
General paper

Structural Change in Glassy Poly(methyl methacrylate) during Stop-Start Stretching

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Abstract: We measured the complex shear modulus, $G^*=G'+iG''$, of glassy poly(methyl methacrylate) (PMMA) during its stop-start stretching processes to investigate the relationship between change in mechanical properties due to aging under a finite strain and relaxation of strain-induced nonequilibrium structures. The yield stress as well as the tensile modulus at the beginning of the re-stretching increased with aging time beyond their initial values in the undeformed state, showing the effect of strain aging appeared in these quantities. The storage shear modulus $G'$ also increased with time elapsed in the stress relaxation period. The development of tensile modulus was observed to be much faster than that of the storage shear modulus. As time scales used for the dynamic measurement is much shorter than that for the macroscopic strain, evolution of tensile modulus due to aging under a finite strain is not ascribable only to the relaxation of nonequilibrium glassy structures induced by large deformation.

Key words: Poly(methyl methacrylate), Yielding, Modulus, Stress relaxation, Dynamic viscoelasticity, Aging

1. INTRODUCTION

A glassy polymer shows nonlinear viscoelastic behaviors with large mechanical stimuli. The yield phenomenon observed under the condition of constant-rate deformation is a typical example of nonlinear behaviors. A concept of structural change due to large deformation has been accepted by many researchers as a fundamental mechanism of the nonlinear behavior [1-8].

Our recent novel analyses on yielding and plastic flow in several glassy polymers [9-11] have indicated that the structure of the glassy polymers is changed into nonequilibrium structures due to large deformation. However, the mechanism of the structural change as well as the mechanism of nonlinear stress relaxation still remains unclear.

In a previous study [12], we have examined the complex shear modulus, $G^*=G'+iG''$, of glassy poly(methyl methacrylate) (PMMA) during its elongation and post-yield stress relaxation processes. In the post-yield relaxation process, the storage modulus $G'$ being lessened upon stretching showed a gradual increase toward its initial value in the undeformed state. The loss tangent $\tan\delta$ varied in an opposite manner to $G'$ in the process. This result led us to a conclusion that strain-induced nonequilibrium structures gradually relaxed during the post-yield stress relaxation process. Thus, variation of dynamic viscoelasticity during large deformation has been found to provide us with information about change in glassy structures.

When a well-annealed glassy polymer is deformed to a finite amount of strain and then left in the stress relaxation state, its modulus and yield stress gradually increase with time beyond their quasi-equilibrium values in the undeformed state. We refer this phenomenon to as "strain aging" [13-16] and we are interested in this phenomenon. Because the development of modulus and yield stress due to strain aging should closely be related to the relaxation of strain-induced nonequilibrium structures and/or nonlinear stress relaxation mechanism in the nonequilibrium glass.

In the present study, we measured the dynamic shear modulus of glassy PMMA during its stop-start stretching processes to investigate the mechanism of strain aging in relation to structural change due to large deformation. For this purpose, the development of tensile modulus due to strain aging was compared to variations of the storage shear modulus.

2. EXPERIMENTAL

A commercial cast sheet of PMMA (Shinkolite L, Mitsubishi Rayon Co.) was used as the experimental material. The glass transition temperature $T_g$ of this material was determined as 116°C by a differential scanning calorimetry run at 1°C min⁻¹. Dumbbell-shaped tensile specimens with a gauge section of 5mm × 5mm × 50mm were machined from the cast sheet. The specimens were used after a thermal conditioning procedure including cooling through $T_g$ at a very slow cooling rate of 3.3°C h⁻¹.

The stop-start stretching of the specimen was performed on an Instron testing machine at a temperature of 90°C. The specimen was stretched at a strain rate $\dot{\varepsilon}_s$ up to a finite strain $\varepsilon_s$ of either 0.03 or 0.06, and then left at $\varepsilon_s$ for a variation of time $t_s$ ranging from 10³ to 10⁵s. This time period $t_s$ was the aging time of the specimen in the strained state. The strain-aged specimen was then re-stretched at the same strain rate as that for the initial stretching. Two nominal strain rates of 1.0 × 10⁻³ and 1.0 × 10⁻⁵s⁻¹ were employed as $\dot{\varepsilon}_s$.

