STRAIN RECOVERY BEHAVIORS AT HEATING
FOR GLASSY POLYMETHYL METHACRYLATE
LARGELY STRETCHED WITH STRAIN RATE JUMPS

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Abstract: To analyze the effect of strain rate upon the state of internal strain energy accumulated in largely stretched glassy polymethyl methacrylate (PMMA), we studied its strain recovery behavior at heating. Specimens were subjected to up- and down-jump schemes of strain rate and stretched to various amounts of strain at a temperature below the glass transition temperature \( T_g \). As an ultimate case of the down-jump scheme, the stress relaxation experiment was also performed for various durations. Comparing transient stress responses due to the strain rate jump imposed on the specimens with their strain recovery behaviors at heating, we found that to increase time length of viscoelastic stress relaxation had an effect of shifting a temperature range of sub-\( T_g \) strain recovery to higher temperatures. Since the strain recovery at less than \( T_g \) has been found to be accompanied by a release of the internal strain energy, the present result allowed us to conclude that molecular kinetics of nonlinear viscoelastic relaxation occurring in the largely deformed polymer had an effect to enhance the thermal stability of the internal strain energy accumulated in the deformed polymer.

Key words: Glassy polymer, Polymethyl methacrylate (PMMA), Large deformation, Strain recovery at heating, Strain rate jump, Nonlinear viscoelasticity, Internal strain energy

1. INTRODUCTION

A glassy polymer shows nonlinear viscoelastic behaviors under intense mechanical stimuli. The yield phenomenon observed under the condition of constant-rate deformation is a typical example of nonlinear behaviors. A number of molecular models explaining the nonlinear behaviors in glassy polymers have been proposed[1-14]. However, the mechanism of large deformation in glassy polymers is still a subject of controversy.

As an experimental approach to study the mechanism of large deformation, deformation recovery behavior of largely deformed glassy polymers has been noticed in connection with their micro-calorimetry. Li et al.[11], Oleynik[12], and Adams et al.[13,14] examined deformation recovery at heating and differential scanning calorimetry (DSC) for several glassy polymers deformed beyond the yield point. According to these studies, the following common features of the deformation recovery behavior and the thermal properties for largely deformed glassy polymers have been found: (a) a plot of the deformation recovery rate against temperature has a broad peak located at less than the glass transition temperature \( T_g \) and another sharp one at a temperature just above \( T_g \), (b) the strain recovery peak in a temperature range below \( T_g \) moves to a higher temperature range with an increase in deformation temperature, and (c) the recovery of the residual strain at less than \( T_g \) is accompanied by a release of internal strain energy. Thus, the large deformation in glassy polymers is very likely a process during which the internal strain energy is accumulated in the glassy polymeric system, yet the mechanism of such energy accumulation still remains unclear.

Taking account of the fact that the state of internal strain energy accumulated in a glassy polymer is closely related to its strain recovery behavior observed at temperatures below \( T_g \), the present authors have examined the relationship between the strain recovery behavior and tensile fracture of fully yielded specimens of glassy polymethyl methacrylate (PMMA). In a previous paper[15], we reported the following results: (a) the residual strain due to a low rate deformation followed by a condition of stress relaxation recovered only at temperatures near \( T_g \) and (b) break down strain was relatively small for the specimens provided with a residual strain being recoverable only at temperatures near \( T_g \). Hence, the relation between the strain recovery behavior and the fracture property has shown that the internal strain energy accumulated in the glassy polymer has a noticeable effect on the macroscopic fracture property of the material and that this effect is enhanced by a decrease in strain rate, a rise in deformation temperature and an advance of stress relaxation.

In the present study, we examined the strain recovery behavior at heating for glassy PMMA uniaxially stretched with strain rate jumps to understand the effect of strain rate upon the state of accumulated internal strain energy. The strain recovery behavior of PMMA specimens subjected to the strain rate jump was discussed in relation to the state of the accumulated internal strain energy and the nonlinear viscoelastic behavior in the glassy polymer.

Received December 1, 1997
2. EXPERIMENTAL PROCEDURES

2.1. Material and Specimen
The material used in this study was a 1.0mm thick commercial cast sheet of atactic PMMA (Acrylite L, Mitsubishi Rayon Co.). The glass transition temperature $T_g$ of this material is 116°C, which was determined as a temperature where the apparent activation energy of linear viscoelastic relaxation gave the maximum value. Dumbbell-shaped specimens with the gauge portion of 50mm×10mm×1.0mm were machined from the sheet. The specimen was annealed at 130°C for 2 hours to erase the thermal and mechanical memories of the material, and then slowly cooled to the room temperature.

