

Phase structure and toughness of silicone-modified epoxy resin with added silicone graft copolymer

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Abstract

To disperse RTV-silicone elastomer as fine particles in a bisphenol-A-type epoxy resin, silicone-methylmethacrylate graft copolymer was added as a compatibilizer. The molecular weight of the silicone segment and the MMA segment between silicone branches in the graft copolymer strongly affected the effectiveness of compatibilizer. It was revealed that the graft copolymer which acts as a more effective compatibilizer was more highly concentrated at the interface between the silicone-dispersed phase and the epoxy matrix. The interfacial tension around the silicone-dispersed phase decreased with the formation of the interphase which is mainly composed of the graft copolymers. The diameter of the dispersed phase decreased with a decrease in the interfacial tension. The fracture toughness of the modified resins increased with a decrease in the diameter of the silicone phase. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Silicone elastomer; Epoxy resin; Silicone-MMA graft copolymer

1. Introduction

Epoxy resin has excellent mechanical, electrical, and bonding properties. This resin is widely utilized as a high performance thermosetting resin in many industrial fields. However, epoxy resin is usually rather brittle, because of its highly crosslinked structure. The toughening of epoxy resin is therefore an important subject in epoxy technology.

Many efforts have been made to improve the toughness of cured epoxy resin. Modification with liquid-elastomers such as CTBN and ATBN [1–3] has been the most successful attempt to improve the toughness of epoxy resin. In these elastomer-modified systems, the toughness and other mechanical properties are necessarily unstable in low and high temperature regions, because the mechanical properties of these elastomers depend strongly on the ambient temperature.

In contrast to these elastomers, silicone rubber preserves stable physical properties over a broad range of temperature. Namely, the modification of epoxy resin with silicone rubber should improve the mechanical properties over this range. However, if epoxy resin is directly modified with silicone elastomer, the silicone is completely separated from the epoxy resin, because the silicone elastomer has no compatibility with the epoxy resin. Sultan et al. [4]

showed that the fracture toughness of a brittle epoxy could be improved by the incorporation of rubber spheres of approximately 1 μm diameter. Therefore, one needs to increase the dispersibility of the silicone for toughening epoxy resin with silicone elastomer. Previously, we have presented [5,6] that the addition of the silicone-PMMA graft copolymer is effective to stabilize the silicone-epoxy interface and thus silicone is uniformly dispersed in the epoxy matrix.

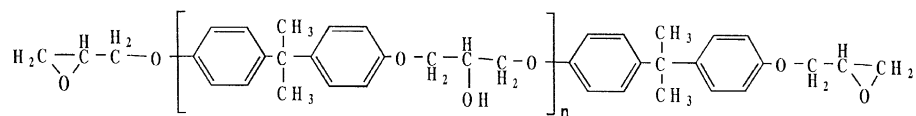
In this work, some types of silicone-PMMA graft copolymers which have different molecular weights to the PMMA and silicone segments are added to improve the dispersibility of the silicone elastomer. We discuss in detail the effects of the chemical structure of the silicone graft-copolymer on the morphology and fracture toughness of the silicone-modified epoxy systems. In addition, the changes in the interfacial tension with the addition of the copolymers are related to the morphology and toughness of the silicone-modified system.

2. Experimental

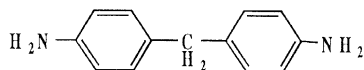
2.1. Materials

The epoxy oligomer used in this work was the diglycidyl ether of bisphenol-A (Epikote 828, Mw:380, Yuka-shell Epoxy Co.).

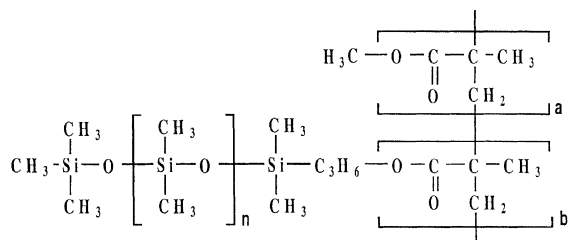
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The curing agent used was 4,4-diaminodiphenylmethane.



The modifier used was Room Temperature Vulcanized (RTV) silicone (KEG 108, Shinetsu Chemical Co., Ltd). Some silicone-PMMA random-graft copolymers in which the molecular weight and contents of the silicone branches were varied were used as compatibilizers.



