Effect of the Low-Temperature Relaxation on Toughness of Cured Epoxy Resins

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SYNOPSIS

The relation between the magnitude of low-temperature relaxation and toughness was investigated for epoxy resins cured with some position isomers of naphthalenediols. A well-defined relaxation was observed near room temperature for a system cured with 2,6-dihydroxynaphthalene. The relaxation was denoted here as the β'-relaxation. The values of the stress intensity factor, K_C, in this system was considerably higher than those of the other cured systems in the temperature region over the β'-relaxation temperature. This is explained by the increase in the plastic deformation region at the crack front with an increase in the temperature near the crack tip caused by the presence of the β'-relaxation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that bisphenol A-type epoxy resin cured with aromatic diamines has a relaxation from −70 to 40°C in the glassy region.[1-5] This relaxation is usually denoted as the β-relaxation. We suggested that the β-relaxation can be interpreted as the sum of the relaxation of hydroxy ether groups and the other parts of the network structure.[6,7]

In previous articles,[8-10] we reported that the cured spiroring-type epoxy resin with methoxy branches has another well-defined relaxation near room temperature, denoted as the β'-relaxation. The relaxation was due to the motion of the hydroxy ether segment being suppressed by the interaction between this group and the methoxy branch. Also, the fracture toughness of the spiro-type epoxy resin with methoxy branches was considerably greater above the temperature region of the β'-relaxation than that of the bisphenol A-type epoxy resin. The increase in the fracture toughness of this system was discussed in terms of the energy dissipation at the crack tip with the presence of the β'-relaxation. But the reason why the toughness of cured resins increases by the presence of a well-defined room-temperature relaxation could not be clearly explained.

In this article, the effect of the room-temperature relaxation on the toughness of cured epoxy resins is investigated using another cured epoxy resin system, i.e., the systems cured with dihydroxynaphthalenes. Further, the mechanism of the increase in the fracture toughness of this system is pursued in detail.
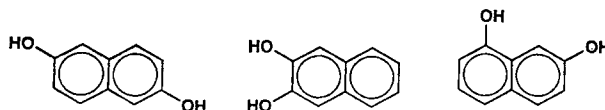
EXPERIMENTAL

Materials

The epoxy resin used was a ortho-cresol novolak-type epoxy resin (EOCN-1020-55, $M_n = 520$, epoxy equivalent 195):
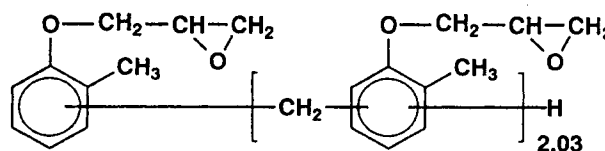
Three isomers of naphthalenediols, i.e., 2,6-, 2,3-, and 1,7-dihydroxynaphthalene (abbreviated to 2,6-DHN, 2,3-DHN, and 1,7-DHN, respectively) were used as the curing agents:

Triphenylphosphine (TPP) was used as an accelerator. These curing agents and accelerator were E.P. grade materials and were used without further purification.

Curing of Epoxy Resin

The epoxy resin was degassed at 130°C under reduced pressure with stirring. Then, stoichiometric amounts of dihydroxynaphthalene were added (one epoxy group corresponds to one active hydrogen of the phenolic hydroxyl group). The mixtures were stirred at 130°C and cooled to 80°C. Triphenylphosphine was added to the mixtures and melted at 80°C. Then, the mixtures were stirred with increasing temperature up to 130°C and were then poured into polytetrafluoroethylene molds. The compounds were cured at 130°C for 2 h and 180°C for 2 h. The samples for mechanical and thermal tests were machined from the cured epoxy resin plates.

Measurements

Dynamic mechanical properties were determined using an inverted, free-oscillation, torsion pendulum (RD-1100AD, Rhesca Co.) according to ASTM D 2236-70. The temperature region from −150 to +250°C was studied. Samples were heated at 0.7°C/min in vacuo.

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. The thickness of the specimens was adjusted between 3.6 and 4.0 mm. A sharp precrack was formed by carefully tapping a fresh razor blade.[11] The specimen was then mounted in an Instron-type tensile machine and loaded at a constant crosshead speed (0.5 mm/min). The load vs. time was recorded. The experiments were conducted over a range of temperature from room temperature to +100°C.

