Non-Newtonian Flow in Polymethyl Methacrylate Glass under Simple Shear Condition

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Large deformation of polymethyl methacrylate (PMMA) glass was examined under the condition of simple shear. Post-yield steady plastic flow was observed over a wide range of strain rate. For the post-yield plastic flow, the logarithm of shear viscosity plotted against the logarithm of shear strain rate showed a non-Newtonian behavior quite resembling the shear thinning behavior observed in polymer solutions and melts. Rate analysis applied to the non-Newtonian flow showed that the fully annealed equilibrium structure of undeformed PMMA glass has been changed into non-equilibrium meltlike structures in the state of steady plastic flow. Comparison of experimental values of the activation enthalpy ΔH and activation entropy ΔS for the plastic flow in simple shear with those in uniaxial tension and compression led us to the conclusion that the meltlike structures under quite different deformation conditions were uniquely expressed by a single characteristic equation relating the activation enthalpy ΔH to the activation entropy ΔS . Evaluation of shear activation volume in simple shear proved that the experimental functional relation of activation volumes in simple shear, uniaxial tension and uniaxial compression was in good agreement with theoretical relations predicted by the Eyring rate theory.

Key words: Polymethyl methacrylate glass / Non-Newtonian flow / Simple shear / Rate analysis / Meltlike structure

1. INTRODUCTION

The matrix of polymeric materials is generally composed of both crystalline and non-crystalline phases. The non-crystalline phase, compared to the crystalline one, is more liable to plastically deform under mechanical stresses, and has smaller strength. Thus the non-crystalline phase in polymeric materials is regarded as domains susceptible to early microcracks eventually leading the materials to ultimate failure. Hence, as an approach to investigating the strength of polymeric materials, large deformation and fracture processes in polymers composed of non-crystalline phase alone, i.e., glassy amorphous polymers, have been studied.

The strength of the glassy polymers is examined quite often in constant rate deformation tests. In these experiments the glassy polymers are occasionally deformed to yield, and flow plastically. Over more than three decades, the yield point of the glassy polymers has been noticed as a state of plastic flow, and rate theory analyses were frequently applied to the yield point^{1)~5)}. The analyses seemed successful except for data obtained at temperatures in the glass transition range, although an essential question has been left about the

relation of the plastic flow at the yield point to another plastic flow observed in the post-yield range.

Our recent rate-analyses applied to post-yield plastic flow of various glassy polymers allowed to provide an interpretation about the relation of the yield point to the post-yield plastic flow, which is presumably more convincing than that obtainable from the analyses of the yield point^{6)~9)}. In the yield process from elastic deformation into post-yield plastic flow, thermodynamically quasi-equilibrium structure of undeformed glassy polymers is changed into non-equilibrium structure with increasing strain. In this course of the structural transition occurring toward a steady plastic flow in the post-yield state, the yield point can only momentarily appear as a state of unsteady plastic flow.

So far, however, we have analyzed the plastic flow of glassy polymers almost solely under conditions of uniaxial tension and compression. Although the uniaxial state of stress is supposed to inherently provide the plastic flow with some effect of hydrostatic component of stress, quantitative experimental analysis on the effect of hydrostatic pressure to the flow has not yet been examined in detail. To study about the effect, experimental data for the plastic flow under conditions free

from the hydrostatic component are desirable to be compared quantitatively with the data in tension and compression. The experiment free from the hydrostatic pressure can be realized in simple shear.

