Abstract: The effect of the amount of applied deformation on a thermally stimulated deformation recovery for a largely deformed epoxy resin under its glass transition temperature was studied in this paper. Two recovery peaks have been observed in the thermally stimulated deformation recovery curves for both epoxy resin and poly(methyl meth acrylate) (PMMA). The lower temperature recovery peak of the PMMA shifts to a higher temperature with increasing applied strain. However, the lower temperature recovery peak of the epoxy resin was independent of the amount of applied strain. The effect of applied strain on the relaxation curves for the epoxy resin was more significant than for the PMMA. Free deformation recovery curves below the glass transition temperature were simulated using a generalized Maxwell model both with and without the dependence of the recovery curve on the amount of applied strain. The model with strain dependence included reproduced the tendency of the experimental results of the epoxy resin more closely than the model without strain dependence. It seems that the structure of the epoxy resin changed after the lower yielding range to a structure which restricts the relaxation of polymeric structures.

Key words: Amorphous polymer, Epoxy resin, Relaxation, Large deformation, Deformation recovery, Polymeric structural change, Linear polymer

1. INTRODUCTION

Glassy epoxy resin is a thermoset resin which is chemically crosslinked. However, glassy epoxy resin shows yielding behavior similar to that of poly(methyl meth acrylate) (PMMA), that is, an upper yielding point followed by a lower yielding range[1, 2]. However, if largely deformed, epoxy resin exhibits strain hardening more clearly than PMMA. It is said that the strain hardening is related to the present of the crosslinks. However, the mechanics of the strain hardening from the molecular point of view is not still clear.

The structure of an amorphous polymer changes under large deformation from a glassy structure to a liquid-like structure [3]. One technique that has been proven to be quite useful for investigating the polymeric structural change is to monitor the thermally stimulated deformation recovery of a polymer after large deformation[4 - 9]. There are two peaks in the thermally stimulated deformation recovery curves for largely deformed polymers. The first peak is below the glass transition temperature, and the other peak is slightly higher than the glass transition temperature. When heated, the sample generated heat in the temperature range close to the first recovery peak. It is considered that molecular motions taking place close to the first recovery peak are not the same to those close to the second recovery peak.

In this study, the thermally stimulated deformation recoveries of a largely deformed glassy epoxy resin were measured. Theoretical free deformation recoveries after large deformation were also calculated using a generalized Maxwell model. The experimental results were compared with those of PMMA. The purpose of this study is to investigate the effect of the crosslinks on the thermally stimulated deformation recovery of the epoxy resin.

2. EXPERIMENTAL

2.1. Sample Preparation

The sample was prepared by curing diglycidyl ether of bisphenol - A epoxy resin EPICLON 850 (DAINIPPON INK AND CHEMICALS, Inc.) with 4, 4' - diamino diphenyl methane. The molar ratio was set to be the stoichiometric ratio. The average molecular weight between crosslinks was estimated to be 385 g/mol, based on the assumption of complete chemical reaction between the epoxy resin and the curing agent.

The epoxy resin was preheated to 70 °C prior to adding the curing agent. After stirred, the mixture was degassed under vacuum, and then, the mixture was cast between preheated glass plates sprayed an FEP mold - releasing agent. The mixture was cured at 70 °C for 12 hours followed at 140 °C for 12 hours. The glass transition temperature, Tg, measured using a differential scanning calorimeter (DSC) was about 175 °C.

Cylindrical specimens were machined from the epoxy plates. The dimensions of the cylindrical specimens were 5mm in height and 4mm in diameter. To remove the thermal history of the specimens, the specimens were heated to 180 °C and kept at the temperature for 2 hours. The heated specimens were cooled down to 105 °C at a cooling rate of 0.05 °C/min and then to room temperature at a cooling rate of 0.1 °C/min.

PMMA was used as a reference material. The PMMA used in this study had a glass transition temperature of about 116 °C. The dimensions of the PMMA specimens were the same as those of the epoxy resin. PMMA specimens were used after a thermal conditioning procedure including very slow cooling through the glass transition temperature[6].
2.2. Testing Methods

An INSTRON type materials testing machine was used to constant rate uniaxial compression tests. The specimens were mounted on the testing machine and kept at test temperature for about 30 min prior to the tests in a heat chamber installed to the testing machine, and then the specimens were compressed at a constant rate of $1.0 \times 10^{-3}$ s\(^{-1}\) to measure stress - strain relations. The test temperature was 130 °C for the epoxy resin and 90 °C for the PMMA.

