Effect of the introduction of methoxy branches on low-temperature relaxations and fracture toughness of epoxide resins

Mitsukazu Ochi, Takashi Shiba, Hidenao Takeuchi, Makoto Yoshizumi and Masaki Shimbo
Department of Applied Chemistry, Faculty of Engineering, Kansai University, Yamate-cho, Suita-shi, Osaka 564, Japan
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Some epoxide resins with or without methoxy branches were cured with an aromatic diamine. A well defined relaxation was observed near room temperature for all cured resins with methoxy branches, independent of the epoxide-resin structure. The relaxation was denoted here as the β'-relaxation. It is suggested that the β'-relaxation can be attributed to suppression of the motion of the hydroxy ether group due to the interaction between this group and the methoxy branch. The effect of the β'-relaxation on the fracture toughness of cured epoxide resins was studied by comparing the stress intensity factor K_c of a spiro-ring type epoxide resin containing a methoxy branch with that of a bisphenol A type resin. The value of K_c in the former system is considerably higher above the β'-relaxation temperature than that of the latter system. This is explained by the increase in the plastic deformation region at the crack front with increase in temperature caused by the presence of the β'-relaxation.

(Keywords: epoxide resins; methoxy branches; relaxation; fracture toughness)

INTRODUCTION

It is well known that bisphenol A type epoxide resin cured with aromatic diamines has a minor relaxation from −70 to −40°C[1–8]. 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 of other parts of the network structure[9,10].

In previous papers[11–13], we reported that the cured spiro-ring type epoxide resin with methoxy branches has another well defined relaxation near room temperature, denoted as the β'-relaxation. It was also revealed that the magnitude of the β'-relaxation depends on the concentration of methoxy branches and was comparable to that of the β-relaxation in the system having two methoxy branches per molecule[13].

It is expected that such a large relaxation near room temperature would considerably affect the mechanical and electrical properties of cured epoxide resins. Moreover, the mechanism for the occurrence of the β'-relaxation is also an interesting subject.

In this paper, the relaxation mechanism for the β'-relaxation is studied by comparing the relaxation behaviour of some epoxide resins with or without methyl or methoxy branches. In addition, the effect of the existence of the room-temperature relaxation on the fracture toughness is discussed for the spiro-ring type epoxide resin cured with an aromatic diamine.

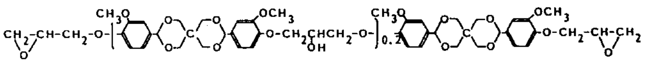
EXPERIMENTAL

Materials

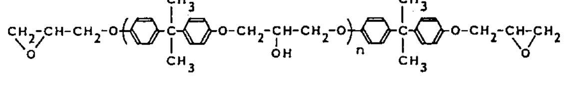
The epoxide resins used were a spiro-ring epoxide resin with methoxy branches, i.e. 3,9-bis[(3-methoxy-4-glycidyl)phenyl]-2, 4, 8, 10-tetroxaspiro[5.5]undecane (BMPTU, Epikote YX-7, epoxide equivalent 280±5), and three kinds of bisphenol A epoxide resins, i.e. 2,2-bis(4-glycidylphenyl)propane (DGEBA, Epikote 828, epoxide equivalent 190±5), 2,2-bis[(4-glycidyl-3,5-dimethyl)phenyl]propane (TMBA, epoxide equivalent 210±10) and 2,2-bis[(4-glycidyl-3-methoxy)phenyl]-propane (DMOBA, epoxide equivalent 244±5).

To compare with these resins, the phenol-novolac type (DMOPN) and the bisphenol F type (DMOBF) epoxide resins with methoxy branches were also used. An aromatic diamine, 4,4′-diaminodiphenylmethane (DDM), was used as the curing agent. The curing agent was EP grade material and was used without further purification.

