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Thermally stimulated recovery of plastic strain in crosslinked and uncrosslinked epoxy/amine systems

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Abstract

Effects of crosslinks on plastic strain recovery in epoxy glass was studied by means of thermally stimulated strain recovery (TSSR) and differential scanning calorimetry (DSC) techniques. Two types of samples were prepared from bisphenol-A type epoxide monomer: one had a crosslinked structure cured by 4,4′-diaminodiphenylmethane and the other had a linear uncrosslinked structure polymerized by aniline. Both specimens were compressed first in the rubbery state and subsequently compressed further in the glassy state. After compressed in the glassy state, the specimens were subjected to the TSSR and the DSC measurements. The TSSR results indicated that the amount of plastic strain recovering at temperatures below the glass transition temperature T_g was larger for the crosslinked sample than for the linear sample. On the other hand, the DSC results indicated that the amount of exothermic heat flow at temperatures below T_g was less for the crosslinked sample than for the linear sample. These results presumably indicate that, for the crosslinked epoxy glass deformed in the glassy state, glass-like strain recovers quite cooperatively with rubber-like strain at temperatures below T_g, in contrast to independent recovery of these strains in the linear epoxy glass.

Keywords: Epoxy glass; Differential scanning calorimetry; Thermally stimulated deformation recovery

1. Introduction

Owing to high specific strength and specific stiffness, epoxy glass is widely used as structural materials. However, epoxy glass has such superior properties in limited ranges of temperature and deformation: at temperatures higher than the ambient temperature, a stress–strain relationship for epoxy glass is frequently non-linear viscoelastic as observed in yielding phenomena.

There exists plastic strain in epoxy glass unloaded after non-linear viscoelastic deformation. To study non-linear viscoelastic deformation mechanisms under large deformation, thermally stimulated strain recovery technique was applied to epoxy glass [1,2], showing that plastic strain after non-linear viscoelastic deformation could be divided into two recovering strain components: one was recoverable with exothermic heat at temperatures below the glass transition temperature (designated as the LTR peak in the references), and the other was recoverable without exothermic heat at temperatures slightly above the glass transition temperature (the HTR peak). The LTR peak indicated that the plastic deformation of polymer glass was accompanied by structural changes, which created a highly excited plastic state, and such an excited plastic state disappeared when the deformed polymer glasses were heated. These authors concluded that the LTR peak reflected the decompositions of the shear defects, which contributed to local shear deformations, and the HTR peak reflects the changes of conformational states of polymer chains. In our previous paper [3], we studied thermally stimulated strain recovery of plastically compressed epoxy glass and found that the structure of epoxy glass changed to a structure which was less susceptible to recover than that of a linear molecular polymer glass.

We also monitored birefringence changes in epoxy glasses under uniaxial elongation [4], and a modified stress-optical rule [5–7] was applied for the experimental results to separate stress into two stress components: glassy stress and rubbery stress. For crosslinked epoxy glass, the glassy stress and the rubbery stress cooperatively increased over deformation, while these stress components increased independently in epoxy glass with a linear molecular structure. To clarify the cooperativity in largely deformed epoxy glass, it is necessary to understand thermodynamic behavior of epoxy glass, which gives

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important informations about thermodynamics in polymer glass.

In the present study, differential scanning calorimetry measurements and thermally stimulated strain recovery tests were performed on plastically deformed epoxy glasses: one has a crosslinked structure and the other has a linear molecular structure. The effects of crosslinks on recovery of plastic strain resulting from non-liner viscoelastic deformation are discussed. This is probably the first application of the TSDR and the DSC technique to study cooperativity in largely deformed epoxy glass.

2. Samples

Bisphenol-A type epoxide precursor (Dainippon Ink and Chemicals, Inc., $M_w \approx 380$, epoxy equivalent weight ≈ 190) was cured by 4,4′-diaminodiphenylmethane (4,4′-DDM) to form a crosslinked structure (sample C). The molar ratio of the epoxy precursor and the amine was that of the stoichiometric ratio. Mixture was cured at 70 °C for 12 h followed by a heat treatment at 160 °C for 12 h. The glass transition temperature T_g of the sample C measured by differential scanning calorimetry (DSC) was about 155 °C. The average molecular weight between crosslinks was about 493 g/mol being calculated from rubber elasticity.

The epoxide precursor was also cured by aniline to form an uncrosslinked structure (sample L). The glass transition temperature of the sample L was about 87 °C, and the number average molecule weight was about 26,000 measured by gel permeation chromatography.

The chemical structures of the curing agents and the samples are shown in Fig. 1. The difference in molecular structure between the samples is that crosslinks exist only in the sample C.

3. Experiments

Cylindrical specimens (diameter, 4.0 mm; height, 5.0 mm) were cut from epoxy glasses. The specimens were annealed at 5 °C above T_g (160 °C for sample C and 92 °C for sample L) for 6 h and then slowly cooled down to room temperature at a cooling rate of 0.1 °C/min.