2.2. Synthesis and characterization of silicone-PMMA graft copolymers

The graft copolymers were prepared by the copolymerization of silicone macromonomers which have different molecular weights (FM711, FM721, Tisso Co., Ltd, X-22-2404, X-22-174DX, Shinetsu Chemical Co., Ltd)

with methylmethacrylate. The copolymerization was carried out at 70°C for 8 h using 0.12 wt% azobis(isobutyronitrile) and MEK as initiator and solvent, respectively, under a nitrogen atmosphere. The graft copolymers were precipitated in methanol and extracted with hexane to remove any unreacted DMS macromonomer.

The characterization of the graft copolymers is shown in Table 1. The molecular weight was determined by gel permeation chromatography (RID-10A, Shinetsu Chemical Co., Ltd). The silicone content in the graft copolymer determined by the H-NMR method was nearly equal to the feed composition. Thus the average molecular weight of the PMMA segments between the silicone branches in the graft copolymer was calculated from the silicone content.

2.3. Curing of epoxy resin

Epoxy resin and silicone-PMMA graft copolymers were completely dissolved in excess THF. The solvent was then removed by evaporating at 80°C for 2 h under reduced pressure (< 3 mmHg). A mixture of RTV silicone and its curing agent was added into the blends of epoxy resin and graft copolymer, adjusting the total content of silicone to about 20 wt%. The compounds were stirred at 80°C for 1 h under the reduced pressure until the RTV silicone was completely dispersed in the system. The stoichiometric amount

Table 1
Characterization of graft copolymer

| Sample | Mw of DMS, | Feed composition (weight ratio) | Mw ^a | Silicone content ^b (weight%) | Mw of MMA segment between side chains ^c |
|--------|------------|------------------------------------|-----------------|--|---|
| 1 | 420 | DMS/MMA = 1/4 | 63 000 | 18.0 | 1920 |
| 2 | 420 | DMS/MMA = 1/10 | 28 000 | 9.4 | 4050 |
| 3 | 420 | DMS/MMA = 1/24 | 30 000 | 3.4 | 11 800 |
| 4 | 420 | DMS/MMA = 1/48 | 44 000 | 1.2 | 34 100 |
| 5 | 1000 | DMS/MMA = 1/4 | 29 000 | 22.7 | 3400 |
| 6 | 1000 | DMS/MMA = 1/10 | 42 000 | 7.9 | 11 600 |
| 7 | 1000 | DMS/MMA = 1/20 | 32 000 | 5.4 | 17 600 |
| 8 | 1000 | DMS/MMA = 1/30 | 68 000 | 3.0 | 32 000 |
| 9 | 1000 | DMS/MMA = 1/40 | 78 000 | 2.9 | 32 900 |
| 10 | 2000 | DMS/MMA = 1/10 | 21 000 | 8.8 | 21 700 |
| 11 | 2000 | DMS/MMA = 1/15 | 66 000 | 7.2 | 25 800 |
| 12 | 2000 | DMS/MMA = 1/20 | 55 000 | 5.0 | 38 100 |
| 13 | 5000 | DMS/MMA = 2/3 | 22 000 | 50.4 | 4920 |
| 14 | 5000 | DMS/MMA = 1/2 | 26 000 | 38.7 | 7900 |
| 15 | 5000 | DMS/MMA = 1/4 | 42 000 | 20.1 | 19 800 |
| 16 | 5000 | DMS/MMA = 1/6 | 35 000 | 16.0 | 26 200 |
| 17 | 5000 | DMS/MMA = 1/9 | 20 000 | 11.3 | 39 400 |

^a Determined by GPC method calibrated with standard polystyrene using an RI detector in THF.

^b Determined by ¹H NMR method in chloroform-*d*.

^c Calculated from silicone content.

of pre-melted curing agent was then added to the compounds at 130°C. The compounds were poured into glass molds which were coated with a thin film of a release agent (tetrafluoroethylene oligomer: Frekote 44, Frekote, Inc.) and cured at 80°C for 2 h followed by 180°C for 4 h.