The uniaxial compression stress relaxation tests were conducted using the same type of specimens and test machine as for the stress - strain measurements. The predetermined deformation was applied at a constant strain rate of $1.0 \times 10^{-3}$ s\(^{-1}\), and then the strain was kept constant to measure the stress relaxation.

For the thermally stimulated deformation recovery tests, the same type of specimens as in the other two tests was compressed to a predetermined strain in a manner identical to the stress relaxation tests, and then, rapidly cooled down to room temperature by blowing cool air on the specimens at constant strain. The specimens were heated from room temperature to 210 °C at a heating rate of 1.0 °C/min to measure thermally stimulated deformation recovery. So as not to disturb recovery of the specimens, the amount of the recovery was measured by using a non-contact displacement sensor.

2.3. Calculation of Free Deformation Recovery after Large Deformation

Free deformation recoveries of a largely deformed epoxy resin at a constant temperature below the glass transition temperature were calculated using a generalized Maxwell model, that is, an array of Maxwell units in parallel. The calculation was separated in three stages: constant rate deformation, removing constraints and free deformation recovery.

The constitutive equation for the \(i\)-th Maxwell unit is

$$\frac{d\sigma_i(t)}{dt} = \frac{1}{E_i} \frac{d\varepsilon_i(t)}{dt} + \frac{\sigma_i(t)}{\eta_i},$$  \hspace{1cm} (1)

where

- \(E_i\) : the modulus of the \(i\)-th Maxwell unit
- \(\eta_i\) : the viscosity of the \(i\)-th Maxwell unit
- \(\sigma_i\) : the stress applied to the \(i\)-th Maxwell unit

In the case of the generalized Maxwell model, the total strain of each Maxwell unit, \(\varepsilon_i(t)\), is equal, thus

$$\varepsilon_i(t) = \varepsilon(t).$$  \hspace{1cm} (2)

2.3.1. Constant rate deformation

During constant rate deformation, the strain rate is kept constant at \(\alpha\);

$$\frac{d\varepsilon(t)}{dt} = \alpha.$$  \hspace{1cm} (3)

Suppose that all Maxwell units are stress - free before deformation;

$$\sigma_{i(0)} = 0.$$  \hspace{1cm} (4)

The stress of the \(i\)-th Maxwell unit at time \(t\) is obtained by solving Eq.(1) under the initial condition (Eq.(4)), giving

$$\sigma_{i(t)} = \alpha \tau_i \varepsilon_i(1 - e^{-t/\tau_i}).$$  \hspace{1cm} (5)

where \(\tau_i = \eta_i/E_i\) is the relaxation time of the \(i\)-th Maxwell unit. The total stress of the generalized Maxwell model at time \(t\) is equal to the sum of stresses applied to each Maxwell unit;

$$\sigma(t) = \sum_i \sigma_i(t) = \alpha \sum_i \tau_i E_i (1 - e^{-t/\tau_i}).$$  \hspace{1cm} (6)

and stress relaxation after deformation ceases at time \(t_0\) is as follows:

$$\sigma(t) = \sum_i \sigma_i(t_0) e^{-\frac{t-t_0}{\tau_i}}.$$  \hspace{1cm} (7)

2.3.2. Removing constrain

Constraint is removed at \(t = t_0\), when total strain reaches to a specified strain. We suppose that only the elastic strain of each Maxwell unit can change immediately after the constraint is removed.

The total strain of each Maxwell unit, \(\varepsilon_i(t_0)\), is divided into elastic strain, \(\varepsilon_{i,e}(t_0)\), and viscous strain, \(\varepsilon_{i,v}(t_0)\),

$$\varepsilon_{i,e}(t_0) = \frac{\sigma_{i(t_0)}}{E_i},$$  \hspace{1cm} (8)

$$\varepsilon_{i,v}(t_0) = \varepsilon(t_0) - \varepsilon_{i,e}(t_0).$$  \hspace{1cm} (9)

The total stress of the generalized Maxwell model is equal to zero after constraint is removed, therefore;

$$0 = \sum_i \sigma_{i(t_0)}.$$  \hspace{1cm} (10)

Substituting Eqs.(7) - (9) into Eq.(10), we obtain the following equation:

$$0 = \sum_i \frac{E_i \varepsilon(t_0) - \varepsilon_{i,v}(t_0)}{E_i}.$$  \hspace{1cm} (11)

By solving Eq.(11), we obtain both elastic and viscous strains of the \(i\)-th Maxwell unit, and hence, the total strain of the generalized Maxwell model at time \(t_0\).