The specimens were first compressed to a fixed amount of strain $\varepsilon^{(R)}$ in the rubbery state ($T = T_g + 5$:160 °C for sample C and 92 °C for sample L) at a constant strain rate of 1.0×10^{-3} [1/s], and then quickly cooled down by blowing room air on the specimens for about 90 s. The length of the specimens was measured immediately after cooling. Then, the pre-strained specimens were compressed further by a strain $\varepsilon^{(G)}$ in the glassy state ($T = T_g - 35$:120 °C for sample C and 52 °C for sample L. Such a choice of test temperature is justified by experimental results [8] and the WLF equation [9] stating that relative molecular mobility is only dependent on $T_g - T$). The strained specimens were quickly cooled down to room temperature by blowing room air to the specimens for about 60 s. Here, strains $\varepsilon^{(R)}$ and $\varepsilon^{(G)}$ are engineering strain calculated from the initial length of an undeformed specimen (i.e. 5.0 mm). After cooled down, the specimens were kept in a desiccator at room temperature for 24 h. As the deformed specimens recovered a portion of there size in the first minutes after unloading, significant deviations in experimental results were caused by small changes in the period of time before following TSSR and DSC tests. To avoid such uncertainties, we studied the effect of the time period on a scatter in TSSR and DSC results and found that the scatter was negligible when the specimens were kept at room temperature for more than 24 h before TSSR measurements or DCS tests.

In TSSR measurements, the strained specimens were heated at a constant heating rate of 1.0 °C/min. The amount of strain

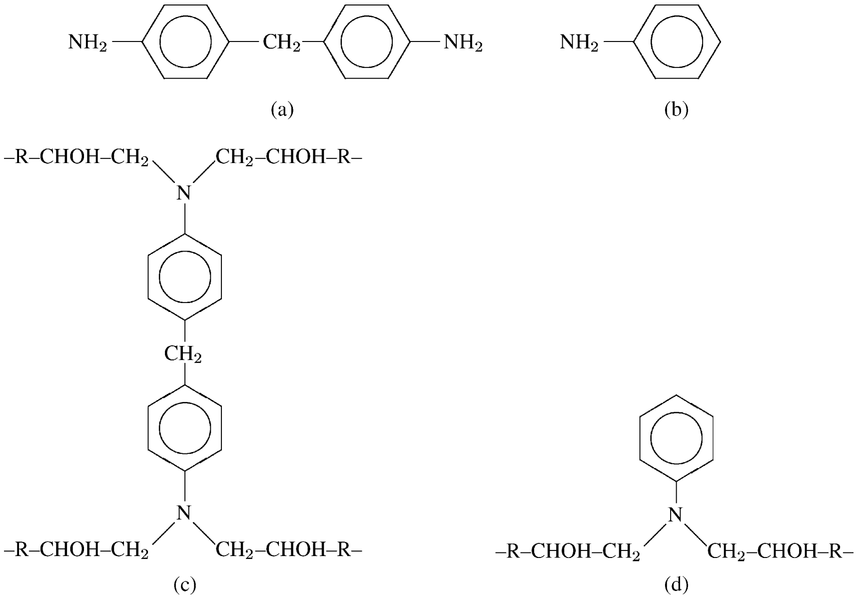

Fig. 1. Molecular structures of curing agents and epoxy glasses. (a) 4,4′-DDM, (b) aniline, (c) sample C (epoxy cured by 4,4′-DDM), (d) sample L (epoxy cured by aniline).

recovery was measured during heating using a non-contact displacement sensor.

The DSC measurement was carried out to the specimens C and L prepared in the same manner as the specimens used to the TSSR measurements. A constant heating rate was set to 1.0 °C/min in order to compare DSC results to TSSR results isochronously.

4. Results

4.1. Stress–strain relationships

Stress–strain curves for pre-strained specimens C compressed in the glassy state are shown in Fig. 2. Each curve is horizontally shifted according to the amount of residual strain before compression in the rubbery state, $\varepsilon_r^{(R)}$. The value of $\varepsilon_r^{(R)}$ and the amount of strain applied in the rubbery state $\varepsilon^{(R)}$ are indicated in the figure. Since a small portion of the strain $\varepsilon^{(R)}$ recovered instantaneously when the specimens were unloaded, the amount of $\varepsilon_r^{(R)}$ was less than $\varepsilon^{(R)}$. The solid curve rising from the origin is a stress–strain relationship for specimen of $\varepsilon^{(R)}=0$. Before the compression, the specimens of $\varepsilon^{(R)}=0$ were subjected to the same thermal treatments as those for other pre-strained specimens: the specimens were kept at 160 °C and then quickly cooled down to room temperature. The horizontal axis is engineering strain ε calculated from the original length of specimens prior to deformation in the rubbery state (i.e. 5.0 mm). The amount of $\varepsilon^{(R)}$ affected stress–strain relationships obtained from the subsequent compression in the glassy state: the value of stress at the upper yield point σ_Y increased with increasing $\varepsilon^{(R)}$.

Fig. 3 shows compressive stress–strain curves for pre-strained specimens L. The values of σ_Y were higher for the specimens L than that of the specimens C, probably because the test temperature for the specimens L was lower than that for the specimens C. For all specimens L pre-strained in the rubbery state, their stress–strain curves in the glassy state were quite similar to that of the specimen L deformed solely in the glassy state ($\varepsilon^{(R)}=0$). For the pre-strained specimens L, the amount of $\varepsilon^{(R)}$ had little effect on the stress–strain curves in the glassy state, and such results are in contrast to the effect of pre-strain on the stress–strain curves for the specimens C.

