Molecular motion of several epoxy resins and influence of electron irradiation

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Electron irradiation effects on the molecular motion of epoxy resins and a composite reinforced by carbon fibre were studied. The materials used were three epoxy resins that were cured by diaminodiphenylmethane: diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of bisphenol F (DGEBF) and tetraglycidyl diaminodiphenylmethane (TGDDM); and carbon-fibre-reinforced TGDDM/diaminodiphenylsulphone. A mechanical loss peak appeared for all epoxy resins in the temperature range from 50 to 100°C. The results of heat treatments indicated that this relaxation is related to the local motion of chains subjected to an internal stress produced during curing. The internal stress was more marked for the tetrafunctional epoxy (TGDDM) than for the difunctional ones (DGEBA and DGEBF). The main reaction induced by irradiation is chain scission, and the order of radiation resistance of the epoxide monomers was revealed to be TGDDM > DGEBF > DGEBA.

(Keywords: DGEBA; DGEBF; TGDDM; DDM; DDS; molecular motion; crosslinking density; electron irradiation)

INTRODUCTION

High-performance fibre-reinforced plastics (FRP) have come to be used in various fields because of their superior properties per unit weight. Advanced carbon-fibre-reinforced plastic (CFRP) is used to make the components of aeroplanes and artificial satellites and is expected to be used as the structural material for space stations in the near future. Also, glass-fibre-reinforced plastic (GFRP) is expected to be used as the insulating material for the superconducting magnets of a magnetically confined fusion reactor.

Since space and fusion reactor environments involve high radiation fields[1–3], knowledge of radiation-induced deterioration in FRP is needed. Several factors can be considered in the deterioration of FRP; for example, damage to the matrix resin, the fibre itself and the fibre–matrix interface. To understand the mechanism of deterioration of composite materials, knowledge of damage to each component is required. In this work, radiation deterioration of the matrix resin has been studied.

Since the epoxy resin used as the matrix in FRP is highly crosslinked, the ultimate elongation was very small, i.e. less than 10%. Therefore, a tensile test, which is usually used for evaluation of damage in elastic polymers, is not adequate to evaluate the damage of epoxy resins. Another quantitative measurement, for example, the measurement of change in crosslink density, is necessary. In this work, the degree of radiation-induced disintegration of the network was evaluated based on changes in the mechanical relaxation behaviour, and the relation between radiation susceptibility and chemical structure was discussed.

EXPERIMENTAL

Diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of bisphenol F (DGEBF) and tetraglycidyl diaminodiphenylmethane (TGDDM) were used as epoxide monomers, and diaminodiphenylmethane (DDM) was used as hardener. Curing of DGEBA/DDM and DGEBF/DDM resins was performed in two steps: the molten mixtures of epoxide monomer (100 phr) and DDM (29 phr) were kept at 120°C for 2 h and then at 150°C for 16 h in a hot press. The TGDDM/DDM resin was cured in three steps: the molten mixture of TGDDM (100 phr) and DDM (40 phr) was kept at 120°C for 2 h, at 150°C for 2 h and then at 170°C for 16 h in a hot press. The chemical structures of the epoxide monomers and the hardeners used are shown in *Figure 1*.

Epoxy–carbon fibre composites were prepared from T-300/3601 (Toray) and IM-6/R6376 (CIBA-GEIGY) prepregs. The four-ply prepregs were laid up to 0°/90° direction and cured under the following conditions: heating to 120°C at a rate of 1.7°C min^{-1}, holding at this temperature for 1 h, heating to 180°C at a rate of 2°C min^{-1}, keeping at this temperature for 2 h and then cooling down at 2.5°C min^{-1} to 60°C in an autoclave. The 3601 resin is an approximately pure TGDDM/diaminodiphenylsulphone (DDS) and the R6376 resin is a TGDDM/DDS resin toughened by the inclusion of a third component.

Specimens (10 mm width, 100 mm length and 0.4 mm thickness) were irradiated in air by a 2 MeV electron beam from an electron accelerator. The dose rate measured by use of a cellulose triacetate (CTA) film dosimeter was 5 $\mathrm{kGy\,s^{-1}}$. To avoid any increase of temperature during irradiation, the specimens were wrapped with aluminium foil (15 μm) and attached with a conductive adhesive onto a stainless-steel radiation table, which was cooled by cold running water. Using this method the temperature of the specimens during irradiation was kept below 50°C.

