

Changes in the Thermomechanical Behavior of Epoxy Glasses Under the State of Strain Aging

Hiroshi Kawakami, Masaomi Watanabe

Department of Mechanical Engineering, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan

Received 24 April 2007; accepted 27 August 2007

DOI 10.1002/app.27248

Published online 1 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Changes in thermomechanical behavior with structural relaxation taking place in epoxy glasses were studied. Differential scanning calorimetry measurements and thermostimulated strain recovery tests were performed for specimens deformed and then aged under fixed strain. In the course of heating, the specimens started to absorb thermal energy, whereas plastic strain was still stable. At higher temperatures, plastic strain started recovery, which was accompanied by exothermic behavior of the specimen. With an increase in the aging duration, the endothermic peak signi-

fied and moved to a higher temperature. These results indicated that the longer the aging duration was, the harder the plastic strain and strain energy were frozen in the glassy structure. This freeze-strain phenomenon was observed for crosslinked epoxy glass, as well as polymeric glasses with linear molecular structures, aged under strain. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2095–2100, 2008

Key words: ageing; amorphous; differential scanning calorimetry (DSC); relaxation; thermosets

INTRODUCTION

Structures of glassy substances relax toward an equilibrium state with the passage of time. The structural relaxation is noticeable in quenched glass. Properties of glassy substances change with structural relaxation; therefore, the relaxation of glassy substances is the hot topic in physics and engineering.¹

For amorphous polymers largely deformed in their glassy states, the structure is similar to that in a melt state and is frozen, remaining far from equilibrium.² The relaxation of glassy polymers subjected to large deformation has been studied.^{3–9}

In our previous studies,^{10,11} on relaxation in epoxy glass aged under large deformation, it was found that the evolution of mechanical properties of epoxy glass left under fixed strain was anisotropic: for epoxy glass that had been twisted clockwise and then aged under strain, the value of the stress at a yield point evolved faster for a clockwise twist than a counterclockwise twist. Such a result indicates that the aging phenomenon of glassy structures under strain is different from those of physical aging of quenched glass, and so we call aging under fixed strain *strain aging*.

In this study, differential scanning calorimetry (DSC) measurements and thermostimulated strain recovery (TSSR) tests were carried out with strain-

aged epoxy glasses to study the evolution of the thermomechanical behavior of polymer glass under the state of strain aging.

EXPERIMENTAL

Samples

A bisphenol A type epoxide precursor (Epiclon 860, Dainippon Ink and Chemicals, Inc., Tokyo, Japan) was cured with 4,4'-diaminodiphenylmethane (4,4'-DDM) to form a sample with a crosslinked structure (sample C). The molar ratio of the epoxy precursor to the amine was the stoichiometric ratio (Table I). The mixture was cured at 343 K (70°C) for 12 h, and this was followed by a heat treatment at 433 K (160°C) for 12 h. The glass-transition temperature (T_g) of sample C, measured by DSC, was about 428 K (155°C). The average molecular mass between adjacent crosslinks was about 493 g/mol, being calculated from rubber elasticity.

The epoxide precursor was also cured with aniline to form a sample with an uncrosslinked structure of linear molecules (sample L). T_g of sample L was about 360 K (87°C), and the number-average molecule mass was about 26,000, as measured by gel permeation chromatography.

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

Cylindrical specimens (diameter: 4.0 mm, height: 5.0 mm, weight: 0.068 g for sample C and 0.073 g for

Correspondence to: H. Kawakami (hkawakam@mech.eng.osaka-cu.ac.jp).

TABLE I
Compositions of the Epoxide Precursor and Hardeners

	Average molecular weight (g/mol)	Amount of hardener (g/100 g of epoxy resin)
Epoxy resin	490	
Aniline	93	19.0
4,4'-DDM	198	20.1

sample L) were cut from the samples. The specimens were annealed at a temperature 5 K higher than T_g [433 K (160°C) for sample C and 365 K (92°C) for sample L] for 6 h and then slowly cooled to room temperature at a cooling rate of 0.1 K/min. Because of this heat treatment, the glass structure of the annealed specimens was expected to be in a thermodynamically quasi-equilibrium state.