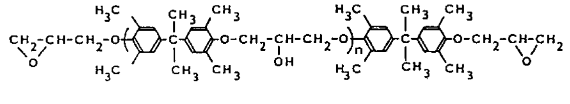
BMPTU



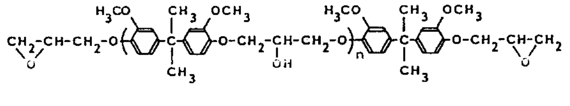
DGEBA



TMBA



DHOBA



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Curing of epoxide resin

The epoxide resins were degassed at 150°C for BMPTU and at 130°C for the other resins, in both cases under reduced pressure with stirring. Then stoichiometric amounts of diamine melted at 130°C in a draught oven were added (one epoxide group corresponds to one active hydrogen of the amino group). The mixtures were quickly stirred at 150°C for BMPTU and at 130°C for the other resins and were then poured into polytetrafluoroethylene moulds. The compounds based on BMPTU were cured at 180°C for 2 h and 200°C for 1 h. The other compounds were cured at 80°C for 2 h and 180°C for 6 h. The samples for the tests were machined from these cured epoxide-resin plates.

Measurements

Dynamic mechanical properties were determined using an inverted, free-oscillation, torsion pendulum (RD-1100AD, Rhesca Co. Ltd) according to ASTM D 2236-70. The temperature range from -160 to $+250$°C was studied. Samples were heated at $0.7°\mathrm{C\,min^{-1}}$ *in vacuo*.

The fracture toughness of the cured epoxide resins was evaluated from the critical value K_c of the stress intensity factor for the initiation of crack growth, which was determined from compact-tension specimens according to ASTM E 399-81. The compact-tension specimen is shown in *Figure 1*. The thickness of the specimens was adjusted from 3.6 to 4.0 mm. A sharp precrack was formed at the base of the slot by carefully tapping a fresh razor blade into the base[14]. The specimen was then mounted in an Instron-type tensile machine and loaded at a constant crosshead speed ($0.5\,\mathrm{mm\,min^{-1}}$). The load P *versus* displacement δ curve was recorded. The experiments were conducted over a range of temperature from -60 to $+150$°C.

The value of K_c was calculated from:

$$K_c = (P_i/Bw^{1/2})f(a/w)$$

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

where P_i is the load at crack initiation and B is the thickness of the specimen; w and a are the width of the specimen and the crack length, respectively, as defined in *Figure 1*: $f(a/w)$ is a geometric factor. It was confirmed for all measurements that the K_c values satisfy the following equation:

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

where σ_y is yield strength.

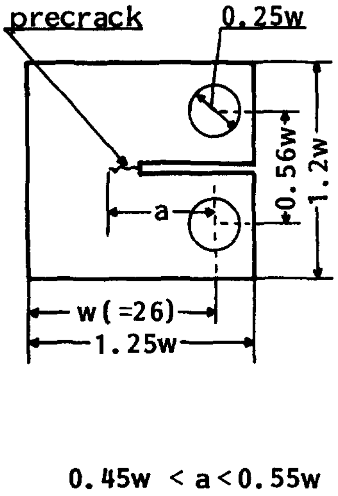

Figure 1 Compact-tension specimen for measuring fracture toughness

The critical value of the strain energy release rate G_c was calculated from the K_c value according to the following equation, assuming the plane-strain state:

$$G_c = K_c^2(1-\nu^2)/E$$

where E and ν are Young's modulus and Poisson's ratio for the cured epoxide resins, respectively. The shear modulus G rather than E was measured in this work. The value of E could be calculated from G by using an assumed value of 0.33 for Poisson's ratio ν and the following equation:

$$E = 2G(1+\nu) = 2.66G$$

The fracture surfaces of the compact-tension specimens were observed using a scanning electron microscope (JSM-35, 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 mechanism of cured epoxide resins with methoxy branches

The mechanical relaxations of various epoxide resins with methoxy branches and of DGEBA without such branches are shown in *Figure 2*. In the DGEBA system, a broad β-relaxation and a small β'-relaxation are observed at about -40 and 50°C, respectively. On the other hand, in the resin systems with methoxy branches, the magnitude and peak temperature of the β-relaxation are decreased and the well defined β'-relaxation is observed. This result shows that the low-temperature relaxations of the cured system are greatly affected by the presence of methoxy branches on the phenyl groups, independent of the epoxide resin structure.