2.2. Preparation of Deformed Specimen
We used two nominal strain rates of $\dot{\varepsilon}_H=1.0\times10^{-3}$ and $\dot{\varepsilon}_L=1.0\times10^{-5}$S$^{-1}$ to stretch the specimens. The straining program used in the strain rate jump experiments was as follows: (1) the stretching was started using either of the two strain rates, (2) at a nominal strain of $\varepsilon=0.10$, where the specimen had been fully yielded as shown in Fig.1, the strain rate was abruptly changed to another one, and then (3) the stretching was continued up to a prearranged strain $\varepsilon$. Hereafter, we refer to the change in the strain rate from $\dot{\varepsilon}_L$ to $\dot{\varepsilon}_H$ as "up-jump" and from $\dot{\varepsilon}_H$ to $\dot{\varepsilon}_L$ as "down-jump", respectively. Stress relaxation experiments were also performed as an ultimate case of the down-jump experiment. In advance of the stress relaxation experiment, the specimens were stretched to $\varepsilon_r=0.10$ at constant strain rates of $\dot{\varepsilon}_H$ and $\dot{\varepsilon}_L$. The control data were also obtained by the constant-rate stretching of specimens to various strains $\varepsilon_i$ using both strain rates. At the end of the stretching accomplished under the above programs, the specimen was unloaded and then immediately quenched to the room temperature. All the straining programs were performed by an Instron type testing machine at a temperature of 80°C. The true stress $\sigma$ calculated on an allowable assumption of isovolume and uniform deformation of the gauge portion was recorded as a function of $\varepsilon$ and time $t_e$ elapsed in the stress relaxation process.

2.3. Strain Recovery Measurement
The strain recovery at heating for the deformed specimens was measured using a laboratory-made apparatus composed of a programmable temperature controller, an environmental chamber and a non-contacting laser-beam displacement instrument. The temperature in the chamber was controlled within ±0.3°C of the programmed temperature. The deformed specimen was heated in the chamber from 30 to 150°C at a constant heating rate of $1.67\times10^{-2}$Cs$^{-1}$ (=1°Cmin$^{-1}$). During the heating, the length of the gauge portion was recorded as a function of heating temperature $T$. The strain recovery was calculated from the length-temperature relation with a correction for the effect of thermal expansion of the material. In this correction, we took the change in length of the gauge portion due to strain recovery into account as a factor affecting the amount of the thermal expansion.

3. RESULTS

3.1. Stress Response under the Deformation Programs
Figure 1 shows the relationships between true tensile stress $\sigma$ and nominal strain $\varepsilon$ obtained by the strain rate jump tests. Dashed lines in the figure are the stress-strain relations at constant-rate elongation at $\dot{\varepsilon}_H$ and $\dot{\varepsilon}_L$. After the down-jump of the strain rate, $\sigma$ began to depart downwards from the $\sigma$-$\varepsilon$ curve obtained at the initial strain rate of $\dot{\varepsilon}_H$ and continued to decrease. After crossing the $\sigma$-$\varepsilon$ relation obtained at $\dot{\varepsilon}_L$, $\sigma$ reached a minimum value at around $\varepsilon=0.11$ and then gradually increased to the same stress level with that of the $\sigma$-$\varepsilon$ relation for the specimen stretched at the constant rate $\dot{\varepsilon}_L$. Thus, a stress-undershoot was observed in comparison to the stress-strain relation at the constant rate $\dot{\varepsilon}_L$. The effect of the down-jump on the stress-strain relation disappeared at about $\varepsilon=0.14$. As for the up-jump straining scheme, the stress $\sigma$ initially grew elastically and then reached a second yield point due to the up-jump at around $\varepsilon=0.12$, where the value of $\sigma$ is much higher than that at the constant rate of $\dot{\varepsilon}_H$. After passing through the second yield point, $\sigma$ decreased gradually, and finally converged to that for the constant-rate condition of $\dot{\varepsilon}_H$ at about $\varepsilon=0.20$. Thus, a stress overshoot was observed in the up-jump condition in comparison to the $\sigma$-$\varepsilon$ relation obtained in the constant-rate straining at $\dot{\varepsilon}_H$.

The relaxation stress $\sigma$ was plotted in Fig.2 against time $t_e$ elapsed after the stop of straining at $\varepsilon_r=0.10$. The stress in a specimen deformed at a higher strain rate relaxed faster. This is a well known strain rate dependence of the stress relaxation behavior observed in largely deformed glassy polymers.

