Plastic Deformation Mechanism in PMMA under Creep Stress*

Yukuo NANZAI**

A rate analysis applied to the plastic flow under creep stress in glassy polymethyl methacrylate (PMMA) is presented. This analysis leads to the conclusion that the structure of the PMMA glass is changed into liquidlike structures during the large deformation under creep stress. Comparisons of various mechanical data obtained from the creep experiment for the polymer with those from the constant-rate deformation experiment indicate that the process of the glass-to-liquid structural change is controlled by the strain and strain rate being imposed on the polymer almost independently of the loading modes.

Key Words: High Polymer Materials, Plasticity, Viscoelasticity, Fracture Toughness, Molecular Kinetics

1. Introduction

On a macroscopic scale, the plastic deformation of a solid polymer is generally observed at its yielding and cold-flow. According to our recent novel analyses⁽¹⁾⁻⁽³⁾ on the yielding and plastic flow in several glassy polymers, it has been experimentally shown that the structure of the glassy polymers is changed into liquidlike structures due to large deformation. This structural change results in drastic decrease in internal viscosity of the glassy polymers⁽¹⁾, hence bringing about great changes in mechanical behavior of the polymers.

Microscopic observation of a local region around a tip of a running crack in the glassy polymers has frequently revealed the appearance of an activated plastic zone preceding the crack tip as schematically shown in Fig. 1^{(4),(5)}. As predicted from results of our experimental analyses on the macroscopic plastic deformation⁽¹⁾⁻⁽³⁾, the mechanical behavior of the

activated plastic zone has been changed from that of the undeformed matrix to that of the liquidlike structure of the polymer. Thus the change in the mechanical behavior of the local crack tip zone has significant effects on the running behavior of the crack, because the crack usually advances into this local plastic zone at its next propagation step. That is, the appearance of the local plastic zone in front of the crack tip can directly be related to the toughness of the solid polymers and thermoplastic composites.

In general the mechanical behavior of a

Fig. 1 Schematic representation of an activated plastic zone at a crack tip frequently observed in glassy polymers

* Received 7th December, 1992.

** Department of Mechanical Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

deforming glassy polymer can be represented by its constitutive relations in terms of mechanical parameters such as stress, strain and their time derivatives. At present, however, the knowledge about details of the contribution of these mechanical parameters to the glass-to-liquid structural change in the glassy polymers remains inadequate. This knowledge is practically important for the construction of nonlinear constitutive relations expressing the large deformation process in the glassy polymers, and can greatly contribute to the analysis of the toughening mechanism in polymeric materials. This may also contribute to the field of kinetics analysis for the machining of polymeric materials.

Our experimental analyses on the structural change so far have been based almost solely on data from the constant-rate deformation test. This strain-controlled deformation mode has hence allowed us limited discussion about the mechanical parameters controlling the structural change. Thus in the present study the plastic deformation mechanism of a glassy polymer is analyzed using data from the constant-stress experiment (i.e., creep test) which is quite different in loading history from the constant-rate deformation test. This creep experiment enables us to further discuss the mechanical parameters controlling the structural change in the polymers.

2. Experimental

The glass-to-liquid structural change has been shown to be due to the shear component of the imposed stress^{(6),(7)}, thus taking place either under tension or under compression. For this reason, the creep experiments in this study were conducted under uniaxial compression to avoid earlier fracture of specimens. Cylindrical specimens of 0.5 cm in diameter and 1.0 cm in height were cut from a commercially available polymethyl methacrylate (PMMA) cast

sheet which had been heat treated at 130°C for 2 hours. The creep deformation tests for the specimens were run between two polished steel plates with no lubricants at temperatures of 40 to 100°C under a condition of constant true stress. This condition was accomplished by stepwise increase of the creep weight proportional to increment of the cross-sectional area of the specimen deforming under the compressive load. The true stress and true strain rate in each specimen were calculated under assumptions of its iso-volume and uniform deformation.

Constant-rate deformation tests for the same specimens were also conducted under uniaxial compression at temperatures of 40 to 100°C using an Instron testing machine.