We proposed in a previous paper[13] that the decrease in the magnitude and peak position of the β-relaxation with the introduction of methoxy branches is caused by suppression of the motion of the hydroxy ether group due to the interaction with the methoxy branch, and that the β'-relaxation is caused by the motion of the constrained hydroxy ether group.

To confirm this interaction, the temperature dependence of the peak position of the hydroxy group was measured by infra-red analysis for three cured epoxide resins, and is shown in *Figure 3*. The absorption maximum of the hydroxy group in the DGEBA system without methoxy branches appears at constant wavenumber, regardless of ambient temperature. However, the absorption maxima in the cured resins with methoxy branches are shifted to lower wavenumber with decrease in the temperature. This result shows that the hydroxy groups in the cured systems containing methoxy branches form a stronger hydrogen bond at low temperature than in the cured system without the branch[15]. The hydrogen bond is weakened with increasing temperature and dissociates substantially near 0°C.

From these results, we conclude that the changes in the β- and β'-relaxation behaviours with the introduction of

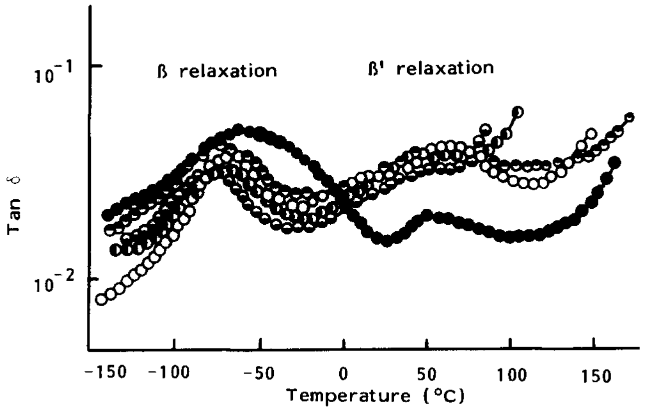

Figure 2 Loss tangent curves of cured epoxide resins with or without methoxy branches. Epoxide resins: (●) DGEBA; (○) BMPTU; (◒) DMOBA; (◐) DMOBF; (⊖) DMOPN. Curing agent: DDM

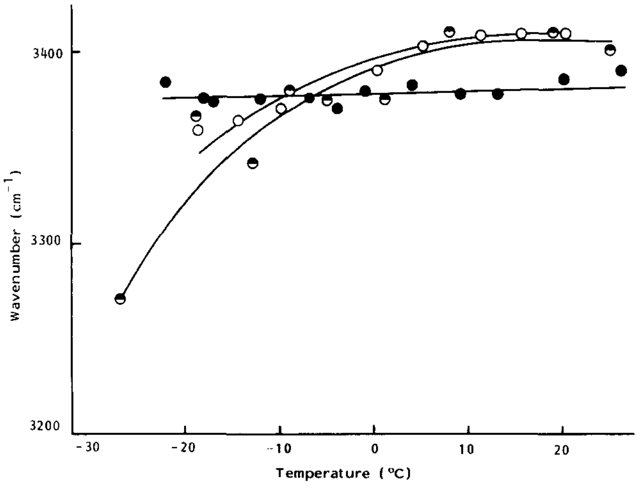

Figure 3 Wavenumber of the hydroxy peak in cured epoxide resins as a function of temperature. Symbols as in *Figure 2*. Curing agent: DDM

methoxy branches is due to the interaction between the hydroxy ether group and the methoxy branch. In addition, the mechanism for the β'-relaxation suggested in the previous paper[13] is reconfirmed from the results of *Figures 2* and *3*.

Mechanical relaxations of bisphenol A type epoxide resins with methyl or methoxy branches and with no branch are shown in *Figure 4*. The β- and β'-relaxation behaviours of the DMOBA with a methoxy branch is considerably different from that of the DGEBA system with no branch, as described in *Figure 2*. However, these relaxations of the TMBA with methyl branches are similar in magnitude and peak position to those of the DGEBA system. This result shows that a non-polar substituent, such as a methyl branch, does not affect the low-temperature relaxations of the cured resins because the non-polar group could not form an interaction with the hydroxy ether group.

