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Thermochimica Acta 282/283 (1996) 345–351

thermochimica acta

Delayed elasticity and viscosity of silicate glasses below the glass transition temperature[1]

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Abstract

The viscosity of pre-annealed lead–silicate glass was studied below the glass transition temperature using the fiber-bending method. The viscosities were determined under conditions of loading and unloading. The delayed elasticity and its effect on the viscosity were also investigated. In the case of equal loading and unloading times, the viscosity was the same for the loading and unloading processes and the delayed elasticity was larger within shorter periods and smaller for longer ones. In addition, the time necessary for the recovery of the delayed elasticity increases with increasing loading time.

Keywords: Delayed elasticity; Fiber-bending method; Glass transition temperature; Lead–silicate glass; Silicate glass; Viscosity

1. Introduction

It is well known that under an external load, viscoelastic materials exhibit three types of strain: elastic, delayed elastic, and viscous strain [1–5]. Elastic strain is instantaneous and recoverable; delayed elastic strain is time-dependent and recoverable. The viscous strain, however, is time-dependent but irrecoverable. The curve of strain versus annealing time is ascending and non-linear if the loading time is short. In the course of the experiment the curve becomes linear, indicating that the delayed elastic deformation is complete and that only viscous flow is taking place. The time at which the delayed elastic strain is complete is not, however, specified. This makes it difficult to

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

PII: S0040-6031(96)02835-3

distinguish between the time-dependencies of the delayed elastic and viscous strains. Viscosity can be determined accurately from the curve of viscous strain versus time. Below the glass transition temperature therefore an accurate determination of viscosity can be obtained only by measurement after a longer duration of loading.

When the load is removed, however, the accumulated elastic and delayed elastic strains disappear. This disappearance leads to the separation of the viscous and delayed elastic strains and so it is possible to measure the viscosity accurately.

Zijstra [6] measured high viscosities of glasses below the glass transition temperature using the fiber-elongation method. As pointed out by Rekhson [7], the relationship between loading and recovery times is important. In order to measure the high viscosity below the glass transition temperature, the recovery, or the time for disappearance of the delayed elastic strain, must be more than ten times the loading time if the temperature is well below the glass transition temperature.

In our previous studies, we reported the apparent viscosity of a glass fiber below the glass transition temperature, the viscosity during loading, and proposed the fiber-bending method for measurement of viscosity at temperatures well below the glass transition temperature.

In the present study, we measured the viscosity and the delayed elasticity of glasses pre-annealed below the glass transition temperature and the effect of re-annealing under unloading condition on the delayed elasticity. The relationship between the delayed elasticity and the viscosity was also investigated.

2. Experimental

Fig. 1 shows a schematic diagram of the relationship between the residual radius of curvature, representing the strain, and the time during loading and unloading for viscoelastic materials. Loading the viscoelastic materials at the initial time causes

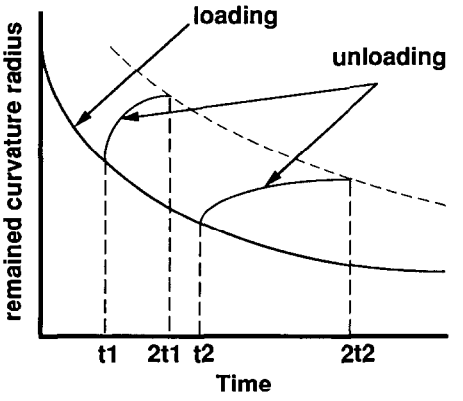

Fig. 1. Schematic diagram of relationship between residual radius of curvature and time during loading and unloading.

instantaneous deformation succeeded by delayed elastic (nonlinear part of the curve) and viscous deformations (linear part of the curve). Opposed to the loading, unloading at any time, t, results in recovery of the instantaneous and delayed elastic deformations in the residual radius of curvature. The viscous deformation formed during loading remains, however. During unloading conditions it is, therefore, possible to separate the deformation due to the viscous deformation from that due to delayed elastic deformation.

The apparent viscosity can be obtained from the slope of the linear deformation curve during loading for longer annealing time, or from the residual deformation (viscous deformation) at equilibrium during unloading. In this study, the viscosity of viscoelastic materials was determined from the loading and unloading curves. The viscosities obtained were compared with each other. The delayed elasticity was also determined on the basis of the difference in deformation between the unloaded fiber at room temperature and that at the same temperature under loading condition.

In this study, the fiber-bending method is used to determine the viscosity of viscoelastic glass fibers below the glass transition temperature. In contrast to the fiber-elongation method, which is based on creep measurement, i.e. strain relaxation, the fiber-bending method is based on the stress relaxation. To the best of our knowledge, this is the first report on the measurement of the viscosity during unloading by the fiber-bending method. The method of determination of the viscosity is explained briefly below.