The value of K_C was calculated from the equation

$$K_C = (P_i/B w^{1/2}) f(a/w)$$

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

where P_i is the load at crack initiation; B, the thickness of the specimen; w and a, the width of the specimen and crack length, respectively; and $f(a/w)$, a geometric factor. It was confirmed for the samples that have a yielding point that their K_C values satisfy the following equation:

$$B \geqslant 2.5(K_C/\sigma_y)$$

where σ_y is the yield strength.

The fracture surfaces of the compact-tension specimens were observed using a scanning electron microscope (JSM-6100, JEOL) at a relatively low accelerating voltage of 15 kV. Prior to the examination, the surfaces were coated with a thin layer of gold in order to improve conductivity and prevent charging.

RESULTS AND DISCUSSION

Relaxation Phenomena of Epoxy Resins Cured with Dihydroxynaphthalene

The dynamic mechanical properties of epoxy resins cured with three dihydroxynaphthalenes are shown in Figure 1. In all cured systems, α-relaxation is observed at about 150°C. The relaxation behavior is independent of the position of phenoric hydroxyl groups on the naphthalene ring. This means that the large-scale motion of the network chains is not affected by the position isomerization of dihydroxynaphthalenes. On the other hand, the well-defined β'-relaxation is observed at about 50°C in the resin system cured with 2,6-DHN. This relaxation is not observed in the other systems. Thus, it is clear that the β'-relaxation is greatly affected by the position of the hydroxyl groups. It has been proposed that a relaxation in the glassy state of an epoxy resin is
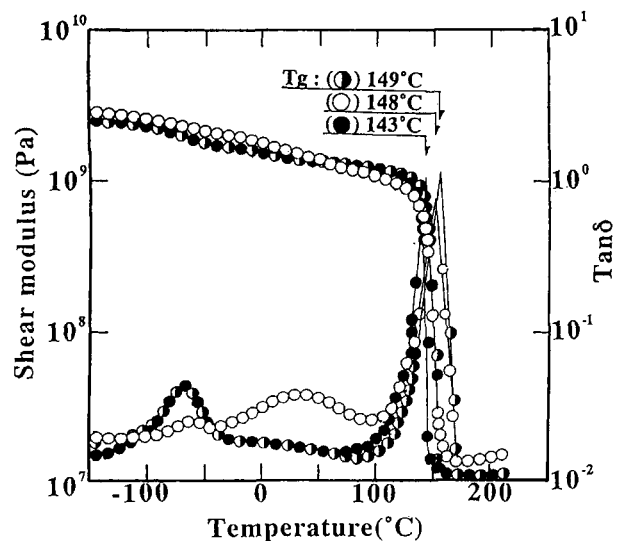
Figure 1 Dynamic mechanical properties of cured epoxy resins. Epoxy resin: o-cresol novolak type epoxy resin. Curing agent: (O) 2,6-DHN; (●) 2,3-DHN; (◐) 1,7-DHN. Accelerator: triphenylphosphine.

due to a local motion of network chains.[6-8] Therefore, it is natural to consider that the β'-relaxation is due to the local motion of the network chains containing 2,6-DHN.

The dynamic mechanical properties of a tetrafunctional epoxy resin cured with the dihydroxynaphthalenes are shown in Figure 2. The 2,6-DHN-cured system has a well-defined tan δ peak near room temperature. This result shows that the β'-relaxation does not depend on the structure of epoxy resin, but only on the position isomerization of naphthalene rings in the curing agents. From the above results, we conclude that the β'-relaxation observed near room temperature is due to the motion of the naphthalene ring bonded to networks through 2,6-positions on the ring.
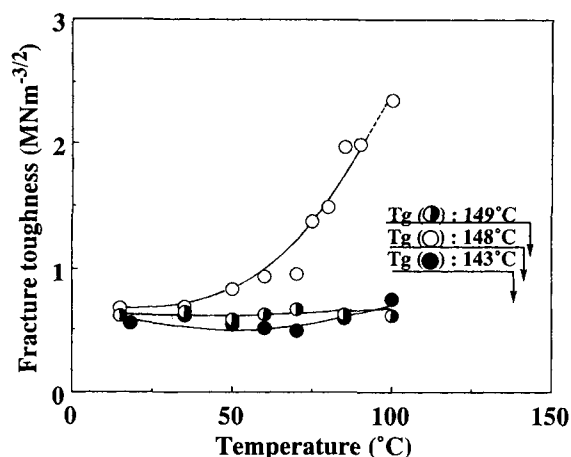
Fracture Toughness of Cured Epoxy Resins