2.4. Measurements

The fracture toughness of cured epoxy resins was evaluated from the critical value K_c of the stress intensity factor for the initiation of crack growth, which was determined from the compact tension specimen according to ASTM E 399–81. The thickness of the specimens was adjusted to between 3.6 and 4.0 mm. A sharp pre-crack was formed by carefully tapping with a fresh razor blade. The specimen was mounted in an Instron-type tensile machine and loaded at a constant crosshead speed (0.5 mm/min). The value of the stress intensity factor, K_c , was calculated from the equation:

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

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

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

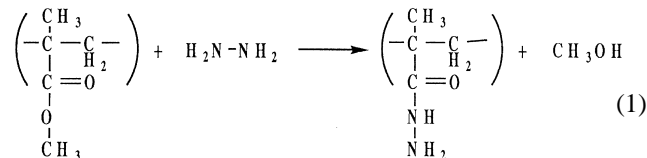
The impact strength of the cured epoxy resin was measured according to DIN–53453. The shape of the specimen was a small rectangular block with dimensions of 15 × 10 × 2 mm.

The morphology of the fracture surfaces was observed using a scanning electron microscope (SEM: JSM–6500, JEOL Co., Ltd). Prior to the examination, the surfaces were coated with a thin layer of gold in order to improve the conductivity and prevent charging. The average diameter D of the dispersed phase was estimated by applying the pin drop test [7] 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 was calculated from the following equation;

$$D = 3Lh/2P$$

where P and h are the total number of intersections, the hit number between the dispersed phases and the test pins, respectively, and L is the length of the test pin. In addition, ultra-thin sections of the modified epoxy resins were observed using a transmission electron microscope (TEM: JSM–1210, JEOL Co., Ltd) to study the phase structure. The specimens for the TEM observations were prepared using an ultramicrotome (REICHERT ULTRA CUT E, Leica Co., Ltd) with a diamond knife. The specimens were stained by osmium tetroxide (OsO_4) [8]. In the staining with OsO_4 , the graft copolymer which is added in the

modified system as a compatibilizer is selectively stained. The specimen was soaked in an aq. hydrazine solution at 80°C for 96 h, and thus the methacrylate groups of the graft copolymer were converted to acrylic acid hydrazide groups as shown in Eq. (1). The hydrazide group was then stained by osmium tetroxide OsO_4 .



Interfacial tension (γ_{SL}) was determined from contact angles (θ) of the graft copolymer against the silicone rubber and epoxy resin, using Young's equation.

$$\gamma_{\text{SV}} = \gamma_{\text{SL}} + \gamma_{\text{LV}} \cos \theta$$

The contact angles of the graft copolymer on the slide glass coated with the silicone or epoxy resin were measured by a goniometer (ELMA Co., Ltd). All experiments for measuring the contact angles were carried out at 25°C ($\pm 2^\circ\text{C}$). The surface tension of the silicone oil and epoxy resin (γ_{LV}) was measured by the ring method using the Du Nouy surface and interfacial tension measuring machine (Shimazu Co., Ltd). The surface tension of the graft copolymer (γ_{SV}) was measured by Maeda's method [9]. Details of these tests can be found elsewhere [9,10].

3. Results and discussion

3.1. Morphology of RTV silicone-modified epoxy system with silicone-PMMA graft copolymer

The morphology of the silicone-modified systems with the added graft copolymers which have different molecular weights of the silicone branches are shown in Fig. 1. The size of the silicone phase in the systems with the added copolymers of which the molecular weight of DMS branches are 420, 1000 and 5000 are about 18, 1, and 2 μm , respectively. This means that the ability of the graft copolymer as a compatibilizer should depend on the molecular weight of the DMS segment, and the copolymer (B) which has an optimum molecular weight of the DMS segment is a more effective compatibilizer for a silicone-modified epoxy system, compared with copolymers (A) and (C) which have a too low or too high molecular weight in the DMS branches. Balazs et al. [11,12] showed that the change in copolymer architecture affects the efficiency of a compatibilizer. These photographs also show that the architecture of the branched copolymer affects the morphology of the silicone-modified system.