Preparation of strain-aged specimens

Annealed specimens were compressed at a constant strain rate of $1.0 \times 10^{-3} \text{ s}^{-1}$ up to a compressive strain value of 0.15. At the moment the strain reached 0.15, it stopped being increased, and specimens were kept under the strain for several aging durations up to $3.0 \times 10^5 \text{ s}$. Immediately after an aging period had passed, the strain-aged specimen was rapidly cooled to room temperature, whereas the strain was kept at 0.15, to freeze the plastic strain in the glassy structure of the specimen. The temperature was kept at $T_g - 35 \text{ K}$ (393 K for sample C and 325 K for sample L) over the strain-aging period and during compression. Such a choice of test tempera-

ture is justified by experimental results¹² and the Williams–Landel–Ferry equation,¹³ which states that relative molecular mobility is dependent on the distance of the temperature from its T_g .

For some strain-aged specimens, increasing the compressive strain resumed at $T_g - 35 \text{ K}$ to obtain stress–strain relationships.

TSSR test

TSSR tests were performed for strain-aged specimens to study the thermal stability of plastic strain. A laboratory-made heat chamber was employed for TSSR measurements. A programmable digital temperature controller (model SR52 digital controller, Shimaden Co., Ltd., Hiroshima, Japan) was installed in the heating chamber; the fluctuation in temperature was less than $\pm 0.1 \text{ K}$. A strain-aged specimen was heated at a constant heating rate of 1.0 K/min, and the amount of strain recovery during the heating was measured with a noncontact displacement sensor (LB-1100 laser sensor, Keyence Co., Osaka, Japan) in order to not disturb the recovery of strain.

DSC measurements

A high-sensitivity differential scanning calorimeter (DSC 6100, Seiko Instruments, Inc., Chiba, Japan) was used for DSC measurements. Specimens subjected to DSC measurements were prepared in the same manner as specimens used for the TSSR tests. A constant heating rate was set to 1.0 K/min to compare DSC results with TSSR results isochronously.

RESULTS

Stress–strain relationships

Stress–strain relationships for strain-aged C specimens are shown in Figure 2 (a schematic diagram of

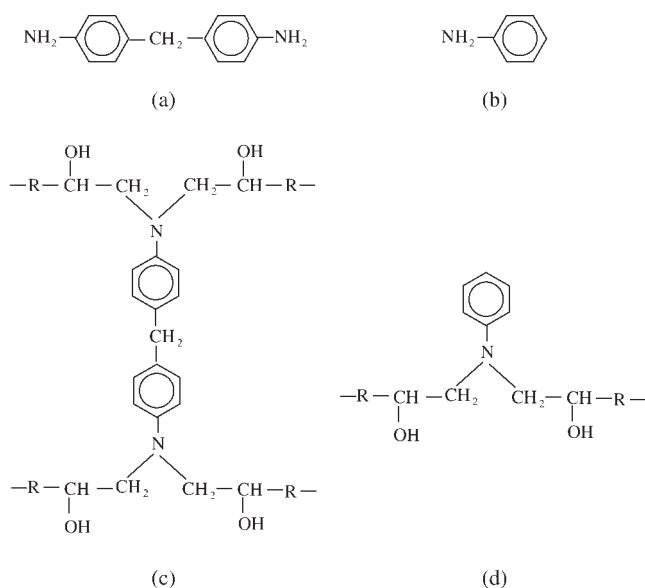


Figure 1 Molecular structures of the curing agents and epoxy glasses: (a) 4,4'-DDM, (b) aniline, (c) sample C (epoxy cured by 4,4'-DDM), and (d) sample L (epoxy cured by aniline).

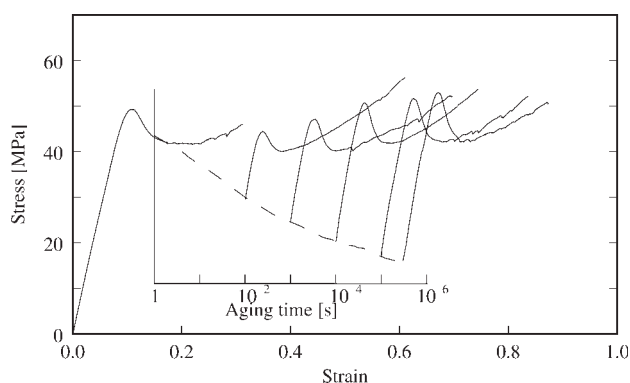


Figure 2 Stress–strain relationships for strain-aged C specimens.

