

Effect of the addition of aramid-silicone block copolymer on phase structure and toughness of cured epoxy resins modified with silicone

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To improve the toughness of silicone-modified epoxy resin, an aramid-silicone block copolymer was used as a compatibilizer. Fine silicone phases could be uniformly and stably dispersed in the epoxy matrix by the addition of the block copolymer. The relative ratio of the molecular weight of epoxy and silicone segments in the block copolymer strongly affected the effectiveness of the compatibilizer. The block copolymer which acted as a good compatibilizer was mainly concentrated in the interfacial area around the silicone phase. The main values of fracture toughness and impact strength in the silicone-modified system increased with a decrease in the diameter of the silicone phases. Their maximum value increased to about 2.0–2.5 times that of the unmodified system. Observations of the damage zone with an optical microscope revealed that the improvement in the toughness in the silicone-modified system is due to the increase in the area of the damage zone caused by the formation of fine silicone phases. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Epoxy resin is one of the most important thermosetting polymers. This resin exhibits many desirable properties, such as high strength and modulus, excellent chemical and solvent resistance, thermal stability and bonding properties. However, epoxy resin is generally brittle because of its highly cross-linked structure.

Many efforts have been made to improve the toughness of the cured epoxy resin. The most successful attempt is modification with some reactive liquid rubber, such as CTBN and ATBN^{1–5}. However, these rubbers lack heat resistance, and thus modification with these rubbers leads to a decrease in the physical properties of cured epoxy resin in the high temperature region. In contrast to these rubbers, silicone rubber preserves stable physical properties over a broad range of temperature. Namely, the modification of epoxy resin with silicone rubber should improve the toughness of the cured resin with no damage to the heat resistance. However, if epoxy resin is directly modified with silicone rubber, the silicone is completely separated from the epoxy resin, because silicone rubber has no compatibility with epoxy resins. Therefore, to improve the toughness of epoxy resin by modification with silicone rubber, increased dispersibility of the silicone in the epoxy matrix is required.

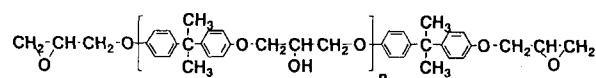
In this study, four types of aramid-silicone block copolymers in which the molecular weight of the silicone block was different were added in silicone-modified epoxy resins as compatibilizers. Effects of the addition of the aramid-silicone block copolymers on the morphology and toughness of the silicone-modified epoxy resins were

examined in detail. Furthermore, the toughening mechanism was investigated by observing the deformation of the silicone phase and the epoxy matrix with various optical and electrical microscope techniques.

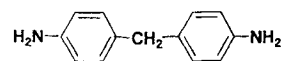
EXPERIMENTAL

Materials

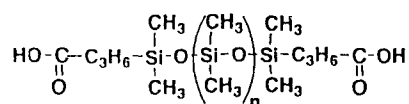
The epoxy resins used in this work were a commercial grade of bisphenol A type resins (Epikote 828, 1001, 1004, and 1007, MW = 380, 900, 1800 and 3800, Yuka-shell Epoxy Co.).



The curing agent used was 4,4-diaminodiphenylmethane.



The silicone oligomer used as a rubber-modifier was carboxyl-terminated dimethylsiloxane (MW = 2600, Shinetsu Chemical Co., Ltd.).

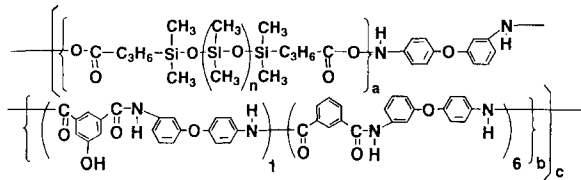


To improve the compatibility between the epoxy resin and the silicone oligomer, the silicone oligomer was pre-reacted with the epoxy resin (Epikote 828, MW = 380).

Some aramid-silicone block copolymers which had

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different molecular weights of the silicone block were used as compatibilizers (Tomoe-gawa Paper Co., Ltd.).