3. Results and Discussion

Variations of the logarithm of true strain rate $\dot{\epsilon}_t$ under various creep stresses at 78°C are plotted against the nominal strain ϵ_n in Fig. 2. After the initial elastic deformation induced by the instantaneous loading of creep weight, $\log \dot{\epsilon}_t$ showed the minimum value at a nominal strain of 0.06 to 0.07. This point shall be designated as point YC (as shown in Fig. 4.). Passing the point YC, $\log \dot{\epsilon}_t$ gradually increased with ϵ_n , and reached the plateaulike maximum value in a range of nominal strain approximately from 0.25 to 0.35. This range shall be referred to as range LC. The ratio of the maximum value of $\dot{\epsilon}_t$ to the minimum one under a constant creep stress is approximately 10. This accelerative increase of the strain rate from the point YC to the range LC is ascribable to gradual softening of the specimen with increasing strain. The softening behavior closely resembles the strain softening observed in the constant-rate deformation experiment as illustrated in Fig. 3. A set of true stress σ against nominal strain curves in Fig. 3 were obtained by constant-rate uniaxial compression tests run at 78°C

Fig. 2 An example of the variation of true strain rate $\dot{\epsilon}_t$ for polymethyl methacrylate (PMMA) under the creep stress plotted against nominal strain ϵ_n

Fig. 3 A set of true stress σ against ϵ_n curves for PMMA obtained under the condition of constant-rate deformation

using the same PMMA specimen. The stress showed the maximum value at a point generally known as the yield point—here referred to as point Y—and then gradually decreased with increasing nominal strain to level off in a strain range of the minimum stress, which is designated as range L. In Fig. 4, both the variations of $\log \dot{\epsilon}_t$ under the creep stress and σ under the constant-rate deformation are schematically reproduced against nominal strain ϵ_n , showing a strong mirror-image resemblance.

Referring to range L, we have shown that a state of steady flow in the glassy polymer exists in this range as mentioned in the previous paper⁽¹⁾. The rate analyses applied to range L for various glassy polymers have led to the conclusion that the structure of the polymers has changed to liquidlike. Thus range LC, being quite similar to range L, is very likely to be a state of steady flow; this motivated us to analyze its behavior with respect to the rate process.

The Eyring equation⁽⁸⁾ was used for the rate analysis of range LC, being expressed in the following form:

$$\frac{\sigma_{LC}}{T} = \frac{9.212k}{v_c} \left(\log \dot{\epsilon}_t - \log CT + 0.4343 \frac{\Delta H}{RT} \right), \quad (1)$$

Table 1 Eyring parameters evaluated from the state of steady plastic flow in polymethyl methacrylate under creep stress

No.	ΔH (kJ/mol)	ΔS (kJ/mol·K)	v_c (nm ³)
1	511	0.949	12.97
2	454	0.812	11.11
3	410	0.706	9.63
4	377	0.627	8.47
5	337	0.531	7.31
6	310	0.466	6.48
7	276	0.390	5.35

Fig. 4 Schematic reproduction of the variations of $\dot{\epsilon}_t$ under creep stress and σ under constant-rate deformation for PMMA plotted against ϵ_n

where

$$C = \left(\frac{2\lambda k}{3\lambda_1 h} \right) \exp \left(\frac{\Delta S}{R} \right). \quad (2)$$

In these equations, σ_{LC} and $\dot{\epsilon}_t$ are the true stress and true strain rate in range LC, respectively, ΔH is the activation energy, ΔS is the activation entropy, v_c is the activation volume evaluated under the condition of uniaxial compressive stress, λ and λ_1 are distances between the adjacent flowing units, R is the gas constant, k is the Boltzmann constant, h is the Planck constant, and T is the absolute temperature.

Experimental data for the stress in range LC, σ_{LC} , divided by temperature T are plotted against $\log \dot{\epsilon}_t$ in Fig. 5. The experimental points at each temperature could be represented by a curve with a slope increasing gradually with $\log \dot{\epsilon}_t$. As illustrated in the previous papers⁽¹⁾⁻⁽³⁾, these curves can be analyzed using the Eyring equation in a novel way: a curve is approximated by successive line elements with different slopes, and parallel line elements at different temperatures represented by Eq. (1) are determined so as to give the best fit to the data. The set of parallel line elements labeled by numbers 1 to 7 in Fig. 5 were obtained in this way, and the corresponding numerical values of the Eyring parameters ΔH , ΔS and v_c are summarized in Table 1. The values of ΔS were calculated from Eq. (2) using the experimental values of C under a reasonable assumption of the same order of magnitude of λ and λ_1 .