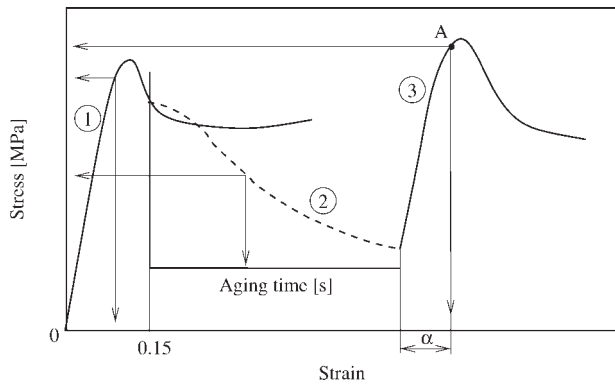


Figure 3 Schematic diagram of stress-strain curves. (1) A stress-strain curve for an annealed specimen. (2) A stress-relaxation curve for a specimen subjected to strain aging under a strain of 0.15. The curve is plotted against the aging time, and the abscissa axis for the curve is placed inside the figure. (3) A stress-strain curve for a strain-aged specimen. As the curve is shifted in a horizontal direction according to its aging duration, the value of the strain at point A is equal to $0.15 + \alpha$. For all curves, including the stress-relaxation curve, the vertical axes, that is, the stress axes, are common.

the stress-strain relationships is shown in Fig. 3) The value of the stress at the upper yield point (σ_{yu}) increased with the aging duration, and those values for strain-aged specimens whose aging period was equal to or longer than 1.0×10^4 s were higher than that for the annealed specimen.

The stress-strain relationships for L specimens are shown in Figure 4. The values of the stress and strain at the upper yield point for an annealed specimen were about 68 MPa and 0.11, respectively. σ_{yu} increased with the aging period.

For C and L specimens, the value of σ_{yu} increased with the aging duration. The stress value at the lower yielding point (σ_{yl}), on the other hand, showed a different evolution: the σ_{yl} value for C specimens increased with the aging duration,

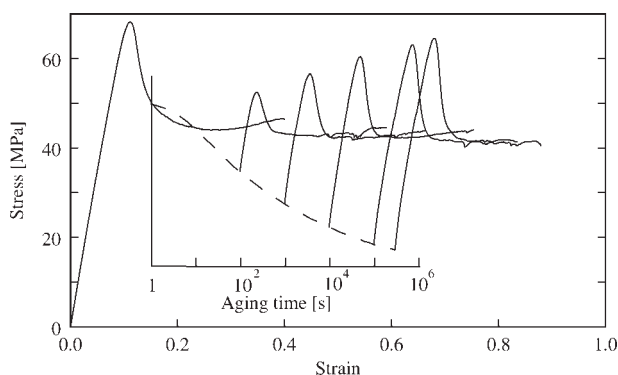


Figure 4 Stress-strain relationships for strain-aged L specimens.

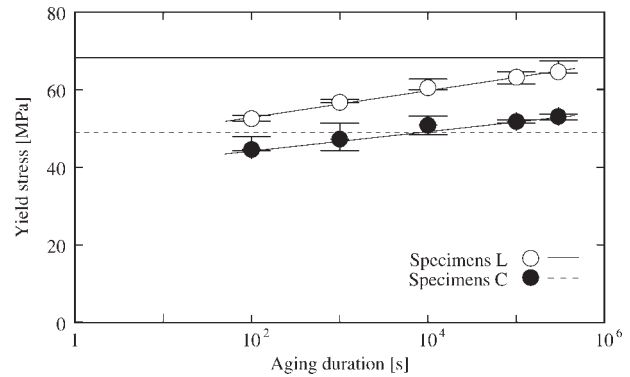


Figure 5 Values of stress at the upper yield point for strain-aged C and L specimens. The horizontal lines indicate the values for annealed specimens. The data are averages from multiple experiments, and bars indicate ranges of error.

whereas for L specimens, the σ_{yl} value was almost constant and was about the same as that of the annealed specimen. The increase in σ_{yl} for sample C was attributed to the following phenomenon: in the crosslinked amorphous polymers, the restriction of rotational motions of the main chains increased with the progression of strain aging.¹⁴

For both specimens, the evolutions of σ_{yu} are summarized in Figure 5. The increase in the σ_{yu} value was almost the same but slightly slower for C specimens.

