Fracture Toughness of Silica Particulate-Filled Epoxy Composite

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ABSTRACT: The relationship between the postcuring conditions and fracture toughness on three silica particulate-filled epoxy composites was investigated. The glass transition temperature, T_g, and the fragility parameter, m, derived from the thermo-viscoelasticity, were used to characterize the composites, which were postcured under various conditions. The glass transition temperature and fragility both depended on both of the curing conditions and the volume fraction of silica particles. The glass transition temperature increased with the postcuring time and temperature, while the fragility generally decreased as the volume fraction increased. There was no direct correlation between the glass transition temperature and fragility. The fracture toughness depended on both the glass transition temperature and fragility. The composites with a high glass transition temperature and low fragility had high fracture toughness. These results indicate that the glass transition temperature and fragility are useful parameters for estimating the fracture toughness of the silica particulate-filled epoxy composites. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2261–2265, 2002

Key words: mechanical properties; viscoelastic properties; fracture, toughness, curing of polymers

INTRODUCTION

Particulate-filled epoxy composites are widely used in various engineering fields because epoxy resin has excellent mechanical characteristics, electric insulation, and adhesion. Many types of epoxide resins and curing agents are used to make epoxy resin. The curing reaction depends on the types used, their combination, and the curing conditions. The curing conditions for obtaining the best mechanical properties depend on the type of resin.

The glass transition temperature is generally used for setting the curing conditions because it is closely related to the degree of the curing reaction. Although the fracture toughness is correlated to the glass transition temperature,[1–3] the fracture property does not have a constant value while the glass transition temperature is constant.[4] This means that a new parameter that can be used to estimate the fracture property is needed for setting the curing conditions.

The purpose of the present study was to clarify the relationship between the curing conditions and the mechanical properties, especially the fracture toughness, of three silica particulate-filled epoxy composites.

A previous study[5] investigated the use of the glass transition temperature and the fragility parameter for characterizing cured epoxy resin. The glass transition temperature, T_g, is generally used to determine the degree of the crosslinking reaction; it increases when the degree of the reaction increases.[6,7] The fragility parameter, m, was proposed by Angell[8] as a basis for classifying supercooled materials according to the variations in their dynamic properties at temperatures above T_g, based on the concept of intermolecular co-operativity. Fragility has attracted much attention as a parameter related to the density heterogeneity thermoplastic resins.[9] The fragility (or the concept of co-operativity) has also been applied to crosslinked polymers,[10–13] which have a heterogeneous microstructure.[14–19] In this study, the fragility was also applied to silica particulate-filled epoxy composites.

These parameters were first derived from the measured thermo-viscoelasticity of composites. Then a fracture toughness test was conducted, and the relation among these parameters and the fracture toughness of the composites was evaluated.

EXPERIMENTAL PROCEDURE

Specimens and curing conditions

The epoxy resin used was bisphenol A type epoxide resin (Yuka Shell, Epikote 828) with methyl-tetrahy-

TABLE I
Characterized Properties of Specimens

Postcuring		Glass Transition	
Temp, K	Time, h	Temp, K	Fragility
Neat Epoxy (Volume Fraction of Particle:0%)			
353	3	343	75
353	9	373	54
353	15	373	49
373	3	377	57
373	9	399	97
373	15	399	62
393	3	387	97
393	9	413	103
393	15	407	53
413	3	389	58
413	9	413	90
413	15	411	46
433	3	391	177
433	9	415	101
433	15	405	53
Composite A (Volume Fraction of Particle:26%)			
353	3	341	117
373	3	395	108
393	3	397	121
413	15	413	107
433	3	411	106
Composite B (Volume Fraction of Particle:35%)			
353	3	351	58
373	3	395	65
393	3	407	80
413	15	413	97
433	3	405	73
Composite C (Volume Fraction of Particle:42%)			
373	3	391	41
393	3	409	42
413	15	409	54
433	3	411	48

Precuring Condition: 353 K, 3 h.

dro-phthalic anhydride as a curing agent (Hitachi Chem., HN-2200R), and 2,4,6-Tris (dimethyl aminomethyl) phenol as an accelerator (Daito Curar, DMP-30). The weight ratio of the resin, the 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% (neat epoxy), 26% (Composite A), 35% (Composite B), and 42% (Composite C).