For the measurement of the complex shear modulus during the stop-start stretching, a laboratory-made equipment was mounted on the testing machine. This
equipment provided specimens under stretching with a forced twisting oscillation around the tensile axis. Dynamic measurement was performed at a frequency ranging from 0.20 to 20Hz. A small angle of 0.016 rad was used as the angular amplitude of the twisting oscillation to obtain the response torque in a form of simple sinusoidal wave. We had confirmed before measurement that the imposition of the twisting oscillation had no effect on uniaxial stress-strain-time relations during the stop-start stretching of the specimen.

3. RESULTS

Figure 1 shows true stress $\sigma$ - nominal strain $\varepsilon_n$ relations during stop-start stretching performed with a nominal strain rate of $\dot{\varepsilon}_n = 1.0 \times 10^{-3} s^{-1}$. Tensile true stress $\sigma$ was calculated with an assumption of isovolume and uniform deformation of the gauge section. In fact, a great majority of stretching run was accomplished without occurrence of visible necking. In each panel, dashed curves plotted against aging time $t_r$ give the stress relaxation behavior during aging period at the finite strain of $\varepsilon_r$. Dash-dotted lines in each panel indicate the magnitude of yield stress for continuous stretching at $\varepsilon_n$. Panel (a) shows the relations for specimens provided with a strain of $\varepsilon_r = 0.03$. The yield stress upon re-stretching of a specimen strain-aged at $\varepsilon_r = 0.03$ for $t_r = 1000s$ was higher than that for continuous stretching. The yield stress increased with aging time $t_r$. A growth of yield stress with $t_r$ was also observed for specimens strained by $\varepsilon_r = 0.06$ (panel (b)). For this case, yield stress for $t_r = 1000s$ was approximately the same as that for continuous stretching. Thus, specimens provided with a smaller amount of $\varepsilon_r$ showed an earlier growth of yield stress. Stress-strain relations obtained by stop-start stretching performed with $\dot{\varepsilon}_n = 1.0 \times 10^{-5} s^{-1}$ are shown in Fig. 2. A growth of yield stress toward higher values than that for continuous stretching was also observed in this case, although the growth appeared at longer times of $t_r$ than that observed in Fig. 1. Specimens aged at $\varepsilon_r = 0.03$ (panel (a)) showed a faster increase of yield stress than those strained by $\varepsilon_r = 0.06$ (panel (b)).

A typical variation of dynamic viscoelasticity during stop-start stretching is depicted in Fig. 3. The storage modulus $G'$ and the loss tangent $\tan \delta$ as well as $\sigma$ are plotted against $\varepsilon_n$ in this figure. The numeric value of $G'$ under large strain was calculated under an assumption of isovolume and uniform deformation of the gauge section. As reported previously [12], $G'$ being lessened upon initial stretching increased with time $t_r$ elapsed in the
Fig. 3. Variation of $\sigma$, storage modulus $G'$ and loss tangent $\tan \delta$ during stop-start stretching.

The loss tangent $\tan \delta$ varied in an opposite manner to $G'$. At long times of $t_r$, $G'$ continued to increase beyond its quasi-equilibrium value at very low strains as will be clearly shown in Fig. 4, whereas $\tan \delta$ approached asymptotically to its quasi-equilibrium value. Variation of the complex shear modulus during the stop-start stretching was qualitatively the same as this result for all straining programs employed in this study.

Tensile moduli $E_2$ at the beginning of re-stretching as a function of $t_r$ are compared to $G'(t_r)$ in Fig. 4. Vertical axes for both moduli $E_2$ and $G'$ are respectively normalized by their quasi-equilibrium values $E_0$ and $G'_0$ at very low strains for convenience to evaluate the progress of strain aging. Values of $E_2/E_0$ were determined from $\sigma-\varepsilon$ relations for individual run of stop-start stretching experiment shown in Figs. 1 and 2. On the other hand, we adopted successively measured $G'/G'_0$ during the longest aging period of $t_r$ for this figure, to avoid the scattering of the data due to occurrence of invisible or quite weak necking.

Figure 4(a) shows the result obtained by stop-start stretching performed with $\dot{\varepsilon}_n = 1.0 \times 10^{-3}$ s$^{-1}$. Amount of strain $\varepsilon_n$, at which specimens were aged, had virtually no effect on the magnitude of $E_2/E_0$ and $G'/G'_0$ throughout the aging period. Numeric values of $E_2/E_0$ increased continuously with $t_r$, showing the effect of strain aging appeared in this property. The storage modulus ratio $G'/G'_0$ observed at all frequencies also increased with $t_r$.