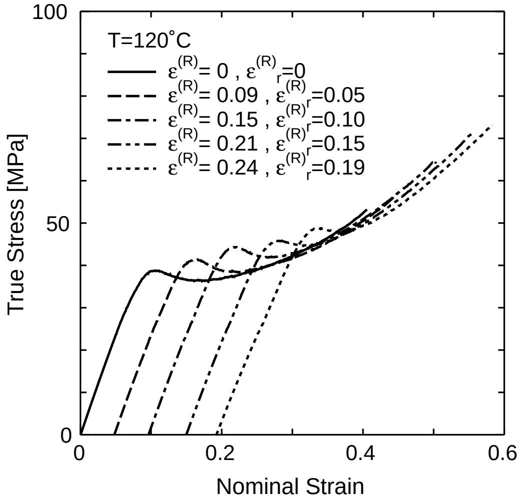

Fig. 2. True stress–engineering strain relationships for the pre-strained specimens C.

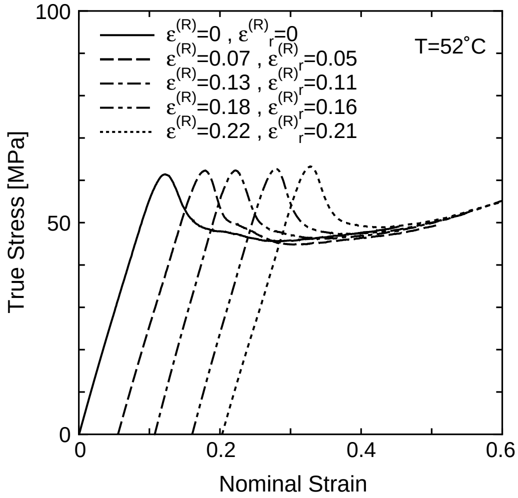

Fig. 3. True stress–engineering strain relationships for the pre-strained specimens L.

4.2. Thermally stimulated strain recovery

Experimental results of thermally stimulated strain recovery for specimens C given three different amount of $\varepsilon^{(R)}$ (i.e. 0, 0.12, 0.24) and the same amount of $\varepsilon^{(G)}=0.45$ are shown in Fig. 4. The vertical solid line in the figure indicates the location of T_g of the sample C. The amount of strain imposed in

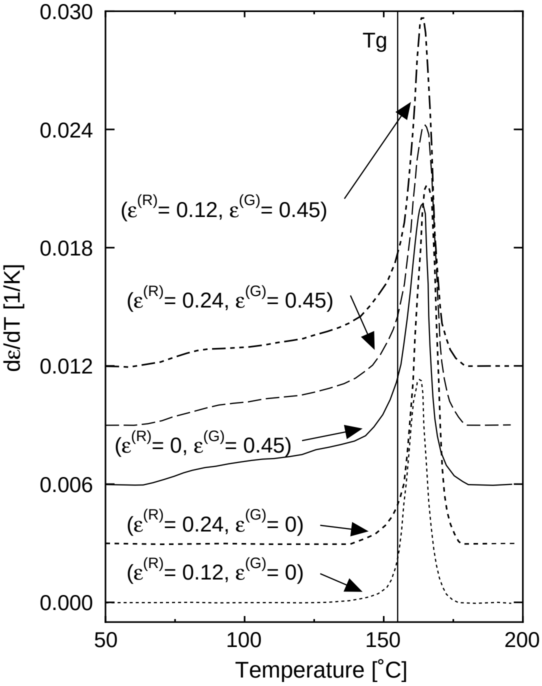

Fig. 4. Thermally stimulated strain recovery curves for the specimens C ($\varepsilon^{(G)}=0.45$). Each curve is shifted systematically at uniform spaced intervals of 0.003.

the rubbery state $\varepsilon^{(R)}$ and those in the glassy state $\varepsilon^{(G)}$ are indicated in the figure. For example, the long-dashed curve labeled as ($\varepsilon^{(R)}=0.12$, $\varepsilon^{(G)}=0.45$) is the TSSR result for a specimen compressed first in the rubbery state by $\varepsilon^{(R)}=0.12$ and then subsequently compressed in the glassy state by $\varepsilon^{(G)}=0.45$. Each TSSR curve indicates that there are two recovering strain components in the specimens compressed in the glassy state: one strain component is ε_L recovering in a broad low temperature range from about 70 to 140 °C, and the other strain component is ε_H recovering in a higher temperature range with a sharp peak at a temperature above T_g (strain recovery at temperatures below the temperature at deformation indicates the specimens were deformed during cooling. This is probably due to thermal shrinkage of test instruments during cooling). For specimens compressed solely in the rubbery state, only a ε_H peak was observed. Below T_g, all curves for specimens given three different amounts of $\varepsilon^{(R)}$ (i.e. 0, 0.12 and 0.24) and the same amounts of $\varepsilon^{(G)}$ (i.e. 0 or 0.45) coincided well with each other. On the other hand, the height of ε_H peak was affected by $\varepsilon^{(R)}$. The ε_H peak height of the specimen ($\varepsilon^{(R)}=0.24$, $\varepsilon^{(G)}=0.45$) was higher than that of the specimen ($\varepsilon^{(R)}=0$, $\varepsilon^{(G)}=0.45$), yet nearly equal to that of the specimen ($\varepsilon^{(R)}=0.24$, $\varepsilon^{(G)}=0$). On the other hand, the ε_H peak height of the specimen ($\varepsilon^{(R)}=0.12$, $\varepsilon^{(G)}=0.45$) was higher than that of the specimen ($\varepsilon^{(R)}=0.12$, $\varepsilon^{(G)}=0$), while being nearly equal to that of the specimen ($\varepsilon^{(R)}=0$, $\varepsilon^{(G)}=0.45$).