The effect of the molecular weight of the MMA segment between the silicone branches in the graft-copolymer on the morphology of the silicone-modified epoxy system is shown

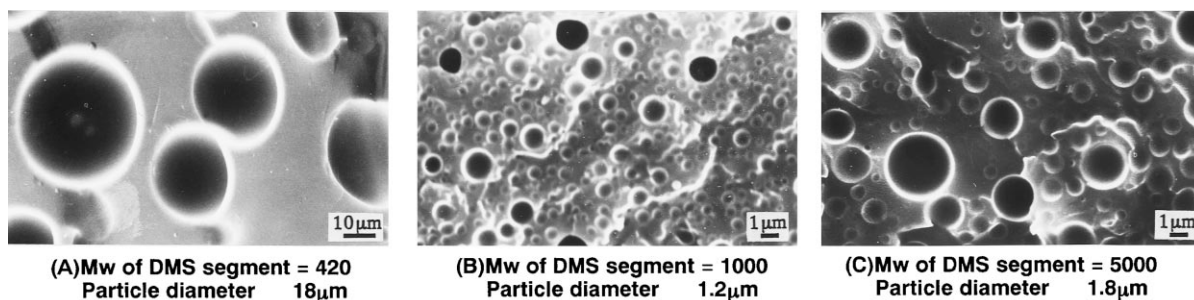


Fig. 1. SEM of fracture surface of epoxy resin modified with RTV silicone. Total silicone; 20 wt%. Graft copolymer content; 1 wt%. Molecular weight of MMA segment between side chains; 10 000.

in Fig. 2. The size of the silicone phase in the system with the added graft copolymer in which the molecular weight of the MMA segment is about 10 000 showed a minimum value. This means that the ability of the graft copolymer as a compatibilizer should also depend on the molecular weight of the MMA segment between the silicone branches. The silicone-PMMA graft copolymers which have a too low or too high molecular weight of the MMA segments between the silicone branches are unsuitable for the compatibilizer.

In order to clarify the importance of the architecture of the graft copolymer in the dispersibility of the silicone elastomer, the relation between the diameter of the silicone-dispersed phases and the molecular weight of the MMA segment between silicone branches is shown in Fig. 3. The diameter of the silicone-dispersed phases had a minimum value at some optimum molecular weight of MMA in all modified systems. In addition, the optimum points in each of the systems are shifted to a high molecular weight of MMA with an increase in the molecular weight of the silicone segments. This shows that the ability of the graft copolymers as a compatibilizer depends on their architecture and the relative ratio of the molecular weight of the MMA segment and the DMS segment in the graft copolymer is the most important factor for determining the dispersibility of the silicone modifier in the graft copolymer-added systems. In addition, the diameter of the silicone-dispersed phase decreased with the molecular weight of the MMA and DMS segments. This means that it should be better for increasing the dispersibility of the

silicone to add a graft copolymer which has more independent silicone and MMA segments.

The silicone-dispersed phase was observed by the transmission electron microscope to confirm the distribution of the graft copolymer in the system with the added graft copolymer. Fig. 4 shows the results of the TEM observation. In these photographs, the graft copolymer was selectively stained with osmium tetroxide. Thus, the area containing the graft copolymer is shown as a dark area. In these photographs, the graft copolymer added in the silicone-modified systems is mainly concentrated in the interfacial area around the silicone phase. This shows that the silicone-dispersed phase is covered with the graft copolymer and thus is dispersed stably in the epoxy resin as fine particles. It is considered from these results that the free energy of the epoxy/silicone interface decreases when the interface is covered with the graft copolymer and thus the large area of the interface could stably exist in the modified system. However, in the system with the added graft copolymer which has a low molecular weight of the MMA segment, a part of the graft copolymer was dissolved in the silicone phase (Fig. 4). This result shows that the graft copolymer which has a high relative ratio of $M_w(\text{DMS})/M_w(\text{MMA})$ has good affinity for the silicone phase. On the other hand, the graft copolymer which has a high molecular weight of the MMA segment is slightly dissolved in the epoxy matrix, because the graft copolymer which has a low relative ratio of $M_w(\text{DMS})/M_w(\text{MMA})$ has a high affinity for the epoxy matrix (Fig. 4). When the graft copolymer which has a good balance between the molecular weight of the MMA and