The quantity ΔH is the activation energy required for a flow unit to pass over the potential energy barrier built up by the intermolecular interaction in the softened state LC of the PMMA glass, and ΔS is the change in entropy at the moment when a

Fig. 5 Ratio of the steady plastic flow stress σ_{LC} under creep load to temperature T plotted against $\log \dot{\epsilon}_t$

flow unit passes over the energy barrier. Thus, both of these quantities are directly related to the state of the softened structure in the range LC of the glassy polymer. That is, a functional relation between the numerical values of ΔH and ΔS seen in Table 1 gives a characteristic equation representing the state of the softened structure of the PMMA glass.

Another functional relation between ΔH and ΔS for the same PMMA sample can be derived from its relaxation or dynamic viscoelastic data above the glass transition temperature T_g . When the empirical WLF equation⁽⁹⁾ holds for the temperature dependence of the relaxation or dynamic data of the PMMA sample, then the functional relation for the structure of the PMMA melt is

$$\sqrt{\Delta H} = \sqrt{T_g - c_f^g} \sqrt{\Delta S} + \sqrt{2.303 R c_f^g c_g^g}, \quad (3)^{(1)}$$

where c_f^g and c_g^g are the WLF parameters reduced to the glass temperature T_g . Numerical values of T_g , c_f^g and c_g^g for the PMMA sample could be determined from the temperature dependence of its stress relaxation data as follows⁽¹⁾:

$$T_g = 389 \text{ K}, \quad c_f^g = 21.1 \text{ and } c_g^g = 66.4.$$

Substitution of these values into Eq. (3) gives

$$\sqrt{\Delta H} = 17.96 \sqrt{\Delta S} + 5.19. \quad (4)^{(3)}$$

This equation is now compared with the characteristic equation for the softened structure of the PMMA glass as shown in Fig. 6. Excellent agreement is seen between the two characteristic equations obtained independently from the softened glass and the melt of the PMMA sample. Consequently, this agreement leads to the conclusion that during the

Fig. 6 Plot of the square root of the activation energy ΔH against the square root of activation entropy ΔS for the plastic flow in the glass under the creep stress and for the stress relaxation in the melt of the same PMMA sample as in Fig. 5

large deformation process under the creep stress the structure of the undeformed glass has been changed to liquidlike, equivalent to those of the melt. The conformational change in polymer molecules is probably the main reason for this glass-to-liquid structural change. The relation of the conformational change to the structural change has been discussed in detail in the previous paper⁽⁷⁾.

Now we examine the mechanical parameters controlling the glass-to-liquid structural change by comparing the results obtained from the creep and constant-rate tests. The true stresses σ_{LC} and σ_L in ranges LC and L, respectively, are plotted against $\log \dot{\epsilon}_t$ in Fig. 7. The difference between σ_{LC} and σ_L at the same strain rates becomes more noticeable with decreasing temperature, yet a relative difference evaluated by the ratio $(\sigma_{LC} - \sigma_L)/\sigma_{LC}$ is always lower than 2.5%. The nominal strain ϵ_{nLC} and ϵ_{nL} at the midpoints of ranges LC and L, respectively, are plotted against $\log \dot{\epsilon}_t$ in Fig. 8. The values of ϵ_{nLC} seem to be slightly larger than those of ϵ_{nL} at the same strain rates, yet the difference is almost within the deviation of the experimental points. A plot of σ_L/T against $\log \dot{\epsilon}_t$ enables us to perform the rate analysis for range L in the same manner as applied to the data shown in Fig. 5, giving the numerical values of the Eyring parameters ΔH , ΔS and v_c for range L. These numerical values are compared with those for range LC in Fig. 9 where CRD stands for the constant-rate deformation. Quite evidently the experimental points of ΔH against ΔS and v_c against ΔS for ranges LC and L lie on straight lines. This indicates that the characteristic equation for the liquidlike structure can be

Fig. 7 Comparison of stresses σ_{LC} and σ_L in ranges LC and L plotted against $\log \dot{\epsilon}_t$

uniquely obtained from the states of steady flow independently of the histories of strain-rate and stress. Accordingly, it is strongly suggested from the comparisons shown in Figs. 7 to 9 that the liquidlike structures in ranges LC and L are nearly the same ones that are uniquely determined by the strain, strain rate and temperature although there are definite differences between the loading histories prior to ranges LC and L.