Fracture toughness of cured epoxide resins

A well defined β'-relaxation is observed near 50°C for all epoxide resins containing methoxy branches. It is expected that such a large relaxation near room temperature would considerably affect the fracture toughness of cured epoxide resins.

The temperature dependence of stress intensity factor K_c for the spiro-ring type resin (BMPTU) with methoxy branches is shown in *Figure 5*, compared with that of the bisphenol A type resin (DGEBA) without methoxy branches. Though the glass transition temperatures (T_g) of both systems are about the same, the temperature dependence of K_c values is considerably different in each system. The values of K_c for the DGEBA system remain nearly constant, independent of temperature. On the other hand, the K_c values for the BMPTU system increase rapidly from near room temperature with an increase in temperature, though the K_c values in the low-temperature region are comparable in both the cured systems.

The temperature region where the K_c values begin to increase is almost compatible with the temperature where the β'-relaxation was observed in *Figure 2*. This may mean that the presence of the β'-relaxation is effective in improving the fracture toughness of the spiro-ring type epoxide resin.

The temperature dependence of strain energy release rate G_c for the spiro-ring type (BMPTU) and bisphenol A type (DGEBA) epoxide resins is shown in *Figure 6*. The value of G_c for the DGEBA system is slightly increased with an increase in temperature, while the G_c

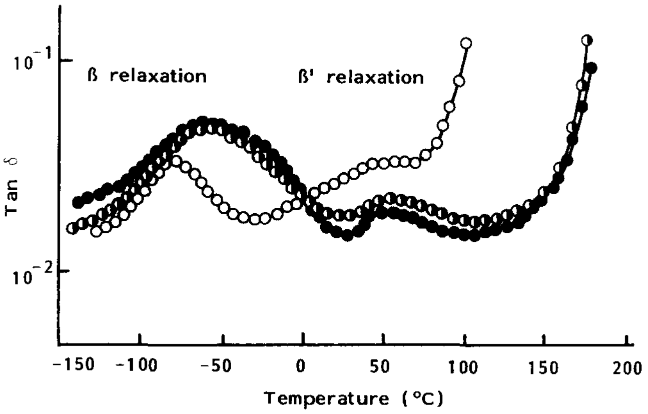

Figure 4 Loss tangent curves of cured bisphenol A type epoxide resins with methyl or methoxy branches and with no branch. Epoxide resins: (●) DGEBA; (○) DMOBA; (◑) TMBA. Curing agent: DDM

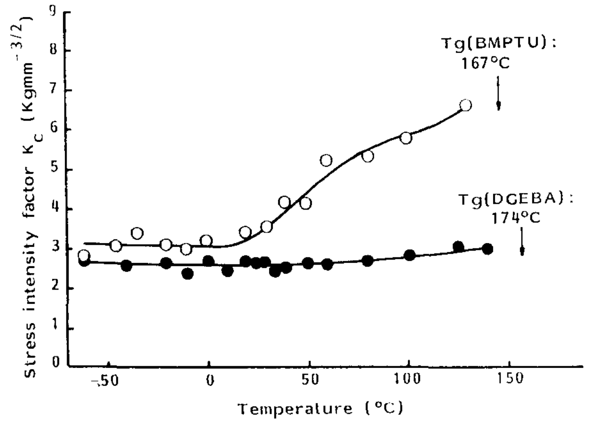

Figure 5 Stress intensity factor (K_c) *vs* temperature of cured epoxide resins. Symbols as in *Figure 2*. Curing agent: DDM

value for the BMPTU system is greatly increased from near room temperature. The G_c value is a direct measure of the fracture energy of samples. Accordingly, it is concluded that the spiro-ring type epoxide resin having the β'-relaxation is tougher above room temperature than the bisphenol A type resin.