Dynamic viscoelastic properties were measured by

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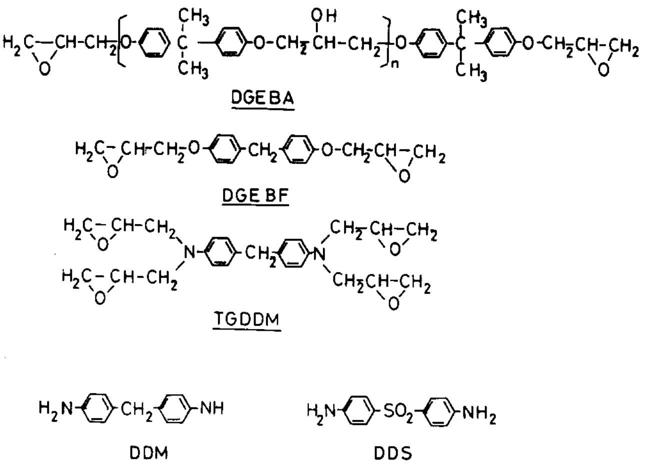

Figure 1 Chemical structures of epoxide monomers and hardeners

using a torsion-pendulum-type viscoelastometer (Rhesca RD-1000 AD) at 0.2 to 1 Hz in the temperature range of −160 to 300°C. Measurements were carried out by heating from −160°C at a rate of 1.5°C min^{-1}. Since the relaxation at low temperature is affected by trace absorbed water molecules[4–7], the specimens were dried on silica gel in vacuum for over 7 days.

RESULTS

The logarithmic decrement and dynamic shear modulus are shown as functions of temperature for the unirradiated DGEBA/DDM epoxy resin in *Figure 2*. The triangles represent the first heating curve (first run) and the circles show the heating curve that was measured again after the first run (second run). Three distinct relaxation peaks are observed at −50, 80 and 170°C in the first run. These relaxations are named γ, γ' and β relaxation from low to high temperature, respectively. The shear modulus decreases abruptly at the temperature corresponding to the β relaxation and then approaches a constant value (rubbery plateau). In the second run, the profile of the γ relaxation is sharpened slightly, the shape of the β relaxation is broadened to the low-temperature side and the modulus in the rubbery plateau decreases slightly.

The relaxation spectra of DGEBA/DDM unirradiated and irradiated with 10 MGy are shown in *Figure 3*. The following changes are induced by irradiation: (a) the γ relaxation peak sharpens slightly and its magnitude decreases, (b) the β relaxation peak shifts from 168 to 149°C, (c) the modulus in the rubbery plateau decreases and (d) a new relaxation appears as a shoulder at 25 to 110°C instead of the γ' relaxation. This new relaxation is named β' relaxation.

Figure 4 shows the results for DGEBA/DDM irradiated with 20 MGy in the first and second runs. The radiation-induced changes are enhanced: (a) the γ relaxation peak becomes sharper and its magnitude decreases further, (b) the β relaxation shifts to lower temperature and (c) the rubbery plateau does not become obvious. In the second run, the β relaxation peak shifts to slightly higher temperature and the β' relaxation disappears.

Figure 5 shows the relaxation spectra of DGEBF/DDM unirradiated and irradiated with 20 MGy. The β relaxation temperature of the unirradiated specimen is lower than that of DGEBA/DDM and its γ' relaxation is not obvious. The changes induced by irradiation are similar to those of DGEBA/DDM: i.e. (a) the magnitude of the γ relaxation peak decreases, (b) the β' relaxation appears, (c) the β relaxation shifts to lower temperature and (d) the modulus in the rubbery plateau decreases.

The relaxation behaviour of unirradiated TGDDM/DDM epoxy resin in the first and second runs is shown in *Figure 6*. Three distinct relaxation peaks are observed

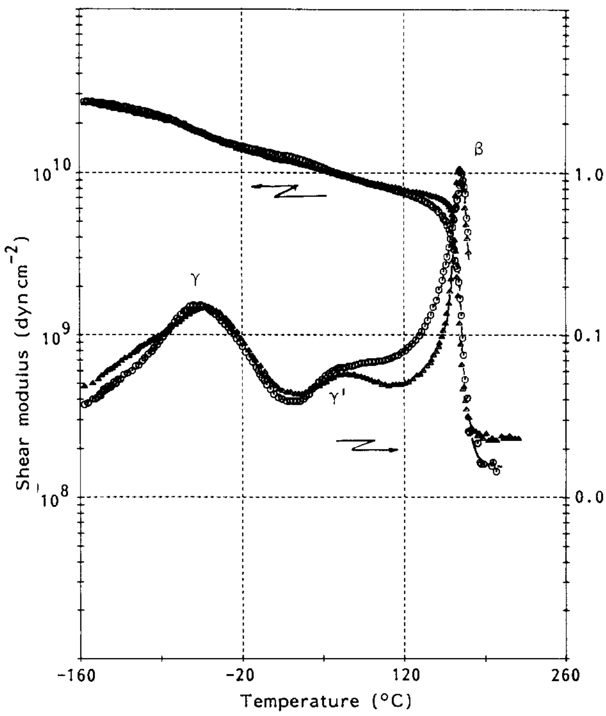

Figure 2 Relaxation spectra of unirradiated DGEBA/DDM resin: (Δ) first and (○) second runs