These block copolymers have phenolic functional groups in the amide segment. The phenolic groups are able to react with the epoxy group. Thus, the amide block in these copolymers appears to be endowed with compatibility in the epoxy matrix by the reaction of the phenolic OH group with the epoxy group.

Curing of epoxy resin

Silicone oligomer was pre-reacted with a large excess of epoxy oligomer (80 g of silicone per 100 g of epoxy oligomer) at 70°C for 30 h. Tetrahydrofuran (THF) and dimethylbenzylamine (DMBA) were, respectively, used as solvent and catalyst in this reaction. On the other hand, amide-silicone block copolymer was also pre-reacted with excess epoxy oligomer (6 g of block copolymer per 100 g of epoxy oligomer) at 80°C for 24 h. In this reaction, N,N-dimethylformamide (DMF) and DMBA were used, respectively, as solvent and catalyst. THF and DMF used as the solvent were then removed by evaporation under reduced pressure (< 3 mmHg) at 80°C for 2 h and 100°C for 2 h, respectively. The pre-reacted silicone and block copolymer and the epoxy resin were dissolved in excess THF to prepare the modified epoxy resins. The total content of silicone in the modified epoxy resins without solvent was adjusted to about 9 wt%. The solvent was then removed by evaporation at 80°C for 2 h under reduced pressure (< 3 mmHg). After removing the solvent, a stoichiometric amount of pre-melted curing agent was added to the mixture at 130°C. The mixture was then poured into 4 mm-thick glass molds which were pre-heated at 180°C. The materials were cured at 180°C for 5 h.

Measurements

The fracture behaviour of epoxy materials was examined using a fracture mechanics approach, and the stress intensity factor, K_c , for the initiation of crack growth was determined from a compact-tension specimen shown in Figure 1 according to ASTM E 399-81. The thickness of the specimens was adjusted to between 3.6 and 4.0 mm. A sharp crack was formed at the base of the slot by carefully tapping the specimen with a fresh razor blade⁶. The specimen was mounted in an Instron type tensile machine (AG-2000E; Shimadzu Co., Ltd.) and loaded at a constant cross-head speed (0.5 mm min⁻¹). The experiments were conducted at room temperature. The value of the stress intensity factor, K_c , was calculated from

$$K_c = P_Q f(a/w) / BW^{1/2}$$

where

$$f(a/w) = (2 + a/w)(0.886 + 4.64a/w - 13.32a^2/w^2 + 14.72a^3/w^3 - 5.6a^4/w^4) / (l - a/w)^{3/2}$$

and where P_Q is the load at crack initiation and a is the crack length, B and W are the thickness and the width of the specimen, respectively. $f(a/w)$ is a geometric factor.

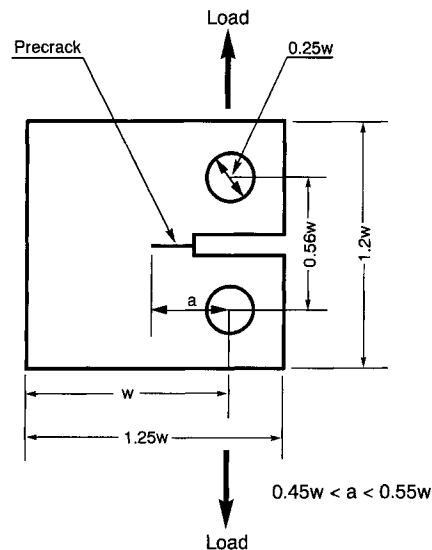


Figure 1 Shape and geometry of compact-tension specimen

The impact strength of cured epoxy resins was measured at room temperature according to DIN-53453. The shape of the specimens is a small rectangular block of 15 × 10 × 2 mm in dimension.

The morphology of the fracture surfaces was observed using a scanning electron microscope (SEM: JSM-6500, JEOL Co., Ltd.) at an accelerating voltage of 15 kV. Prior to the examination, the surfaces were coated with a thin layer of gold in order to improve conductivity and prevent charging. The average diameter D of the dispersed phase was estimated by applying the pin drop test⁷ to the scanning electron microphotographs, assuming that the dispersed phase is spherical in shape and is homogeneously dispersed in the matrix resin. In this test, the average diameter D is calculated from the following equation:

$$D = 3Lh/2P$$

where P and h are the total number of intersections and the hit number between the dispersed phases and the test pins, respectively, and L is the length of the test pin.