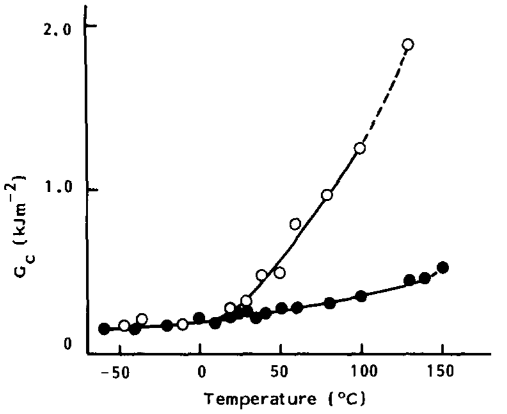

Figure 6 Strain energy release rate (G_c) *vs* temperature of cured epoxide resins. Symbols as in *Figure 2*. Curing agent: DDM

Morphology of fracture surfaces of cured epoxide resins

Scanning electron micrographs of the fracture surfaces of the compact-tension specimens are shown in *Figure 7* for the bisphenol A type epoxide resin and in *Figure 8* for the spiro-ring type resin, respectively. For both the cured resins, a plastic deformation zone in the immediate neighbourhood of the crack initiation line is clearly observed. 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 bisphenol A type resin, even if the measuring temperature increases. In this resin system, the values of K_c and G_c also remain nearly constant regardless of the temperature, as shown in *Figures 5* and *6*. However, the length of the plastic deformation zone for the spiro-ring type resin increases with increase in