![Fig. 1. Stress-strain relations for glassy polymethyl methacrylate (PMMA) obtained by strain rate jump stretching and constant-rate stretching.](image-url)
3.2. Strain Recovery at Heating

In all the cases of the straining histories used here, the residual strain left in the deformed specimen was completely recovered by heating up to 150°C. First, as the control data, we show strain recovery behaviors for the specimens stretched at constant rates in Fig. 3, giving strain recovery behaviors obtained from specimens stretched to various strains of $\varepsilon_i$ at (a) $\dot{\varepsilon}_H=1.0\times10^{-3}\text{s}^{-1}$ and (b) $\dot{\varepsilon}_L=1.0\times10^{-5}\text{s}^{-1}$. The quantity on the vertical axis, $-d\varepsilon/dT$, gives a change in the amount of residual strain with an increment of heating temperature $T$, which will be referred to as "strain recovery rate" for simplicity. The negative sign of the quantity corresponds to the fact that the recovery is observed as shrinkage of the gauge portion. In the same way as already reported [12,14,15], the strain recovery rate curves showed one broad peak in a range of temperature below $T_g$ and another sharp one at a temperature just above $T_g$. When the specimen was stretched at the higher strain rate, the recovery started at a lower temperature. With increasing strain in a strain range well beyond the yield strain, the recovery rate curve moved upwards in a temperature range above 70°C as shown in Fig.3(a) and above 85°C as in Fig.3(b).

The strain recovery rate curves for specimens subjected to the up-jump straining are shown in Fig.4(a). The curve for $\varepsilon_i=0.10$ gives the recovery behavior of a specimen unloaded and quenched immediately before the instant of the strain rate jump. In a strain range of $\varepsilon_i=0.10$ to 0.12, where the stress increased elastically due to the up-jump of strain rate (Fig.1), there was virtually no difference among the strain recovery behaviors. In the strain range larger than $\varepsilon_i=0.12$, where $\sigma$ decreased gradually as shown in Fig.1, the increase in the residual...
strain was observed mainly in two separate temperature ranges, i.e., below ca. 80°C and above ca. 95°C. The recovery curve for the specimen with ε₀=0.18 was almost identical with that observed for the specimen stretched up to the same amount of strain at the constant rate of ε₁.

The effect of the down-jump of strain rate upon the strain recovery behavior is depicted in Fig.4(b). In a strain range of ε=0.10 to 0.11, strains recoverable in the lowest temperature range gradually decreased with increasing ε whereas the recovery rate in a higher temperature range increased. For the specimens stretched beyond ε=0.11, their recovery rate curves changed with strain in the similar manner as those observed in the case of constant rate stretching at ε₁ (Fig.3(b)). Especially, the effect of the down-jump of strain rate upon the recovery rate curve was no longer observed for specimens stretched to ε larger than 0.14.

Figure 5 shows an example of the change in strain recovery caused by the stress relaxation process. This result was obtained for the specimens stretched to a strain of ε₀=0.10 at the strain rate of ε₁ and then stress-relaxed for a time tᵣ. With increasing time tᵣ, a tail of the recovery rate curve at lower temperatures as well as the recovery rate peak observed below Tₑ progressively moved towards higher temperatures. The height of the peaks located below and above Tₑ was intensified in this process. This change is quite similar to those observed in a short time range after the down-jump of strain rate as shown in Fig.4(b). The similar effect of stress relaxation on the strain recovery behavior was also observed for the specimen stretched at another strain rate ε₂.

4. DISCUSSION

As shown in Figs.1, 3 and 4, the influence of the strain rate jump on both of the stress-strain relation and the strain recovery behavior gradually weakened and finally disappeared with the increase of strain added after the strain rate jump. That is, both of the stress-strain relation and the strain recovery behavior came to be determined by the amount of strain and the strain rate after the strain rate jump. This result indicates that the state of the residual strain, i.e., the state of the internal strain energy, is closely related to the viscoelastic stress response of the material in its deformed state. Hence, we will fully discuss in the following about the relation of the viscoelastic response (stress strain relation) to the strain recovery behavior, especially, to that at temperatures below Tₑ.

With the advancement of stress relaxation, the residual strains recoverable at lower temperatures gradually decreased whereas the strains recoverable at higher temperatures increased as seen in Fig.5. Since the amount of macroscopic strain was kept constant throughout this process, this result indicates that the thermal instability of the residual strain is gradually suppressed by the stress relaxation. Thus, the stress relaxation in the largely deformed polymeric glass is likely to have an effect of changing the state of the accumulated strain energy to another one in which the internal strain energy is thermally more stable. In the down-jump experiment, as shown in Fig.1, the stress steeply fell to a minimum value at ε=0.11. That is, the stress relaxed rapidly in a short time after the down jump of the strain rate. In this relaxation process, as shown in Fig.4(b), the strain recovery rate curve has been changing in the same manner with that observed in the stress relaxation experiment (Fig.5). This observation shows that, even in the process of increasing deformation, the relaxation of the macroscopic stress has an effect to lessen the thermal instability of the residual strain.