The ultra-thin sections of modified epoxy resins were observed using a transmission electron microscope (TEM: JEM-1210, JEOL Co., Ltd.) to study the phase structure and the subsurface damage. The specimens for TEM observations were prepared using an ultramicrotome (Reichert Ultracut E, Leica Co., Ltd.) with a diamond knife. The specimens were stained with osmium tetroxide (OsO₄) or ruthenium tetroxide (RuO₄). In the staining using OsO₄ vapour, the block copolymer which is added in the modified system is selectively stained. On the other hand, in the staining with RuO₄ vapour, the entire silicone dispersed phase in the modified system is stained.

A transmission optical microscope (OM: BH-2, Olympus Co., Ltd.) was employed to examine the subsurface damage in the compact-tension specimens. The thin sections for OM observations were produced using a petrographic polishing technique described by Holic *et al.*⁸. The thickness of the thin sections was less than 35 μm. These sections were viewed with transmitted light, with and without crossed polarizers.

RESULTS AND DISCUSSION

Morphology of silicone-modified epoxy system with amide-silicone block copolymer

The changes in the morphology of the silicone-modified

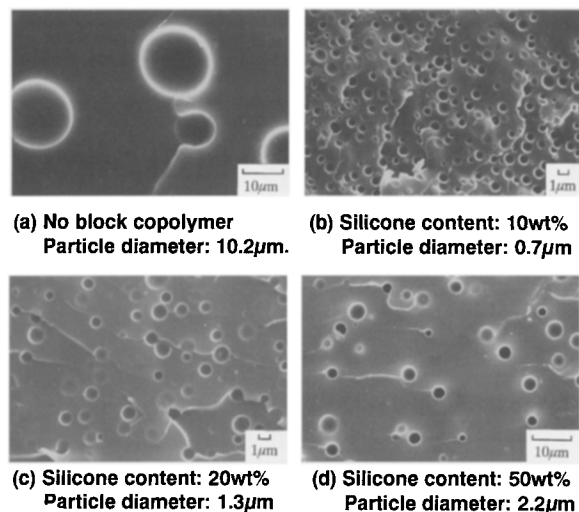


Figure 2 SEM of fracture surfaces of epoxy resin modified with silicone. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. Block copolymers were pre-reacted with epoxy monomer whose molecular weight was 380 g mol⁻¹

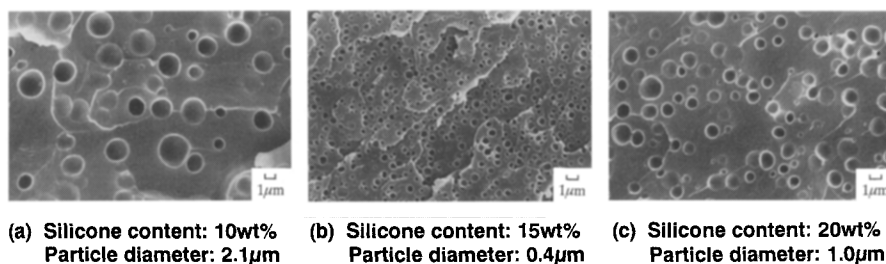


Figure 3 SEM of fracture surfaces of epoxy resin modified with silicone. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. Block copolymers were pre-reacted with epoxy monomer whose molecular weight was 900 g mol⁻¹