Thermally stimulated strain recovery curves for specimens C given three different amount of $\varepsilon^{(R)}$ and the same amount of $\varepsilon^{(G)}=0.2$ are shown in Fig. 5. The TSSR curves for the specimens C of $\varepsilon^{(G)}=0.2$ were similar to those of the specimens C of $\varepsilon^{(G)}=0.45$, except that the amount of ε_L was smaller than those of the specimens C $\varepsilon^{(G)}=0.45$.

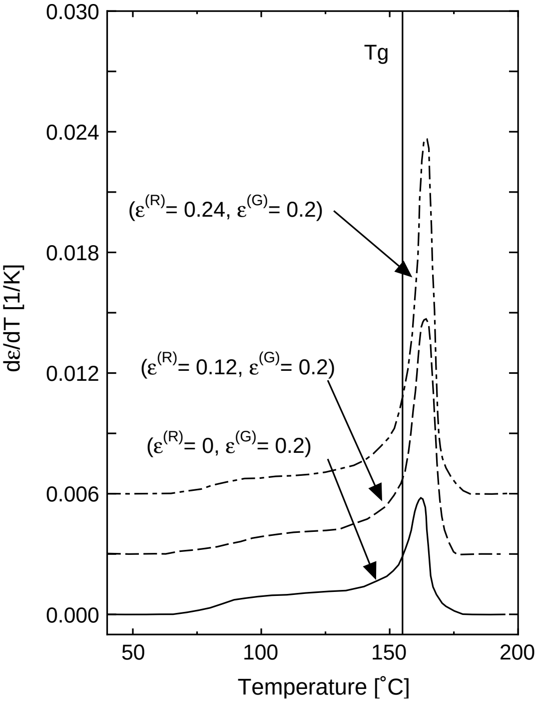

Fig. 5. Thermally stimulated strain recovery curves for the specimens C ($\varepsilon^{(G)}=0.2$). Each curve is shifted systematically at uniform spaced intervals of 0.003.

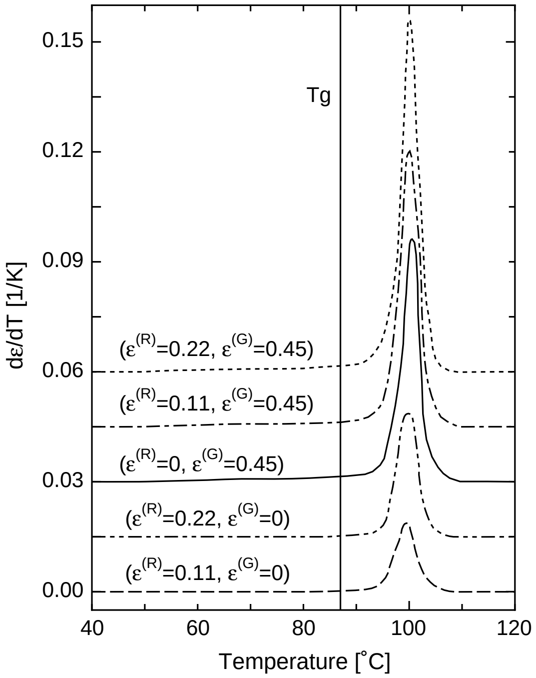

Fig. 6. Thermally stimulated strain recovery curves for the specimens L ($\varepsilon^{(G)}=0.45$). Each curve is shifted systematically at uniform spaced intervals of 0.015.

For specimens L, the TSSR curves are shown in Figs. 6–9. Similarly to the TSSR results for the specimens C, each TSSR curve for the specimens L showed two recovering strain components: one is ε_L recovering in a broad low temperature range from about 50 to 80 °C and the other is ε_H recovering in a higher temperature range with a sharp peak at a temperature above T_g. Below T_g, the curves of all specimens given different $\varepsilon^{(R)}$ (i.e. 0, 0.11 and 0.22) and the same $\varepsilon^{(G)}$ coincided with each other in a temperature range below T_g (Figs. 7 and 9).

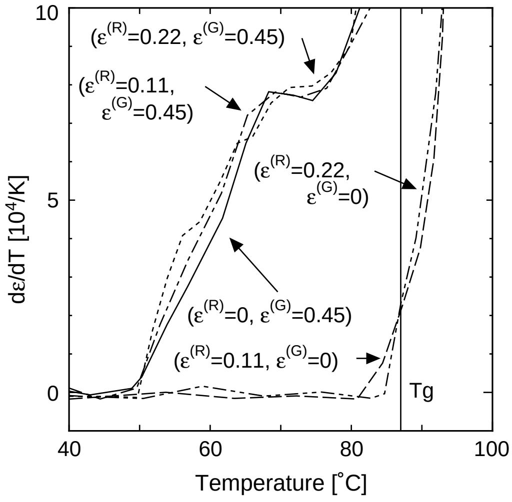

Fig. 7. Thermally stimulated strain recovery curves for the specimens L ($\varepsilon^{(G)}=0.45$). Each curve is shifted systematically at uniform spaced intervals of 0.003.