The equation of viscosity is;

$$\eta(t) = \frac{\sigma(r,t)}{3(\mathrm{d}\varepsilon_{re}(r,t)/\mathrm{d}t)} \tag{1}$$

where,

$$\sigma(r,t) = \sigma(r,0) - \sigma_{re}(r,t) \tag{2}$$

where $\sigma(r,0)$ and $\sigma(r,t)$ are loads at the initial time and time t, respectively. $\sigma_{re}(r,t)$ is the relaxed load at time t and is determined by means of Eq. (3)

$$\sigma_{re}(r,t) = E \times \varepsilon_{re}(r,t) = E \times (r/R(t)) \tag{3}$$

where $\varepsilon_{re}(r,t)$ is the residual strain and $R(t)$ is the radius of curvature at time t.r is the radius of the fiber. The method used for measurement of $R(t)$ was reported in Refs. [8,9].

The chemical composition, Young's modulus, and glass transition temperature of the glass fibers used in this study are shown in Table 1. The glass transition temperature was determined by differential thermal analysis (DTA) which was performed on a powder sample at a heating rate of 10 K min^{-1}. Glass fibers of about 100 μm diameter were wound around quartz cylinders of radius 30 mm. These fibers were then heated at constant temperatures for various periods of time. After heat treatment, the fibers were released and the bending radii of the deformed fibers were measured by means of a telescope to an accuracy of $\pm$ 1%. Some specimens were pre-annealed as shown in Table 2 before viscosity measurement. The residual radii during loading and unloading were measured and used for the determination of the viscosity under loading and unloading conditions.

Table 1
The chemical composition, Young's modulus, and glass transition temperature of the glass fiber

Glass	Composition/mol%		Young's modulus/Pa	T_g/°C [b]
	SiO_2	PbO		
SP55	50	50	4.41×10^{10} [a]	403

[a] Ref. [10].
[b] Programming rate 10 K min^{-1}.

Table 2
Heating conditions used for bending of the glass fiber

Glass sample no.	Loading		Unloading	
	Temp./°C	Time/min	Temp./°C	Time/min
1	390	300	–	–
2	390	300	390	60
3	390	300	390	300
4	390	300	390	1440
5	390	720	–	–
6	390	720	390	720
7	390	720	390	2880

3. Results

Fig. 2 shows the profile of the residual radius of curvature of SP64 glass pre-annealed at 430°C for 10 h versus the loading and unloading time at different temperatures below the glass transition temperature ranging from 390 to 410°C. Loading and unloading times are the same in this case. Solid lines are the residual radius of curvature of the deformed fibers under loading conditions and dashed ones are those under unloading conditions. The bending radius during loading decreases with loading time and annealing temperature. The decrease occurs rapidly if loading was for a short time only. The decrease is, however, slow for longer periods of loading and unloading time. For shorter periods of time, the difference between the residual radius of curvature due to loading and unloading is larger compared with that for longer periods of time.

The viscosity during loading and unloading was determined using Eq. (3) and is shown in Fig. 3 as a function of loading and unloading time. The loading and unloading times were the same and the temperature was 390°C. The viscosity increases rapidly within a short time and then continues to increase gradually for both loading and unloading. No remarkable difference is observed between the viscosity determined under loading and that under unloading.

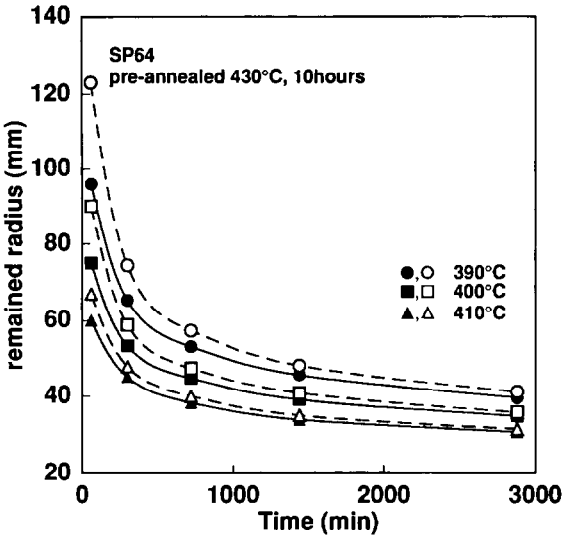

Fig. 2. The profile of the residual radius of curvature versus the loading and unloading time below the glass transition temperature.

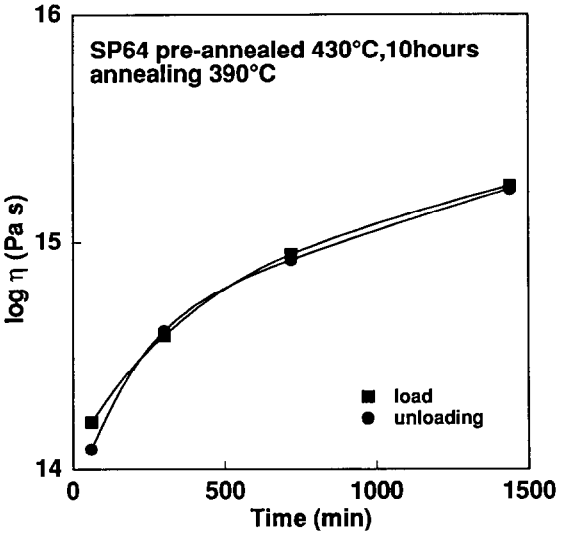

Fig. 3. The viscosity during loading and unloading below the glass transition temperature.

