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

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Abstract

To improve the toughness of silicone-modified epoxy resin, aramid–silicone block copolymer was used as a compatibilizer. Fine silicone phases could be uniformly and stably dispersed in epoxy matrix by the addition of the block copolymer grafted with epoxy oligomers. The architecture of the block copolymer, such as the silicone content of the block copolymer and the molecular weight of epoxy and silicone segments, strongly affected the effectiveness of a compatibilizer. The block copolymer that acts as a good compatibilizer was mainly concentrated in an interfacial area around the silicone phase. The thickness of the interphase depended on the architecture of the block copolymer and decreased with an increase in the chain length of the epoxy segment. The values of fracture toughness in the silicone-modified system increased with a decrease in the diameter of the silicone phases. Their maximum value increased to about 2.0 times that of the unmodified system. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Toughening; Silicone elastomer

1. Introduction

Epoxy resin is one of the most important thermosetting polymers. This resin exhibits many desirable properties, such as high thermal stability and excellent electric properties. However, epoxy resin is generally rather brittle, because of its highly crosslinked structure. Improving the toughness of this resin is very important for epoxy technology.

Many efforts have been made to improve the brittleness of the cured epoxy resin. The most successful attempt is the modification with some reactive liquid rubbers, such as CTBN and ATBN [1–5]. However, these rubbers lack heat resistance, and thus the modification with these rubbers leads to a decrease in the thermal stability of the cured epoxy resin over the high-temperature region. In contrast to these rubbers, silicone rubber preserves stable physical properties over a broad range of temperatures. Namely, the modification of epoxy resin with the silicone rubber should produce an improvement in the toughness of the cured resin with no damage in the high-temperature properties. However, if epoxy resin is directly modified with silicone rubber, the silicone is completely separated from the epoxy resin, because silicone rubber lacks compatibility with epoxy resins [6–8]. Therefore, to improve the toughness of the epoxy resin by the modification with silicone rubber, an increase in the dispersibility of silicone into the epoxy matrix is needed. In the previous report [8], we investigated improving the dispersibility of RTV silicone by adding the aramid–silicone block copolymer as a compatibilizer. Thus, it was concluded that the block copolymer acts as a useful compatibilizer for the silicone-modified epoxy system and is mainly concentrated in the interfacial area around the silicone dispersed phases.

In this work, four kinds of aramid–silicone block copolymers in which the molecular weight of the silicone block differed were added in silicone-modified epoxy resins as compatibilizers. The effects of the addition of the aramid–silicone block copolymers on the morphology of the silicone-modified epoxy resins are discussed in detail. Further, the structure of the interfacial area between the silicone phase and epoxy matrix was investigated by observing the distribution of the block copolymer in the modified resin with an electrical microscope technique.

2. Experimental

2.1. Materials

The epoxy resins used in this work were a commercial

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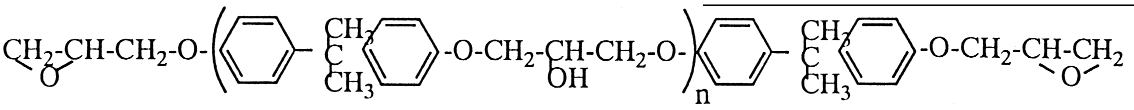
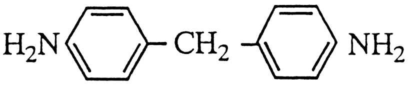
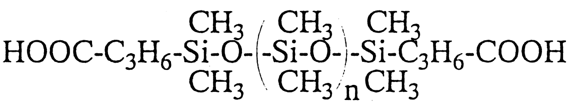
grade of diglycidyl ether of bisphenol-A (Epikoto 828, 1001, 1004, and 1007, $n = 0.1$, 2, 4, and 9, Yuka-shell Epoxy Co.):



The curing agent used was 4,4′-diaminodiphenylmethane:



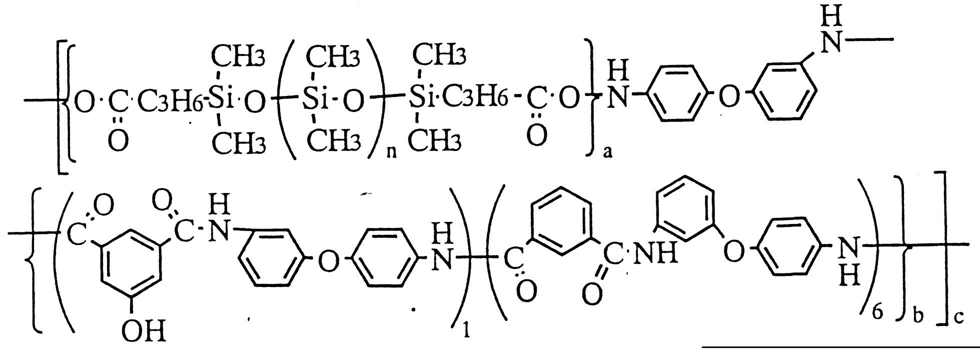
The silicone oligomer used as a rubber modifier was carboxyl-terminated dimethyl siloxane ($M_w = 2600$, Shinetsu Chemical Co., Ltd.):



$$HOOC\text{-}C_3H_6\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\left(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\right)_n\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}C_3H_6\text{-}COOH$$

To improve the compatibility between the epoxy resin and the silicone oligomer, the silicone oligomer was pre-reacted with an epoxy monomer (molecular weight 380).

Four aramid–silicone block copolymers with different molecular weights of the silicone block were used as compatibilizers (M_w = ca. 85 000, Tomoegawa Paper Co. Ltd.):



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

2.2. Curing of epoxy resin

The silicone oligomer was pre-reacted with a large excess of epoxy oligomer (80 g silicone per 100 g epoxy oligomer) at 70°C for 30 h. In this reaction, tetrahydrofuran (THF) and dimethylbenzylamine (DMBA) were used as solvent and catalyst, respectively. In contrast, the aramid–silicone block copolymer was also pre-reacted with an excess amount of epoxy oligomer (6 g block copolymer per 100 g epoxy oligomer) at 80°C for 24 h. In this reaction, *N*,*N*-dimethylformamide (DMF) and DMBA were used as solvent and catalyst, respectively. THF and DMF used as the solvents were then removed by evaporating 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 also the epoxy resin were dissolved into an excess amount of THF in order to prepare the modified epoxy resins. The total content of the silicone was adjusted to about 9 wt.%. The solvent was then removed by evaporating at 80°C for 2 h under reduced pressure (<3 mmHg). After removing the solvent, the stoichiometric amount of pre-melted curing agent was added to the mixture at 130°C. The mixture was then poured into a 4 mm thick glass mold which was pre-heated at 180°C. The materials were cured at 180°C for 5 h.

2.3. Measurements

The morphology of the fracture surfaces was observed by 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 to improve the conductivity and prevent charging. The average diameter, *D*, of the dispersed phase was estimated by applying the pin drop test [9] to the scanning electron microphotographs, assuming that the dispersed phase is spherical in shape and is homogeneously dispersed in a 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

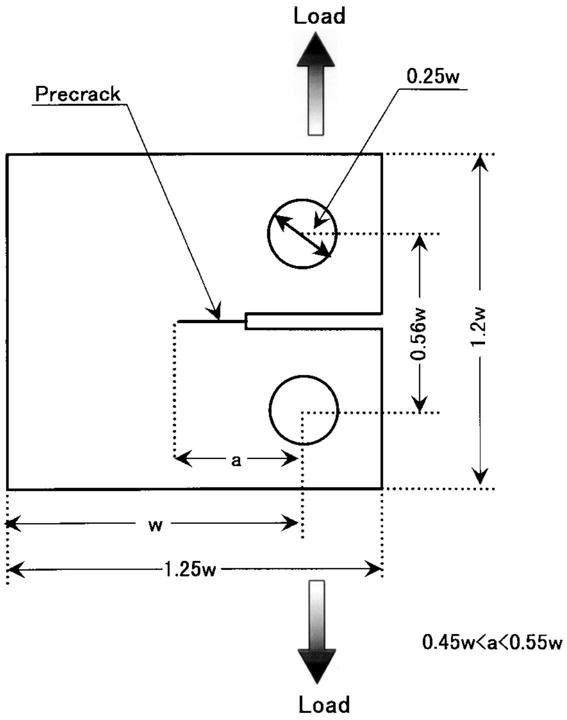


Fig. 1. Shape and geometry of compact-tension specimen.

hit number between the dispersed phases and the test pins, respectively, and L is the length of the test pin.