In addition, one of our present subjects of interest is the non-Newtonian behavior observed for the post-yield plastic flow of glassy polymers in the state of non-equilibrium structure, because it is quite similar with the shear-thinning non-Newtonian behavior generally observed in condensed solutions and melts of polymers at relatively high shear rates. That is, the logarithm of viscosity is almost inversely proportional to the logarithm of strain rate. Physical meaning of the similarity between the non-Newtonian behaviors of glassy polymers and polymer solutions or melts must be an attractive subject of controversy. To study on the relation between nonlinear viscosities in the melt and solid polymers, it will be necessary to obtain experimental data under the same condition of deformation, such as in simple shear. Up to the present, however, the experiment on the plastic flow of glassy polymers in simple shear has not substantially been attempted. Thus, in the present study nonlinear flow in a glassy polymer is experimentally examined under the condition of simple shear which has also quite often been used to study the nonlinear behaviors in solutions and melts of polymers.

2. EXPERIMENTAL

A commercial polymethyl methacrylate (PMMA) cast sheet with 0.8 mm thickness produced by Mitsubishi Rayon Co. was used as the test material. Specimens shown in Fig. 1 were cut from the cast sheet which had been heat-treated at 130°C for 2 hours. The specimen was fastened firmly to a laboratory-made shearing device as shown in Fig. 2, and the device was installed on an Instron testing machine. The specimen was kept at a required testing temperature for 20 min in a temperature controlling cabinet, and then the device was pulled at a constant rate in the vertical direction as

Fig. 1 Specimen of polymethyl methacrylate (PMMA) glass for large deformation in simple shear.

Fig. 2 Laboratory-made shearing device to which the specimen was fastened firmly as shown by hatching. Abrasive papers were placed between the specimen and the fastening plates to avoid slippage.

pointed by a couple of arrows to give simple shear to experimental portions 5 mm wide and 25 mm long of the specimen. Abrasive papers placed between the specimen and the fastening plates were effective to avoid slippage between the specimen and the shearing device.

The dynamic viscoelasticity of the test sample was measured by DMS210 of Seiko Instruments Inc. in a temperature range from 71 to 195 °C at frequencies of 0.005 to 10 Hz. From the dynamic data, the glass transition temperature T_g of the sample was evaluated as a temperature giving the maximum value of the apparent activation energy of linear viscoelastic relaxation. The WLF parameters c_1^g and c_2^g were also evaluated by an application of the time-temperature superposition principle to the dynamic data at temperatures above T_g .

3. RESULTS

3.1 The Glass Transition Temperature and WLF Parameters of PMMA

The glass transition temperature defined as a temperature at which the apparent activation energy of linear viscoelastic relaxation showed the maximum value was determined as 114°C. The WLF parameters at the glass temperature, c_1^g and c_2^g , were also determined from frequency and temperature dependencies of the data of G' and G'' as follows:

$$c_1^g = 13.86 \quad \text{and} \quad c_2^g = 49.1.$$

3 • 2 Stress-Strain Relation and State of Steady Flow in PMMA under Simple Shear Condition

Figure 3 shows an example of plots of shear stress τ against shear strain γ for PMMA obtained at various strain rates. Passing through the yield point, the stress τ decreased to level off to the horizontal axis γ . This post-yield constant stress range can be regarded as a state of steady flow as far as the deformation of the specimen is uniform. For the PMMA specimen used in the present study, its shear deformation up to $\gamma = 1.0$ could approximately be considered as uniform on the basis of macroscopic observation of the shape of sheared portions. Hence, the post-yield range was regarded as a state

Fig. 3 Stress-strain relations for PMMA glass during large deformation in simple shear.

of steady flow and shear viscosity η could be evaluated for this steady flow state.

The logarithm of shear viscosity η calculated as $\tau_i/\dot{\gamma}$ from the data of the shear stress τ_i and shear strain rate $\dot{\gamma}$ in the state of steady flow was plotted against the logarithm of the strain rate in Fig. 4. The quantity $\log \eta$ decreases linearly with increasing $\log \dot{\gamma}$ and the magnitude of each slope of these double logarithmic plots is a little less than unity. Thus the strain rate dependence of the viscosity is seen to be quite similar to the shear thinning behavior frequently observed in polymer solutions and melts.