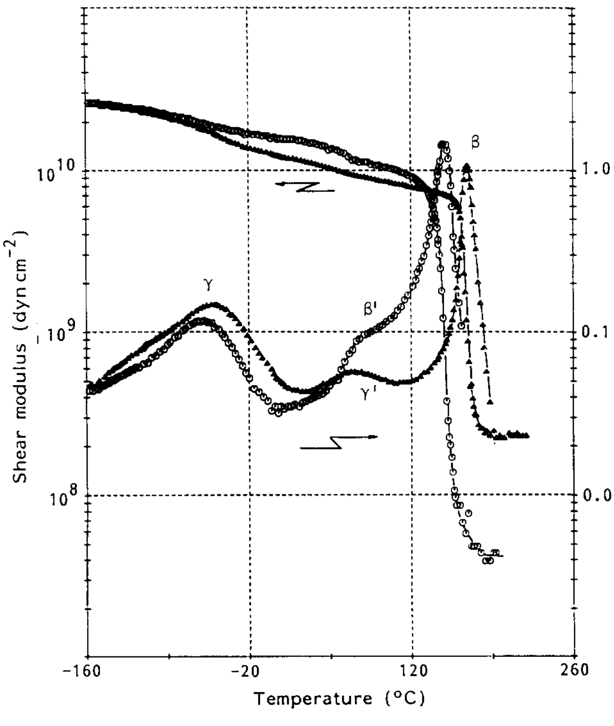

Figure 3 Relaxation spectra of DGEBA/DDM resin in the first run: (Δ) unirradiated and (○) irradiated with 10 MGy

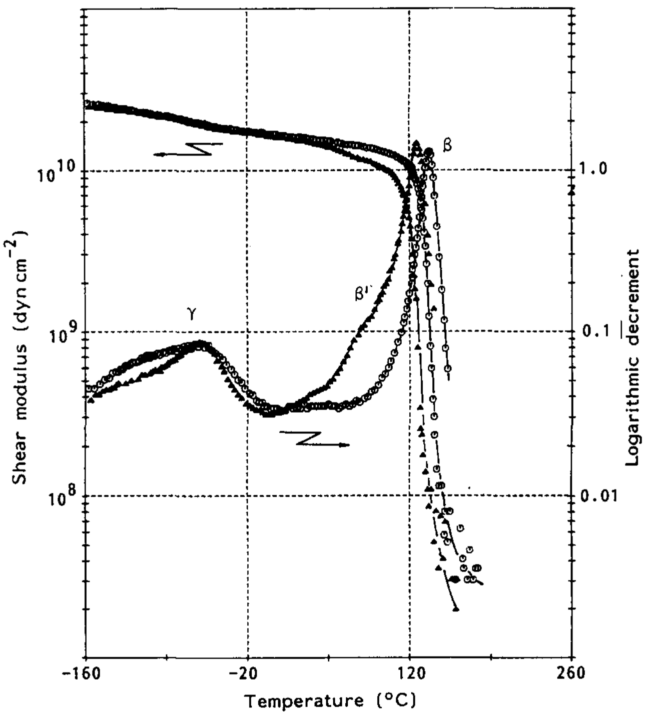

Figure 4 Relaxation spectra of DGEBA/DDM resin irradiated with 20 MGy: (Δ) first and (○) second runs

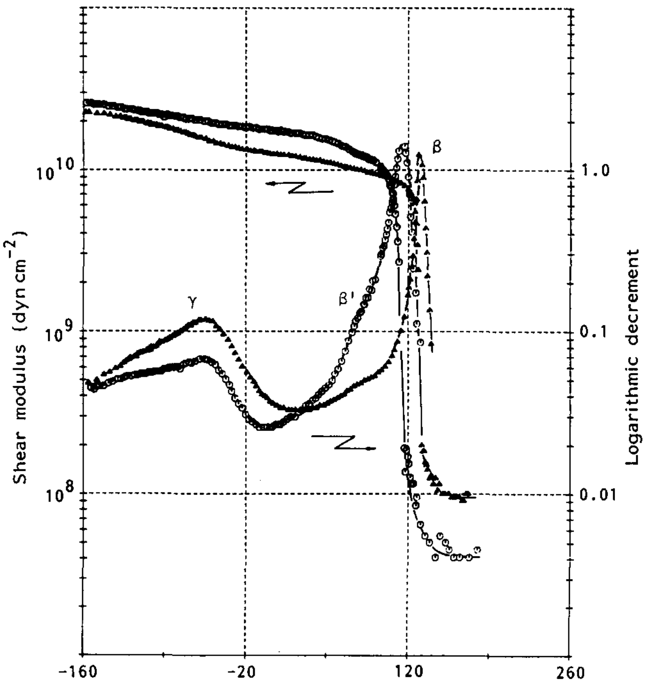

Figure 5 Relaxation spectra of DGEBF/DDM resin in the first run: (Δ) unirradiated and (○) irradiated with 20 MGy

in the first run, but in the second run the γ and γ' relaxation peaks become diffuse. The β relaxation peak in the first run is observed at 249°C, but the shear modulus decreases monotonically even above the β relaxation temperature. In the second run, the β relaxation peak temperature shifts to 180°C and the rubbery plateau becomes obvious.