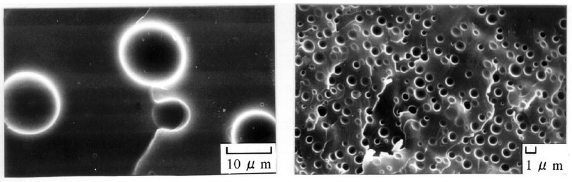
The ultrathin sections of modified epoxy resins were observed using a transmission electron microscope (TEM: JEM-1210, JEOL Co. Ltd.) to study the phase structure and the subsurface damage. The specimens for TEM observations were prepared by an ultramicrotome (REICHERT ULTRACUT E, Leica Co. Ltd.) with a diamond knife. The specimens were stained by osmium tetraoxide (OsO_4). In the staining with a vapor of OsO_4, the block copolymers that are added into the modified system are selectively stained.

The stress intensity factor, K_c, for the initiation of crack growth of the cured epoxy resins was determined from a compact-tension specimen, shown in Fig. 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 with a fresh razor blade [10]. The specimen was mounted in an Instron-type tensile machine (AG-2000E; Shimazu Co. Ltd.) and loaded at a constant crosshead speed (0.5 mm/min). The experiments were conducted at room temperature. The value of the stress intensity factor, K_c, was calculated from

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

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

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



(a) No block copolymer
Particle diameter: 10.2 μ m

(b) Copolymer content: 2.6 wt%
Particle diameter: 2.3 μ m

Fig. 2. SEM of fracture surfaces of epoxy resin modified with silicone: total silicone, 9 wt.%; M_w of epoxy branch, 380; and silicone content in the block copolymer, 20 wt.%.

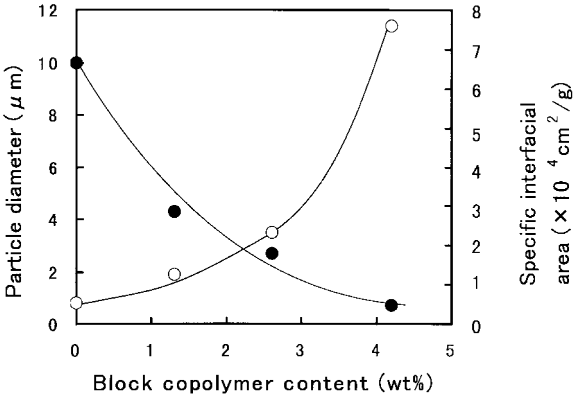
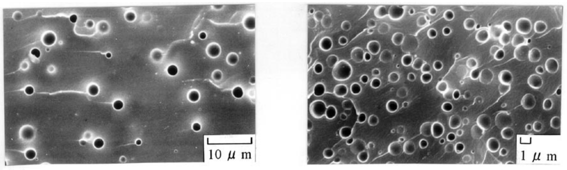


Fig. 3. Relation between the diameter of the silicone phases and block copolymer content. Total silicone: 9 wt.%.

3. Result and discussion

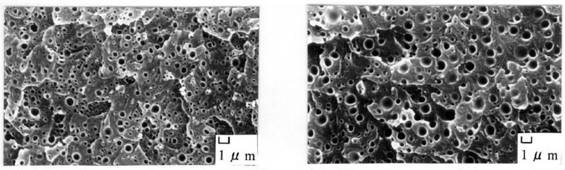
3.1. Morphology of silicone-modified epoxy system with aramid–silicone block copolymer

The changes in the morphology of the silicone-modified epoxy system with the addition of aramid–silicone block copolymers are shown in Fig. 2. In the system without added block copolymer (Fig. 2(a)), it is clearly observed that large silicone phases are dispersed in the epoxy matrix. The average diameter of the dispersed phases was about 10 μm. In previous research works [6,7], we reported that a silicone is completely separated from an epoxy resin if the epoxy resin is directly modified with the silicone. In this work, the silicone oligomer could be dispersed in the epoxy matrix, because the compatibility between the epoxy resin and the silicone oligomer was improved by the pre-reaction described in the previous section. However, for improving the toughness of cured epoxy resins by the modification with silicone elastomer, the average diameter of the dispersed silicone phase must be decreased to sub-micron order [11]. Therefore, in this investigation, aramid–silicone