2.3.3. Free deformation recovery

Supposing that the deformation recovery rate, \(d\varepsilon/dt\), was constant for a brief period of time, \(\Delta t\), thus Eq.(1) is written as follows:

$$\frac{d\varepsilon_n}{dt} = \frac{1}{E_i} \frac{d\sigma_{i(t)}}{dt} + \frac{\sigma_{i(t)}}{\eta_i}.$$  \hspace{1cm} (12)

where \(\dot{\varepsilon}_n\) is the constant deformation recovery rate at the \(n\)-th time interval. From Eq.(12), the stress of each Maxwell unit after the \(n\)-th interval, \(\sigma_{n,i}\), is expressed as

$$\sigma_{n,i} = \dot{\varepsilon}_n \tau_i E_i (1 - e^{1-\Delta t/\tau_i}) + \sigma_{n-1,i} e^{1-\Delta t/\tau_i},$$  \hspace{1cm} (13)
where $\sigma_{n-1,i}$ is the initial stress of the n-th interval. The total stress is equal to zero during free deformation recovery,

$$0 = \sum_{i} \sigma_{n,i}$$

$$= \varepsilon_{n} \cdot \sum_{i} \left\{ \tau_{i} E_{i} (1 - e^{1-\Delta t/\tau_{i}}) + \sigma_{n-1,i} \cdot e^{1-\Delta t/\tau_{i}} \right\}.$$  

(14)

Strain rate at the n-th interval, $\varepsilon_{n}$, is obtained by substituting $\sigma_{n-1,i}$ into Eq. (14) and solving for $\varepsilon_{n}$. Then, the stress of each Maxwell unit after the n-th interval, $\sigma_{i,n}$, is obtained by substituting $\varepsilon_{n}$ into Eq.(13). And the total strain recovery after the n-th interval is

$$\varepsilon_{n} = \sum_{n} \varepsilon_{n} \cdot \Delta t.$$  

(15)

The relaxation curves obtained from relaxation tests and dynamic mechanical spectrometer (DMS) tests (see, Appendix) were used to calculate both the modulus and the relaxation times used in the above calculations. The relaxation times were determined by dividing the time range of relaxation curves into equal parts on logarithmic time scale. These relaxation times were used in Eq.(7) and then fitted to the relaxation curves so as to find the sets of modulus giving the best description of the curves.

### 3. RESULTS

#### 3.1. Stress - Strain Relation

Figure 1 shows the stress - strain relations for the epoxy resin and the PMMA under uniaxial compression. The vertical axis is true stress which was calculated assuming a uniform deformation and isovolume of the specimen during deformation. The stress - strain curve for the epoxy resin was similar in shape to that for the PMMA. For both the epoxy resin and the PMMA, the stress was almost proportional to the strain in the small strain range. As the strain increased, the stress decreased after upper yield point and appeared the lower yield range in which the stress was almost constant. However, for the epoxy resin, the lower yield range was shorter than that of the PMMA and the stress resumed increasing soon after the lower yielding range.

#### 3.2. Stress Relaxation

Figures 2 and 3 show the stress relaxation curves for the epoxy resin and the PMMA respectively. The amounts of applied strain are indicated in the figures. The effect of the amount of applied strain, $\varepsilon_{d}$, has more significant effects on the relaxation curves for the epoxy resin than for the PMMA. In the case of the epoxy resin, the ratios of stress relaxed to the initial stress during measurements decreased with increasing applied strain, while in the case of the PMMA, the ratios did not depend significantly on the amounts of applied strain. However, when the PMMA was strained by 0.5, the amount of stress decreased was smaller than that of the samples strained by 0.1 and 0.3.