Figure 7 shows the relaxation spectra of the TGDDM/DDM resin irradiated with 30 MGy in the first and second runs. On irradiation, a decrease of the magnitude of the γ relaxation, the appearance of β' relaxation and a shift of the β relaxation peak temperature from 249 to 202°C were observed. In contrast to the case of the unirradiated specimen, a rubbery plateau is observed even in the first run. In the second run, broadening of the γ relaxation, the appearance of the γ' relaxation and a shift of the β relaxation peak to slightly higher temperature were observed.

Figure 8 shows the temperature dependence of the

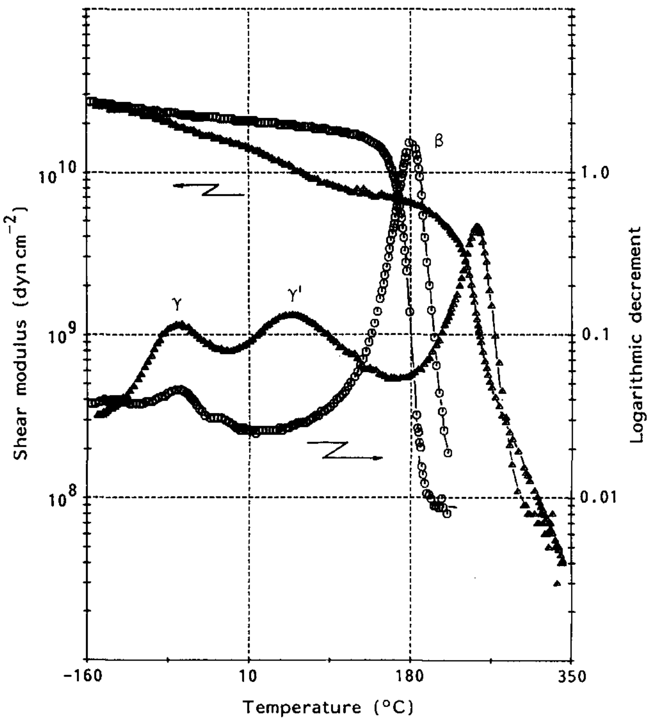

Figure 6 Relaxation spectra of unirradiated TGDDM/DDM resin: (Δ) first and (○) second runs

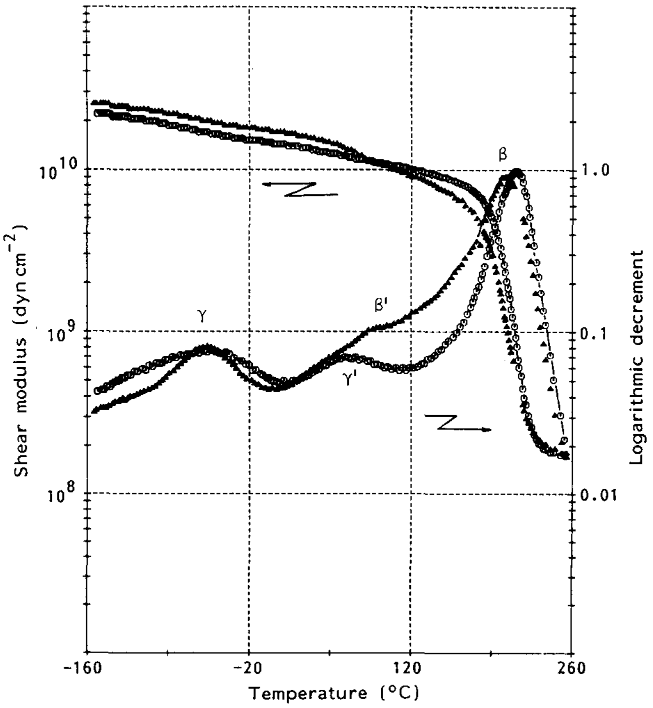

Figure 7 Relaxation spectra of irradiated TGDDM/DDM resin with 30 MGy: (Δ) first and (○) second runs