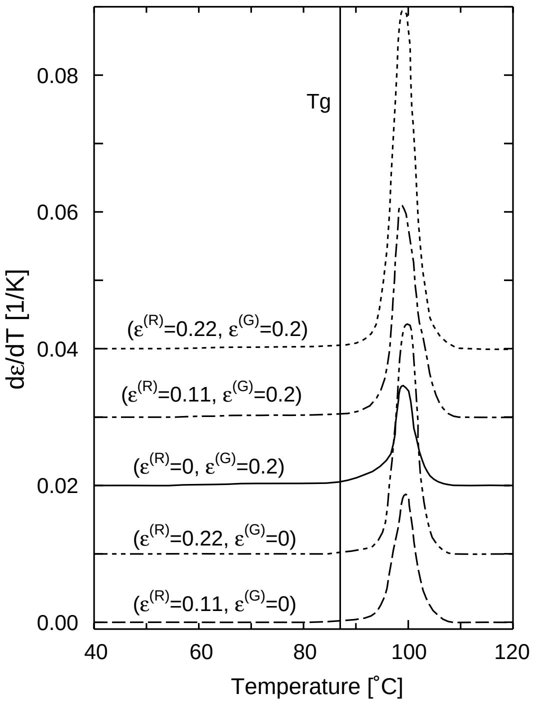

Fig. 8. Thermally stimulated strain recovery curves for the specimens L ($\varepsilon^{(G)}=0.2$). Each curve is shifted systematically at uniform spaced intervals of 0.003.

On the other hand, the height of ε_H peak increased with increasing the amount of $\varepsilon^{(R)}$.

4.3. Differential scanning calorimetry

Results of differential scanning calorimetry measurements for the specimens C are shown in Figs. 10 and 11. The solid DSC curves labeled as 'quenched' are a result for an undeformed specimen quenched from 160 °C to room temperature, and is drawn as a reference curve. Upward deviation from the reference curve indicates exothermic behavior of the deformed specimens. The DSC curve of the specimen compressed only in the rubbery state ($\varepsilon^{(G)}=0$) coincided with the reference curve. On the other hand, the DSC curves of all specimens compressed in the glassy state similarly deviated upward from the reference curve in the temperature range below T_g, and the temperature at which the deviation started was equal to the temperature at which ε_L recovering started in the TSSR results. The amount of deviation is larger

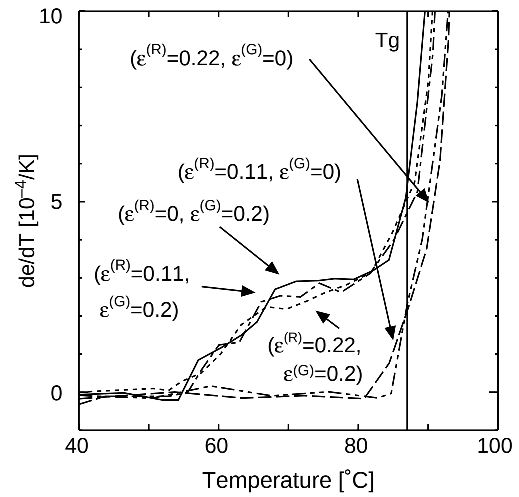

Fig. 9. Thermally stimulated strain recovery curves for the specimens L ($\varepsilon^{(G)}=0.2$). Each curve is shifted systematically at uniform spaced intervals of 0.0006.

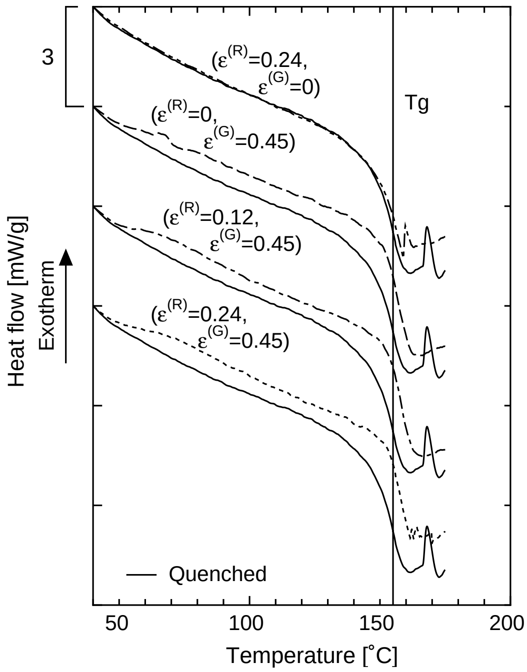

Fig. 10. Differential scanning calorimetry thermograms for specimens C ($\varepsilon^{(G)}=0.45$). Each curve is shifted systematically at uniform spaced intervals of three.