3 • 3 Rate Analysis of the Steady Flow in Simple Shear

Nonlinear steady flow in PMMA under simple shear condition was analyzed using the Eyring equation expressed in the following form¹⁰⁾:

$$\dot{\gamma} = \frac{2\lambda kT}{\lambda_i h} \exp \left(-\frac{\Delta H - T\Delta S + p\Delta V}{RT} \right) \sinh \left(\frac{\tau v_s}{2kT} \right) \quad (1)$$

where τ is the shear stress, $\dot{\gamma}$ the shear strain rate, ΔH the activation enthalpy, ΔS the activation entropy, p the hydrostatic component of stress, ΔV the pressure activation volume, v_s the shear activation volume, k the Boltzmann constant, h the Planck constant, R the gas constant, and λ and λ_i a

Fig. 4 Logarithm of shear viscosity η in the state of post-yield steady flow in PMMA glass plotted against logarithm of shear strain rate $\dot{\gamma}$, showing a typical non-Newtonian behavior.

couple of constants giving spatial distances for an elementary jumping motion of a rearranging molecular unit. In simple shear the value of the component p is zero, and for the case of plastic flow under high shear stress Eq. (1) is approximated by the following equation¹¹⁾:

$$\frac{\tau_i}{T} = \frac{4.606k}{v_s} \left(\log \dot{\gamma} - \log \frac{\lambda kT}{\lambda_i h} + 0.4343 \frac{\Delta H - T\Delta S}{RT} \right) \quad (2)$$

where τ_i is the shear stress of the steady plastic flow. According to the Eyring model, the value of the ratio λ/λ_i can reasonably be approximated to be of the order of unity.

To apply Eq.(2) to the data of nonlinear flow, experimental quantity τ_i/T is plotted against $\log \dot{\gamma}$ as shown in Fig. 5. The best fit of Eq.(2) to the experimental plot was accomplished by sectioning nonlinear curves of τ_i/T against $\log \dot{\gamma}$ into straight line elements labeled 1 to 9 as shown in Fig. 5. Experimental values of the Eyring parameters ΔH , ΔS , and v_s obtained by the best fit of Eq.(2) to the plot are summarized in Table I. In Fig. 6, ΔH and ΔS were plotted against v_s , giving linear relations between ΔH and v_s , and between ΔS and v_s , respectively.

Structure of glassy PMMA in the state of steady shear flow can be compared with the structure of the equilibrium melt through a comparison of their respective plots of the activation enthalpy ΔH against the activation entropy ΔS in the same manner as previously demonstrated for plastic flows in uniaxial tension and compression^{6)~9)}. According to the time-temperature superposition principle, the quantities ΔH and ΔS for the equilibrium melt of PMMA are expressed in the following WLF equations¹²⁾:

Fig. 5 Ratio of shear stress τ_i in the state of steady plastic flow to temperature T plotted against logarithm of strain rate $\dot{\gamma}$. Line segments labeled 1 to 9 were determined by best fitting the Eyring equation to the experimental points.

Table I Experimental values of Eyring parameters obtained from the steady plastic flow in PMMA glass in simple shear.

No.	ΔH (KJ/mol)	ΔS (KJ/mol · K)	v_s (nm ³)
1	314.0	0.4940	6.35
2	334.9	0.5419	7.14
3	351.6	0.5809	7.70
4	380.9	0.6530	8.42
5	427.0	0.7612	10.09
6	470.9	0.8726	11.08
7	514.9	0.9799	12.47
8	573.5	1.1263	14.29
9	673.1	1.3773	17.18

$$\Delta H = \frac{2.303Rc_1^g c_2^g T^2}{(T - T_g + c_2^g)^2} \quad (3)$$

and

$$\Delta S = \frac{2.303Rc_1^g c_2^g (T_g - c_2^g)}{(T - T_g + c_2^g)^2} \quad (4)$$