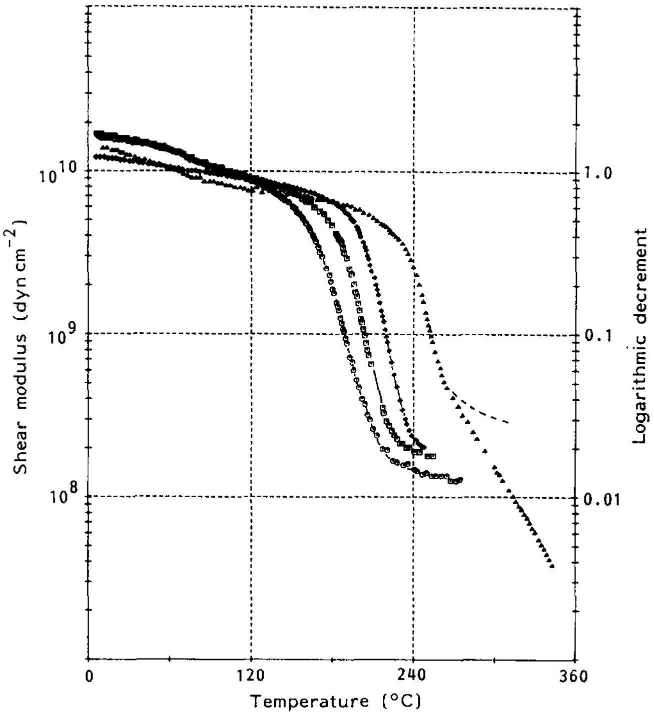

Figure 8 Temperature dependence of shear modulus around the glass transition temperature for TGDDM/DDM resin irradiated with various doses: (Δ) unirradiated, (◇) 30 MGy, (□) 60 MGy, and (○) 120 MGy

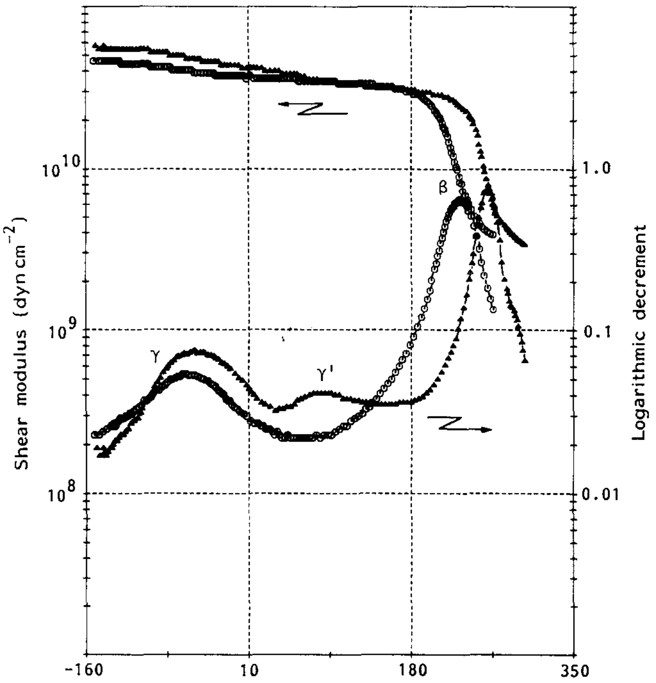

Figure 9 Relaxation spectra of unirradiated T-300/3601 composite: (Δ) first and (○) second runs

shear modulus for TGDDM/DDM resin irradiated with various doses. The shear modulus decreases sharply at the temperature corresponding to the β relaxation. The temperature of the sharp decrease shifts to lower values with increase of dose. The rubbery plateau is absent in the unirradiated specimen, but it becomes obvious in the irradiated specimens, and the modulus at the rubbery plateau decreases with dose.

The relaxation spectra for the unirradiated T-300/3601 composite is shown in *Figure 9*. In the first run the three relaxation peaks are observed distinctly. In the second run the γ' relaxation disappears and the β relaxation peak shifts from 263 to 233°C. These findings are the same as for unirradiated TGDDM/DDM epoxy resin.

Figure 10 shows the results for unirradiated IM-6/R6376 composite in the first and second runs. In this case, the difference between the relaxation spectra for the first and second runs is smaller than that of T-300/3601 composite.

Figure 11 shows the relaxation spectra for the T-300/3601 composite unirradiated and irradiated with 30 MGy. The changes induced by irradiation are almost the same as for the TGDDM/DDM epoxy resin, i.e. the narrowing of the γ relaxation peak, the appearance of β' relaxation and a shift of the β relaxation to lower temperature. The β relaxation peak temperature is shown as a function of dose for T-300/6301 and IM-6/R6376 composites in *Figure 12*. The decreasing rate per dose of T-300/3601 composite in the initial stage is larger than that of IM-6/R6376 composite, but it becomes rather less in the higher dose region.

DISCUSSION

Origin of relaxation

All of the as-cured epoxy resins used in this work showed three distinct relaxations. The β relaxation appearing in the highest temperature region can be attributed to the three-dimensional motion of chains between crosslinking points (main chain) during the glass transition process, because the shear modulus decreases sharply at the same time.