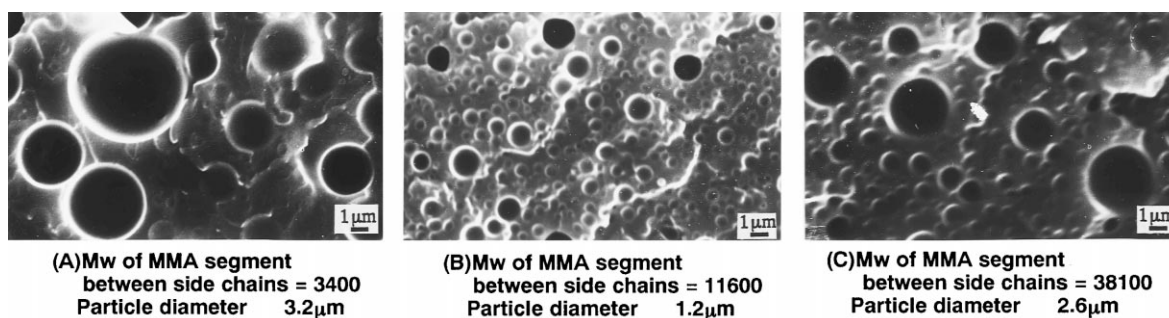


Fig. 2. SEM of fracture surface of epoxy resin modified with RTV silicone. Total silicone; 20 wt%. Graft copolymer content; 1 wt%. Molecular weight of DMS segment; 1000.

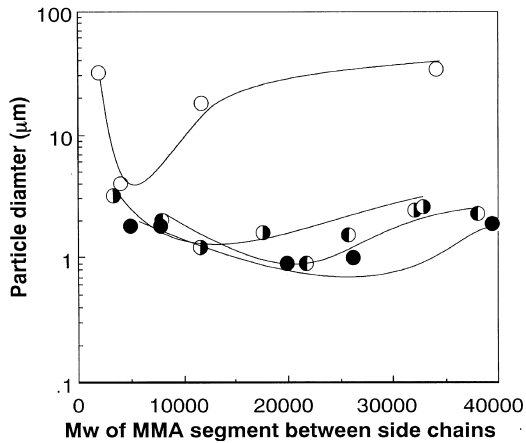


Fig. 3. Relation between particle diameter of silicone phases and molecular weight of MMA segment between side chains. Total silicone; 20 wt%. Graft copolymer content; 1 wt%. Molecular weight of DMS segment (○) 420, (◐) 1000, (◑) 2000, (●) 5000.

DMS segments is added to the silicone-modified systems, the graft copolymer is mainly concentrated in the interfacial area around the silicone dispersed-phases.

These results mean that the graft copolymer which has a good balance in the ratio of Mw(DMS)/Mw(MMA) is more effectively concentrated at the interface between the silicone and epoxy phases and thus could stabilize a larger area of the silicone-dispersed phase.

3.2. Reduction of interfacial tension in silicone/epoxy blends by the addition of silicone graft copolymer

Interfacial tension is an important parameter characterizing the interface in immiscible polymer blend systems. The schematic model of the relationship between the morphology and interfacial tension in the silicone-modified epoxy system with the added graft copolymer is shown in Fig. 5. In the case of epoxy matrix systems, four morphologies are predicted depending on the balance between interfacial tensions [13,14]. Here, E, S, and G