The raw material mixture was poured into an aluminum mold coated with a Teflon sheet, which had been set up in an oven. The dimensions of the mold in length, width, and depth were 260, 5, and 180 mm, respectively.

The curing was performed in two steps. First, in precuring, the specimen was kept at 353 K for 3 h to gel the matrix resin. Then, in postcuring, which greatly affects the crosslinking reaction of the resin, the specimen was kept under various conditions, which are summarized in Table I. The heating rate from precuring to postcuring was a constant 72 K/h for each process.

Thermo-viscoelasticity measurement

The thermo-viscoelastic properties of the cured composites were examined with a dynamic viscoelastometer (Orientec, Rheovibron DDV-III-EA). Tensile vibrations at 3.5, 11, 35, or 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. Master curves at the standard frequency, 3.5 Hz, were made according to the time–temperature equivalence principle with a shift factor, a_T.

The glass transition temperature T_g increased monotonically with the crosslinking degree until the crosslinking reaction saturated.[6,7] The fragility parameter m has attracted much attention as a parameter related to the heterogeneous of density of resins.[9] The T_g and m, derived from the thermo-viscoelasticity measurement results,[5] were used to classify the neat epoxy resin and the composites, which were postcured under various conditions.

The temperature at the maximum value of the *apparent* 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.[8] Böhmer et al. expressed m as:[20]

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

where τ and T are the relaxation time and absolute temperature, respectively.

Neat epoxy and its composites have been experimentally shown as a themorheologically simple materials,[21–23] so a_T can be expressed as:[24]

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

where T_0 is the standard temperature. Substitution of eq. (2) into eq. (1) enables m to be expressed by a_T:

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

Hence, m can be derived from the slope of a_T with the reciprocal of the temperature normalized by T_g, which is essentially equal to the *apparent* activation energy.[25,26]

Elastic properties measurement

To measure Young's modulus, E, and Poisson's ratio, ν, the specimens were cut from cured plates. They were 250 mm long, 25 mm wide, and 5 mm thick. A

tensile test was carried out at a deformation rate of 2 μm/s and a temperature of 293 K with a universal material testing machine (Instron 8501). The longitudinal and transverse strains were measured at the mid point of the specimen with strain gauges (Kyowa, KFG-2-120-D16).

Fracture toughness test

A tensile test of a double edge-cracked plate was carried at room temperature (293 K) to measure the mode I fracture toughness. The specimen shape and deformation rate were the same as the ones for the measurement of elastic properties. Precracks, 5 mm long, were induced on both sides of the middle position of the specimen. 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, linear elastic fracture mechanics could be applied to the experimental results to determine the fracture toughness. The mode I stress intensity factor, K, is given by:[27]
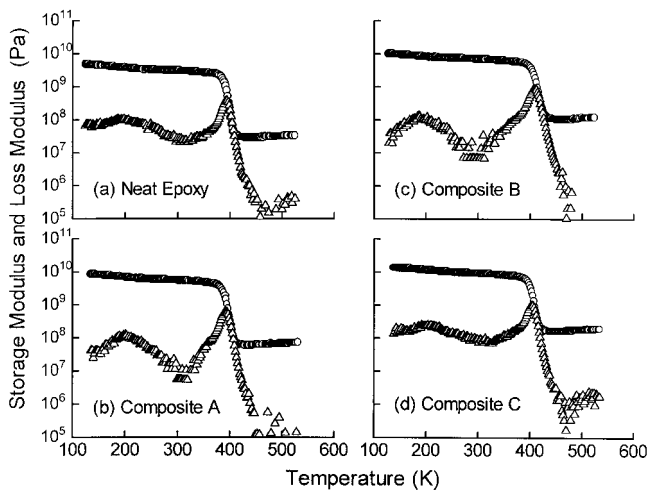
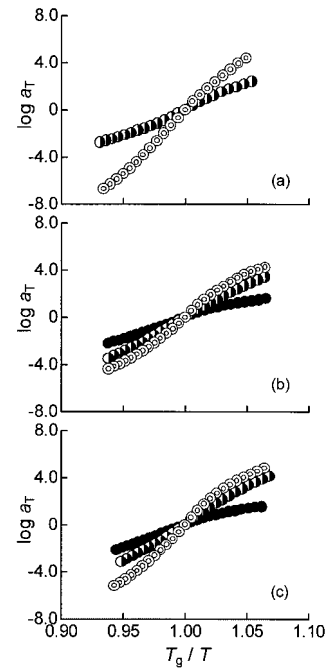$$K = \frac{P}{BW}\sqrt{\pi a} \cdot f(\xi) \tag{4}$$