epoxy system with the addition of aramid-silicone block copolymers are shown in *Figure 2*. In the system with no added block copolymer [*Figure 2(a)*], large silicone phases are clearly observed to be dispersed in the epoxy matrix. The average diameter of the dispersed phases was about 10 μm. In previous studies^{9,10}, we reported that the silicone was completely separated from the epoxy resin if the epoxy resin was directly modified with the silicone. In this study, the silicone oligomer could be dispersed in the epoxy matrix without the addition of the block copolymer as a compatibilizer, because the compatibility between the epoxy resin and the silicone oligomer was improved by the pre-reaction described in the experimental section. However, for the purpose of the improvement of the toughness in the silicone-modified system, the average diameter of the dispersed silicone phase must be decreased to the sub-micron order. Sultan and McGarry¹¹ showed that the fracture toughness of a brittle epoxy could be improved by the incorporation of rubber spheres of approximately 1 μm diameter. Therefore, aramid-silicone block copolymers which were pre-reacted with epoxy monomers were added as a compatibilizer for improving the dispersibility of the silicone oligomer in the epoxy matrix. *Figure 2(b)* shows the morphology of the system with added block copolymer whose silicone content was about 10 wt%. The block copolymer added was pre-reacted with a low-molecular-weight epoxy resin (Epikote 828; MW = 380). In this system, the silicone formed well-defined dispersed phases and was uniformly dispersed in the epoxy matrix.

The average diameter of the dispersed phases was smaller compared with that of the system modified with the silicone oligomer only [*Figure 2(a)*] and reached less than 1 μm. This photograph shows that fine silicone phases could be uniformly and stably dispersed in the epoxy matrix by the addition of the block copolymer.

Figure 2(c) and *(d)* shows the morphology of the systems with added block copolymers whose silicone contents were about 20 and 50 wt%, respectively. These block copolymers were pre-reacted with the same epoxy monomer used in *Figure 2(b)*. As seen in *Figure 2(b)–(d)*, the diameter of the silicone-dispersed phases increased with an increase in the silicone content in the block copolymer. This means that the block copolymer whose silicone content is low acts as a good compatibilizer when the block copolymer was pre-reacted with a low-molecular-weight epoxy monomer. Lyatskaya *et al.*¹² showed that the change in copolymer architecture affects the efficiency of a compatibilizer. These photographs also show that the architecture of the block copolymer affects the morphology of the silicone-modified epoxy system.

Figure 3 shows the morphology of the system with added block copolymer which was pre-reacted with the epoxy resin whose molecular weight was 900. These photographs show that, in the system with added block copolymer (silicone content: 15 wt%), more fine silicone phases could be uniformly and stably dispersed in the epoxy matrix, compared with the modified systems with other added block copolymers. This means that the block copolymer whose silicone content was about 15 wt% could act as a good compatibilizer when the block copolymer was pre-reacted with the epoxy monomer whose molecular weight was 900. *Figure 4* shows the morphology of the system with added block copolymer which was pre-reacted with epoxy resin whose molecular weight was 3800. The diameter of the silicone-dispersed phases decreased with an increase in silicone content in the block copolymer. In particular, in the system with the added block copolymer whose silicone content was about 50 wt%, the diameter of the dispersed phases reached less than 0.1 μm and its distribution also became comparatively narrow. This result shows that the block copolymer whose silicone content was about 50 wt% was more effective for improving the distribution of the silicone phases. As seen from *Figures 2–4*, it is thought that the block copolymer whose silicone content is higher can act as a better compatibilizer, when the block copolymer was pre-reacted with a higher molecular weight epoxy monomer. These photographs show that the balance between the contents of the silicone block and epoxy oligomer in the pre-reacted block copolymer is an important

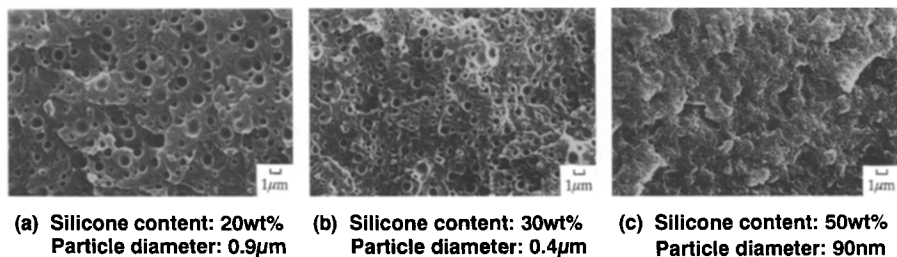


Figure 4 SEM of fracture surfaces of epoxy resin modified with silicone. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. Block copolymers were pre-reacted with epoxy monomer whose molecular weight was 3800 g mol^{-1}

