Fracture Toughnesses of Bisphenol a Type Epoxy Resin and Silica Particulate-Filled Epoxy Composite*

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Using Raman spectroscopic analysis and the fractographical analysis, we investigated the relationship between the glass transition temperature, T_g , the fragility parameter, m , and the fracture toughness, K_{Ic} , of epoxy resin and composite. T_g and m derived from the thermo-viscoelasticity were used to characterize the epoxy resin and composite post-cured under various conditions. The Raman spectroscopic analysis showed that the T_g is directly related to the degree of cross-linking reaction of the epoxy resin and the matrix of composite. The fractography showed that m of the epoxy resin depends on the heterogeneous microstructure. The m of the composite was dominated by the volume fraction. K_{Ic} of the epoxy resin increased as m decreased when the T_g was saturated at approximately 400 K. A composite with a high T_g and a low m had a high K_{Ic} value.

Key Words: Fracture Toughness, Fractography, Composite Material, Epoxy Resin, Thermo Visco Elasticity

1. Introduction

Epoxy resins and its composites are widely used in various engineering fields, because of their excellent mechanical characteristics, electric insulation, and ease of casting. The curing condition effects on the properties of cured epoxy resins. The glass transition temperature, T_g , is generally used for setting the curing conditions of epoxy resin, because it is closely related to the degree of curing reaction. Although it is well known that the fracture toughness is correlated to T_g (Refs.(1) - (3)), the fracture property does not have a constant value even when T_g is the same (Ref.(4)). This means that an alternative parameter for setting the curing conditions is needed to estimate the fracture property.

The purpose of the present study is to clarify the effect of the curing condition on the fracture toughness of a bisphenol-A type epoxy resin cured with acid

anhydride and a silica particulate-filled epoxy composite, using a glass transition temperature and a fragility parameter, m . The former is related to the degree of the cross-linking reaction (Refs.(5) and (6)). The latter was proposed by Angell (Ref.(7)) as a basis for classifying of supercooled materials according to the variations in their dynamic properties at temperature above T_g , based on the concept of intermolecular cooperativity. It has attracted much attention as a parameter related to the density heterogeneity of thermoplastic resins (Ref.(8)). Fragility or the concept of cooperativity has been also applied to cross-linked polymers (Refs.(9) - (12)), which have a heterogeneous microstructure (Refs.(13) - (18)).

In our previous studies (Refs.(19) - (21)), we proposed using T_g and m to evaluate the fracture properties of the epoxy resins and composites. In this study, based on the Raman spectroscopic analysis and fractographical analysis, we investigated the relationship between T_g , m , and the fracture toughness, K_{Ic} , in detail. T_g and m were derived from the thermo-viscoelasticity in order to characterize the resins and composites made under various curing conditions.

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The specimens were examined using a laser Raman spectrophotometer. Then a fracture toughness test was performed at room temperature (293 K), and the fracture surfaces were observed with a differential interference microscope, a scanning electron microscope, and an atomic force microscope. The relationship between T_g , m or K_{Ic} was discussed, based on the Raman micro-spectroscopic analysis and the fractography of microscopic roughness.

2. Experimental Procedures

The epoxy resin used in the experiment was a blend of bisphenol-A type epoxide resin (Yuka Shell, Epikote 828) with methyl-tetrahydro-phthalic anhydride as a curing agent (Hitachi Chem., HN-2200R) and 2-4-6 tris phenol as an accelerator (Daito Curar, DMP-30). The weight ratio of the resin, curing agent and the accelerator was 100:80:0.5. The filler was fused silica particles (Tasumori, Fuselex ZA-30), with an average diameter of 5.5 μm . The volume fractions of the silica particles were 0% (Epoxy), 26% (Composite A), 35% (Composite B), and 42% (Composite C). The raw material mixture was cast in a mold after it was agitated and degassed in vacuum, then cured in a thermostatic oven.

The curing was performed in two steps. First, in pre-curing, the specimen was kept at 353 K for 3 hours to gel the matrix resin. Then, in post-curing, which greatly affects the cross-linking reaction of the resin, the specimen was kept at 353 to 433 K for 3 to 15 hours.