(a) Mw of epoxy branch: 380
Particle diameter: 1.3 μm

(b) Mw of epoxy branch: 900
Particle diameter: 1.0 μm



(c) Mw of epoxy branch: 1800
Particle diameter: 0.2 μm

(d) Mw of epoxy branch: 3800
Particle diameter: 0.9 μm

Fig. 4. Morphology of modified epoxy resins with added block copolymer: total silicone, 9 wt.%; block copolymer content, 4.2 wt.%; and silicone content in the block copolymer, 20 wt.%.

block copolymers which were pre-reacted with epoxy oligomers ($M_w = 380, 900, 1800, 3800$) were added for dispersing the silicone oligomer as fine particles in the epoxy matrix. Fig. 2(b) shows the morphology of the system with added block copolymer which is pre-reacted with a low molecular weight epoxy resin (Epikote 828; $M_w = 380$). In this system, the silicone oligomer formed well-defined dispersed phases and was uniformly dispersed in the epoxy matrix. The average diameter of the dispersed phases was much smaller compared with that of the system modified only with the silicone oligomer (Fig. 1(a)) and reached less than 1 μm. This photograph shows that the block copolymer pre-reacted with epoxy oligomer should act as a good compatibilizer for the silicone-modified epoxy system. In addition, it is expected that the toughness of the silicone-modified system would increase with the addition of the block copolymer, because the average diameter of the silicone phases is on the submicron order.

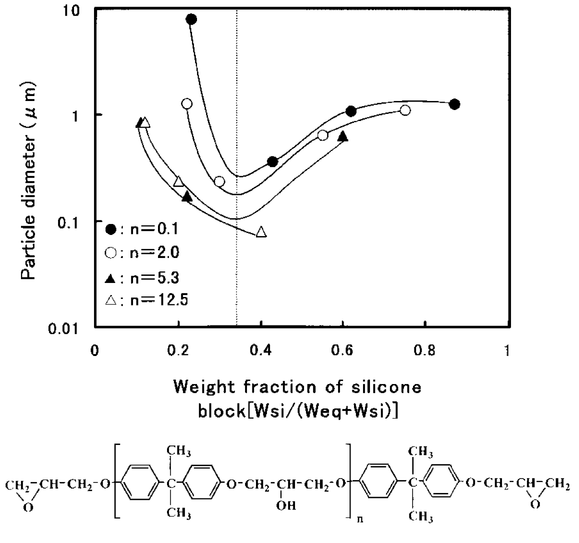
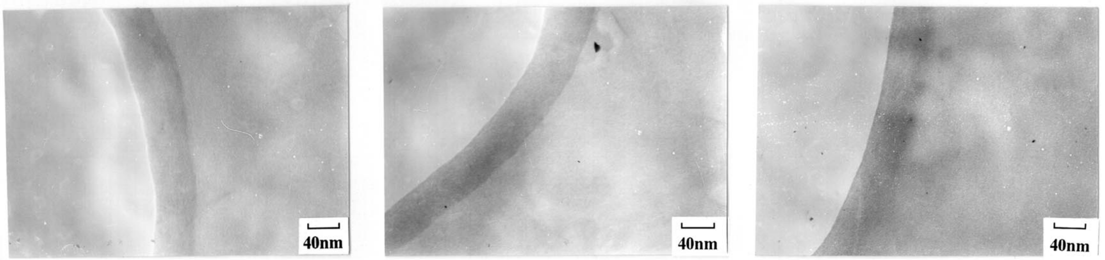


Fig. 5. Relationship between the particle diameter of the dispersed phases and the weight fraction of the block: total silicone, 9 wt.%; and block copolymer content, 4.2 wt.%.

Fig. 3 shows the relationship between the average diameter and specific interfacial area of the dispersed silicone phases and the content of the added block copolymer. The diameter of the dispersed phases decreased in inverse proportion with the amounts of the block copolymer. In contrast, the interfacial area of the dispersed phases increased with an increase in the block copolymer. These results demonstrate that the block copolymer added should stabilize the interface between the silicone dispersed phase and the epoxy matrix, and thus a larger area of the epoxy/silicone interface could exist with the addition of greater amounts of block copolymer. In the previous article [12], it was described that a good compatibilizer for silicone-modified epoxy system could cover the dispersed phases and decrease the free energy of the interfacial area. Also in this work, it is expected that the block copolymer which acts as a good compatibilizer is mainly concentrated in the interfacial area around the silicone dispersed phases and decreases the interfacial free energy of the silicone-modified epoxy system.

