

Fracture Toughness of Bisphenol A-Type Epoxy Resin

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ABSTRACT: The relationship between the postcuring conditions and the fracture toughness of a bisphenol A-type epoxy resin cured with acid anhydride was investigated. The glass transition temperature and fragility parameter, derived from the thermo-viscoelasticity, were used to characterize the epoxy resin postcured under various conditions. Relationship between these two parameters and the fracture toughness was then investigated, based on the fractography results of a microscopic roughness examination of a fractured surface. The values of the glass transition temperature and fragility greatly depended on the postcuring conditions. The glass transition temperature was approximately 400 K when the crosslinking reaction was saturated. The fragility was independent of the saturation of the reaction and varied

between 50 and 180. The results of the fracture test and fractography examination showed that there was no direct correlation between the glass transition temperature, the fracture toughness, and the roughness. On the other hand, there was a correlation between the fragility, fracture toughness, and roughness when the glass transition temperature saturated (at 400 K). As the fragility decreased from 180 to 50, the fracture toughness increased from 0.6 to 1.1 MPa · m^{1/2} at the same glass transition temperature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2266–2271, 2002

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

INTRODUCTION

Epoxy resins are widely used in various engineering fields, due to their excellent mechanical characteristics, electric insulation, and adhesion. Many types of epoxide resins and curing agents are used to make epoxy resins. The curing reaction depends on types used, their combination, and the curing conditions. The curing conditions vary with the type of epoxy resin for obtaining the best mechanical properties.

The glass transition temperature is generally used for setting the curing conditions, because it is closely related to the degree of 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 a different parameter is needed for setting the curing conditions, one that can be used to estimate the fracture property.

The purpose of the present study was to clarify the relationship between the curing condition and the fracture toughness of bisphenol A-type epoxy resin cured using acid anhydride. The resin was postcured under various conditions, then characterized by the glass transition temperature and fragility parameter. The glass transition temperature, T_g , is related to the

degree of the crosslinking reaction—it increases with the degree.^{5,6} The fragility parameter, m , was proposed by Angell,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.⁸ The fragility (or the concept of cooperativity) has been also applied to crosslinked polymers,^{9–12} which have a heterogeneous microstructure.^{13–18}

In the present study, first, the glass transition temperature and fragility were derived from the measured thermo-viscoelasticity of epoxy resin. Based on the results of a fracture toughness test and fractography examination, the relations among these parameters, the fracture toughness, and the microscopic roughness of a fractured surface were investigated.

EXPERIMENTAL PROCEDURES

Specimens and curing conditions

The epoxy resin used in the present 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, the curing agent, and the accelerator was 100 : 80 : 0.5. The blend

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TABLE I
Characterized Properties of Specimens

Postcuring		Glass transition	
Temp, K	Time, h	Temp, K	Fragility
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

Precuring condition: 353 K, 3 h.

was cast in a mold after it was agisted and degassed in vacuum, then cured in a thermostatic oven.

Epoxy resin blended with an acid anhydride curing agent is generally cured in two stages: precuring for gelation, and postcuring for promotion of the crosslinking reaction. A preparatory experiment demonstrated that the precuring conditions negligibly affect the mechanical properties of the cured resin. The specimens were thus made under fixed precuring conditions, at 353 K for 3 h, and under various postcuring conditions, at 353 to 433 K for 3 to 15 h, as summarized in Table I.

Hermo-viscoelasticity measurement

The dynamic storage modulus, E' , of the specimen was measured using a dynamic viscoelastometer (Orienteq, Rheovibron DDV-III-EA). The measuring temperature ranged from 298 to 523 K, and the frequency was 3.5, 11, 35, or 110 Hz.

Epoxy resin is a thermo-viscoelastic material that depends on both temperature and time. To enable both dependencies to be evaluated, a master curve of E' was 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 .