TSSR

TSSR curves for strain-aged C specimens are shown in Figure 6. In the figure, each curve can be divided into two parts: one below T_g with a broad, shoulder-like peak and the other in a short temperature range above T_g with a peak at about 435 K. Therefore, plastic strain remaining in a glassy structure after strain

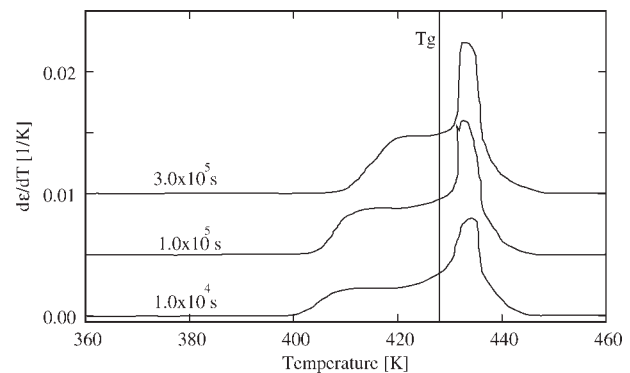


Figure 6 TSSR curves for strain-aged C specimens. Each curve is shifted systematically at uniformly spaced intervals of 0.005 K^{-1} . The vertical axis is the strain recovery rate ($d\epsilon/dT$). The vertical line indicates the position of T_g .

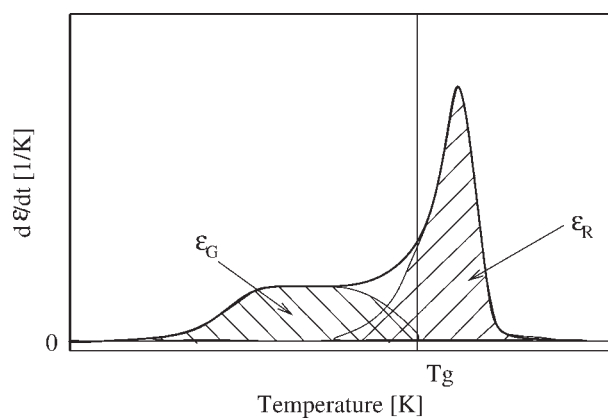


Figure 7 Schematic diagram showing definitions of ε_G and ε_R . The recovering plastic strain can be divided into two strain components: ε_G , recovering in a broad temperature range below T_g , and ε_R , recovering at higher temperatures with a sharp peak at a temperature above T_g . In the temperature range in which ε_G and ε_R recover simultaneously, both strain components contribute to the total amount of the recovery rate ($d\varepsilon/dT$). As the result, the lower recovering peak is like a shoulder.

aging can be divided into two strain components (Fig. 7): ε_G , recovering below T_g , and ε_R , recovering mainly above T_g . The temperature at which ε_G started recovery moved to a higher temperature and the shoulder height increased with the aging duration. The peak height of ε_R became higher with the aging duration, whereas the temperature at the ε_R peak was independent of the aging duration.

Figure 8 shows TSSR curves for strain-aged L specimens. The evolution of the TSSR curves was qualitatively the same as that of C specimens: the ε_G shoulder height became higher and the ε_G recovering temperature range moved to a higher temperature, whereas the ε_R peak became higher and the peak temperature remained the same.

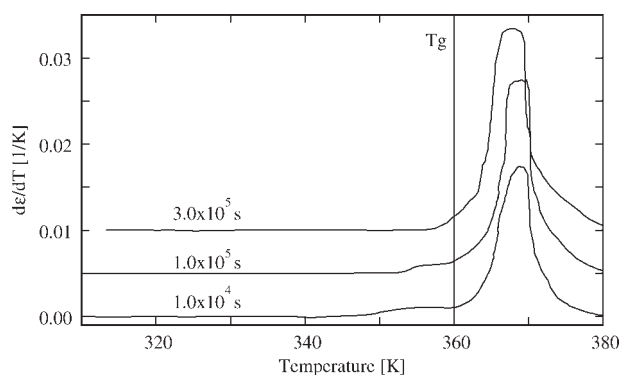


Figure 8 TSSR curves for strain-aged L specimens. Each curve is shifted systematically at uniformly spaced intervals of 0.005 K^{-1} . $d\varepsilon/dT$ is the recovery rate.

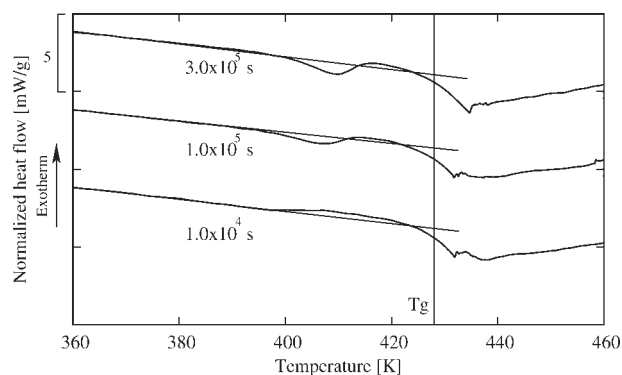


Figure 9 DSC thermograms for strain-aged C specimens. Each curve is shifted systematically at uniformly spaced intervals of 5 mW/g . The fine lines are base lines extended from DSC curves in a lower temperature range and are drawn for reference.