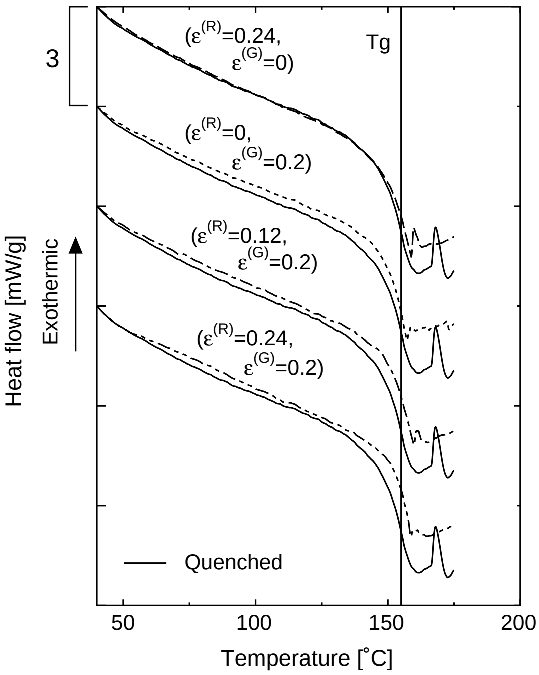

Fig. 11. Differential scanning calorimetry thermograms for specimens C ($\varepsilon^{(G)}=0.2$). Each curve is shifted systematically at uniform spaced intervals of three.

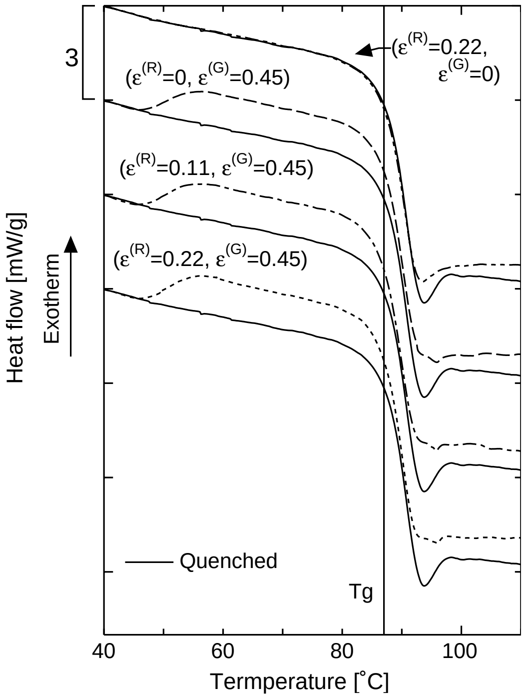

Fig. 12. Differential scanning calorimetry thermograms for specimens L ($\varepsilon^{(G)}=0.45$). Each curve is shifted systematically at uniformly spaced intervals of three.

for the specimens of $\varepsilon^{(G)}=0.45$ than for the specimens of $\varepsilon^{(G)}=0.2$.

The DSC results for the specimens L are shown in Figs. 12 and 13. The DSC curves for the specimens L were qualitatively the same as those of the specimens C: the DSC curves of specimens L compressed only in the rubbery state ($\varepsilon^{(G)}=0$) coincided with the reference curve, and the DSC curves of all specimens compressed in the glassy state deviated upward from the reference curve in a temperature range below T_g, and the magnitude of the deviation was the same as that of the specimens L given the same amount of $\varepsilon^{(G)}$.

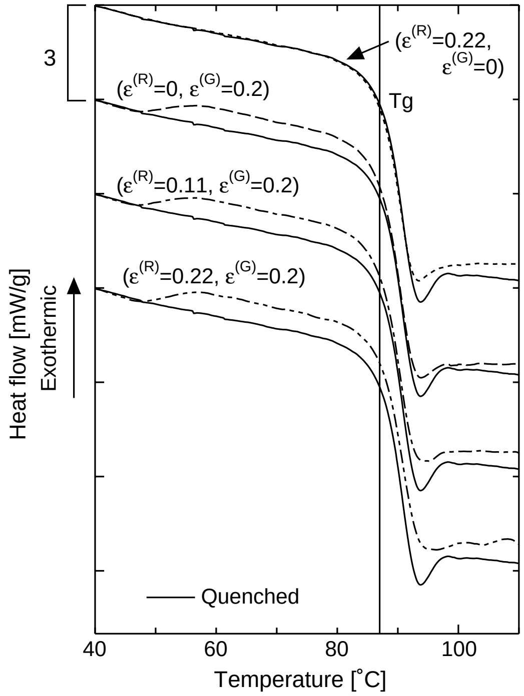

Fig. 13. Differential scanning calorimetry thermograms for specimens L ($\varepsilon^{(G)}=0.2$). Each curve is shifted systematically at uniformly spaced intervals of three.

5. Discussion

In our experiments, the deformed specimens were annealed at room temperature for 24 h before subjected to DSC tests or TSSR measurements. Hence, the β motions, whose peak temperature is around or below $-50\,^{\circ}\mathrm{C}$ [10,11], should relax before DSC tests, and, therefore, the β motions has little effect on experimental results measured in temperature ranges above room temperature. For highly crosslinked epoxy glass, such as the sample C, there may appear an additional ω relaxation located slightly above room temperature [12]. The ω relaxation, if exists, can reduce the amount of exothermic heat in DSC results. We measured the dynamic mechanical spectra of the annealed specimen C and confirmed that there was no such an additional ω relaxation above the room temperature (Fig. 14).