Glass transition temperature and fragility parameter

The glass transition temperature, T_g , increases monotonically with the crosslinking degree until the crosslinking reaction saturates.^{5,6} The fragility parameter, m , suggested by Angell,⁷ has attracted much attention as a parameter related to the density heterogeneity of resins.⁸ The values of T_g and m , obtained

from thermo-viscoelasticity measurement results, were used to classify the epoxy resin 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, where the abscissa is scaled to T_g of the material.⁷ Böhmer et al. expressed m as:¹⁹

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

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

Epoxy resin has been experimentally shown to be a themorheologically simple material,^{20,21} so a_T can be expressed as:²²

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

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

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

Hence, m can be derived from the slope of a_T , with the reciprocal of the temperature normalized by T_g , which is essentially equal to the *apparent* activation energy.^{23,24}

Fracture toughness test

A tensile test was performed on a double-edge precracked specimen to measure the mode I fracture toughness. The test was carried out under a constant displacement rate of 2 $\mu\text{m/s}$ at room temperature (298 K), using a universal testing machine (Instron 8501). The specimen had a length of 250 mm, a width of 25 mm, and a thickness of 5 mm. The precrack lengths on both sides were 5 mm. Because the load–displacement curve of each specimen was linear until brittle fracture occurred, the critical stress intensity factor was used as the fracture toughness, K_{Ic} .²⁵

$$K_{Ic} = \sigma_c \sqrt{\pi a} \cdot f(\xi) \quad (4)$$

$$\sigma_c = \frac{P_c}{BW}$$

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

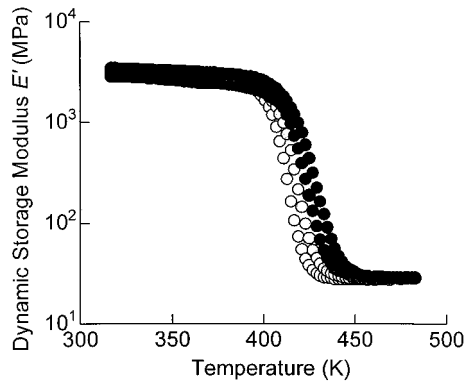


Figure 1 Typical dynamic storage modulus (postcuring conditions: 393 K, 15 h); measuring frequency: open circles: 3.5, light shaded circles: 11, medium shaded circles: 35, solid circles: 110 Hz.

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

and P_c is the maximum load; B , W , and a are the thickness, width, and precrack length of the specimen. The average value of five measurements was used as the fracture toughness.

Fractography

After the fracture toughness test, the fractured surface was observed with a differential interference microscope and an atomic force microscope (Seiko, SPI3800) to evaluate the microstructure of the cured epoxy resin visually and quantitatively. First, the overall fractured surface was observed, and then the region where the effect of the microstructure was most remarkable was precisely observed. The average surface roughness, R_a , was estimated to quantify the microscopic observation of the fractured surface. It was defined similar to that in JIS B0601 (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. The estimate of R_a was done in an area $5 \times 5 \mu\text{m}$, which is sufficiently large to determine the microscopic roughness of the fractured surface.

RESULTS AND DISCUSSION

Relationship between T_g , m , and curing conditions

The typical dynamic storage modulus, E' , is shown in Figure 1. It depended on both temperature and time.

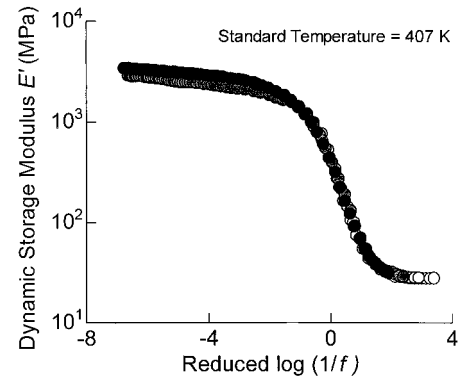


Figure 2 Typical master curve of dynamic storage modulus (postcuring conditions: 393 K, 15 h); measuring frequency: open circles: 3.5, light shaded circles: 11, medium shaded circles: 35, solid circles: 110 Hz.

The master curve derived from Figure 1 is shown in Figure 2, and the typical shift factor, a_T , is shown in Figure 3. The slope at T_g , namely fragility m , for the specimen postcured at 413 K for 9 h was larger than that for the one postcured at 393 K for 15 h. Both specimens had approximately the same T_g (400 K). The T_g and m for each specimen are summarized in Table I.

The relationship between T_g and the postcuring condition is shown in Figure 4. At the postcuring temperatures above 393 K, T_g converged to approximately 400 K as the postcuring time approached 10 h, indicating that the crosslinking reaction saturated.^{5,6} The reaction was estimated to have been 80% by then.²⁶ At a postcuring temperature of below 373 K, T_g was lower and saturated at a temperature below 400 K, indicating that the degree of crosslinking was insufficient.