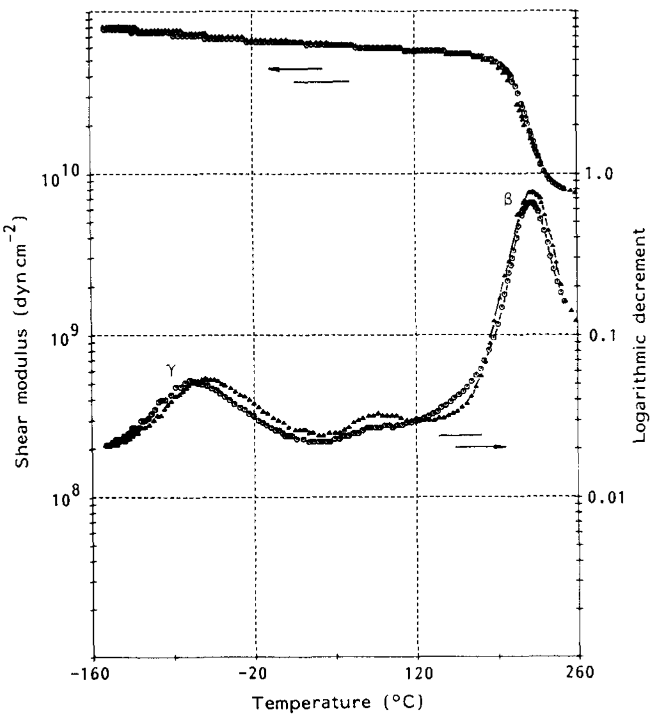

Figure 10 Relaxation spectra of unirradiated IM-6/R6376 composite: (Δ) first and (○) second runs

The β relaxation peaks of the unirradiated TGDDM/DDM resin and T-300/3601 composite having TGDDM/

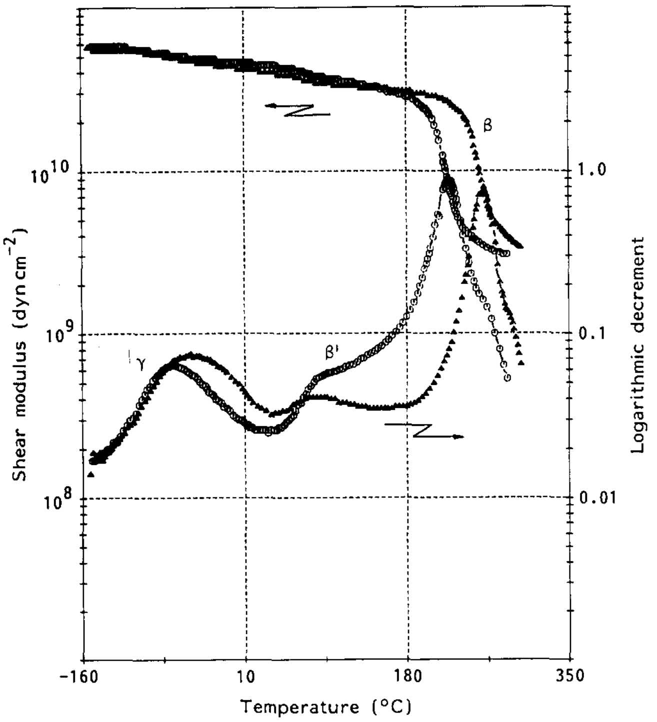

Figure 11 Relaxation spectra of T-300/3601 composite: (Δ) unirradiated and (○) irradiated with 30 MGy

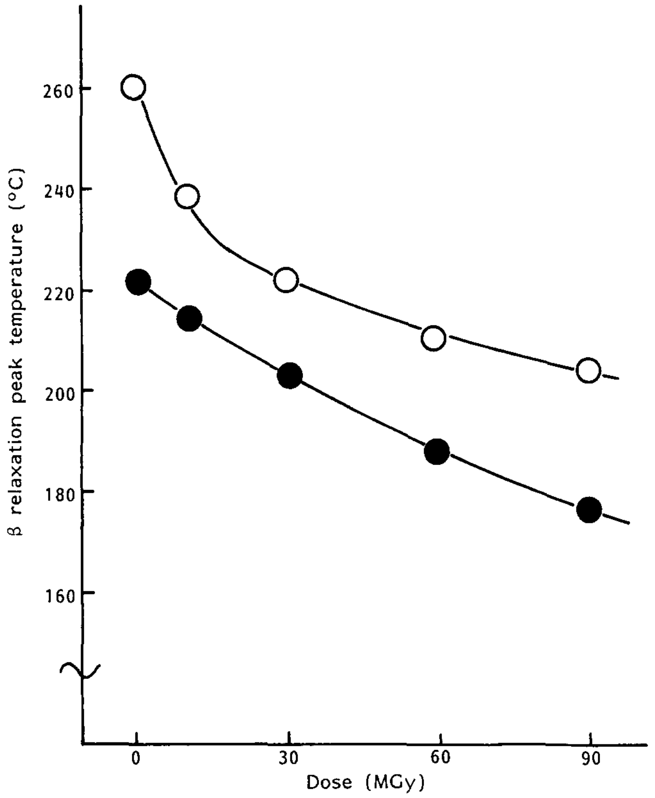

Figure 12 Dose dependence of glass transition temperature for T-300/3601 (○) and IM-6/R6376 (●) composites