In the same way as already reported [1,13], the recovery of plastic strain of both these samples is divided in two strain components, i.e. ε_L recovering below T_g with exothermic heat flow and ε_H recovering above T_g without exothermic heat flow. The amount of exothermic heat was larger for the specimens L than for the specimens C, whereas the ε_L shoulder height was much lower for the specimens L than for the specimens C. These results indicate that the amount of exothermic heat released per unit strain recovery was larger for the specimens L than for the specimens C. In the following, we will discuss this matter.

For both samples C and L, the TSSR curves of all specimens applied the same amount of $\varepsilon^{(G)}$ coincided with each other in a lower recovering temperature range. Such results indicate that for both samples, the amount of ε_L is determined solely by the amount of $\varepsilon^{(G)}$, but not by the amount of $\varepsilon^{(R)}$. On the other hand, the ε_H peak height is affected by the amount of $\varepsilon^{(R)}$: the ε_H peak height increased with increasing $\varepsilon^{(R)}$.

To quantitatively investigate the effect of $\varepsilon^{(R)}$ on the ε_H peak height of the specimens L, we evaluated TSSR results for the specimens L by adding results for the specimens L compressed solely in the rubbery state ($\varepsilon^{(G)}=0$) to results for the specimens L compressed solely in the glassy state ($\varepsilon^{(R)}=0$). For example, the TSSR curve for the specimen ($\varepsilon^{(R)}=0.22$, $\varepsilon^{(G)}=0.45$) was evaluated as follow:

$$\left[\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}(T)\right]_{\text{for }(\varepsilon^{(R)}=0.22,\ \varepsilon^{(G)}=0.45)}=\left[\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}(T)\right]_{\text{for }(\varepsilon^{(R)}=0.22,\ \varepsilon^{(G)}=0)}+\left[\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}(T)\right]_{\text{for }(\varepsilon^{(R)}=0,\ \varepsilon^{(G)}=0.45)} \tag{1}$$

The evaluated curves agree well with their corresponding experimental results (Fig. 15), indicating that the superposition rule is valid for the ε_H peak height of the specimens L.

For the ε_H peak height of the sample C, the superposition rule is not valid. The ε_H peak height of the specimen ($\varepsilon^{(R)}=$

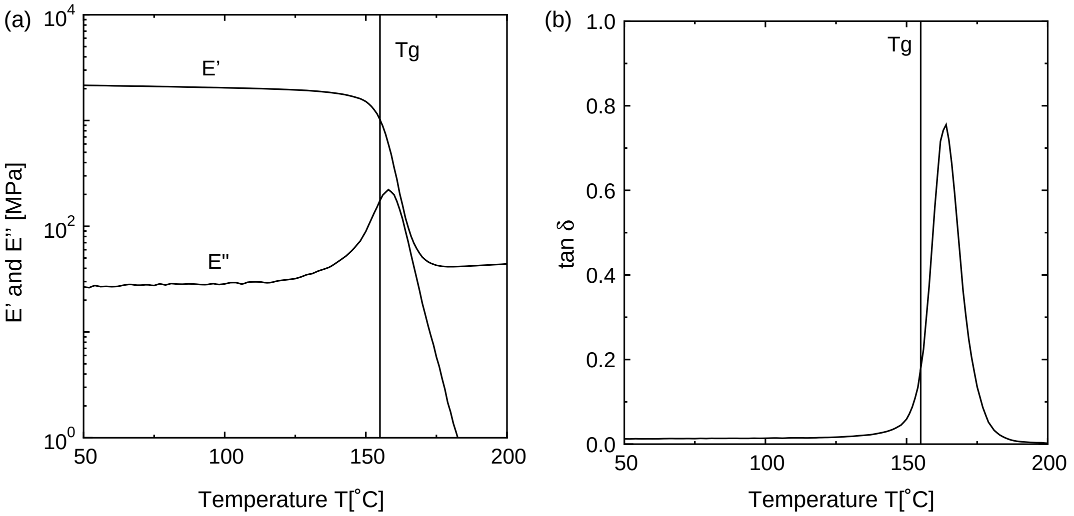

Fig. 14. Dynamic mechanical spectra for the annealed sample C. The tests were carried out in tension mode using a rectangular specimen. The rate of heating was 1.0 °C/min and frequency was 1 Hz.

0.12, $\varepsilon^{(G)}=0$) was higher than that of the specimen ($\varepsilon^{(R)}=0.12$, $\varepsilon^{(G)}=0$), and the former height was equal to that of the specimen ($\varepsilon^{(R)}=0$, $\varepsilon^{(G)}=0.45$). And, the ε_H peak height of the specimen ($\varepsilon^{(R)}=0.24$, $\varepsilon^{(G)}=0.45$) was higher than that of the specimen ($\varepsilon^{(R)}=0$, $\varepsilon^{(G)}=0.45$), and the former height was equal to that of the specimen ($\varepsilon^{(R)}=0.24$, $\varepsilon^{(G)}=0$).