#### 3.3. Thermally Stimulated Deformation Recovery after Large Deformation

The results of the thermally stimulated deformation recovery measurements of the PMMA are summarized in Fig.4, in which the strain recovery rate, $d\varepsilon/dT$, is plotted against temperature. The amounts of applied strain, $\varepsilon_{d}$, are indicated in the figure together with the residual strain in parentheses. The residual strain started recovering at lower temperature than at which the specimens had been deformed, and the strain recovered gradually in the temperature range below the glass transition temperature. The effect of the amount of applied strain on the strain recovery rate was not significant in this range. After the glass transition temperature, the strain recovered rapidly and peaked at slightly higher temperature than the glass transition temperature. The higher temperature recovery peaks increased in height with increasing the amount of applied strain.

Figure 5 shows the thermally stimulated recovery curves for the epoxy resin. The recovery curves were similar in shape to those for the PMMA. However, the effect of the amount of applied strain on the strain recovery rate was more significant. Namely, the larger the applied strain,
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4. DISCUSSION

It is considered that when PMMA is stretched, the structure of the polymer changes to a liquid-like structure in which stress relaxes more easily, causing a steady plastic flow to occur in the lower yielding range on the stress-strain curve [3]. As shown in Fig. 1, the stress-strain curve for the epoxy resin was similar in shape to that for the PMMA in the lower yielding range. This similarity indicates that the epoxy resin and the PMMA might share the same polymeric structural change in the lower yielding range, that is, the structural transition of a quasi-equilibrium solid state to a viscous liquid-like structure. The polymer with a liquid-like structure relaxes more easily than that having a solid structure, thus stress remains almost constant with increasing strain. However, the epoxy resin exhibited significant strain hardening after the lower yielding range. For the epoxy resin, the structural change occurring in this range might be different from that in the lower yielding range, and the strain hardening might relate to the change in the relaxation curves with increasing strain.

The amount of applied strain had more significant effect on the relaxation curves for the epoxy resin than for the PMMA (Figs. 2 and 3). For the epoxy resin, the larger the applied strain was, the smaller the ratio of recovered stress to the initial stress. It seems that the polymeric structural change which occurred after the lower yielding range restricts polymer relaxation and is different from that which occurs in the lower yielding range. When the PMMA was strained by 0.5, the amount of stress relaxed was lower than those strained by 0.1 and 0.3. This decrease in the amount of the stress relaxed might be due to the same mechanics as the epoxy resin, because as shown in Fig. 1, the stress of the PMMA already resumed increasing when the sample was strained by 0.5.

One of the authors has studied about the effect of aging on the thermally stimulated deformation recovery of largely deformed PMMA [6]. They found that the lower temperature recovery peak moved to higher temperature with aging time. The shift of the lower temperature recovery peak was attributed to the relaxation of a polymeric structure from a liquid-like structure to a meta-stable structure. This structural change reduced the ratio of the strain component which recovered close to the lower temperature peak ($\varepsilon_L$) to total residual strain and increased the ratio of the strain component which recovered close to the higher temperature recovery peak ($\varepsilon_H$) to total residual strain. Figure 6 shows the thermally stimulated deformation recovery curves for the PMMA. The vertical axis expresses the strain recovery rate normalized by the amount of residual strain to highlight the study of the effect of the amount of applied strain on the behavior of the peaks. In this figure, although the lower temperature peak is not clear, it seems that the strain recovering below the glass transition temperature is $\varepsilon_L$, and the strain recovering over the glass transition temperature is $\varepsilon_H$ (Fig. 7). The ratio of $\varepsilon_L$ to total residual strain decreased and the ratio of $\varepsilon_H$ increased with increasing applied strain. These changes in
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Fig. 8. Normalized thermally stimulated deformation recovery curves for epoxy resins.

The ratio might be attributed to the relaxation of $\varepsilon_L$ during deformation.

Figure 8 shows the thermally stimulated deformation recovery curves for the epoxy resin. The ratios of $\varepsilon_L$ and $\varepsilon_H$ to the residual strain were almost independent of the amount of applied strain. This might be explained as follows: the amount of the applied strain affected the relaxation curves of the epoxy resin more seriously than of the PMMA, and the larger the applied strain is, the greater the relaxation during the deformation (i.e., the relaxation of $\varepsilon_L$) is restrained. Therefore, in the case that epoxy resin was largely deformed, the rates of $\varepsilon_L$ and $\varepsilon_H$ to the total strain did not change seriously with increasing applied strain, and the strain hardening in the stress-strain relation was clearer than that of the PMMA.