The thermo-viscoelastic properties of the cured epoxy resins and composites were examined with a dynamic viscoelastometer (Orientec, Rheovibron DDV-III-EA). Tensile vibrations at 3.5, 11, 35, and 110 Hz were applied to the specimen every 2 K from 123 to 523 K to measure the complex moduli, E' and E'' . The specimens were 70 mm long, 5 mm wide, and 3 mm thick. Epoxy resin and its composite are known as thermo-viscoelastic materials that depend on both temperature and time. Their master curves of E' were made from the temperature dependence curve of E' shifted along the frequency axis according to the temperature-time equivalent principle with a shift factor, a_T .

Then, we derived T_g and m from the results of the thermo-viscoelasticity measurement (Refs.(19) - (21)). These parameters were used to classify the epoxy resins and the composites, which were post-cured under various conditions. The temperature at the maximum value of the thermal activation energy, given by an Arrhenius plot of a_T , was defined as T_g . By definition, m is the slope at T_g of the viscosity or the relaxation time in an Arrhenius plot with an

abscissa scaled to the T_g of the material (Ref.(7)). Böhmer et al. expressed m as (Ref.(22)):

$$m = \frac{d(\log \tau)}{d(T_g/T)} \quad \text{at } T = T_g \quad (1)$$

where τ and T are the relaxation time and absolute temperature, respectively. Neat epoxy and its composite have been experimentally shown as a thermorheologically simple materials (Refs.(23) - (25)), so a_T can be expressed as (Ref.(26)):

$$a_T = \frac{\tau(T)}{\tau(T_0)} \quad (2)$$

where T_0 is the standard temperature. Substituting Eq.(2) into Eq.(1) enables us to express m in terms of a_T :

$$m = \frac{d(\log a_T)}{d(T_g/T)} \quad \text{at } T = T_g \quad (3)$$

Hence, m can be derived from the slope of a_T with the reciprocal of the temperature normalized by T_g , which is substantially equal to the *apparent* activation energy (Refs.(27) and (28)).

A laser Raman spectrophotometer (NRS-1000, JASCO) was used at room temperature (293 K) to determine the curing degree of the specimens. The epoxy specimens and the epoxy resin matrix of the composites were examined with a space resolution of 2 μm . A green laser with wavelength 532.3 nm and power 100 mW were used, and a spectral slit was 40 μm wide. The exposure time was 420 s for the epoxy resins and 600 s for the composites. The specimens were less than 500 μm thick and their surfaces were polished smoothly, in order to reject background stray light.

A tensile test of a double edge-cracked plate was performed to measure the mode I fracture toughness. The specimens were 250 mm long, 25 mm wide, and 5 mm thick. Pre-cracks, 5 mm long, were induced on both sides of the middle position of the specimen. The test was carried out at a deformation rate of 2 $\mu\text{m/s}$ and a temperature of 293 K with a universal material testing machine (Instron 8501). The load-deformation curve of each specimen was linear until brittle breaking occurred, meaning that the stress field near the crack tip was small scale yielding. Therefore, the method of linear elastic fracture mechanics could be applied to the experimental results to determine the fracture toughness. The mode I stress intensity factor, K_I , is given by (Ref.(29)):

$$K = \frac{P}{BW} \sqrt{\pi a} \cdot f(\xi) \quad (4)$$

where

$$f(\xi) = \frac{1.122 - 0.561\xi - 0.205\xi^2 + 0.471\xi^3 - 0.190\xi^4}{\sqrt{1-\xi}},$$

$$\xi = \frac{2a}{W}$$

The P , W , B , and a are the load, width, thickness, and

crack length. Substituting of the maximum load $P_{\max}$ into P in Eq.(4), we can determine the fracture toughness, K_{Ic} . We took the average value of five results as the fracture toughness.

After the fracture toughness test, we observed the fractured surface was observed to evaluate the microstructure of the specimens visually and quantitatively. The overall fractured surface of the epoxy resin was measured with a differential interference microscope. Then the surfaces were finely observed with an atomic force microscope (Seiko, SPI3800) for the epoxy resin and a scanning electron microscope for the composite. Then the average surface roughness, R_a , in an area $5 \times 5 \mu\text{m}$ was estimated to quantify the observation by the atomic force microscope. The R_a was similar to that in JIS B 0601 (1994) :

$$R_a = \frac{1}{S_0} \int_{S_0} |z| dS \quad (5)$$

where S and S_0 are the actual surface area and the area projected from the actual surface to the flat plane; z denotes the distance from the projected plane to the actual surface.