Eqs. (3) and (4) give a relation between ΔH and ΔS as

$$\sqrt{\Delta H} = \sqrt{T_g - c_2^g} \sqrt{\Delta S} + \sqrt{2.303Rc_1^g c_2^g} \quad (5)$$

Hence, substitution of the numerical values of T_g , c_1^g and c_2^g shown above into Eq. (5) gives

$$\sqrt{\Delta H} = 18.39\sqrt{\Delta S} + 3.61 \quad (6)$$

Eq. (6) is plotted in Fig. 7 as a solid line, showing an approximate agreement with the experimental points of $\sqrt{\Delta H}$ and

Fig. 6 Activation enthalpy ΔH and activation entropy ΔS plotted against shear activation volume v_s for the steady plastic flow in PMMA glass.

$\sqrt{\Delta S}$ labeled 1 to 9 obtained from the shear plastic flow in the PMMA glass.

Fig. 7 Square root of ΔH as a function of square root of ΔS

4. DISCUSSION

4 · 1 Shear-Induced Isothermal Glass-to-Melt Structural Change in PMMA

In the steady state of plastic flow, molecular segments in a glassy polymeric system probably make successive rearrangement at a constant rate under the actuation of high shear stress. When a polymer segment or a cluster of segments makes a single step rearrangement against the intermolecular secondary bonding forces, it has to obtain an amount of activation enthalpy ΔH to pass over a potential

energy barrier. The profile of this potential energy barrier is constructed by the intermolecular secondary bonding forces which have made up the spatial arrangement of the polymer molecules or in other words the structure of the polymeric system. In consequence, the value of the activation enthalpy ΔH is uniquely determined by the structure of the polymeric system in the state of steady plastic flow. The value of the activation entropy ΔS is also controlled by the structure of the polymeric system because it is an amount of change in entropy for a mole of rearranging units passing over the potential energy barrier. Accordingly, both the values of the activation enthalpy ΔH and activation entropy ΔS are uniquely determined by the structure of the polymeric glass in the state of steady plastic flow. It can be convinced in a similar manner that the relation of the parameters ΔH and ΔS with the structure of the polymeric system mentioned above also holds for linear viscoelastic relaxation processes in polymer melts.

Now, as shown in Fig. 7, the plot of $\sqrt{\Delta H}$ against $\sqrt{\Delta S}$ obtained from the plastic flow in the PMMA glass is approximately in agreement with the plot of $\sqrt{\Delta H}$ and $\sqrt{\Delta S}$ for the viscoelastic relaxation in the equilibrium melt of PMMA. Since both the values of ΔH and ΔS are determined by the structure of the polymeric system at the time of their evaluation as discussed above, the agreement seen in Fig. 7 allows us to conclude that the PMMA glass in the shear plastic flow has a structure similar to that of the equilibrium melt. In addition, the experimental points of $\sqrt{\Delta H}$ and $\sqrt{\Delta S}$ obtained from plastic flow in the PMMA glass can be seen to align successively along a line corresponding to successive variations of strain rate and temperature. That is, the meltlike structure in the state of steady plastic flow is continuously changeable in response to the successive variations of strain rate and temperature.

Meaning of the meltlike structure in a glassy polymer can in an explicit way be understood in terms of the molecular conformations. If a polymer melt being in thermodynamic equilibrium at a temperature T_h above T_g is instantaneously quenched to a temperature T_l below T_g and no physical aging occurs, then the molecular conformation in the melt will be preserved still in the glass at the temperature T_l . What is different between the equilibrium structure of the melt at T_h and the non-equilibrium structure of the frozen glass at T_l is solely their temperatures. Accordingly, the melt structure in the PMMA glass mentioned above can be regarded as a non-equilibrium structure similar to that obtained by quenching the melt.