A well-defined β'-relaxation is observed near 50°C for the resin system cured with 2,6-DHN. It is expected that such a large relaxation near room temperature would considerably affect the fracture toughness of the cured epoxy resins. The temperature dependence of the stress intensity factor K_C for the systems cured with dihydroxynaphthalenes is shown in Figure 3. Though the values of glass transition temperature (T_g) for all the systems are almost same (Fig. 1), the K_C values only for the 2,6-DHN-cured system increase rapidly from near room temperature with an increase in ambient temperature.

The temperature region where the K_C values begin to increase is almost compatible with the tempera-
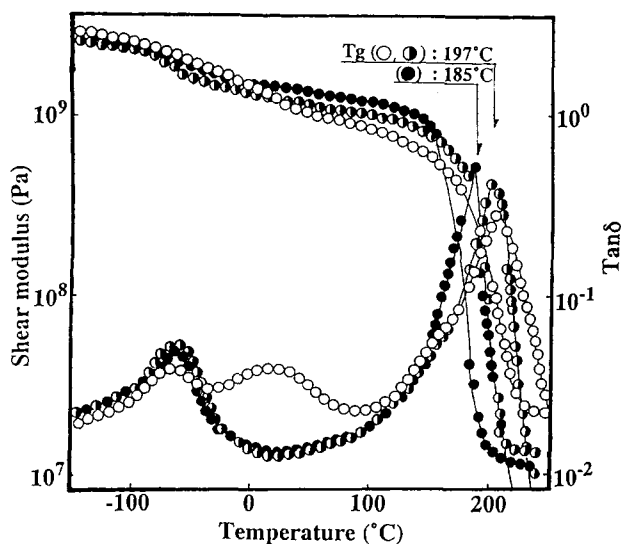
Figure 3 Fracture toughness of cured epoxy resins. Broken line shows the region where a large-scale deformation is observed. Symbols as shown in Figure 1.
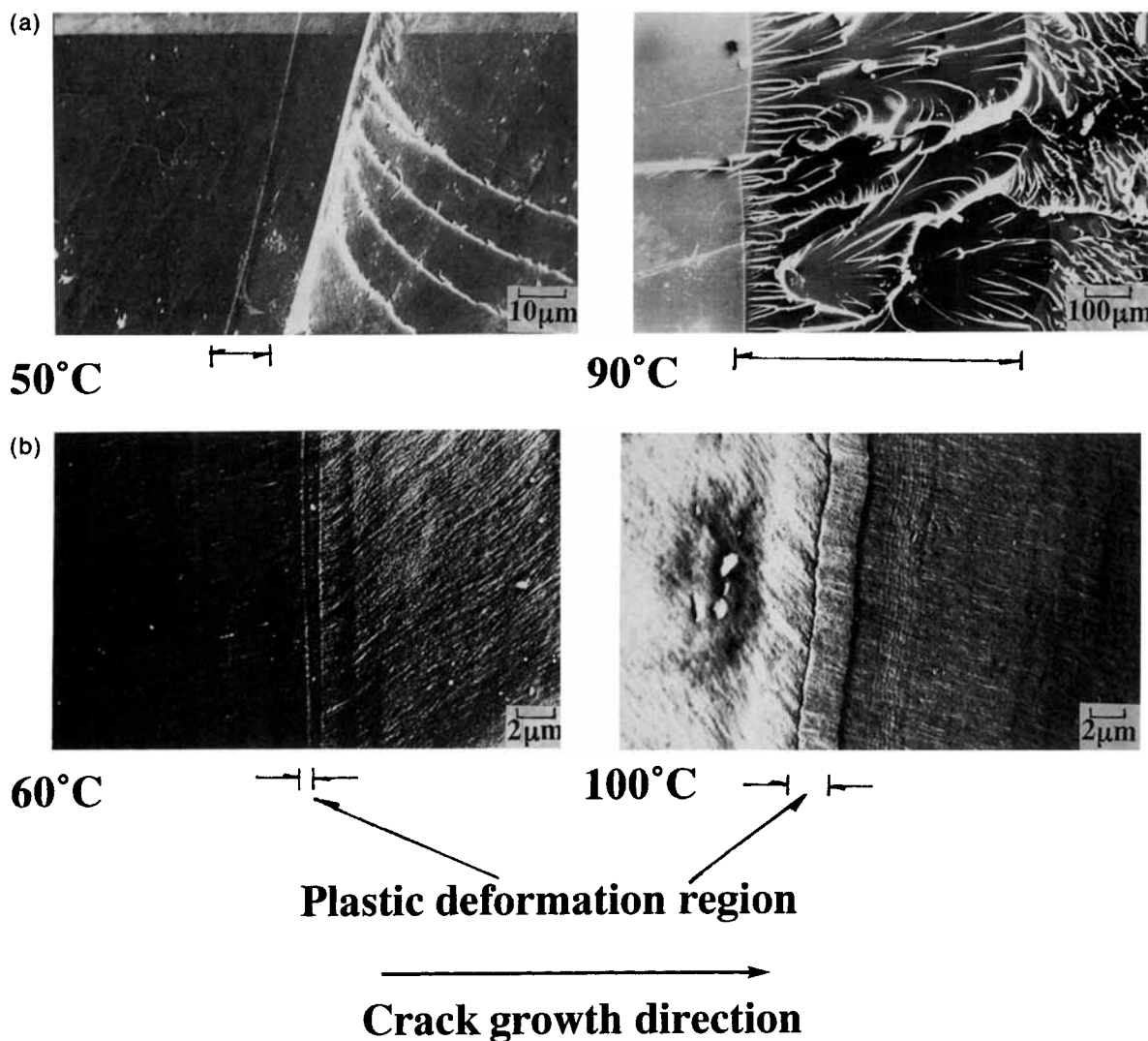
ture region where the β'-relaxation was observed in Figure 1. In addition, the large-scale deformation region that is shown as a broken line in this figure is observed at lower temperature in the 2,6-DHN-cured system compared with that of the other systems. These results may mean that the presence of the β'-relaxation is effective in improving the toughness of cured epoxy resins. It is an interesting subject for the toughening of epoxy resins to pursue the reason why the epoxy system having the β'-relaxation is tougher above room temperature than are the other systems.