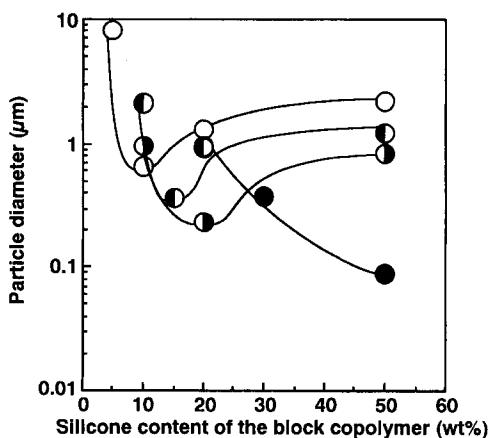


Figure 5 Fig. 5Relation between particle diameter of dispersed phases and silicone content in aramid-silicone block copolymer. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. Molecular weight of epoxy monomer pre-reacted (g mol^{-1}): (○) 380; (○) 900; (●) 1800; (●) 3800

factor in determining the effectiveness of the block copolymer as a compatibilizer.

In order to clarify the importance of the balance between the silicone and epoxy contents in the block copolymer, the

relation between the diameter of the silicone-dispersed phases and the silicone content of the block copolymers which were pre-reacted with four kinds of epoxy monomer ($\text{MW} = 380, 900, 1800, 3800$) is shown in *Figure 5*. The diameter of the silicone dispersed phases had a minimum value at some optimum silicone content in all modified systems. The optimum points in each system shifted to a high silicone content with an increase in the molecular weight of epoxy monomer pre-reacted with the block copolymer. This means that the relative ratio of the molecular weight of the epoxy segment and the silicone segment in the block copolymer strongly affects the ability of the compatibilizer composed of the block copolymer. In addition, the diameter of the silicone phase at the optimum points decreased with an increase in the silicone content of the block copolymer. This result shows that the block copolymer in which the characteristics of the silicone and epoxy segments are more independently observed should act as a more effective compatibilizer. The silicone dispersed phase was observed with a transmission electron microscope to confirm the distribution of the block copolymer in the system with added block copolymer. *Figure 6* shows the results of the TEM observation. In these

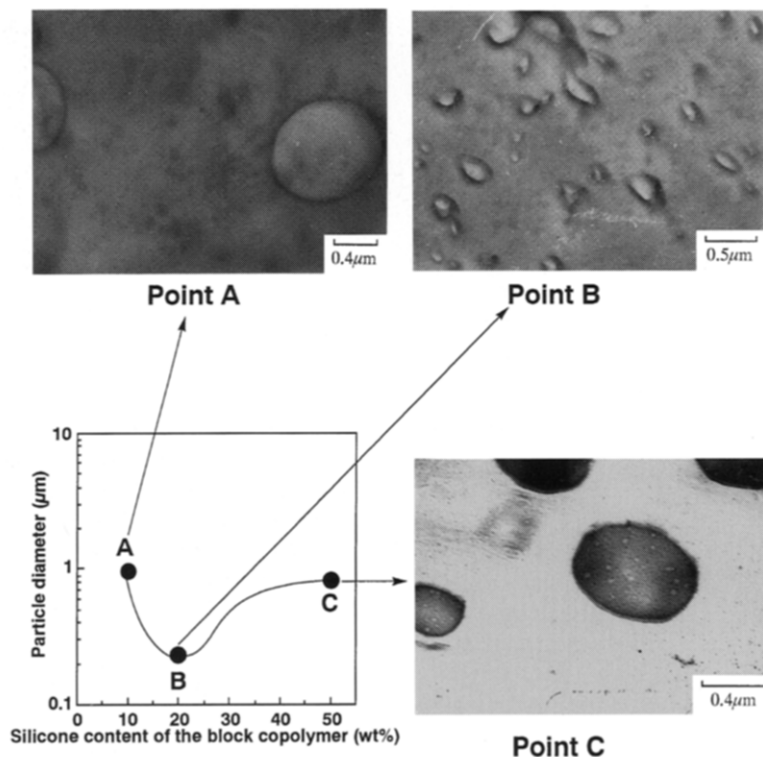


Figure 6 Fig. 5TEM micrographs of epoxy resins modified with silicone. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. Block copolymers were pre-reacted with epoxy monomer whose molecular weight was 1800 g mol^{-1}