Fig. 4 shows the morphology of the silicone-modified systems with added block copolymer which were pre-reacted with four kinds of epoxy oligomer ($M_w = 380$, 900, 1800, and 3800). When the block copolymer was pre-reacted with the epoxy oligomer whose molecular weight was 1800, the finest silicone phases could be uniformly and stably dispersed in the epoxy matrix. If the molecular weight of the epoxy oligomer is more or less than 1800, a larger silicone phase is observed in the silicone-modified systems. This means that the block copolymer that was pre-reacted with the optimum molecular weight of the epoxy oligomer could act as a more effective compatibilizer. From this result, it is expected that the balance between the contents of the silicone block and epoxy oligomer in the pre-reacted block copolymer is an important factor in determining the effectiveness of the block copolymer as a compatibilizer. Lyatskaya et al. [13] showed that the change in copolymer architecture affects the efficiency of a compatibilizer. Our results also show that the architecture of the block copolymer affects the morphology of the silicone-modified epoxy system.

In order to clarify the importance of the balance between the silicone and epoxy contents in the block copolymer, the relationship between the diameter of the silicone-dispersed phases and the weight fraction of the silicone block in the block copolymer pre-reacted with four kinds of epoxy oligomer ($M_w = 380, 900, 1800, 3800$) is shown in Fig. 5. In each system with added block copolymers, the diameter of the silicone-dispersed phase had a minimum value at some optimum point in the weight fraction of the silicone block. The optimum points in each system were observed at the point of



(a) Copolymer content: 1.3 wt%
Thickness of interface: 48.3 nm

(b) Copolymer content: 2.6 wt%
Thickness of interface: 47.1 nm

(c) Copolymer content: 4.2 wt%
Thickness of interface: 47.2 nm

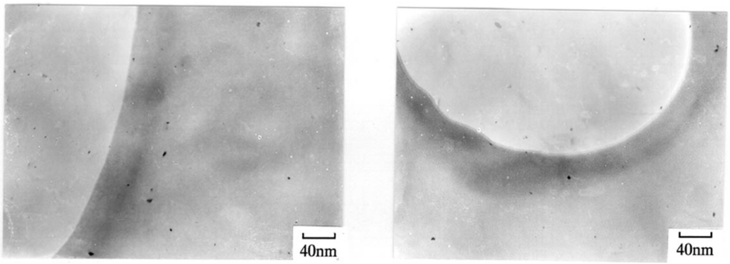
Fig. 6. TEM of the silicone-modified epoxy resin with block copolymer that has a good balance in the affinity for epoxy and silicone phases: total silicone, 9 wt.%; M_w of epoxy branch, 380; and silicone content in the block copolymer, 20 wt.%.

about the same weight fraction, even though the silicone content of the block copolymers and the molecular weight of the epoxy oligomers pre-reacted with the copolymers are completely different. This means that the balance in the weight fraction of the epoxy segment and silicone block in the block copolymer strongly affects the ability of the block copolymer as a compatibilizer. Namely, it is concluded that the balance between the affinity for the epoxy matrix and the silicone dispersed phases is the most important factor for determining the effectiveness of the block copolymer as a compatibilizer.

In addition, the diameter of the silicone phase at the optimum points decrease with an increase in the molecular weight of the epoxy oligomers. This result shows that the block copolymer in which the characters of the silicone block and epoxy segment are more independently observed should act as a more effective compatibilizer.

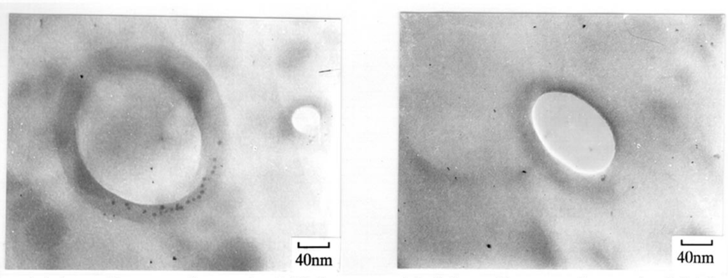
3.2. Interphase composed of block copolymer pre-reacted with epoxy oligomer