Morphology of Fracture Surfaces of Cured Epoxy Resins

Scanning electron micrographs of fracture surfaces of the compact-tension specimens are shown in Figure 4 for the systems cured with 2,6- and 2,3-DHNs. For both systems, a plastic deformation zone is observed in the immediate neighborhood of the crack initiation line. This shows that energy loss is caused by plastic deformation at the crack front prior to unstable crack propagation.

The length of the plastic deformation zone is nearly constant for the resin systems cured with 2,3-DHN, even if a measuring temperature increases. However, the length of the plastic deformation zone for the resin system cured with 2,6-DHN increases with an increase in the ambient temperature. This shows the ease of yielding at the crack front of the cured system that has the β'-relaxation near room temperature.

The temperature dependence of the length of the plastic deformation zone is shown in Figure 5. In the system cured with 2,6-DHN, the length of the plastic deformation zone increases near the peak

Figure 2 Dynamic mechanical properties of cured epoxy resins. Epoxy resin: 1,1,2,2-tetraphenylglicidyletherethane. Symbols as shown in Figure 1.

(a)

50°C ⊢—⊣

90°C ⊢————————⊣

(b)

60°C

100°C

Plastic deformation region

Crack growth direction

Figure 4 SEM of fracture surface of cured epoxy resins: (a) 2,6-DHN; (b) 2,3-DHN.

temperature of the β'-relaxation, though the length of those zones in the other systems is kept nearly constant regardless of the ambient temperature. It is well known that the energy dissipation during sample deformation reaches a maximum at the relaxation process of the sample. Accordingly, the presence of the β'-relaxation should increase the generation of heat with the plastic deformation at the crack front. Thus, we consider that the increase in the plastic deformation zone in the 2,6-DHN-cured system is attributed mainly to the generation of heat at the crack front caused by the presence of the β'-relaxation.

### Estimation of the Increase in Temperature at the Crack Front

The correlation between the K_C values and the length of the plastic deformation region in the system cured with three dihydroxynaphthalenes is

shown in Figure 6. The K_C values for the system cured with 2,6-DHN are increased with increasing the length of the plastic deformation region,[11] whereas in other systems, the K_C values are nearly constant because the length of the plastic deformation region is scarcely changed. We conclude from this result that the increase in the K_C value in the 2,6-DHN-cured system is due to the increase in the plastic deformation region at the crack front.