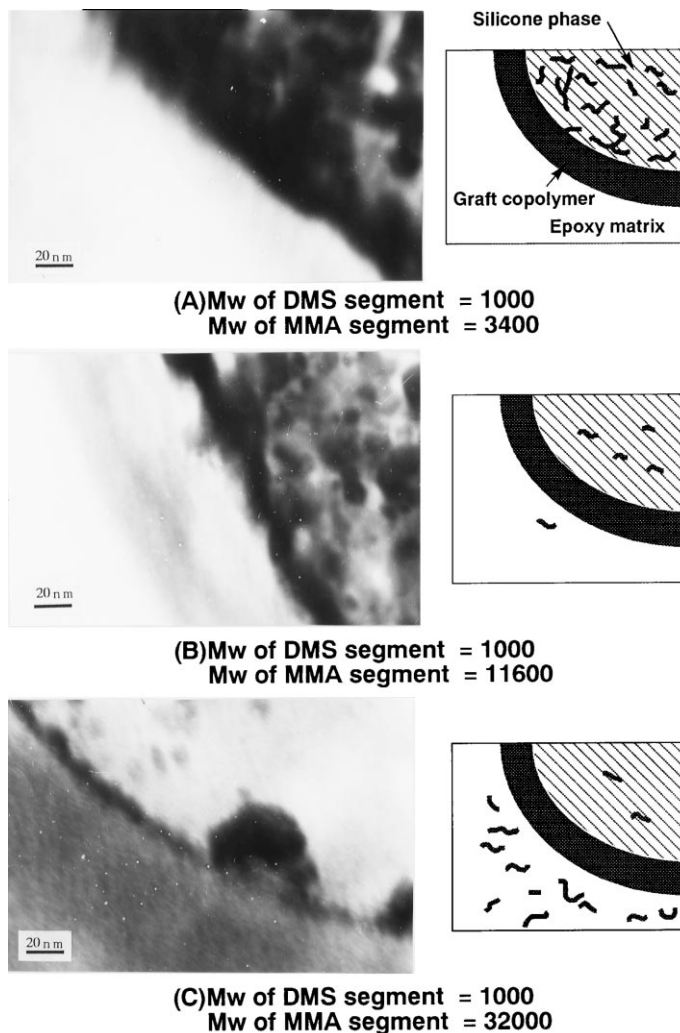


Fig. 4. TEM of epoxy resin modified with RTV silicone. Total silicone; 20 wt%. Graft copolymer content; 1 wt%.

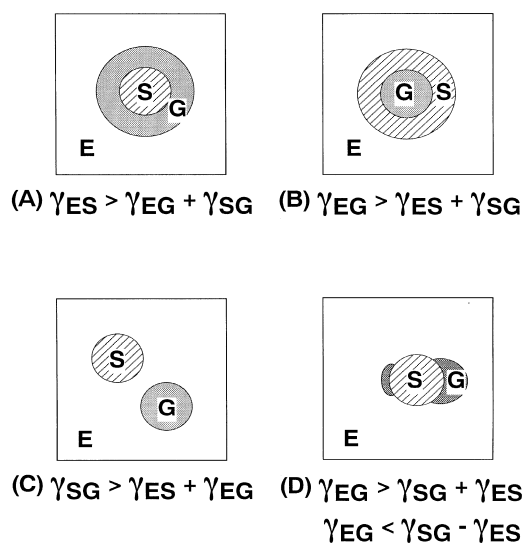


Fig. 5. Morphology models of three-component polymer blends.

mean epoxy resin, silicone oil, and graft copolymer, respectively, and γ_{ij} is the interfacial tension between components i and j

When γ_{ES} is larger than the total of γ_{EG} and γ_{GS} , the silicone-dispersed phase should be covered with a layer of graft copolymer (Fig. 5a). When γ_{EG} or γ_{SG} are larger than the total of the other two interfacial tensions, the graft copolymer should be dissolved in the silicone-dispersed phase or should form separate dispersed phases in the epoxy matrix, respectively (Fig. 5b and c). Under the other conditions, dispersed phases composed of graft copolymer and silicone oil adhered together (Fig. 5d). As shown in the previous section, the silicone-MMA graft copolymer is mainly concentrated in the interfacial area around the silicone-dispersed phase, thus, it is predicted in this work that the addition of the graft copolymer reduces the interfacial tension of the silicone-modified epoxy system and the interfacial tension depends strongly on the architecture of the graft copolymer.

In order to evaluate the changes in the interfacial tension with the addition of the graft copolymer, γ_{EG} and γ_{SG} were determined from the contact angles between the graft copolymer and the silicone oil or epoxy resin. To measure the contact angle between the silicone and epoxy resin, a low viscosity silicone oil was used instead of the RTV-silicone. The values of γ_{EG} , and γ_{SG} in the system with the added graft copolymer are shown in Table 2. In all modified systems, γ_{EG} decreased and γ_{SG} increased with an increase in the molecular weight of the MMA segment between the silicone branches. This means that the graft copolymers which have a high molecular weight for the MMA segments have a good affinity for the epoxy matrix. Moreover, the values of γ_{SG} decreased with an increase in the molecular weight of the silicone branches. This is reasonable, because the affinity of the graft copolymer for silicone should increase as the length of the silicone branches increases.

