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Thermal shock resistance of hybrid particulate-filled epoxy composites with hard and soft fillers

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Abstract—For improvement in toughness of epoxy casting materials, the technology of filling the epoxy with hard and soft particles is effective. In this study, thermal shock tests were carried out for a hybrid composite system that consisted of silica particulate as hard filler, methacrylate–butadiene–styrene rubber as soft filler and matrix of epoxy resin. The testing method was established by the authors, and the thermal shock resistance of materials could be evaluated by using a disc-type specimen with a sharp notch. Fracture toughness of the hybrid composite materials improved remarkably by using both silica and MBS filler. However, the contribution of particle filling effect to thermal shock resistance was relatively small. These results were mainly due to debonding of silica filler/matrix resin interface.

Keywords: Thermal shock; epoxy resin; hybrid filler; fracture toughness; particulate-filled composite; thermal shock test; silica filler; MBS rubber.

1. INTRODUCTION

Epoxy resin has many useful properties for electric insulating materials, such as good insulation resistance, adhesive property, and moldability. Hence, epoxy resin based materials are widely used for the encapsulation of electrodes or other electric and electronic devices. Unfortunately, epoxy casting materials usually show low cracking resistance. Therefore, second phase materials are added to the resin for improvement in toughness. The second phase materials often consist of either a hard inorganic filler [1] or a soft rubbery material [2]. The hard

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particulate shows a branching-off effect and pinning effect on crack propagation, which improves fracture toughness. This type of filler also reduces residual stress due to decrease of thermal expansion. On the other hand, soft particulate promotes the deformation of matrix resin and the fracture toughness increases because of the energy consumption of matrix deformation. Since these toughening mechanisms are effective individually, new composites such as hybrid particulate-filled epoxy resins have been reported as highly toughened insulating materials [3, 4]. For these composites, in which both hard and soft particles are filled, a large improvement in toughness can be expected.

In application of these epoxy based composites in electric and electronic fields, high resistance to the thermal shock is required to guarantee high reliability. Thermal shock failure is a complex phenomenon because it is affected by many factors, such as the geometry of the material, thermal and mechanical properties, and so forth.

We have already proposed a new test method to evaluate the thermal shock resistance of the epoxy resins and particulate filled resins [5–9]. The thermal shock test is easily conducted in the laboratory, and the thermal shock resistance is evaluated analytically based on linear fracture mechanics. In our previous studies, the thermal shock resistance of hard particulate filled resin and soft second phase filled resin were reported. Both types of toughened resins showed improvement in thermal shock resistance.

In this study, the effect of hybrid filler on thermal shock resistance using silica particulate as a hard filler and MBS rubber particulate as a soft filler was examined.

2. EXPERIMENTAL

2.1. Materials

The thermal shock test was conducted for neat resin, silica filled composite, rubber filled composite, and silica and rubber hybrid type composites. The neat resin or the matrix resin of the other composites was bisphenol-type epoxy (epoxy equiv. wt. = 0.18–0.20 kg) cured with acid anhydride hardener. The hard filler was fused silica which was angular-shaped particulate without any surface treatment, and the average diameter of the filler was about 13 μm. The Methacrylate–Butadiene–Styrene (MBS) rubber was used as soft filler material. This filler consisted of under micron-size particles, which made about 100 μm size cluster.

Two series of mono-filler composites and two series of hybrid-filler composites were used. The silica filler content was varied from 0 to 300 phr (0 to 0.43 of volume fraction), and the MBS filler content was varied from 0 to 15 phr (0 to 0.082 of volume fraction), respectively. The term phr means ‘parts (by weight) per hundred resin’. The content of hard filler and soft filler in hybrid filler composites were also changed as shown in Table 1.