3. Results and Discussion

The relationship between T_g , m , and the post-curing condition is shown in Fig.1. The T_g of the epoxy resins and composites increased as the curing temperature and time increased. It approached to approximately 400 K when the post-curing temperature was more than 400 K. The m of each epoxy resins was low, after being post-cured for 15 hours at every post-curing temperature. The m of the composites strongly depended on the volume fraction of silica particles. There was no direct correlation between T_g and m for any specimen; in particular m of the epoxy resins varied considerably even after T_g saturated at approximately 400 K.

Figure 2 shows typical Raman spectra of the biphenol-A type epoxide resin (DGEBA), the epoxy resin and the epoxy resin matrix of the composites for the $600 - 1800 \text{ cm}^{-1}$ spectral region. All the specimens had common spectral features in the range $300 - 4000$

cm^{-1} . The Raman spectra at about $2800 - 3200 \text{ cm}^{-1}$, $1500 - 1800 \text{ cm}^{-1}$ are attributed to CH and CH_2 stretching, CH_2 deformation vibration, respectively (Refs. (30) - (32)). The peaks at 1123 , 1196 cm^{-1} are associated with bisphenol-A backbone vibrations (Refs. (32) - (34)). The bands at 835 , 927 , and 1256 cm^{-1} are associated with the epoxide ring vibration (denoted by black triangles in Fig.2). The intensity of these bands decreases as the cross-linking reaction proceeds (Refs.(33) and (34)). The intensity of the 1256 cm^{-1} band, I_{epo} , was used to determine the cross-linking degree of the specimens. And the intensity of the 1186 cm^{-1} band, I_{ref} , was chosen as an internal standard because the bands associated with the bisphenol-A backbone do not depend on the curing reaction. The relationship between the normalized intensity of the epoxide ring, I_{epo}/I_{ref} , and T_g is shown in Fig.3.

Fig. 1 Relationship between post-curing condition and T_g , m

Fig. 2 Raman spectra of DGEBA, Epoxy, and Composite A (Post-curing condition: 413 K, 15 h)

The cross-linking degrees of the epoxy resins and the matrix of the composites had a good correlation with the T_g of them. These results show that the T_g derived from the thermo-viscoelasticity expresses the cross-linking degree of the epoxy resin and the matrix resin of the composite, and that the T_g of the composite primarily depends on the thermo-viscoelastic property of the matrix resin. In contrast, the m of the specimens did not have any relation to the cross-linking reaction, therefore it is possible that the m is due to a physical structure.

The relationship between T_g , m and K_{Ic} is shown in Fig. 4. Figure 4(a) shows that the K_{Ic} of each composite increased with T_g , although that of the epoxy was not directly related to it. For example, the K_{Ic} of Composites A increased from 1.1 to 1.6 MPa·m^{1/2} as T_g increased from 340 to 410 K, while that of the epoxy resins varied from 0.6 to 1.1 MPa·m^{1/2} even when the T_g were approximately the same. Figure 4(b) shows that the K_{Ic} of the epoxy resin depended on m when T_g was saturated at approximately 400 K. As the m decreased from 180 to 50 when the T_g was

Fig. 3 Relationship between I_{epo}/I_{ref} and T_g

(a) Glass transition temperature T_g

(b) Fragility m

Fig. 4 Relationship between T_g , m , and K_{Ic}

about 400 K, the K_{Ic} of the epoxy increased from 0.6 to 1.1 MPa·m^{1/2}. Comparison of the composites demonstrated that the K_{Ic} of Composites C, which generally had a higher volume fraction and lower m than the other composites, showed a high value.