DDS as matrix resin shifted extensively to low temperature in the second run. Wilson *et al.*[8] reported also that the β relaxation peak of TGDDM/DDS resin shifts to lower temperature on cyclic heat treatment through 280°C. It is known in highly crosslinked materials that the glass transition temperature and the modulus at the rubbery plateau are related to the crosslink density[9]: the glass transition shifts to higher temperature and the modulus increases with increase of crosslink density. Since the lowering of the glass transition temperature indicates a decrease of the crosslink density, disintegration of the network structure takes place partially by heat treatment over the glass transition temperature.

In contrast, the changes in the molecular motions induced by heat treatment for DGEBA/DDM are small (*Figure 2*). Also, the molecular motions of DGEBF/DDM are scarcely altered by the heat treatment during the first run. These facts indicate that the thermal resistance of the cured resin of the difunctional epoxide is greater than that of the tetrafunctional epoxide. It can be easily supposed that the tetrafunctional epoxide monomer creates a non-uniformity in the network structure during the cure process, such as a large distribution of the molecular weight of network chains. The non-uniformity of the crosslinking structure would give a stress to the chains. The marked thermal deterioration seen in TGDDM/DDM resin and T-300/6376 composite would be caused by preferential disintegration of network chains that are subjected to the internal stress.

The continuous decrease of the modulus above the glass transition temperature seen in the unirradiated TGDDM/DDM resin indicates that the network structure is successively disintegrated during heating. If disintegration of the network does not take place, the modulus *versus* temperature curve would change to the broken curve in *Figure 8*. In the case of IM-6/R6376 composite, the effect of heat treatment is small. Since R6376 resin is modified by the addition of a third component, the internal stress might be lowered.

The γ relaxation at the lowest temperature has been assigned to the local motion of main chains in the glassy state[10–18]. Especially, Keenan assigned it to crankshaft rotational motion of the glycidyl moiety[14]. The γ' relaxation (ω relaxation in Keenan *et al.*'s terminology or β relaxation in almost all other researchers' terminology) has usually been assigned to the motion of chains existing in a region with low crosslink density and/or of unreacted epoxide moiety[14,18]. The assignment of the γ' relaxation, however, has not necessarily been clarified yet.

If the γ' relaxation is due to the motion of chains existing in a region with low crosslink density, this relaxation should appear in a lower temperature region than that of the relaxation, because the restriction due to the crosslinking points would be lower than that for chains in a region fully crosslinked. The tailing-off of the β relaxation peak towards the low-temperature side is observed in the second run of DGEBA/DDM (*Figure 2*). Since the modulus at the rubbery plateau decreases at the same time, this tailing-off would be brought about by an increase of the region of low crosslink density. However, the profile and the magnitude of the γ' relaxation in the second run can be regarded as being scarcely altered. It is better to assign the γ' relaxation to the motion of a chain restricted further by crosslinking points.

The latter alternative assignment, i.e. the motions of unreacted epoxide moiety, would also be unreasonable. Mikolajczak *et al.*[18] reported that the magnitude and peak temperature of the γ' relaxation of DGEBA/DDM (β in their terminology) are scarcely affected by further curing after a normal cure. It is difficult to assign the γ' relaxation to the motion of unreacted epoxide moiety.

Finally, from the disappearance of the γ' relaxation accompanied by disintegration of the network structure (*Figures 6* and *9*), it should be noted that this relaxation should be assigned to the local motion of chains restricted heavily by crosslinking points, which were produced by a heterogeneous crosslinking reaction.

Effects of irradiation

Narrowing of the γ relaxation peak, the appearance of the β' relaxation and a shift of the glass transition to lower temperature with increase of dose were observed in all of the epoxy resins studied. Changes in the properties of polymeric materials caused by ionizing radiation have mainly been ascribed to chemical reactions like chain scission and/or formation of crosslinks. It has been reported also in epoxy resins that further curing and/or chain scission are produced by irradiation of γ-rays and electrons[19–26].

The relaxation termed β' appears on irradiation in all of the resins and composites (*Figures 3*, *4*, *5*, *7* and *11*). This relaxation disappears in the second run (*Figures 4* and *7*). The same relaxation was observed in irradiated polymers having high glass transition temperatures, and was assigned to molecular motion related to the chain ends produced by chain scission[7,27,28]. Appearance of the β' relaxation is proof of the occurrence of radiation-induced chain scission.