Table 1.
Composition of tested materials. Open symbols represent the combination of silica and MBS filler tested in this study. Closed circles denote hybrid composites

MBS rubber	Silica filler (phr)					
filler (phr)	0	100	200	250	300	320
0	○	○	○		○	
5	○		●			
10	○	●	●	●	●	●
15	○		●			

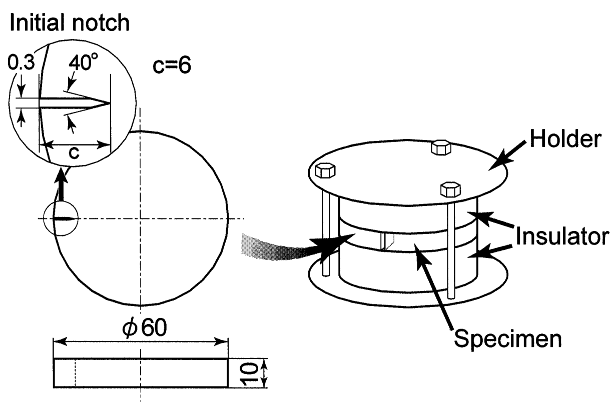


Figure 1. The size and shape of thermal shock test specimen.

2.2. Thermal shock test method

In this test, a pre-notched disk shaped specimen was checked to see whether a crack was initiated or not from the tip of the notch after thermal shock. The test specimen of 60 mm diameter and 10 mm thickness disk has a radial direction pre-notch of 6 mm length as shown in Fig. 1. This specimen held between two heat insulators was put into the cooling bath, which consisted of dry ice and pentane coolant system (about -70°C). Then, thermal stress for mode-I fracture induced at the tip of the pre-notch, because the disk was cooled from the cylindrical surface to the center along the radius. The temperature difference, ΔT was controlled by changing the initial temperature of the specimen, and the thermal chock resistance was evaluated quantitatively as the minimum temperature difference ΔT_c at which initial notch propagated.

2.3. Morphological study

Fracture toughness was measured by three-point bending with single edge notched (SEN) specimen and was calculated according to the ASTM E-399. The notches of specimens were made by a similar method to that for the thermal shock specimens. The fracture surfaces of the thermal shock test and the fracture toughness test were observed with a scanning electron microscope (SEM) equipped with back scattering image (BEI) detector, which could easily distinguish inorganic filler from matrix resin.

3. RESULTS AND DISCUSSION

3.1. Mono-filler composites

The silica filled composite and rubber filled composite increased both fracture toughness and thermal shock resistance in comparison with neat resin. Figure 2 shows thermal shock test results on (a) silica and (b) MBS filled resin, respectively. In these figures the open circle denotes that the crack propagated and the solid circle shows that the crack did not propagate. The critical temperature difference, which corresponds to the minimum temperature difference to initiate the crack, clearly increases with silica and MBS filler content, as shown in Fig. 2a and b. Thus, the value of thermal shock resistance ΔT_c is evaluated at the boundary of open and solid symbols. In Fig. 2b, a solid triangle denotes that the crack propagation does not occur but the notch deformed obviously due to plastic deformation. In our study, the degree of thermal shock ΔT is defined as the difference between the temperature of specimen in oven and the temperature of the cooling bath (dry ice/pentane). If severe thermal shock is required, the specimen should be put into high temperature oven. Thus, when the temperature at the crack tip equals (or is greater than) the glass transition temperature of the tested materials, the initial notch largely opens by plastic deformation and the crack does not propagate.

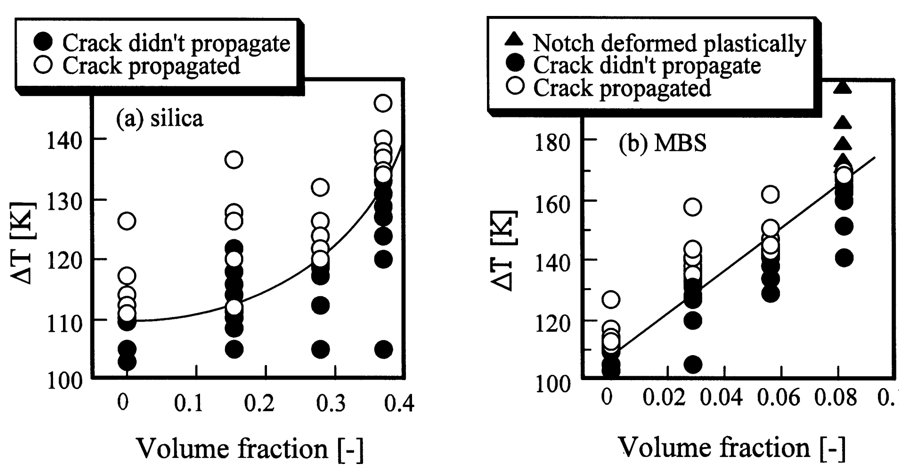


Figure 2. Effect of filler content on thermal shock resistance.