It has been reported that the K_C values of polymers depend on the length r_P of the plastic deformation region.[12,13] The relationship between these two factors is described fairly well with Dugdale's equation[14]:

$$r_P = \frac{\pi}{8}\left(\frac{K_C}{\sigma_y}\right)^2 \tag{1}$$

where σ_y is the yield stress of the sample.
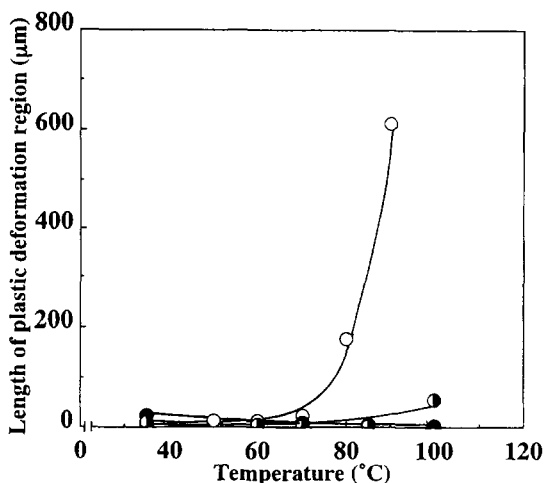
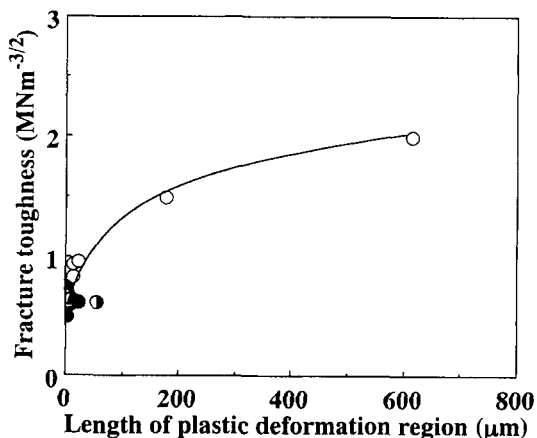**Figure 5** Length of plastic deformation region vs. temperature of cured epoxy resins. Symbols as shown in Figure 1.

Figure 7 Fracture toughness vs. square root length of plastic deformation region of cured epoxy resins. Symbols as shown in Figure 1.
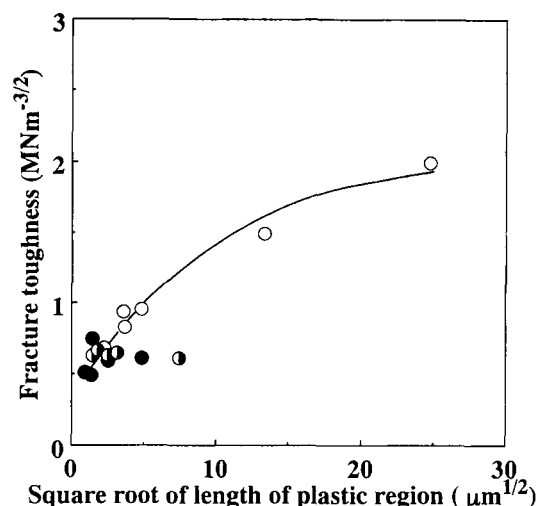
By modifying Dugdale's equation, the K_C values are functions of both the yield stress σ_y and a half-power of the r_P values as shown in eq. (2):

$$K_C = \sigma_y \left(\frac{8}{\pi}\right)^{1/2} r_P^{1/2} \qquad (2)$$

Then, the correlation between the K_C values and a half-power of the r_P values in all the systems is plotted in Figure 7. The values of K_C increased with an increase in the $r_P^{1/2}$ values and was asymptotic to same constant value for all cured systems. This result shows that Dugdale's equation can be applied to these resins. Moreover, a slope of this curve should correspond to the σ_y values of samples. This figure means that the σ_y values decrease with an increase

in the $r_P^{1/2}$ values, i.e., an increase in the ambient temperature.