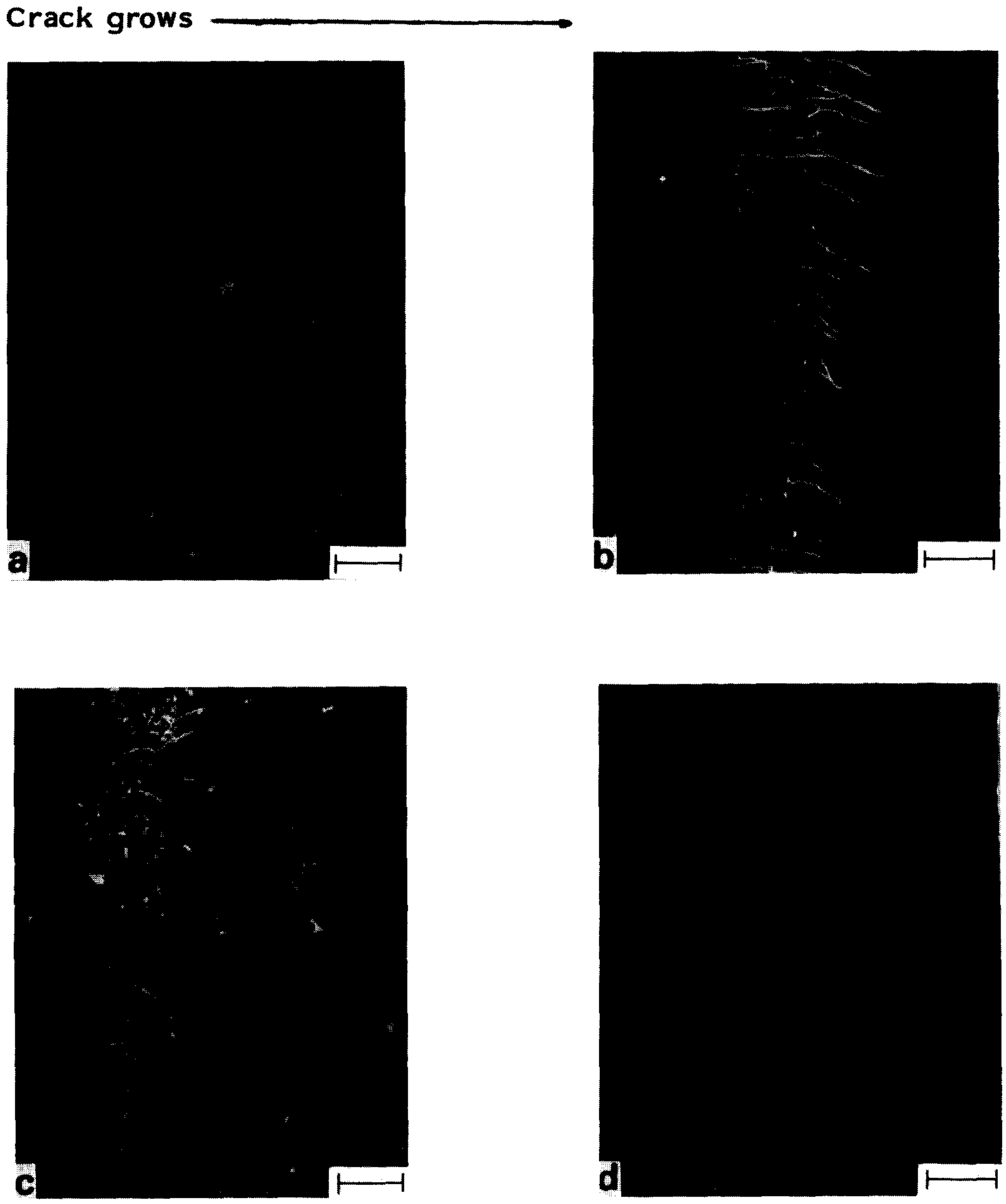

Figure 7 Scanning electron micrographs for fracture surfaces of the bisphenol A type resin system. Epoxide resin: DGEBA. Curing agent: DDM (a) 20°C; (b) 50°C; (c) 60°C; (d) 80°C. Scale bar = 0.1 mm