The relationship between m and the postcuring condition is shown in Figure 5. At a postcuring temperature of 433 K, m decreased from 180 to 50 as the postcuring time was increased from 3 to 15 h. At 413, 393, and 373 K, m varied from 50 to 100. That of the

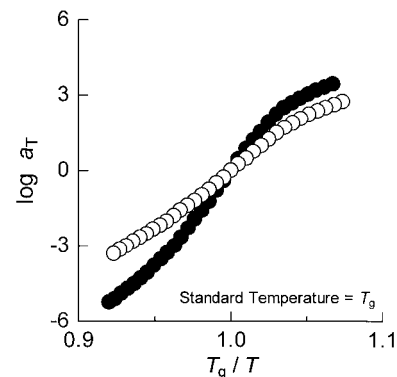


Figure 3 Typical shift factor. Postcuring condition: open circles: 393 K, 15 h ($T_g = 407$ K, $m = 53$), filled circles: 413 K, 9 h ($T_g = 413$ K, $m = 90$).

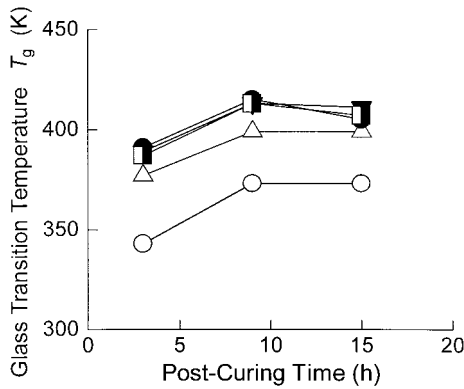


Figure 4 Relationship between glass transition temperature and postcuring condition. Postcuring temperature: open circles: 353, open triangles: 373; half open, half filled squares: 393; filled triangles: 413, filled circles: 433 K.

specimen postcured at 353 K was below 80. At every postcuring temperature, after being postcured for 15 h, each specimen had an m of approximately 50.

As shown by the results illustrated in Figures. 4 and 5, both T_g and m greatly depended on the postcuring condition and m varied independently after T_g saturated at approximately 400 K.

Relationship between T_g , m , and fracture toughness

The relationship between K_{Ic} and T_g is shown in Figure 6. Even though some specimens had approximately the same T_g , K_{Ic} varied from 0.6 to 1.1 $\text{MPa} \cdot \text{m}^{1/2}$. Because there was no direct correlation between T_g and K_{Ic} , hence K_{Ic} cannot be estimated based only on T_g .

The relationship between K_{Ic} and m is shown in Figure 7. The K_{Ic} of the specimens postcured at 353 and 373 K, which had a low T_g , did not exceed 1.0 $\text{MPa} \cdot \text{m}^{1/2}$. That of the specimens postcured at 393, 413, and 433 K, which had a T_g of approximately 400

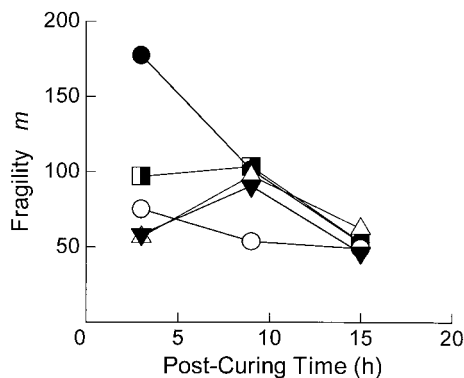


Figure 5 Relationship between fragility and postcuring condition. Postcuring temperature: open circles: 353, open triangles: 373; half open, half filled squares: 393; filled triangles: 413, filled circles: 433 K.

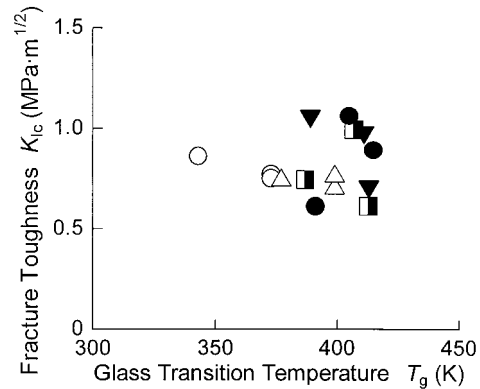


Figure 6 Relationship between fracture toughness and glass transition temperature. Postcuring temperature: open circles: 353, open triangles: 373; half open, half filled squares: 393; filled triangles: 413, filled circles: 433 K.