DSC

For strain-aged C specimens, DSC curves are shown in Figure 9. For the specimen strain-aged for $1.0 \times 10^4 \text{ s}$, the DSC curve deviated upward from the baseline at about 395 K and then dropped from the temperature came closer to T_g . For the specimens strain-aged for 1.0×10^5 or $3.0 \times 10^5 \text{ s}$, before the upward deviation, the DSC curve first deviated downward from the baseline and then turned to recover, finally passing the baseline. Such a downward deviation intensified as the aging duration was longer, and the temperature range in which the DSC curve was below the baseline moved to a higher temperature with increasing aging duration.

Figure 10 shows DSC curves for L specimens. The specimen strain-aged for $1.0 \times 10^4 \text{ s}$ exhibited a downward deviation before the upward deviation. The downward deviation intensified and moved to a higher temperature with increasing aging duration.

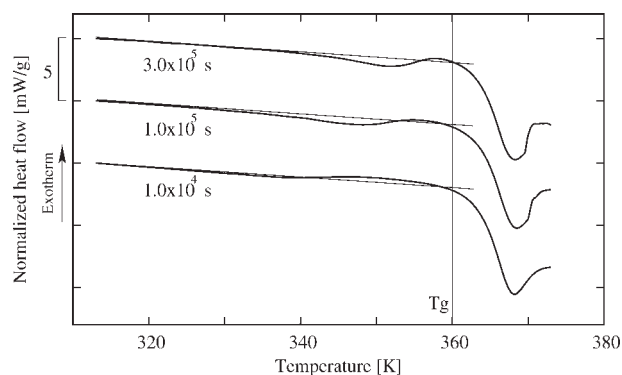


Figure 10 DSC thermograms for strain-aged L specimens. Each curve is shifted systematically at uniformly spaced intervals of 5 mW/g . The fine lines are base lines extended from DSC curves in a lower temperature range and are drawn for reference.

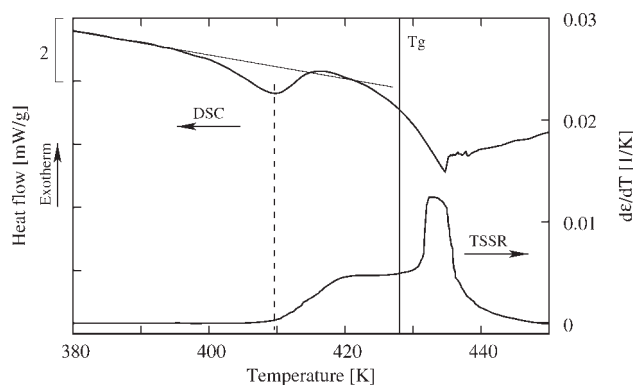


Figure 11 DSC curve and TSSR curve for the C specimen strain-aged for 3.0×10^5 s. The fine line is a base line extended from the DSC curve at lower temperatures and is drawn for reference.

DISCUSSION

For the C specimen strain-aged for 3.0×10^5 s, the DSC curve and the TSSR curve are shown isochronously in Figure 11. The figure shows that the downward deviation of the DSC curve started before strain recovery. Such a result indicates that plastic strain in the specimen recovered only after the strain-aged glassy structure absorbed a certain amount of thermal energy.

In addition, the TSSR curve in Figure 9 indicates that strain component ϵ_G started recovery at a temperature of 410 K. At the same temperature, the DSC curve started recovering from its downward deviation. When strained polymers are heated, some amount of strain energy is released as exothermic heat at temperatures below T_g .^{15–19} It is, therefore, necessary to take into account the effects of the exothermic heat when we study DSC curves for strained polymers. The fact that the strain recovery and the recovery of the DSC curve from its downward deviation started at the same temperature indicates that once plastic strain starts recovery, the heat energy that drives strain recovery is compensated by strain energy released as plastic strain recovers. The origin of the exothermic heat should be strain energy, which is accumulated in the glassy structure during deformation and is frozen in the glassy structure during strain aging.