$$(\varepsilon^{(R)}=0.12,\ \varepsilon^{(G)}=0) < (\varepsilon^{(R)}=0,\ \varepsilon^{(G)}=0.45) = (\varepsilon^{(R)}=0.12,\ \varepsilon^{(G)}=0.45) < (\varepsilon^{(R)}=0.24,\ \varepsilon^{(G)}=0.24,\ \varepsilon^{(G)}=0.45) = (\varepsilon^{(R)}=0.24,\ \varepsilon^{(G)}=0) \tag{2}$$

Hence, the ε_H peak height was determined solely by the amount of $\varepsilon^{(G)}$ when $\varepsilon^{(R)}$ was relatively small (i.e. $\varepsilon^{(G)}=0$, 0.12), whereas the ε_H height was determined by the amount of $\varepsilon^{(R)}$ when $\varepsilon^{(R)}$ was relatively large. Furthermore, the ε_H peak height of the specimen ($\varepsilon^{(R)}=0.12$, $\varepsilon^{(G)}=0.45$) was equal to that of the specimen ($\varepsilon^{(R)}=0$, $\varepsilon^{(G)}=0.45$) even though the amount of $\varepsilon^{(R)}$ was increased from 0 to 0.2, and they were lower than the ε_H peak height of the specimen ($\varepsilon^{(R)}=0.24$, $\varepsilon^{(G)}=0.45$). These results indicate that the ε_H peak height increases only when $\varepsilon^{(R)}$ exceeds a threshold value which depends on the amount of $\varepsilon^{(G)}$. As the amount of $\varepsilon^{(G)}$ also determines the amount of ε_L, the threshold value is also related to the amount of ε_L.

In comparison with the sample L, the characteristics of the plastic strain recovery of the sample C are as follows:

From the DSC results,

- recovery of ε_L generates relatively less heat. And, from the TSSR results,
- the relatively higher ε_L shoulder
- the relatively lower ε_H peak height
- the ε_H peak height increases only when $\varepsilon^{(R)}$ exceeds a threshold value depending on the ε_L shoulder height.

These features indicate that some amount of entropic strain in the sample C recovers cooperatively with the enthalpic strain below the glass transition temperature (Fig. 16). In other word, when epoxy glass is subjected to plastic strain and then heated, the conformational changes occur cooperatively at temperatures below T_g. And, presumably, the crosslinks and an excited state make the changes of conformation below T_g be possible. The ε_L component, thus, contains entropic strain more than that of the sample L, and the amount of generated heat is 'diluted' with the cooperatively recovering entropic strain which recovers without exothermic behavior.

For these samples C and L, cooperativity in stress results from and stress resulting from is also observed [4].

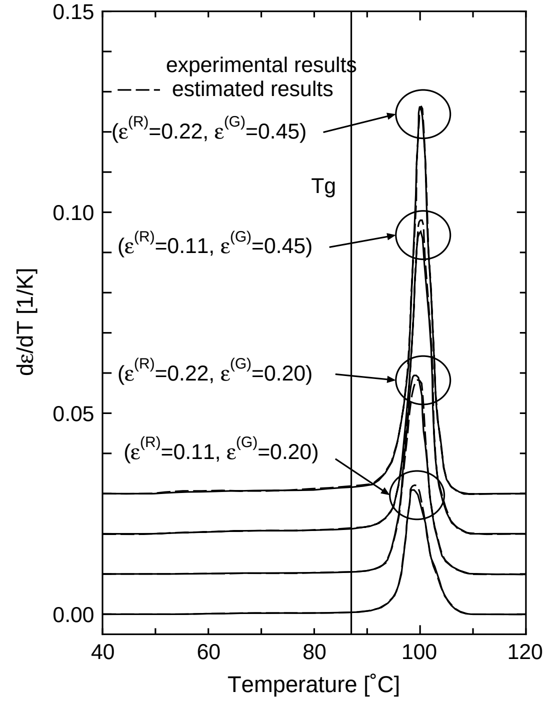

Fig. 15. Comparisons of the TSSR curves for the specimens L between experimental and evaluated results.

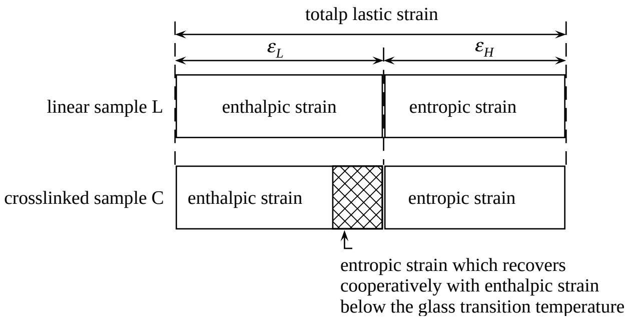

Fig. 16. Schematic representation of the inelastic strain components of the linear sample L and the crosslinked sample C.

6. Conclusion

The amount of plastic strain recovering at temperatures below T_g was larger for the crosslinked sample than the linear molecular sample, while the amount of exothermic heat flow was less for the crosslinked sample than the linear molecular sample. Such results indicate that, for plastic strain recovery of crosslinked epoxy glass plastically deformed in the glassy state, some amount of entropic strain recovers cooperatively with enthalpic strain in a temperature range below T_g. In other word, when epoxy glass is largely deformed and then heated, the conformational changes occur cooperatively at temperatures below T_g. And, presumably, the crosslinks and an excited state make the change of conformation be possible below.

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