In the previous section, we demonstrated that the aramid–silicone block copolymer which has an optimum balance between the affinity for the epoxy matrix and the silicone-dispersed phase acts as a good compatibilizer for the silicone-modified epoxy system. Thus, the silicone-dispersed phase was observed by a transmission electron microscope to confirm the distribution of the block copolymer that has an optimum balance in the modified system. Fig. 6 shows the results of the TEM observation. In these photographs, the block copolymer was selectively stained with OsO_4. In these photographs the area containing the block copolymer is shown as a dark area. In all the systems, the block copolymer that acts as a good compatibilizer is mainly concentrated in the interfacial area, and the interphase containing



(a) Mw of epoxy branch: 380
Thickness of interphase: 47 nm

(b) Mw of epoxy branch: 900
Thickness of interphase: 34 nm



(c) Mw of epoxy branch: 1800
Thickness of interphase: 29 nm

(d) Mw of epoxy branch: 3800
Thickness of interphase: 22 nm

Fig. 7. TEM of the silicone-modified epoxy resin with added block copolymer which has a good balance in the affinity for epoxy and silicone phases: total silicone, 9 wt.%; and silicone content in the block copolymer, 20 wt.%.

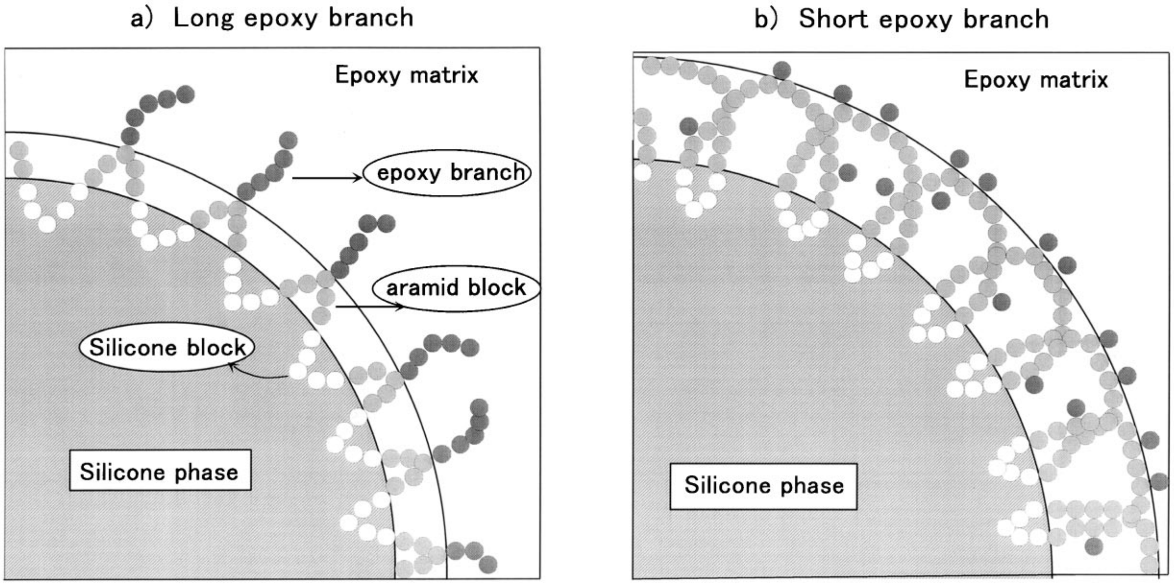


Fig. 8. Schematic models of interphases in the silicone-modified epoxy systems with added block copolymers as compatibilizers.

the high concentration of the block copolymer was clearly observed around the dispersed silicone phase. This means that, in the system with the added block copolymer which has a good balance between the affinity for the epoxy and silicone phases, the silicone phases are covered with the block copolymer and thus their interfacial energy decreases with the addition of the block copolymer. This is the reason why the diameter of the dispersed phase had a minimum value, as shown in Fig. 5, when the effective compatibilizer is added to the silicone-modified system.

In addition, the thickness of the interphase maintained a constant value, if the amount of the block copolymer added was changed. This means that the area of the epoxy/silicone interface which could be covered with the block copolymer increases with an increase in the amount of the block copolymer added; thus the diameter of the silicone phase decreased with the addition of the block copolymer as shown in Fig. 3.