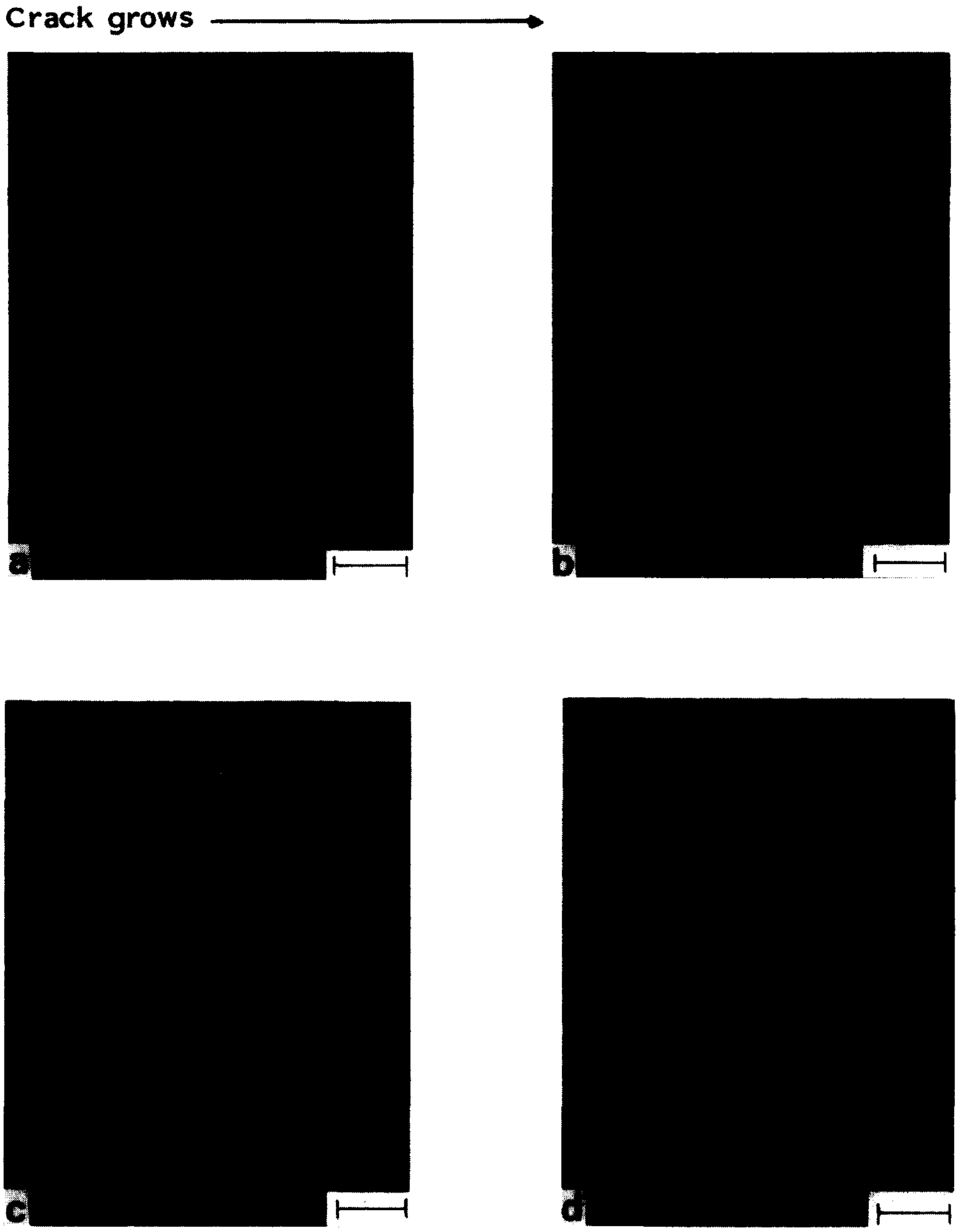

Figure 8 Scanning electron micrographs for fracture surfaces of the spiro-ring type resin system. Epoxide resin: BMPTU. Curing agent: DDM (a) 20°C; (b) 50°C; (c) 60°C; (d) 80°C. Scale bar = 0.1 mm

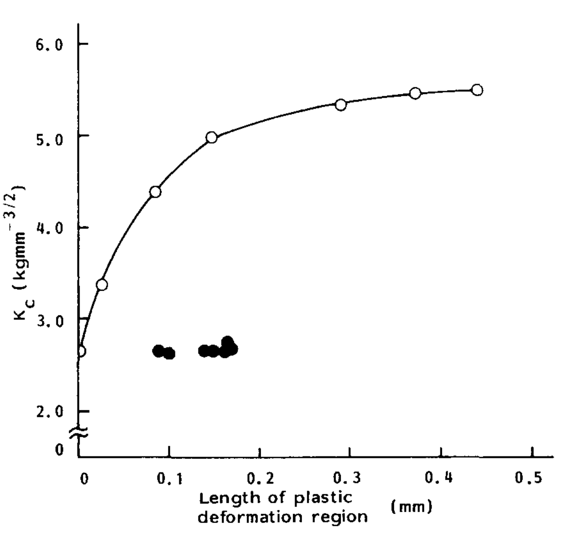

Figure 9 Relation between the values of K_c and the length cf plastic deformation region. Symbols as in *Figure 2*.Curing agent: DDM

temperature, especially in the temperature region where the β'-relaxation is observed. It is well known that the energy dissipated as heat during sample deformation becomes a maximum at the relaxation process of the sample. Accordingly, the presence of the β'-relaxation should increase the generation of heat on plastic deformation at crack front. Thus, we consider that the increase in the plastic deformation zone in the spiro-ring resin system is mainly attributed to the increase in temperature at the crack front due to the presence of the β'-relaxation.

The relation between the K_c values and the length of the plastic deformation region in the cured epoxide resins is shown in *Figure 9*. The K_c values for the spiro-ring type resin are increased with increasing length of the plastic deformation region[16,17]. The K_c values for the bisphenol A type resin 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 spiro-ring type resin is due to the increase in the plastic deformation region at the crack front.

CONCLUSION

Some epoxide resins with or without methoxy branches were cured with an aromatic diamine. The effect of the introduction of the methoxy branches on the low-temperature relaxation of the cured epoxide resins was studied in detail. In addition, the relation between the fracture toughness and the relaxation behaviour of cured epoxide resins was also investigated for the spiro-ring type and bisphenol A type resins. From these results, the following conclusions were reached.

(i) A well defined relaxation is observed near room temperature for the cured epoxide resins with methoxy branches. The relaxation was denoted here as the β'-relaxation.

(ii) The β'-relaxation is due to the motion of the hydroxy ether segment being suppressed by the interaction between this group and the methoxy branch.

(iii) The fracture toughness of the spiro-ring type epoxide resin with methoxy branches is considerably greater above the temperature region of the β'-relaxation than that of the bisphenol A type resin. The increase in the fracture toughness of the former system is explained by the increase in the plastic deformation region due to the presence of the β'-relaxation.

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