Table 2

The calculated values of interfacial tension

| Mw of DMS segment | Mw of MMA segment between side chains | Interfacial tension (10^{-3} N/m) | |
|-------------------|---------------------------------------|--------------------------------------|---------------|
| | | γ_{EG} | γ_{SG} |
| 420 | 1920 | 6.2 | 1.2 |
| | 4050 | 1.7 | 2.2 |
| | 11 800 | 1.0 | 4.2 |
| 1000 | 34 100 | 1.3 | 4.7 |
| | 3400 | 2.7 | 0.6 |
| | 11 600 | 0.7 | 1.3 |
| | 32 000 | 0.8 | 2.3 |

As shown in Fig. 5, it was predicted in the silicone-modified system with the added graft copolymer that the value of γ_{ES} is larger than the total of γ_{EG} and γ_{SG} . To confirm this prediction, The values of $\gamma_{EG} + \gamma_{SG}$ in the system with the added graft copolymer are plotted against the molecular weight of the MMA segment between chains in Fig. 6. In this figure, the dashed line shows the value of γ_{ES} in the system with no added graft copolymer. In all systems, the total of γ_{EG} and γ_{SG} was smaller than the value of γ_{ES} . This result is consistent with the TEM observations (Fig. 4) in which the silicone-dispersed phase is covered with a layer of the graft copolymer. Namely, the graft copolymer which is added to the silicone-modified system decreases the interfacial tension between the silicone modifier and the epoxy matrix and thus stabilized the silicone-dispersed phases in the epoxy matrix. In addition, the sum of γ_{EG} and γ_{SG} was a minimum value at some optimum molecular weight of the MMA segment in each of the systems. This means that the graft copolymer which has an optimum segment structure has good affinity for both the epoxy matrix and the silicone-dispersed phases and thus reduces the interfacial tension more effectively.

Compared with the results of Fig. 3, it is clear that the diameter of the silicone phases has a minimum value at the point where the total of γ_{EG} and γ_{SG} has a minimum value. This result shows that the size of the silicone-dispersed phase depends strongly on the interfacial tension in the modified systems. Fig. 7 shows the relation between the diameter of the silicone-dispersed phase and the interfacial tension which is the total of γ_{EG} and γ_{SG} . The diameter of the silicone-dispersed phase decreased with a decrease in the interfacial tension of the epoxy-silicone interface ($\gamma_{EG} + \gamma_{SG}$) and is independent of the architecture of the graft copolymers. This means that the addition of the graft copolymer decreases the interfacial tension and thus a large area of the interface could exist stably in the modified systems.

3.3. Toughening of silicone-modified epoxy system with silicone graft copolymer

The relation between fracture toughness and the diameter of silicone-dispersed phases in the silicone-modified system

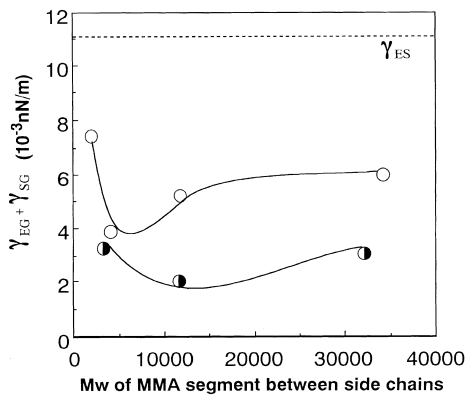


Fig. 6. Relation between molecular weight of MMA segment between side chains and interfacial tension which is the sum of γ_{EG} and γ_{SG} . Molecular weight of DMS segment; (○) 420, (●) 1000.

is shown in Fig. 8. The fracture toughness of the silicone-modified system with the added graft copolymer increased with a decrease in the diameter of the silicone phase. 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 graft copolymer. It is well known that the toughness of elastomer-modified epoxy systems increases with a decrease in the diameter of the elastomer-dispersed phase. Kunz-Douglas et al. [15] have reported that large (40 μm) particles are not efficient in providing an increase in fracture toughness compared with that of smaller (1 μm) particles. Pearson and Yeel [16] showed that small particles provide an increase in the toughness of the CTBN-modified system.