K, increased from 0.6 to 1.1 $\text{MPa} \cdot \text{m}^{1/2}$ as m decreased from 180 to 50. This means that K_{Ic} closely correlates with m when T_g is saturated.

Fractography

The fractured surface was observed mostly using the differential interference microscope. The typical observed surfaces are shown in Figure 8. These specimens had approximately the same T_g , 400 K, but a different m . The specimens shown in Figure 8(a) and (b) both had a smooth, mirror-like surface near the initial crack tip. As the crack propagated, 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 becomes rougher. These surfaces differed in the origination and propagation of the parabolic patterns. The source of the parabolic pattern, which is obviously the pits,

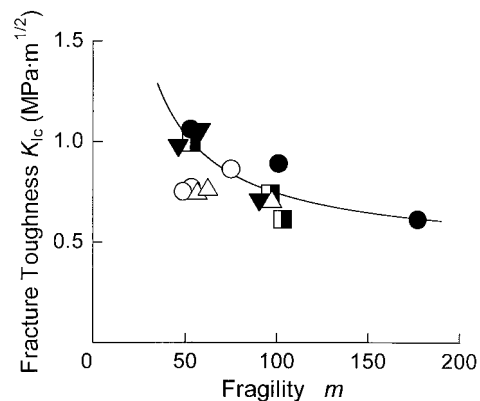


Figure 7 Relationship between fracture toughness and fragility. Postcuring temperature: open circles: 353, open triangles: 373; half open, half filled squares: 393; filled triangles: 413, filled circles: 433 K.

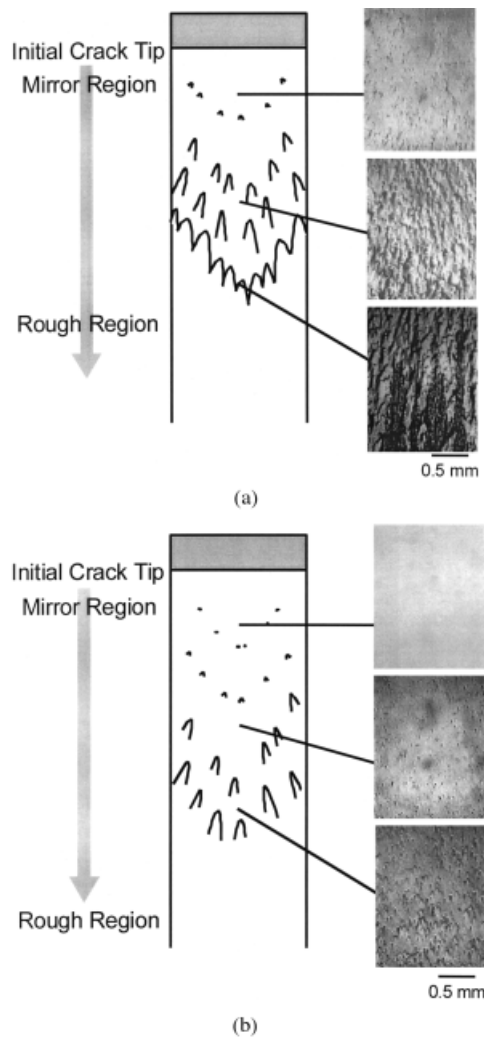


Figure 8 Typical fractured surfaces observed using differential interference microscope. (a) Postcuring conditions: 393 K, 15 h ($T_g = 407$ K, $m = 53$). (b) Postcuring conditions: 413 K, 9 h ($T_g = 413$ K, $m = 90$).

greatly depended on the microstructure of the cured epoxy resin.

The region where the pits appeared was precisely observed using an atomic force microscope. Typical images are shown in Figure 9. The surface roughness depended on m when T_g was the same (400 K).

The images of the atomic force microscope were quantified using the average surface roughness, R_a . The relationship between R_a and T_g is shown in Figure 10. Even though T_g was approximately the same, R_a varied from 5 to 13 nm; i.e., there was no correlation between R_a and T_g . This is probably because T_g is the parameter used to express the average crosslinking degree of the cured epoxy resin.