The behaviors observed in the DSC curve and the TSSR curve shown in Figure 11 can also be observed in experimental results for other specimens strain-aged for various aging durations, except the C specimen strain-aged for 1.0×10^4 s. For the C specimen strain-aged for 1.0×10^4 s, endothermic behavior was hardly seen, and this indicates that the threshold value of thermal energy necessary to induce strain recovery is quite small. [Also, largely

deformed but not strain-aged specimens (i.e., aging time (t_a) = 0) did not exhibit the endothermic behavior.¹⁵] In consideration of this result, the fact that the endothermic peak signified and shifted to a higher temperature with increasing aging duration indicates that the threshold value of thermal energy increases with an increase in the aging duration. In other words, plastic strain and strain energy become hardly frozen in the glassy structure in the course of structural relaxation under the state of strain aging. Such a structural relaxation can be rotation of side groups, which is the major change taking place in epoxy glass aged under strain.¹⁴ As a result of the freeze-strain phenomenon, the σ_{yu} value increases with the aging duration.

Because experimental results for sample L were qualitatively the same as those for sample C, the freeze-strain phenomenon under the state of strain aging takes place also in polymer glass with linear molecules, as reported in refs. 20 and 21. However, the progress of the structural relaxation seems to be slower in sample C than in sample L, as shown in Figure 5. Such a result agrees with an experimental result from a previous study in which a change in birefringence was measured in the course of strain aging.¹⁴

CONCLUSIONS

For epoxy glasses left under the state of strain aging, the plastic strain and strain energy are frozen more hardly in a glassy structure with aging time. The threshold value of thermal energy necessary to initiate strain recovery increases with an increase in the aging duration. Such a freeze-strain phenomenon takes place in polymeric glasses under the state of strain aging, yet the progress of the structural relaxation seems to be slower in a crosslinked glassy polymer than in a glassy polymer with linear molecules.

The authors thank Dainippon Ink and Chemicals, Inc., for kindly supplying the epoxy resin used.

References

1. Relaxations in Complex Systems 5, Proceedings of the Fifth International Discussion Meeting on Relaxations in Complex Systems, Lille, France, July 7–13, 2005; Affouard, F.; Descamps, M.; Ngai, K. L., Eds. Elsevier: Amsterdam, Netherlands, 2006.
2. Nanzai, Y. *Prog Polym Sci* 1993, 18, 437.
3. Bernstein, B.; Kearsley, A. E.; Zapas, L. Z. *Trans Soc Rheol* 1963, 7, 391.
4. McKenna, G. B.; Zapas, L. *J Polym Eng Sci* 1986, 26, 725.
5. Lee, A.; McKenna, G. B. *Polymer* 1990, 31, 423.
6. Santore, M. M.; Duran, R. S.; McKenna, G. B. *Polymer* 1991, 32, 2377.
7. Aboulfaraj, M.; G'Shell, C.; Mangelinck, D.; McKenna, G. B. *J Non-Cryst Solids* 1994, 172, 615.

8. Waldron, W. K., Jr.; McKenna, G. B. *J Rheol* 1995, 39, 471.
9. Colussi, D. M.; O'Connell, P. A.; McKenna, G. B. *Polym Eng Sci* 1997, 37, 1469.
10. Kawakami, H.; Otsuki, R.; Nanzai, Y. *Polym Eng Sci* 2005, 45, 20.
11. Kawakami, H.; Souda, K.; Nanzai, Y. *Polym Eng Sci* 2006, 46, 630.
12. Cook, W. D.; Mayer, A. E.; Edward, G. H. *Polymer* 1998, 39, 3725.
13. Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
14. Kawakami, H.; Kishimoto, K.; Nanzai, Y.; Sato, Y. *J Non-Cryst Solids* 2006, 352, 4956.
15. Kawakami, H.; Yamanaka, H.; Nanzai, Y. *Polymer* 2005, 46, 11806.
16. Oleinik, E. *Prog Colloid Polym Sci* 1989, 80, 140.
17. Nanzai, Y.; Miwa, A.; Cui, S. Z. *JSME Int J Series A* 1999, 42, 479.
18. Nanzai, Y.; Miwa, A.; Cui, S. Z. *Polym J* 2000, 32, 51.
19. Kawakami, H. *Nihon Reoroji Gakkaishi* 2007, 35, 119.
20. Cui, S. Z.; Nanzai, Y. *Polym J* 2001, 33, 444.
21. Nanzai, Y. *J Non-Cryst Solids* 2002, 307, 481.