4 • 2 Structure of PMMA Glass for the Non-Newtonian Flow in Simple Shear Compared with Those in Uniaxial Tension and Compression

Transforming Eq.(1) into expressions available to the cases

of plastic flow under uniaxial tensile stress σ_t and uniaxial compressive stress σ_c , we have the following equations⁽¹¹⁾:

$$\frac{\sigma_t}{T} = \frac{9.212k}{v_s} \left(\log \dot{\epsilon}_t - \log \frac{2\lambda kT}{3\lambda_s h} + 0.4343 \frac{\Delta H - T\Delta S}{RT} \right) \quad (8)$$

and

$$\frac{\sigma_c}{T} = \frac{9.212k}{v_c} \left(\log \dot{\epsilon}_c - \log \frac{2\lambda kT}{3\lambda_c h} + 0.4343 \frac{\Delta H - T\Delta S}{RT} \right) \quad (9)$$

where $\dot{\epsilon}_t$ is uniaxial tensile strain rate, v_t the apparent shear activation volume under the condition of uniaxial tension, $\dot{\epsilon}_c$ uniaxial compressive strain rate and v_c the apparent shear activation volume in uniaxial compression. The quantities v_t and v_c are expressed using v_s and Δv as

$$v_t = v_s + \frac{4}{3}\Delta v \quad (10)$$

and

$$v_c = v_s - \frac{4}{3}\Delta v \quad (11)$$

where Δv given as $\Delta v = \Delta V/N_0$ (N_0 is the Avogadro number) is the pressure activation volume for a single moving unit.

Applications of Eqs.(8) and (9) to the data of plastic flows in the PMMA glass under uniaxial tension and compression have given the numerical values of the Eyring parameters ΔH , ΔS , v_t and v_c as reported elsewhere⁽⁹⁾. The PMMA sample used in these uniaxial tension and compression tests was also the material produced by Mitsubishi Rayon Co. and of the same grade as that used in the present study. Hence, these PMMA samples enable us to analyze the relations of the numerical values of the Eyring parameters obtained from the same grade samples under the conditions of simple shear, uniaxial tension and uniaxial compression. The relations of ΔH and ΔS obtained under the three different conditions of deformation is plotted in Fig. 8. As seen in the figure, an outstandingly linear relation is found between ΔH and ΔS although the experimental points were obtained from the three quite distinguishable deformation modes. As discussed above, both of the quantities ΔH and ΔS represent uniquely the spatial arrangement of polymer molecules in the steady plastic flow. Thus, it is concluded that in the state of plastic flow the fully annealed PMMA glass has changed its structure in accordance with the single characteristic equation between ΔH and ΔS expressing the non-equilibrium structure of the glassy polymeric system under various conditions of stress. The least-square method applied to experimental points in Fig. 8 gives a functional relation between ΔH and ΔS as

$$\Delta H = 402\Delta S + 115 \text{ (kJ/mol)} \quad (12)$$

which is shown by a dotted line. This is the characteristic equation constraining the variation of structures of the PMMA glass under various stress conditions for the steady plastic flow.

Fig. 8 Plot of activation enthalpy ΔH against activation entropy ΔS obtained from the steady plastic flow in PMMA glass under the conditions of simple shear, uniaxial tension and uniaxial compression, giving an outstandingly linear relation.

In Fig. 8, the non-equilibrium structure in the plastic flow was seen to vary in line with the characteristic relation between ΔH and ΔS , i.e. Eq.(12), irrespective of the difference in deformation modes. That is, the non-equilibrium structure of the glass induced by uniaxial tension or compression was shown to be entirely reproducible by simple shear. With regard to the state of stress in the plastic flow, the uniaxial stress σ produces shearing stress $\tau (= \sigma/2)$ and hydrostatic component $p (= \pm \sigma/3)$: positive and negative signs correspond to the stresses of compression and tension, respectively), whereas the simple shear includes no hydrostatic component. Hence, the characteristic functional relation shown in Fig. 8 leads us to the conclusion that the shearing stress probably plays a leading role in inducing the non-equilibrium structure in the glassy polymer.