The free deformation recovery after large deformation was calculated using general Maxwell models both with and without considering the dependence of recovery curves on the amount of applied strain to examine the effect of the change in the relaxation curves on the deformation recovery. Supposing an Arrhenius type dependence of relaxation times on temperature, the elapsed time in free deformation recovery at constant temperature corresponds to rising temperature in thermally stimulated deformation recovery measurements. For the linear model, only one set of the modulus and relaxation times calculated from DMS data was used. In this method, the same set of values was used regardless the amount of strain. This model did not take the strain dependence of relaxation into account. For the non-linear model, the sets of the modulus and the relaxation times obtained from both the DMS and the stress relaxation data of epoxy resin were used to change those sets as the strain increased. For example, in a calculation of the free deformation recovery of a sample strained to 0.5, the set of the values calculated from DMS data was used in the calculations until the generalized Maxwell model was strained by 0.05. The set of the values obtained from the stress relaxation data at strain equal to 0.1 was used in the calculation until the model strained up to 0.2, and then, the set of the values obtained from the stress relaxation data at strain equal to 0.3 was used during straining from 0.2 to 0.4. The set of the values from the data at 0.5 was used until strain reached 0.5, as well as the following processes: that is, removing the constrain and the free deformation recovery. This method took into consideration the strain dependence on relaxation.

Fig. 9. Comparison of calculated residual strain with experimental result.

Figure 9 shows the ratios of the residual strain to the amount of applied strain obtained from the experiments and the calculations. The results calculated from the linear model increased with increasing applied strain. In the calculation using non-linear model, the ratios decreased with increasing applied strain. These results indicate that the non-linear model in which the relaxation properties depend on the amount of the applied strain reproduces the experimental results of the epoxy resin more precisely than the linear model.

In the experiments, the specimens were cooled down to room temperature at constant strain. The cooling rate should be fast enough to freeze the molecular structure. However the cooling ratio was finite. Therefore, there was enough time interval for the molecular structural to recover. It seems that this recovery might account for the differences between the experimental results and the calculations from non-linear model.

The ratios of $\varepsilon_L$ to residual strain, $\varepsilon_r$, were also calculated. It is considered that $\varepsilon_L$ corresponds to the strain which recovers in a short time period in the free deformation recovery tests below the glass transition temperature[4]. In the calculations, the deformation recovery occurred in times shorter than $10^8$ s and the strain remained almost constant after $10^8$ s. Therefore, the amount of $\varepsilon_L$ was calculated as the strain recovered in times shorter than $10^8$ s.

The calculations are summarized in Fig.10. The computed results from linear model showed that the ratios decreased with increasing applied strain. This tendency was the same as that in the experimental results of thermally stimulated deformation recovery curves for the PMMA (Fig.6). In the case that the non-linear model was used,
the ratios slightly increased with increasing applied strain. However, the dependence of the ratios on applied strain in the non-linear model was weaker than that in the linear model. These comparisons indicate that, the relaxation of the largely deformed epoxy resin is restricted with increasing strain and, as a result of this restriction, the ratios of $\varepsilon_L$ and $\varepsilon_H$ to residual strain, $\varepsilon_r$, are independent of the amount of applied strain.

The molecules of an epoxy resin are chemically crosslinked to each other. The strain above the lower yielding range may be large enough for the crosslinks to restrain the molecular movement, and then the structure of the epoxy resin changes to a structure which restricts structural relaxation. This structural change occurring in the range in which stress resumes increasing after the lower yielding range seems to be a reason for the difference between the thermally stimulated deformation recovery curves for the epoxy resin and that for the PMMA.

5. CONCLUSION

In this study, the thermally stimulated deformation recovery of largely deformed epoxy resin was investigated. The applied strain did not affect the ratio of $\varepsilon_L$ and $\varepsilon_H$, probably because after the lower yielding range, the structure of epoxy resin changed to a structure which restricted the relaxation.

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APPENDIX

Dynamic Mechanical Test The dynamic mechanical behaviors of each substance was measured with a Seiko DMS 6100 system. Small elongation was cyclically applied to rectangular shaped specimen having 20.0 mm in gage length and 7.5 mm$^2$ in cross sectional area. Frequency range was from 0.1 Hz to 1.0 Hz. Temperature was risen from 50 °C to 190 °C at a constant rate of 0.1 °C/min. Results were reduced to 130 °C to compose a master carve.

REFERENCES