3.2. Hybrid-filler composites

Figures 3 and 4 indicate the results of fracture toughness test and thermal shock test for hybrid-filler composites. The value of thermal shock resistance is the boundary of the open and solid circle and the fracture toughness is shown as the open triangle mark.

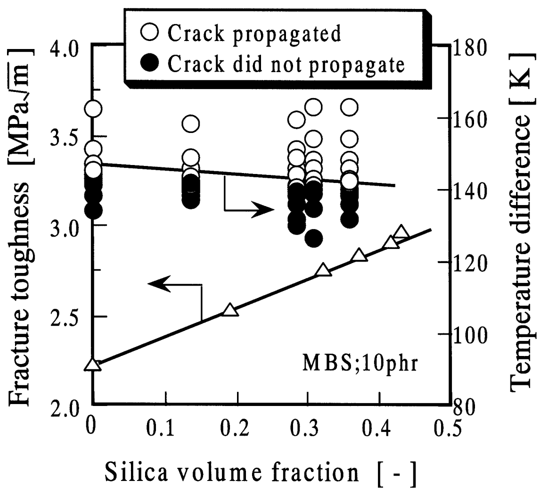


Figure 3. Effect of silica filler content on fracture toughness and thermal shock resistance of hybrid composite (rubber: MBS 10 phr).

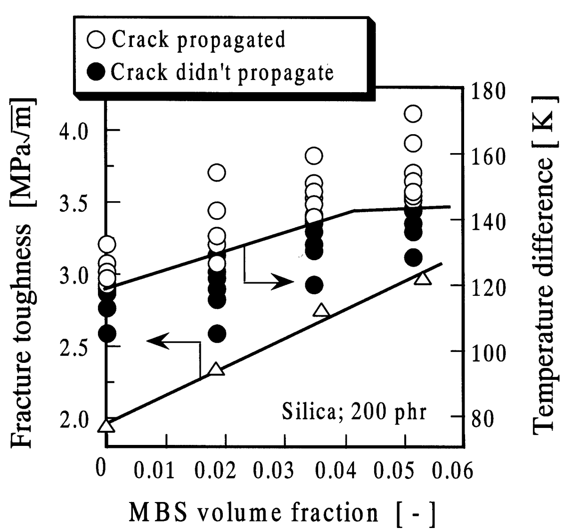


Figure 4. Effect of MBS rubber filler content on fracture toughness and thermal shock resistance of hybrid composite (silica: 200 phr).

In Fig. 3, MBS rubber content is fixed at 10 phr and silica filler content is varied. Fracture toughness of the hybrid composite is clearly improved by filling silica particulate. However, thermal shock resistance gradually decreases with increasing silica filler content.

In Fig. 4, silica filler content is fixed at 200 phr and MBS rubber content is varied. The increase of MBS rubber content also contributes to the improvement in fracture toughness. On the other hand, thermal shock resistance increases with increasing MBS rubber content. However, the effect of filling rubber particle is small at high rubber content.

3.3. Evaluation of thermal shock resistance based on fracture mechanics and fractography

To discuss the effect of filler content on thermal shock resistance, the stress intensity factor induced by thermal stress was evaluated with some thermal and mechanical properties. Based on our previous study [5, 9], the thermal shock resistance ΔT_c is expressed as;

$$\Delta T_c = \frac{(1-\nu)\cdot K_{IC}}{\alpha \cdot E} \cdot \frac{C_1}{\sqrt{R}} + \frac{k\cdot(1-\nu)\cdot K_{IC}}{\alpha \cdot E} \cdot \frac{C_2}{h\cdot\sqrt{R^3}}, \qquad (1)$$

where α is coefficient of thermal expansion, E is elastic modulus, K_{IC} is fracture toughness, ν is Poisson's ratio, k is thermal conductivity, h is heat transfer coefficient, R is the radius of the disk specimen and C_1, C_2 are constants determined by the condition of the thermal shock test, respectively. The coefficients of thermal shock resistance, i.e. the fraction $(1-\nu)K_{IC}/\alpha E$ in the first term and the fraction $k(1-\nu)K_{IC}/\alpha E$ in the second term, are measured experimentally and are shown in Fig. 5. Because h and R are constant under the same experimental conditions,