As for the activation volumes v_s , v_t and v_c , their experimental values are plotted against ΔH in Fig. 9, where the quantity ΔH is adopted as a parameter quantitatively expressing the non-equilibrium structure of the polymeric glass in the state of plastic flow. Three straight lines could approximately be drawn through the data obtained in uniaxial tension, simple shear and uniaxial compression, respectively. The line for the case of simple shear can be seen to lie almost in the middle between the lines for the uniaxial tension and compression. According to Eqs.(10) and (11), v_s is given as

Fig. 9 Activation volumes in simple shear, uniaxial tension and compression related to activation enthalpy ΔH for PMMA glass. The line for simple shear lies almost in the middle between the lines for uniaxial tension and compression.

$$v_s = \frac{1}{2}(v_t + v_c) \quad (13)$$

i.e., the mean value of v_t and v_c , thus it is seen that the experimental values of v_s are consistent with those predicted by Eq. (13) using the experimental values of v_t and v_c . Eqs.(10) and (11) give equations also for Δv as

$$\Delta v = \frac{3}{4}(v_t - v_s) \quad (14)$$

$$\Delta v = \frac{3}{4}(v_s - v_c) \quad (15)$$

and

$$\Delta v = \frac{3}{8}(v_t - v_c) \quad (16)$$

Either of these equations can provide the experimental value of Δv . The volume Δv and a ratio of Δv to v_s could be roughly evaluated from the data in Fig. 9, and were plotted against ΔH in Fig. 10. It is seen that the value of Δv is not constant but linearly increases with ΔH . Moreover, it should be noticed that the quantity Δv is always positive in spite of the opposite sign of the hydrostatic components p in uniaxial tension ($p = -\sigma/3$) and uniaxial compression ($p = +\sigma/3$). Hence, the experimental determination of the value and sign of Δv enabled us to conclude that the increase in the volume of an activated moving unit had no concern with the hydrostatic component of stress. Probably, the quantity Δv was caused solely by the shear stress. This can be deduced also from the unique relation between Δv and ΔH shown in Fig.

Fig. 10 Pressure activation volume Δv and a ratio of Δv to shear activation volume v_s plotted against ΔH .

10. This is because the volume Δv uniquely related to the structural parameter ΔH verifies that the quantity Δv is an alternative structural parameter quantitatively expressing the non-equilibrium glassy structure which is entirely induced by the simple shear stress alone as illustrated above. That is, the volume Δv is caused by the shear stress alone. As shown in Fig.10, the ratio of Δv to the amount of shear activation volume v_s could be evaluated as 4 to 6 percent. Thus, in the state of plastic flow the volume of a moving unit at the instance of activation is presumably expanded by 4 to 6 percent of the volume of v_s solely by the shear stress.

5. CONCLUSION

The results obtained by the application of the Eyring rate theory to non-Newtonian plastic flow in PMMA glass under the condition of simple shear are summarized as follows:

1) The structure of the PMMA glass in the state of steady simple shear flow is very likely to be similar with that of the equilibrium PMMA melt.

2) Comparison of the non-Newtonian flows in the PMMA glass under the conditions of simple shear, uniaxial tension and uniaxial compression has led us to the conclusion that a

variation of the non-equilibrium structure of the PMMA glass in the state of plastic flow is uniquely represented by a single characteristic equation between the activation enthalpy ΔH and the activation entropy ΔS irrespective of the presence of hydrostatic component of stress. Accordingly, the transition into non-equilibrium glassy structure can probably be accomplished by the shearing stress alone.

3) From the numerical difference between the shear activation volumes in simple shear, uniaxial tension and compression, the experimental value of the pressure activation volume Δv could be determined as 4 to 6 percent of the shear activation volume. The value of Δv was always positive, thus having no concern with the hydrostatic component of stress. Hence it is certain that the quantity Δv is caused by the shearing stress alone.

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