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. Substitution of the maximum load P_{max} into P in eq. (4), enables the fracture toughness,

Figure 1 Complex moduli (postcuring conditions:433 K, 3 h). ○: Storage modulus; △: loss modulus.

Figure 2 Angell's plots of shift factors. Postcuring conditions: (a) 353 K, 3 h, (b) 373 K, 3 h, (c) 393 K, 3 h. Volume fraction—◎ : composite A (26%); ◑: composite B (35%); ●: composite C (42%).

K_{Ic}, to be determined. The experimental results shown in the figures are the averaged values of five measurements.

EXPERIMENTAL RESULTS AND DISCUSSION

Thermo-viscoelasticity

Typical master curves of E' and E'' of specimens postcured for 3 h at 433 K are shown in Figure 1. The relationship between a_T and the reciprocal of the temperature over the normalized T_g is shown in Figure 2. As shown in Table I, T_g and m depended on both the postcuring conditions and the volume fraction of silica particles. The T_g of the composites increased with the postcuring time and temperature, while m generally decreased as the volume fraction increased. As shown in Figure 3, there was no direct correlation between T_g and m.

Elastic modulus

As shown in Figure 4, the E of each specimen was approximately constant regardless not only of T_g but also of m. Moreover ν was constant (not shown in the figures). For example, the E and ν of Composite A were constantly about 7.0 GPa and 0.350, respectively. Therefore, the elastic properties of the specimens did not depend on either T_g or m.
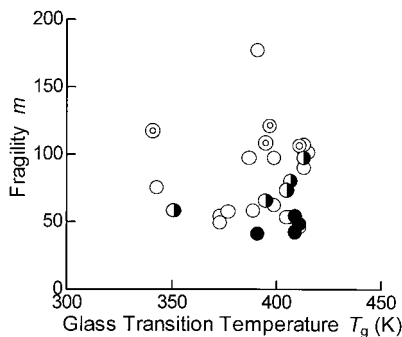
Figure 3 Relationship between fragility and glass transition temperature. Volume fraction—○: neat epoxy (0%); ◎ : composite A (26%); ◑: composite B (35%); ●: composite C (42%).

The experimentally derived E was compared with theoretical predictions. The predicted modulus was calculated using Nielsen's equation:[28]
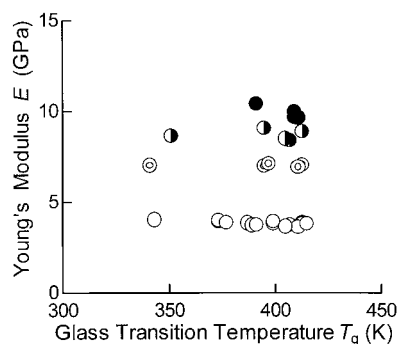
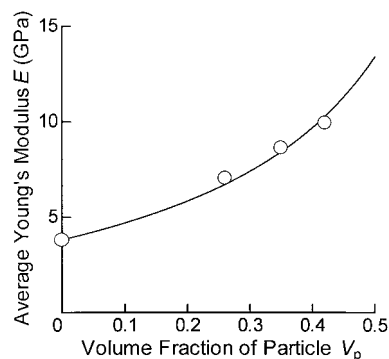$$E = E_M \frac{1 + ABV_P}{1 - B\psi V_P} \qquad (5)$$