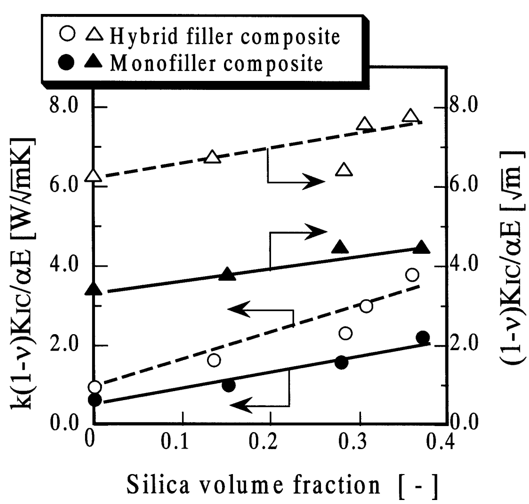
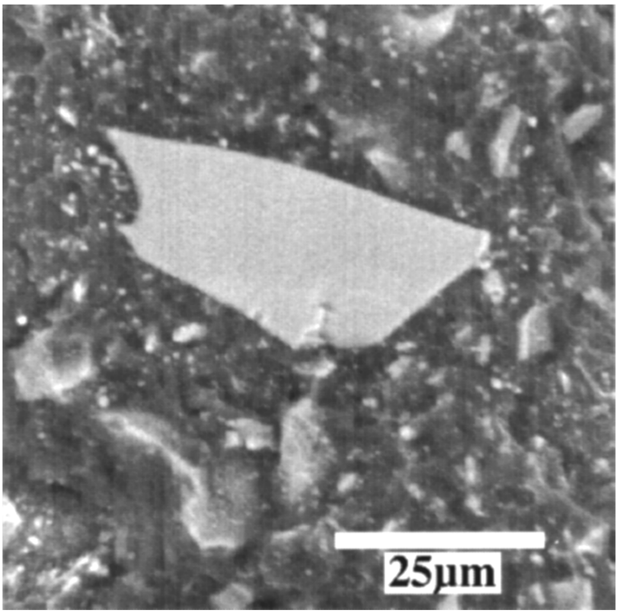


Figure 5. Silica filled effect on coefficients of thermal shock resistance.

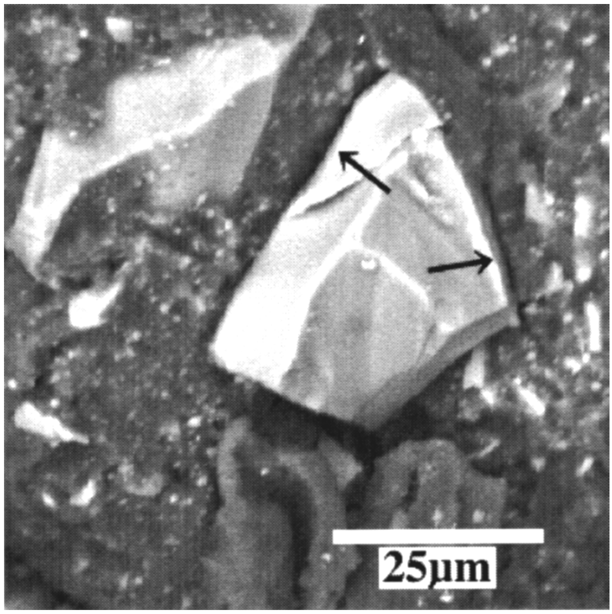
these values, $(1 - \nu)K_{IC}/\alpha E$ and $k(1 - \nu)K_{IC}/\alpha E$, indicate the magnitude of thermal shock resistance qualitatively. Figure 5 shows that both $(1 - \nu)K_{IC}/\alpha E$ and $k(1 - \nu)K_{IC}/\alpha E$ increase with increase of silica filler content for mono-filler (only silica) composite and hybrid filler composite. Consequently, the coefficients of thermal shock resistance obtained by thermal and mechanical properties suggest that the thermal shock resistance should increase by filling silica particulate for mono-filler and hybrid filler composites tested here.