Figure 5 shows the appearance of typical surfaces of general surfaces of the epoxy resins observed using the differential interference microscope. These specimens had approximately the same T_g of 400 K, but different values of m . The specimens both had a smooth, mirror-like surface near the initial crack tip. As the crack propagated, small pits began to appear on the surface and developed into parabolic patterns, so that the surface gradually became rough. As the crack propagates further, the parabolic patterns are superposed on each other and the surface became rougher. The source of the parabolic pattern, which is obviously the pits, greatly depended on the microstructure of the epoxy resin. The region where the pits appeared was finely observed using the atomic force microscope and the results were quantified using the average surface roughness, R_a . The relationship between R_a and m is shown in Fig. 6. R_a decreased as m increased at constant T_g . The morphology of fractured surface is related to network heterogeneity on a scale of several nm to μ m in cross-linked resin (Refs.(15) and (17)), and this heterogeneity affects the fracture property (Refs.(1), (17) and (18)). Kanaya et al.(Ref.(8)) reported that m expresses the density heterogeneity of the thermoplastic resins. Previous research and our experimental results suggest that m expresses the density heterogeneity of cross-linking in the epoxy resin. This hypothesis explains well the relationship between K_{Ic} and m of the epoxy resin shown in Fig. 4(b).

Figure 7 shows typical surfaces of the epoxy

Fig. 5 Fracture surface of epoxy resin

Fig. 6 Relationship between R_a and m of epoxy resin (Post-curing temperature: 393, 413, and 433 K)

composites observed using the scanning electron microscope. The fracture surface of the composite was mostly rough due to many steps compared with that of the epoxy resin. Such steps have been attributed to silica particles and the interparticle spacing (Ref. (35)), and the creation of the steps requires energy to form the fracture surface. The specimens shown in Figs. 7(a) - (c) had the same volume fraction but different T_g values. The number of the steps increased with increasing T_g , when the volume fraction was the same. The steps of the composite were strongly influenced by the filled particles when the cross-linking reaction of the matrix had sufficiently proceeded. The specimens shown in Figs. 7(c) - (e)

had approximately the same T_g but different volume fractions. The number of step increased with increasing volume fraction when T_g was almost the same. This is because the composite with a high volume fraction had a small interparticle spacing. Since the composites with a high T_g and high volume fraction, such as Composite C cured at 413 K for 15 h, had many steps on their fracture surface, they had high K_{Ic} .

These experimental results showed that the epoxy resins have a high K_{Ic} when T_g is about 400 K and a low m . The K_{Ic} of the epoxy resin increases with the increasing heterogeneity of the microstructure, when the cross-linking reaction has almost finished. The results also indicate that the epoxy composites with a high T_g and low m have a high K_{Ic} . The m of the composite depended on the volume fraction of the silica particles, because the viscosity of the composite may be mainly dominated by not the matrix resin but the interaction between the matrix and the particles, which primarily depends on the volume fraction. The filling of the particles increased the energy required to form the fracture surface, so the K_{Ic} increases with decreasing m . When the volume fraction was constant, a change in the interaction, following the proceeding of the cross-linking reaction in the matrix, may greatly affect the fracture properties.

4. Conclusions

The relationships between the post-curing condi-

	(a)	(b)	(c)	(d)	(e)
Specimen	Comp. A	Comp. A	Comp. A	Comp. B	Comp. C
Volume fraction (%)	26	26	26	35	42
Post-curing condition	353 K, 3 h	393 K, 3 h	413 K, 15 h	413 K, 15 h	413 K, 15 h
T_g (K)	341	397	413	413	409
m	117	121	107	97	54
K_{Ic} (MPa · m^{1/2})	1.11	1.40	1.62	1.73	1.85

Fig. 7 Fracture surface of silica particulate-filled epoxy composite

tions and the fracture toughness, K_{Ic} , of a bisphenol-A type epoxy resin and silica particulate-filled epoxy composite were discussed. The glass transition temperature, T_g , and the fragility parameter, m , derived from the thermo-viscoelasticity were used in order to characterize the epoxy resin and composite post-cured under various conditions. Raman spectroscopic analysis showed that T_g expresses the degree of the cross-linking reaction of the epoxy resin and the matrix in the composite. The fractography results showed that m of the epoxy resin depends on the heterogeneous microstructure. The m of the composite was dominated by the volume fraction. The K_{Ic} of the epoxy resin increased as m decreased when T_g was saturated at approximately 400 K. The K_{Ic} of the composite with a high T_g and low m was high. Based on our experimental results, we suggest that T_g and m are very useful for estimating the fracture toughness of epoxy resin and its composites.

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