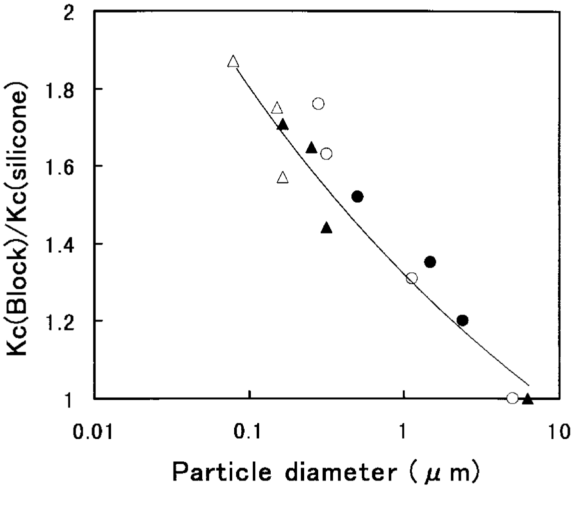


Fig. 9. Relationship between particle diameter of silicone phases and K_c (Block)/K_c (Silicone) in cured epoxy resins modified with silicone. Total silicone, 9 wt.%. M_w of epoxy branch: (●) 380; (○) 900; (▲) 1800; (△) 3800.

Fig. 7 shows the transmission electron micrographs of the silicone-dispersed phases in the systems with the block copolymers having a good balance between the affinity for the epoxy and silicone phases. Also in these photographs, the area containing the block copolymer is shown as a dark area by staining with OsO_4. In all the systems, the interphase containing the high concentration of the block copolymer was clearly observed at the interfacial area. This result also demonstrates that the block copolymer with an optimum affinity is selectively concentrated in the epoxy/silicone interface. The thickness of the interphase decreased with an increase in the molecular weight of the epoxy oligomer which is pre-reacted with block copolymers, therefore, the block copolymer which has longer epoxy branches could cover and thus stabilize the larger area of the silicone/epoxy interface. This is the reason why the diameter of the silicone phase at the optimum points decreased in Fig. 5 with an increase in the molecular weight of the epoxy monomer.

Schematic models of the interphase composed of the block copolymers are shown in Fig. 8. In the system with the added block copolymer that has a long epoxy branch, a long branch could cover the large area of the interface between the silicone phase and the epoxy matrix, and thus the thin interphase should be formed around the silicone phase. In contrast, in the system with the added block copolymer that has a short epoxy branch, a short branch could only cover the narrow interface. Therefore, a large amount of the block copolymer and thus the thick interphase is needed for stabilizing the silicone/epoxy interface.

3.3. Toughening of silicone-modified epoxy system with aramid–silicone block copolymer

As shown in the previous sections, the addition of aramid–silicone block copolymer is effective in improving the dispersibility of the silicone modifier in the epoxy matrix. Therefore, the effects of the improvement in the dispersibility of the silicone on the toughness of the silicone-modified epoxy system were studied. Fig. 9 shows the relationship between fracture toughness and the diameter of the silicone-dispersed phases in the silicone-modified system with added block copolymer. The numbers on the vertical axis show the relative ratio of the fracture toughness in the system with and without the addition of the block copolymer. The increase in the fracture toughness with 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 the added block copolymer increases to over 1.9 times that of the system modified with the silicone oligomer only. This means that the increase in the fracture toughness is due to the improvement in the dispersibility of the silicone rubber with the addition of the block copolymer.

Many investigators have already suggested [1,6–8,14–18] that a toughening mechanism for the rubber-modified epoxy system is the cavitation of the rubber-dispresed phases and the shear deformation of the epoxy matrix near the crack tip. In previous articles [6,8], we suggested that, also in the silicon-modified system, cured epoxy resin is toughened by the same toughening mechanism, if we could significantly improve the dispersibility of the silicone oligomer into the epoxy resin. The results shown in Fig. 9 also support this toughening mechanism.

4. Conclusions

To improve the toughness of the silicone-modified system, aramid–silicone block copolymers were added as compatibilizers. The distribution of the block copolymer in the modified system was investigated by some microscopic techniques. 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 copolymer used acted as a compatibilizer for improving the dispersibility of the silicone oligomer.
2. In the system with the added block copolymer that has a good balance between the affinity for the epoxy matrix and silicone phases, it was clearly shown by the TEM observations that the silicone dispersed phase is covered with the block copolymer.
3. The thickness of the interphase containing the high concentration of the block copolymer decreased with an increase in the molecular weight of the epoxy oligomer pre-reacted with the block copolymer. This result means that the block copolymer in which the characters of the silicone block and epoxy segment are more independently observed should act as a more effective compatibilizer.

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