Fig. 4. Growing behaviors of modulus $E_2$ and $G'$ during stress relaxation process. Both moduli are normalized by their quasi-equilibrium values at very small strains.
The value of $E_2/E_0$ had exceeded unity by $t=10^5$s, while $G'/G'_0$ attained unity at around $t=3.0 \times 10^3$s for $f=20$Hz, at which $G'/G'_0$ showed the fastest growth in this condition. This result shows that the growth of $E_2/E_0$ due to strain aging is much faster than that of $G'/G'_0$ obtained at frequencies of 0.20 to 20Hz.

Comparison of $E_2/E_0$ and $G'/G'_0$ obtained with $\dot{\varepsilon}_s = 1.0 \times 10^5$s$^{-1}$ is shown in Fig. 4(b). Magnitude of $\varepsilon_s$ had also little effect on growing behavior of $E_2/E_0$ and $G'/G'_0$ in this case. As can be seen in Fig. 4(b), modulus ratio $E_2/E_0$ as well as $G'/G'_0$ at $t=1000$s was lower than unity. That is, both moduli $E_2$ and $G'$ were lower than their initial quasi-equilibrium values for this case. Then both ratio increased with $t_1$ to values higher than unity due to strain aging. The ratio $E_2/E_0$ attained unity at about $t_1=3.0 \times 10^5$s. The ratios $G'/G'_0$ for all frequencies attained their quasi-equilibrium values at around $t_1=1.0 \times 10^5$s. Thus, an earlier growth of $E_2/E_0$ compared to $G'/G'_0$ was also observed in this stop-stop stretching condition.

4. DISCUSSION

Both of the yield stress (Figs. 1 and 2) and tensile modulus $E_2$ (Fig. 4) observed in the re-stretching process increased with aging time $t$, beyond their initial quasi-equilibrium values in the undeformed state, showing the effect of strain aging appeared in these quantities. The increase of yield stress depended on both the strain rate $\dot{\varepsilon}_s$ at stretching and the strain $\varepsilon_t$ at which specimens were aged. On the other hand, the growing behavior of $E_2$ was affected only by the strain rate $\dot{\varepsilon}_s$. This observation indicates that the yield stress and the modulus $E_2$ of the strained material governed by some different mechanisms. As the yielding phenomenon can only be observable by imposing a large deformation, the yield stress at re-stretching should greatly be affected by structural change due to re-stretching. On the other hand, the tensile modulus can be determined even at very small strain. Hence, the modulus $E_2$ is more suitable quantity for discussing its relation to the nonequilibrium structures of the glass. From this point of view, we will limit our discussion on the relation of growing behaviors of $E_2$ and $G'$.

An increase of $G'$ accompanying decrease of $\tan \delta$ during stress relaxation process (Fig. 3) indicates that strain-induced nonequilibrium structures relax with time during the stress relaxation process [12]. Experimental time scales of our dynamic measurement ranging from 0.20 to 20 Hz are much shorter than that of the stop-start stretching. Thus, the change in $G'$ observed here shows relaxing behavior of very local structures compared to those related to macroscopic nonlinear relaxation. As seen in Fig. 4, the tensile modulus $E_2$ observed at a time scale longer than that of $G'$ grew much faster than $G'$. In other words, the development of tensile modulus $E_2$ due to strain aging was found to be much faster than relaxation of local structures. This result reveals that the growth of $E_2$ as a result of strain aging does not directly depend on the relaxation of strain-induced nonequilibrium structures. The strain aging observed as an increase of tensile modulus is likely to be related to molecular mechanism of nonlinear stress relaxation under large deformation. Further discussion on the molecular mechanism of the nonlinear stress relaxation will require more sophisticated experimental studies and will be presented in subsequent papers.

5. CONCLUSIONS

An increase of tensile modulus of PMMA due to stress relaxation at a finite strain was quantitatively compared to a variation of the storage shear modulus to discuss the relationship between the mechanism of strain aging and relaxation of strain-induced nonequilibrium structures. The tensile modulus at the beginning of re-stretching showed much faster increase than the storage modulus. As time scales used for the dynamic measurement is much shorter than that for the macroscopic straining, evolution of tensile modulus due to aging under a finite strain is found to be not ascribable only to the relaxation of strain-induced nonequilibrium glassy structures.

REFERENCES