photographs, the block copolymer was selectively stained with osmium tetroxide. Thus, the area containing the block copolymer is shown as a dark area. At point A, most of the block copolymer is dissolved in the epoxy matrix. This result shows that the block copolymer which has low silicone content has a good affinity for the epoxy matrix. On the other hand, at point B, the block copolymer is mainly concentrated in the interfacial area around the silicone dispersed phases. Namely, at point B, the silicone phases are covered with the block copolymer and thus their diameter had a minimum value. This means that the larger area of the interface could exist stably in the system with added block copolymer which has an optimum balance between the affinity for the epoxy matrix and the silicone dispersed phase. At point C, the block copolymer is mainly dissolved in the silicone phases. This result shows that the added block copolymer at this point has a high affinity for the silicone oligomer, because of its high silicone content. From these results, it is concluded that the addition of the block copolymer which has a good balance of the affinity for the epoxy matrix and for the silicone phase could more effectively improve the dispersibility of the silicone phases.

Toughening of silicone-modified epoxy system with aramid-silicone block copolymer

The relation between fracture toughness and the diameter of the silicone dispersed phases in the silicone-modified system is shown in Figure 7. The fracture toughness on the vertical axis is shown as the relative ratio to that of the systems with no added block copolymer. The improvement in the fracture toughness in the silicone-modified system by the addition of the block copolymer increased with a decrease in the diameter of the silicone phases. The maximum value of the fracture toughness of the system with added block copolymer increased to over 1.9 times that of the system modified with silicone oligomer only. This means that the increase in the fracture toughness is due to the improvement in the dispersibility of silicone rubber with the addition of the block copolymer.

Figure 8 shows the relation between the impact strength and the diameter of the silicone dispersed phase in the modified system. The increase in the impact strength by the addition of the block copolymer increased with a decrease in the diameter of the silicone dispersed phases. The maximum value of the impact strength of the system with added block copolymer increased to over 2.5 times that of the system modified with silicone only. This result also shows that the

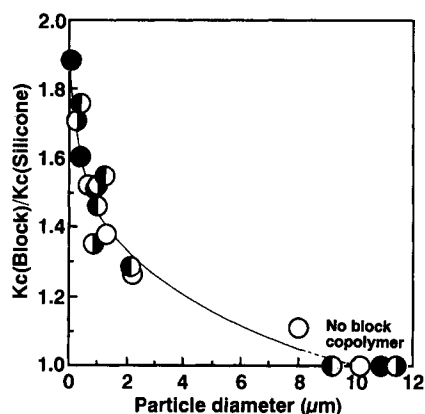


Figure 7 Relation between K_c (block)/ K_c (silicone) and particle diameter of silicone phases. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. MW of pre-reacted epoxy monomer (g mol^{-1}): (○) 380; (◐) 900; (◑) 1800; (●) 3800

toughness of the silicone-modified system is considerably increased by the addition of the block copolymer as a third component.

Toughening mechanism in the system with added block copolymer

As shown in the previous sections, the addition of aramid-silicone block copolymer is effective for improving the toughness of the silicone-modified system. Therefore, the toughening mechanisms in the silicone-modified systems were studied using some microscopic techniques. Figure 9 shows the area we observed using the microscopes. First, we applied the stress which was about 90% of the crack initiation stress on the compact tension specimen. A small block in the vicinity of the crack was then cut from this specimen. From this small block, a thin section was produced using the petrographic polishing technique, and an ultrathin section for TEM was removed using an ultramicrotome. The damage zone was viewed along the direction of the arrow shown in this figure.