Thus, the increase in temperature at the crack front was estimated on the basis of eq. (1) for the system cured with 2,6-DHN. First, the yield stress at the crack front is estimated from the K_C value and the length of plastic deformation region according to the following equation:

$$\sigma_y = \left(\frac{\pi}{8r_P}\right)^{1/2} K_C \qquad (3)$$

The calculated value of the yield stress estimated from eq. (3) is compared with the values of the observed yield stress as shown in Figure 8. The calculated values of σ_y obtained at 80 and 90°C correspond to the observed σ_y values that are measured

Figure 6 Fracture toughness vs. length of plastic deformation region of cured epoxy resins. Symbols as shown in Figure 1.
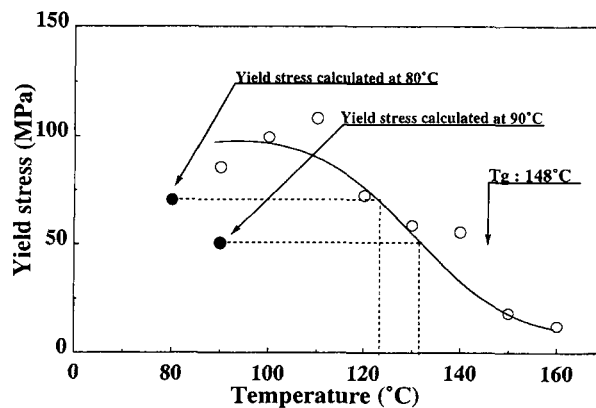
Figure 8 Yield stress vs. temperature of cured epoxy resin. Curing agent: 2,6-DHN. Open circles show the values of observed yield stress.
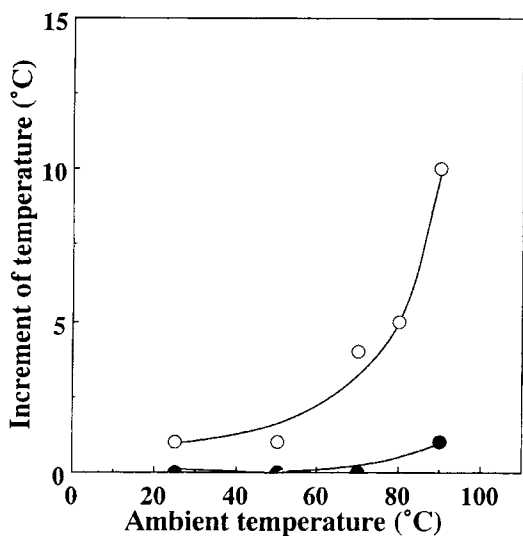
Figure 9 Increment of temperature at crack front deformation process of cured epoxy resins. Curing agent: (O) 2,6-DHN; (●) 2,3-DHN.

by a bending test near 120 and 135°C, respectively. This may mean that the temperature at the crack front in the system with 2,6-DHN is about 40°C higher than the ambient temperature.

To confirm the above consideration, we tried to observe the increase in temperature at the crack front. A highly sensitive thermocouple that has very low heat capacity was inserted in the cured resins 0.5 mm from a crack tip. The cycle load corresponded to 70% of the ultimate strength applied to the specimen. The changes in the output level of the thermocouple were recorded during the cycle deformation at the crack front. The increment of temperature measured by this experimental procedure is plotted in Figure 9. The increase in temperature at the crack front is clearly observed for the 2,6-DHN-cured system, though the temperature at the crack front is kept nearly constant in the 2,3-DHN-cured system during the cycle test. In addition, the increment of temperature increases rapidly over the β'-relaxation temperature. These results show that the increase in temperature at the crack front of the former system is due to the high-energy dissipation ability with the presence of the β'-relaxation. Thus, we conclude that the increase in the K_C values in the system cured with 2,6-DHN is attributed to the increase in the temperature at the crack front caused by the high-energy dissipation ability of this cured system.

CONCLUSION

The correlation between the low-temperature relaxation and the toughness of the epoxy resin cured with three dihydroxynaphthalene was investigated. Thus, we reached the following conclusions:

(i) A well-defined relaxation is observed near room temperature for the epoxy resin cured with 2,6-DHN. The relaxation was denoted here as the β'-relaxation.

(ii) The toughness of the cured epoxy resin having the β'-relaxation is considerably greater above the temperature region of the β'-relaxation than that of the cured resin without the β'-relaxation. The increase in the toughness of the former system is attributed to the increase in the temperature at the crack front caused by the presence of the β'-relaxation.

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