Tobolsky *et al.*[29] derived the following relation between the shear modulus G' at the rubbery plateau and the number-average molecular weight of the chain between crosslinking points M_c:

$$G' = \rho(r_i^2/r_f^2)RT/M_c[1 - (2M_c/M_n)] \qquad (1)$$

where ρ is the density, r_i^2/r_f^2 is the ratio of the mean-square end-to-end distance of the polymer chains in the sample in the solid state to that in a randomly coiled chain (in solution), R is the gas constant, T is the absolute temperature at G', and M_n is the molecular weight of the backbone chain. Of these parameters, determination of the ratio r_i^2/r_f^2 is difficult. If it is assumed that, in the solid state, polymer chains exist in random coil conformation, the ratio becomes 1.0. The factor $[1 - (2M_c/M_n)]$ is a term correcting for the chain-ends effect. This term is also equal to 1.0, because $M_n \gg M_c$ in highly crosslinked polymers. Consequently, equation (1) is simplified to:

$$G' = \rho RT/M_c \qquad (2)$$

By using this relation, Murayama *et al.*[30] succeeded in determining M_c of epoxy resins with various crosslink densities, which were prepared by varying the ratio of epoxide monomer to hardener. In *Table 1* the value of M_c calculated by applying this method and the crosslink density ν_e ($\nu_e = \rho/M_c$) are summarized together with raw data.

For the three epoxide systems, M_c increases and ν_e decreases with dose, indicating that chain scission takes place mainly during irradiation. The crosslink density of DGEBA/DDM decreases to 36% of the original value on irradiation with 10 MGy, whereas that for DGEBF/DDM only decreases to 39% of the initial value even on 30 MGy irradiation. This shows that the radiation resistance of DGEBF/DDM is better.

The crosslink density of unirradiated TGDDM/DDM cannot be calculated because of the absence of the rubbery plateau, but this resin is more radiation-resistant than DGEBF/DDM judging from the high crosslink

Table 1 Changes in crosslink density on irradiation

(a) DGEBA/DDM

Dose (MGy)	0	5	10	30
T_g (°C)	168	152	145	127
G' ($\times 10^{-8}$ dyn cm^{-2})	2.31	1.50	0.791	0.227
Temp. at G' (°C)	219	185	190	153
M_c	195	279	535	1722
ν_e ($\times 10^3$ mol cm^{-3})	6.1 (1.0)	4.3 (0.71)	2.2 (0.36)	0.7 (0.12)

(b) DGEBF/DDM

Dose (MGy)	0	5	10	20	30
T_g (°C)	129	126	117	108	105
G' ($\times 10^{-8}$ dyn cm^{-2})	1.01	0.765	0.410	0.382	0.360
Temp. at G' (°C)	172	179	165	160	170
M_c	403	539	976	1033	1124
ν_e ($\times 10^3$ mol cm^{-3})	3.0 (1.0)	2.2 (0.73)	1.2 (0.40)	1.2 (0.40)	1.1 (0.37)

(c) TGDDM/DDM

Dose (MGy)	0	10	30	60	90
T_g (°C)	250	223	202	193	189
G' ($\times 10^{-8}$ dyn cm^{-2})	–	2.02	1.81	1.42	1.30
Temp. at G' (°C)	–	280	255	279	275
M_c	–	209	243	323	417
ν_e ($\times 10^3$ mol cm^{-3})	–	5.8	4.9	3.7	2.9

density after irradiation with 90 MGy. In contrast to the unirradiated TGDDM/DDM resin (*Figure 6*), the irradiated specimen showed the rubbery plateau even in the first run, and its β relaxation peak shifted to rather higher temperature after heat treatment over the glass transition temperature (*Figure 7*). This result means that thermal degradation is suppressed by irradiation. Radiation-induced suppression of thermal degradation would result from preferential disintegration of network chains subjected to internal stress.

The decreasing rate per dose of the β relaxation temperature of T-300/3601 composite is marked up to 30 MGy, and it becomes moderate in the higher dose region. Also, TGDDM/DDM resin shows similar behaviour against dose (*Table 1*). These facts might result from radiation-induced preferential disintegration of network chains subjected to internal stress in the low-dose region. In contrast, the β relaxation temperature of IM-6/R6376 composite decreases monotonically with dose. This fact indicates also that the internal stress is lowered by the inclusion of a third component.

SUMMARY

Thermal and irradiation effects on difunctional (DGEBA and DGEBF) and tetrafunctional (TGDDM) epoxy resins cured by DDM and a composite having TGDDM/DDS resin as the matrix are summarized as follows.

The γ' relaxation appearing between the γ relaxation (local motion of chains) and the β relaxation (glass transition) is assigned to local motion of chains subjected to the internal stress caused by non-uniformity in the crosslinking structure. This stress for tetrafunctional epoxy resin is larger than for difunctional ones. Network chains subjected to the internal stress are preferentially disintegrated by heat treatment over the glass transition temperature and irradiation.

The main reaction induced by irradiation is chain scission (disintegration of networks). The order of radiation resistance of epoxide monomers is deduced as follows:

$$\mathrm{TGDDM} > \mathrm{DGEBF} > \mathrm{DGEBA}$$

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