracture toughness of epoxy resin modified with mixture of AT900/AT3000, AT900/AT3880 shows about 15–20% increase in fracture toughness when compared to the neat epoxy resin.
4. The concentration of dispersed polysiloxane particles increases, and the interparticle distance decreases with a decrease of polysiloxane particle size.
5. The small particle size and high concentration of polysiloxane particles improve the fracture toughness of epoxy resin.
6. Toughening mechanisms are energy dissipation by easy debonding of the polysiloxane particles to epoxy matrix and shear yielding in the ATPDMS-modified epoxy systems.

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