As for the mechanical parameters controlling transient structural states during the transition to the liquidlike structure, stresses σ_{YC} and σ_Y and strains

Fig. 8 Comparison of nominal strains ε_{nLC} and ε_{nL} at the midpoints of ranges LC and L plotted against $\log \dot{\varepsilon}_t$

Fig. 9 Comparison of the plots of ΔH against ΔS obtained from the steady plastic flows under creep stress and constant-rate deformation (CRD)

ε_{nYC} and ε_{nY} at points YC and Y can be compared. This is because the yield point Y of the glassy polymers has successfully been interpreted as a transient state during the structural change⁽¹⁾. In Fig. 10, σ_{YC} and σ_Y are plotted against $\log \dot{\varepsilon}_t$. At higher temperatures the value of σ_{YC} is lower than that of σ_Y by 10% at most. This difference is ascribed to the different loading histories. Yet, the value of σ_{YC} approaches that of σ_Y with decreasing temperature. Figure 11 shows a plot of ε_{nYC} and ε_{nY} against $\log \dot{\varepsilon}_t$, indicating no significant difference between the two strains. These numerical values of the stress and strain at points YC and Y should reflect the transient structural states of the polymer glass at these points. Thus, it can be concluded from the comparisons shown in Figs. 10 and 11 that the transient structures of the polymer at points YC and Y are almost the same and are

Fig. 10 Comparison of the stresses σ_{YC} and σ_Y at points YC and Y plotted against $\log \dot{\varepsilon}_t$

Fig. 11 Comparison of the nominal strains ε_{nYC} and ε_{nY} at points YC and Y plotted against $\log \dot{\varepsilon}_t$

uniquely determined by the strain rate at these points and the temperature.

As a whole, the comparisons illustrated above for ranges LC and L and points YC and Y lead to the conclusion that the strain and strain rate are the key parameters controlling the structural change either under the creep stress or under the constant-rate deformation, whereas the change in strain rate or stress during the large deformation process is likely to contribute less to the structural change in these loading modes. Accordingly, the plastic deformation in PMMA under the creep stress can be understood as a kinetic process quite similar to that under the constant-rate deformation: Upon deformation the internal viscosity between the polymer molecules falls from an extremely high value in the undeformed glass to a steady value in range LC, and this softening process, probably due to the molecular conformational change, is controlled almost solely by the strain and strain rate being imposed on the polymer glass.

4. Conclusions

The rate analysis applied to the creep flow in the PMMA glass has verified that due to the large deformation under the creep stress the structure of the glass is changed to liquidlike. The comparisons of the data obtained from the creep experiment with those from the constant-rate deformation experiment have led to the conclusion that the glass-to-liquid structural change is almost totally controlled by the strain and strain rate being imposed on the PMMA glass in

the loading modes.

References

- (1) Nanzai, Y., Transition Mechanism from Elastic Deformation to Plastic Flow in Poly(Methyl Methacrylate), *Polym. Eng. Sci.*, Vol. 30, No. 2(1990), p. 96.
- (2) Nanzai, Y., Strain-Induced Liquid-Like Structures in Glassy Polymers, *J. Non-Crystalline Solids*, Vol. 131-133(1991), p. 516.
- (3) Nanzai, Y., Konishi, T. and Ueda, S., Structural Transition in Poly(Methyl Methacrylate) due to Large Deformation at Temperatures below the Equilibrium Second-Order Transition Temperature, *J. Mater. Sci.*, Vol. 26(1991), p. 4477.
- (4) Narisawa, I. and Ishikawa, M., Crazing in Semicrystalline Thermoplastics, *Advances in Polymer Science*, 91/92(1990), p. 353.
- (5) Struik, L. C. E., Some Problems in the Non-Linear Viscoelasticity of Amorphous Glassy Polymers, *J. Non-Crystalline Solids*, Vol. 131-133(1991), p. 395.
- (6) Nanzai, Y., Plastic Flow of Poly(Methyl Methacrylate) in Uniaxial Compression, *Kobunshi Ronbunshu*, (in Japanese), Vol. 41, No. 5(1984), p. 285.
- (7) Nanzai, Y., Molecular Kinetics of Yield Deformation and Ductile Fracture in Polymer Glasses, *Prog. Polym. Sci.*, Vol. 18, No. 3(1993), p. 437.
- (8) Glasstone, S., Laidler, K.J. and Eyring, H., *The Theory of Rate Processes*, (1941), p. 480-483, McGraw-Hill, New York.
- (9) Ferry, J.D., *Viscoelastic Properties of Polymers*, 3rd Ed., (1980), p. 289-290, John Wiley & Sons, New York.