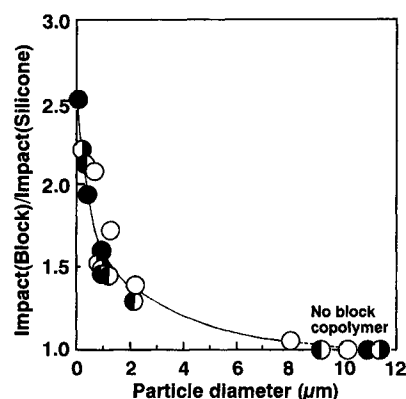


Figure 8 Relation between impact strength (block)/impact strength (silicone) and particle diameter of silicone phases. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. MW of pre-reacted epoxy monomer (g mol^{-1}): (○) 380; (◐) 900; (◑) 1800; (●) 3800

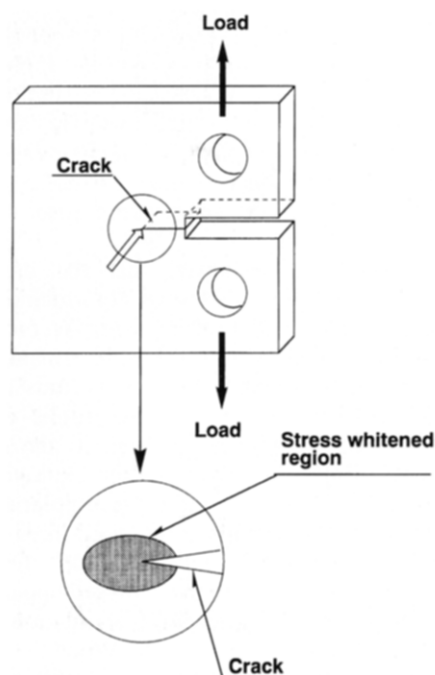


Figure 9 Area of TEM and OM observations

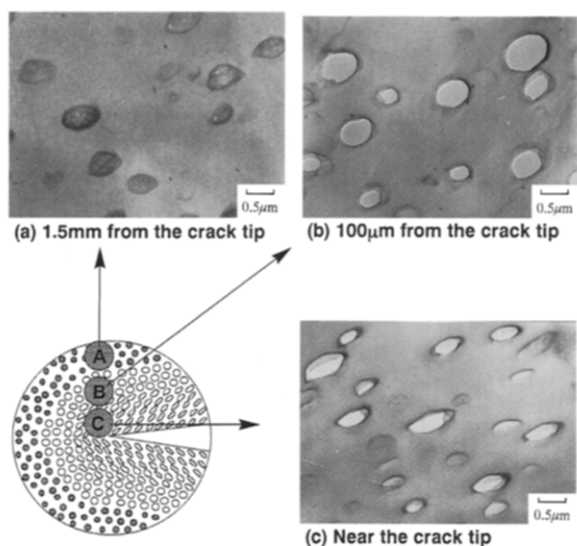


Figure 10 TEM of epoxy resin modified with silicone. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. Samples were stained with RuO_4 . Silicone content of copolymer: 50 wt%. MW of pre-reacted epoxy monomer: 1800 g mol^{-1}

The transmission electron micrographs of the ultrathin section taken near the crack tip are shown in *Figure 10*. At point A, which is about 1.5 mm from the crack tip, the silicone dispersed phases are circular in shape and they are filled with silicone rubber. At point B, which is fairly close to the crack tip, the diameter of the silicone dispersed phases is greater than that at point A and the silicone dispersed phases are not filled with silicone rubber. This result shows that cavitation of the silicone dispersed phases occurred at point B. At point C, which is very close to the crack tip, the silicone dispersed phases are clearly deformed from circular to ellipsoidal along the direction of applied stress. At this point, deformation of the epoxy matrix clearly occurred. From these micrographs, we concluded that the toughening mechanism in the system with added block copolymer is cavitation of the silicone dispersed phases followed by deformation of the epoxy matrix.

Many investigators have already reported^{1,9,13–16} a similar toughening mechanism for the rubber-modified epoxy system. They reported that the cavitation of rubber dispersed phases and the shear deformation of the epoxy matrix near the crack tip constitute the main mechanism for toughening of the rubber-modified system. Our results obtained from the TEM observation also support this toughening mechanism.