The relationship between R_a and m is shown in Figure 11. The roughness decreased as m increased with T_g constant. The morphology of fractured surface is related to network heterogeneity on a scale of several nm to μm in crosslinked resins,^{15–17} and this

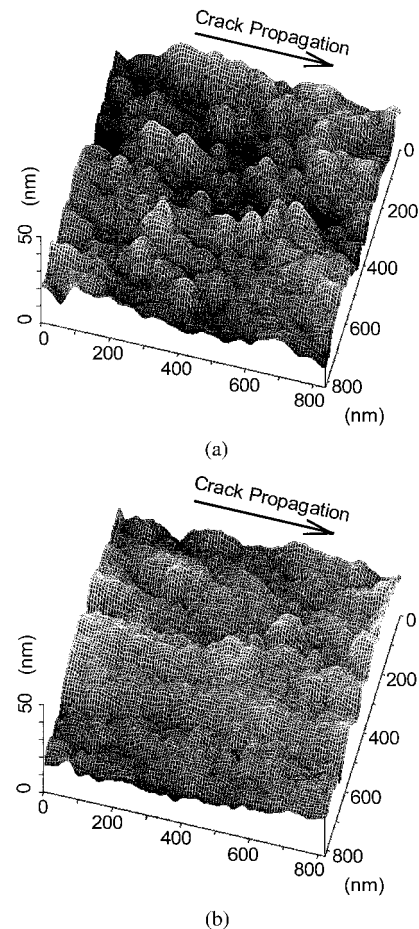


Figure 9 Typical fractured surfaces observed using atomic force microscope. (a) Postcuring conditions: 393 K, 15 h ($T_g = 407$ K, $m = 53$). (b) Postcuring conditions: 413 K, 9 h ($T_g = 413$ K, $m = 90$).

heterogeneity affects the fracture property.^{1,17,18} Kanaya et al.⁸ reported that m expresses the density heterogeneity of the thermoplastic resins. Previous research and our experimental results suggest that m

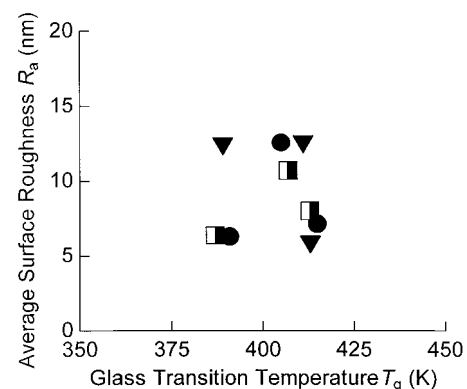


Figure 10 Relationship between average surface roughness and glass transition temperature. Postcuring temperature: half open, half filled squares: 393, filled triangles: 413, filled circles: 433 K.

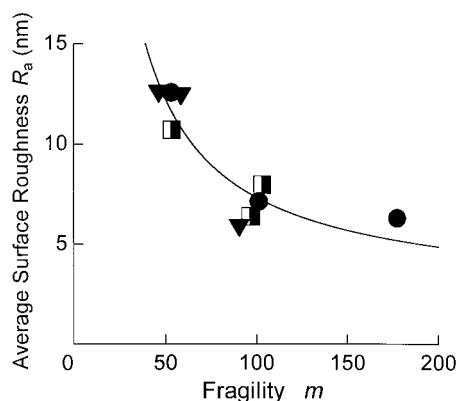


Figure 11 Relationship between average surface roughness and fragility. Postcuring temperature: half open, half filled squares: 393, filled triangles: 413, filled circles: 433 K.

expresses the density heterogeneity of crosslinking in the epoxy resin. This hypothesis explains well the relationship between K_{IC} and m shown in Figure 7.

CONCLUSION

The relationship between the postcuring conditions and the fracture toughness of a bisphenol A-type epoxy resin cured with acid anhydride was investigated. The values of T_g and m greatly depended on the postcuring conditions. The value of T_g was approximately 400 K when the crosslinking reaction saturated. Despite this saturation, m independently varied. Although there was no direct correlation between K_{IC} or R_a and T_g , there was a correlation between K_{IC} , R_a , and m when T_g saturated (at 400 K). As m decreased

from 180 to 50 under the saturated T_g , K_{IC} oppositely increased from 0.6 to 1.1 $\text{MPa} \cdot \text{m}^{1/2}$.

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