Pearson and Yee [17] also showed that the improvement in the toughness of the CTBN-modified system is due to the cavitation of the rubber-dispersed phase followed by the shear deformation of the epoxy matrix. Wu et al. [18,19] suggested that such a toughening effect depends on the thickness of the matrix between the rubber particles in the rubber-modified polyamide. We also suggest that the

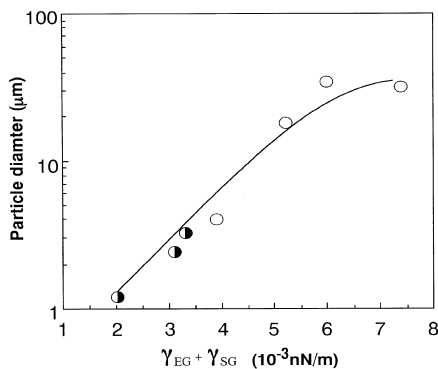


Fig. 7. Relation between interfacial tension which is the sum of γ_{EG} and γ_{SG} and particle diameter of the silicone phase. Molecular weight of DMS segment (○) 420, (●) 1000.

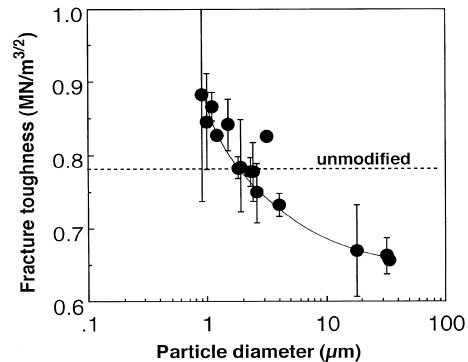


Fig. 8. Relation between particle diameter and fracture toughness of cured epoxy resins modified with RTV silicone. Total silicone; 20 wt%. Graft copolymer content 1 wt%.

toughness of the CTBN-modified epoxy system increases with a decrease in the diameter of the CTBN phase because of the increase in the area of the damage zone near the crack tip [20].

In the silicone-modified system of this report, the stress whitening area increased with a decrease in the diameter of the silicone phase. In the damage zone, the cavitated rubber phases were observed using a transmission electron microscope. These results suggested that the toughening mechanism of the silicone-modified system is the cavitation of the dispersed phase following by shear deformation of the epoxy matrix [5,6].

Fig. 9 shows the relation between the impact strength and the diameter of the silicone-dispersed phase in the modified system. The impact strength also increased with a decrease in the diameter of the dispersed phase. In the region where the diameter of the silicone phase is less than about 1 μm , the impact strength of the modified system became higher than that of the unmodified system. This result also shows that the toughness of the silicone-modified system is considerably increased by the addition of the graft copolymer as a compatibilizer.

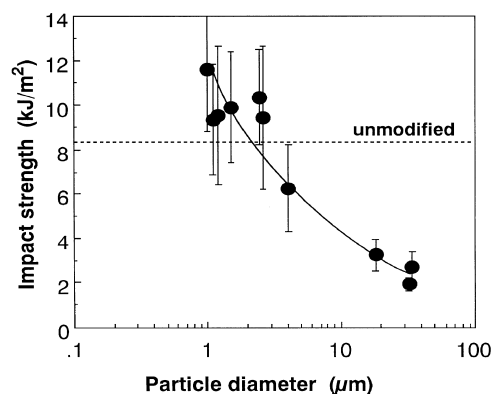


Fig. 9. Relation between particle diameter and impact strength of cured epoxy resins modified with RTV silicone. Total silicone; 20 wt%. Graft copolymer content; 1 wt%.

4. Conclusions

To improve the toughness of the silicone-modified systems, a silicone/PMMA graft copolymer was added as a compatibilizer. The effects of the chemical structure of the graft copolymer on the morphology and fracture toughness of these systems were investigated in detail. The following conclusions were reached:

1. We can uniformly disperse fine silicone particles in the epoxy matrix by the addition of the silicone/PMMA graft copolymer. The graft copolymer acts as an effective compatibilizer for the epoxy/silicone blend system. The efficiency of the compatibilizer was influenced by the molecular weight of the silicone segment and the MMA segment between silicone branches in the graft copolymer.
2. The morphology of the silicone/epoxy blend is dependent on the interfacial tension between the silicone phase and the epoxy matrix. The size of the silicone-dispersed phase in these blends decreased with a decrease in the interfacial tension with the addition of the silicone/PMMA graft copolymer.

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