where

$$A = \frac{7 - 5\nu_M}{8 - 10\nu_M}, \; B = \frac{(E_P/E_M) - 1}{(E_P/E_M) + A}, \; \psi = 1 + \frac{1 - V_{PM}}{V_{PM}^2}$$

and V_P, V_{PM}, and E_P are volume fraction, maximum volume fraction, and Young's modulus of the particles, respectively. E_M and ν_M are Young's modulus and Poisson's ratio of the matrix resin. Assuming that each particle is a sphere, V_{PM} is 0.74. The E_P was 73.1 GPa for the fused silica, and E_M is the measured value for the neat epoxy.

The values calculated using eq. (5) and the experimental results are shown in Figure 5. The theoretical values for the neat epoxy agreed with the experimental results, demonstrating that Nielsen's equation produces reasonable results.

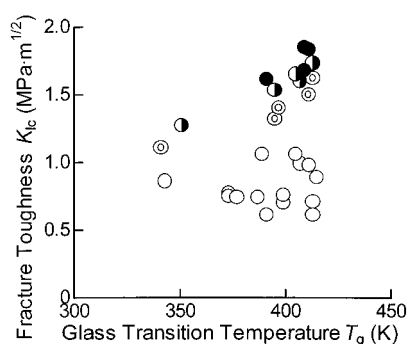**Figure 5** Nielsen's prediction of Young's modulus. — Nielsen's equation; ○: experiment.

Fracture toughness

Figure 6 shows that the K_{Ic} of the composites increased with T_g, while that of the neat epoxy was not directly related to its T_g. 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. Figure 7 shows that K_{Ic} of the neat epoxy resin depended on m when T_g was saturated (at approximately 400 K).[5] The K_{Ic} of the composites increased as m decreased. These results indicate that epoxy composites with a high T_g and low m have a high K_{Ic}. For example, Composite C with an m of about 50 and a T_g of about 410 K, had a K_{Ic} generally above 1.5 MPa · m$^{1/2}$. That of the neat epoxy increased from 0.6 to 1.1 MPa · m$^{1/2}$ as m decreased from 180 to 50 when T_g was approximately 400 K.

In summary, T_g and m are very useful for estimating the fracture toughness of epoxy resin and its composites. The physical meaning of m for epoxy resin was previously discussed.[5] For epoxy composites, the interaction between epoxy resin and the silica particle should also be investigated.

CONCLUSIONS

The relationship between the postcuring conditions and the fracture toughness on three silica particulate-

Figure 4 Relationship between Young's modulus and glass transition temperature. Volume Fraction—○: neat epoxy (0%); ◎ : composite A (26%); ◑: composite B (35%); ●: composite C (42%).

Figure 6 Relationship between fracture toughness and glass transition temperature. Volume fraction—○ neat epoxy (0%); ◎ : composite A (26%); ◑: composite B (35%); ● composite C (42%).
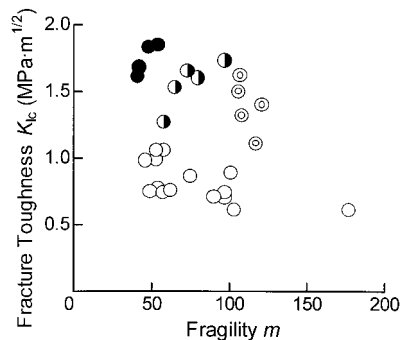
Figure 7 Relationship between fracture toughness and fragility. Volume fraction—○: neat epoxy (0%); ◎ : composite A (26%); ◑: composite B (35%); ●: composite C (42%).

filled epoxy composite was investigated. Experiments showed that T_g and m depended on both the curing conditions and the volume fraction of silica particles. The T_g of the composites increased with the postcuring time and temperature and m generally decreased as the volume fraction increased. There was no direct correlation between T_g and m. While the fracture toughness of the neat epoxy depended on m when T_g saturated (at about 400 K), the fracture toughness of the composites depended on both T_g and m. The composites with a high T_g and low m had a high K_{Ic}.

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