Pearson and Yee¹⁷ showed that the crossed nicol technique is useful for observing deformations near the crack tip that induce a birefringence. According to this technique, the overall view of the deformation near the crack tip was observed using transmission optical micrographs. *Figure 11* shows the result of the OM observation. The micrographs shown in the left section were viewed using bright light and the photographs in the right section were viewed using crossed polarized light. In the bright field micrographs, the dark area shows the aggregations of cavitated rubber particles. On the other hand, the bright area in the crossed polarized field micrographs shows the molecular orientation caused by the deformation of the epoxy matrix. When the diameter of the silicone phases is over about $2 \mu\text{m}$, the cavitation of silicone dispersed phases and the deformation of the epoxy

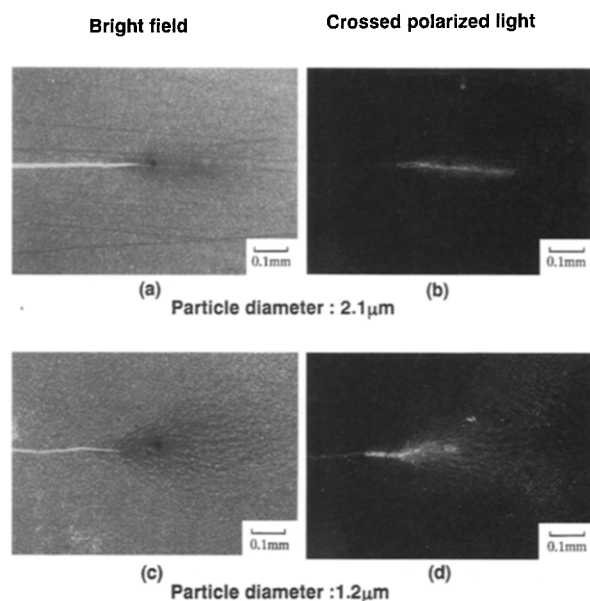


Figure 11 Optical micrographs taken at the sub-fracture surface of epoxy resins modified with silicone. Total silicone: 9 wt%. Block copolymer content: 4.2 wt%. Silicone content of block copolymer (wt%): (a) and (b) 10; (c) and (d) 20. MW of pre-reacted epoxy monomer (g mol): 900

matrix are observed only in the limited area which is very close to the crack tip [*Figure 11*(a) and (b)]. When the diameter of the silicone phases is about $1 \mu\text{m}$, the damage zone is observed in the larger area as shown in *Figure 11*(c) and (d). This result shows that the area of the damage zone becomes larger as more fine silicone phases are uniformly dispersed in the epoxy matrix. Wu^{18,19} showed that the deformability of a matrix resin depends on interparticle distance between the surfaces of two nearest neighbouring particles. He suggested that the shear yielding of matrix resin occurs when the interparticle distance decreases below some critical value. It is clear that the interparticle distance decreases with a decrease in the diameter of dispersed rubber phases if the rubber content remains constant. Thus the addition of the aramid-silicone block copolymer should decrease the interparticle distance between two neighbouring silicone particles, and thus induce the shear yielding of the matrix in a larger area near the crack tip. Therefore, it can be concluded that the improvement in the toughness with the addition of aramid-silicone block copolymer is due to the increase in the area of the damage zone caused by the formation of fine silicone phases.

CONCLUSIONS

To improve the toughness of the silicone-modified system, aramid-silicone block copolymers were added as compatibilizers. Thus, we reached the following conclusions:

- (1) The diameter of the silicone phases considerably decreased with the addition of aramid-silicone block copolymers. The block copolymers served as compatibilizers for improving the dispersibility of the silicone oligomer.
- (2) In the system with added block copolymer which acts as a good compatibilizer, it was clearly shown by TEM observations that the silicone dispersed phase is covered with the block copolymer. The balance between the silicone and epoxy contents in pre-reacted block

copolymers is an important factor in the effectiveness of the compatibilizer.

- (3) The toughness of the silicone-modified system increases considerably with the increase in the dispersibility of the silicone rubber. The improvement in the toughness by the addition of the aramid-silicone block copolymer is due to the increase in the area of the damage zone caused by the formation of fine silicone phases.

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