4. Discussion

As delayed elasticity is time-dependent, it increases and decreases with loading and unloading times, respectively. If the glass fiber is unloaded at room temperature after it has been loaded at 390°C for different periods of time, no change in the residual radius

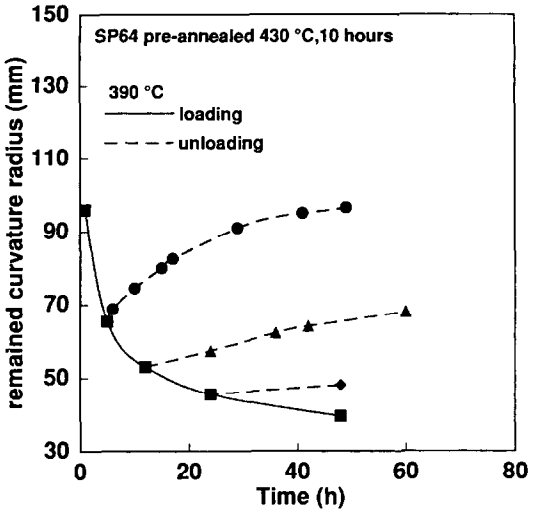

Fig. 4. The profile of the residual radius of curvature versus time for a glass fiber loaded and unloaded at 390°C.

of curvature is observed. This indicates that the delayed elasticity could not recover even after longer periods of time. In order to accelerate the recovery of the delayed elasticity, the unloaded fiber is re-annealed. In this case, the re-annealing was done at 390°C and the re-annealing time is the same as that for loading. The result is shown in Fig. 2. A clear recovery of the delayed elasticity is observed and this is represented by the change of the residual radius of curvature observed as a result of changes in unloading time. The delayed elasticity is larger within shorter periods of time compared with that for longer periods of loading and unloading time in the case of equal loading and unloading times. It was found that for periods of time longer than 3000 min, the difference between the residual radius of curvature of the fiber unloaded at room temperature and that at 390°C is nearly zero. This is an indication of total relaxation of delayed elasticity for periods longer than 3000 min. This led us to unload the fiber for much longer periods than those for loading conditions.

Fig. 4 shows a plot of the residual radius of curvature versus time for glass fiber loaded and unloaded at 390°C. After loading for 5, 12 and 24 h, the recovery time for the delayed elastic deformation was investigated. The loading time was considered as the time for the formation of the delayed elastic deformation during loading. It is clear from the shape of the curve that during unloading the time necessary for the relaxation of the delayed elastic deformation formed during loading is much longer than its formation time; this is in agreement with observation reported by Rekhson [7]. Further investigations are necessary to clarify the origin of the shape of the curve of the change in the residual radius of curvature during unloading. As indicated in Fig. 3, the viscosity determined under loading and unloading conditions was nearly the same. As seen in Fig. 4, the delayed elastic deformation does not recover in a period of time equal to its

formation during loading, an indication of the presence of the delayed elastic deformation during deformation of the viscosity. It is suggested that the deformation due to the residual delayed elasticity is very small compared with that due to the viscous flow. Investigation of the shape of the curve may lead to the discovery of two different viscosities during loading and unloading and hence the difference between them will shed a light on the delayed elasticity. The effect of re-annealing temperature on the recovery of the delayed elasticity and on the separation of the viscous flow from the delayed elasticity also needs further investigation.

The unloading process was also used for investigation of the relaxation mechanism. The stretching parameter is a characteristic of the relaxation mechanism. It expresses the distribution of relaxation time. The stretching parameter under unloading conditions was determined in similar way, reported previously [8,9], to that under loading conditions. It was found that this latter has a value of 0.42. Compared with that for loading conditions, 0.39, there was no large difference between them. This small difference between the stretching parameter obtained under loading and unloading conditions indicates further that the residual elastic deformation is small in comparison with viscous deformation.

5. Conclusion

The viscosity of pre-annealed lead–silicate glass was determined by the fiber-bending method during loading and unloading processes. The delayed elasticity under loading and unloading conditions was also investigated. There was no change in deformation due to the delayed elasticity at room temperature. Re-annealing, however, promoted the relaxation of the delayed elasticity. For equal loading and unloading times, the delayed elasticity was found to be larger for shorter periods of time than for longer periods. It was also found that the viscosity determined during loading and unloading is nearly the same. The time necessary for recovery of the delayed elasticity was, on the other hand, found to be longer for longer loading times.

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