As for the up-jump experiment, in contrast to the stress relaxation and the down-jump experiments, the stress initially increased elastically, and then after passing through a second yield point at ε=0.12 it decreased gradually with increasing strain (Fig.1). As a result of this transient viscoelastic process, the strain recovery rate curve has evolved mainly in two separate temperature ranges above ca. 95°C and below ca. 80°C as seen in Fig.4(a). The strain being recoverable in the temperature range above 95°C increased with strain in a similar manner to that observed in any other constant rate straining condition, yet the amount of the increase was relatively small. As a much more characteristic feature observed under the up-jump condition, the increase in strain being recoverable in the temperature range below 80°C is noticed. This feature was observed along with the appearance of the second yield point. The appearance of the second yield point followed by the decrease in true stress indicates that the relaxation flow begins in the glassy polymer in order to follow the new higher strain rate. Hence, the viscoelastic relaxation of a shorter relaxation time is likely to produce residual strains having a lower degree of thermal stability. In other words, the internal strain energy accumulated in a thermally more instable state is closely related to molecular kinetics of relaxation with a shorter relaxation time. This is consistent with the following other experimental observations: (1) the strains recoverable in the lower temperature range disappear in the early stage of stress relaxation process (Fig.5) and also in a
short time after the down-jump of strain rate (Fig. 4(b)),
(2) the residual strains introduced by a relatively higher
strain rate begins to recover at a relatively lower heating
temperature (Fig. 3).

As discussed above, an increase in time length of vis-
coelastic stress relaxation for the largely deformed poly-
meric glass is found to have an effect of shifting the tem-
perature range of sub-$T_g$ strain recovery to higher temper-
atures. That is, the thermal instability of the residual
strains recoverable at temperatures below $T_g$ is gradually
lessened in the progress of stress relaxation. This finding
leads us to a reason why a single maximum strain recov-
ery rate was observed at a temperature below $T_g$; as men-
tioned above, in the process of viscoelastic relaxation in
the deformed polymer, strains recoverable at a heating
temperature is changing into those requiring a higher
temperature to recover. Since the distribution of charac-
teristic times of this change ranges from shorter ones for
strains recoverable at temperatures much lower than $T_g$ to
longer ones for those recovering at high temperatures just
below $T_g$, the largest amount of strains are presumably
accumulated in a state in which the characteristic time of
the change (i.e., the viscoelastic relaxation time) is
numerically comparable to the experimental time scale.
Accordingly, a maximum strain recovery rate is observed
at a moderate heating temperature below $T_g$. Strain rate
dependence of the peak temperature can also be interpret-
ed by the same reason as just mentioned.

The relation between the residual strain recoverable at
lower temperatures and the stress relaxation with rela-
tively shorter relaxation times is qualitatively rather sim-
ple because of its similarity to the time-temperature
equivalence observed in the linear viscoelastic regime.
The present result shows, however, that the relation can
not quantitatively be described by the simple time-tem-
perature superposition. As shown in Fig. 5, for example,
the residual strain recovering at sufficiently high tempera-
tures near $T_g$ significantly increased even at short times
of stress relaxation. This fact indicates that molecular
motions with very long characteristic times in the stress-
free state can occur in a very short time under the condi-
tion of large deformation. The molecular origin of non-
linear viscoelastic behaviors of a polymeric glass is prob-
able related to this complexity in the accumulation mech-
anism of the residual strain. Further discussion on the
accumulation mechanism will require more sophisticated
experimental studies and will be presented in subsequent
papers.

5. CONCLUSIONS

The strain recovery behavior at heating for glassy
PMMA largely stretched with strain rate jumps was
examined in connection to the transient stress response
due to the strain rate jump. The viscoelastic relaxation in
the largely deformed glassy polymer is found to lessen
the thermal instability of strains having been imposed on
the system. Since the strain recovery at less than $T_g$ has
been found to be accompanied by a release of the internal
strain energy, the present results allowed us to conclude
that molecular kinetics of nonlinear viscoelastic relax-
ation occurring in the largely deformed polymer
enhanced the thermal stability of the internal strain ener-
gy accumulated in the deformed polymer.

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