Figure 6 shows the fractured surface of (a) fracture toughness test and (b) thermal shock test for the specimen of silica 320 phr and MBS 10 phr hybrid system. Fractured specimen by fracture toughness test shows some flat silica surfaces (a). This means that the crack propagates with destruction of the particles. It also suggests good adhesion of resin and a particle. On the other hand, thermal shock fracture surface indicates the filler original surface as shown in Fig. 6b. Furthermore, some clearance or space between matrix resin and silica filler can also be observed at the points of the arrows. This clearance or space may be caused by the silica/epoxy interfacial debonding and subsequent plastic deformation around the silica particle. Generally, silica filler has good adhesion with epoxy resin. In this study, mono-filler composite indicates good interfacial adhesion for both fracture toughness test and thermal shock test. However, for hybrid filler composite, especially at high silica content, thermal shock test specimens indicate interfacial debonding due to difference of thermal expansion coefficient between filler and resin as shown in Fig. 6b. Then it can be concluded that thermal shock resistance



(a) Fracture toughness test

Figure 6. SEM photographs of fracture surfaces of hybrid composite (silica 320 phr and MBS 10 phr).



(b) Thermal shock test

Figure 6. (Continued).

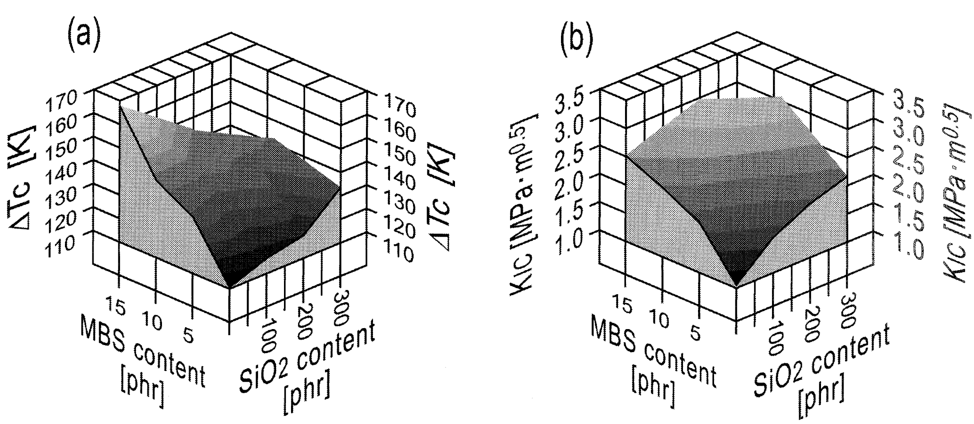


Figure 7. Silica and MBS hybrid filler effect on (a) thermal shock resistance and (b) fracture toughness.

does not clearly increase by filling particles for hybrid filler composite is caused by the interfacial debonding.

The results are summarized in Fig. 7. Thermal shock resistance and fracture toughness are plotted against the volume fraction of silica and MBS filler. Fracture toughness is explicitly improved by filling both soft and hard particle as shown in Fig. 7b. The effect of filling soft and hard particle on thermal shock resistance seems to be a little complicated as shown in Fig. 7a. For mono-filler composite, thermal shock resistance obviously increases with increasing both soft and hard filler content. In the case of hybrid filler composite, the effect of filling particle is not always positive.

4. CONCLUSIONS

Thermal shock resistance of hybrid particulate (silica particulate as hard filler and MBS rubber as soft filler) filled epoxy composites was investigated.

1. Thermal shock resistance was estimated as temperature difference that required developing crack at the notch in the specimen suffered quenching thermal shock.
2. For silica filled composite and MBS rubber filled composite, thermal shock resistance was improved by filling particle.
3. For hybrid particulate filled composite, thermal shock resistance was not clearly improved by filling particle. On the other hand, fracture toughness was comprehensively increased with increasing both silica and MBS filler content.
4. Thermal shock resistance was evaluated on the basis of the linear fracture mechanics. The calculated results suggested that thermal shock resistance should be increased by filling silica particulate for mono-filler and hybrid filler composites. It is clarified by microscopic observations that the difference between experimental results and calculated results was caused by silica/resin interfacial debonding.

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