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The viscosity of a soda-lime silica glass was measured at high strain rates. The data show non-Newtonian viscous flow in this inorganic oxide glass with the viscosity values below the expected Newtonian value. Following the imposition of large, steady strain rates, the observed stress increases with time to a maximum and then decreases to a time-independent value. A comparison of the viscosity behavior of this glass with the molecular dynamics results in a "Lennard-Jones" glass shows a number of points of correspondence and suggests the interpretation of the non-Newtonian behavior as resulting from structural rearrangements in the material. The combined data show that the sustained, steady-state stress asymptotically approaches a maximum at very high strain rates. This limiting stress is interpreted as the actual cohesive strength of the material and is calculated to be $1.4 \times 10^8 N/m^2$ (20 000 psi) for the glass under study.

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INTRODUCTION

The strain rate response of non-crystalline materials under an applied stress has generally been observed to be linear (Newtonian) for low stress or strain rates. Organic materials have exhibited large deviations from Newtonian behavior both in the pseudoplastic direction (below Newtonian viscosity) and the dilatant direction (above Newtonian viscosity).[1] Since a correspondence between specific structural changes and the non-Newtonian response has not been determined for these materials, it has been generally surmised that the non-Newtonian behavior is a result of complex molecular chain kinetics such as unfolding, stretching, cross linking, etc.

Recent "experiments" with Lennard-Jones spheres in a glassy state using molecular dynamics (MD) calculations have also shown the onset of non-Newtonian behavior under increasing strain rates or applied stresses.[2,3] The calculations show that when an applied shear strain rate is imposed on a box containing Lennard-Jones spheres, the resulting stress is proportional to the applied strain rate, $\dot{e}$, only for low strain rate values ($\dot{e}\tau_0 \ll 1$, where τ_0 is the shear isothermal relaxation time in the Newtonian region). At higher strain rates, the measured stresses and the corresponding viscosity do not reach their expected Newtonian value, with the deviation growing for increasing strain rates. The resulting behavior is shown in Fig. 1. Since in Lennard-Jones glasses the atoms interact only via central forces, it seems clear that the observed nonlinear behavior in MD calculations is a fundamental property of the liquid or glassy state.

Oxide glasses consist of ions which bind with both ionic and covalent character. For example, the alkali metal modifiers form ionic bonds with oxygen, while the silicon-oxygen bonds have more covalent character.[4] In general, silicate glasses exhibit no chain characteristics; thus, they may offer a set of real materials whose behavior may be compared to MD Lennard-Jones glasses. Similarities are expected in measurements of properties controlled by the central force behavior of the bonds and differences are expected when bond direction plays a significant role in the material behavior. Thus, in general, silicate and MD Lennard-Jones glasses

may exhibit similar qualitative behavior in studies of viscous flow processes but will probably differ quantitatively.

Measurements by Li and Uhlmann on rubidium silicate glasses[5] have shown the existence of a non-Newtonian region in the viscoelastic response of the glass to an applied constant load. As is the case for MD glasses, the deviation from Newtonian behavior was in the pseudoplastic direction. However, the dynamics of the non-Newtonian behavior of the glass were not studied in detail. We have analyzed their data, and a comparison of their results to MD experiments and to our results is presented below.

In this paper a stable silicate glass was selected for an investigation of non-Newtonian behavior. The glass is a
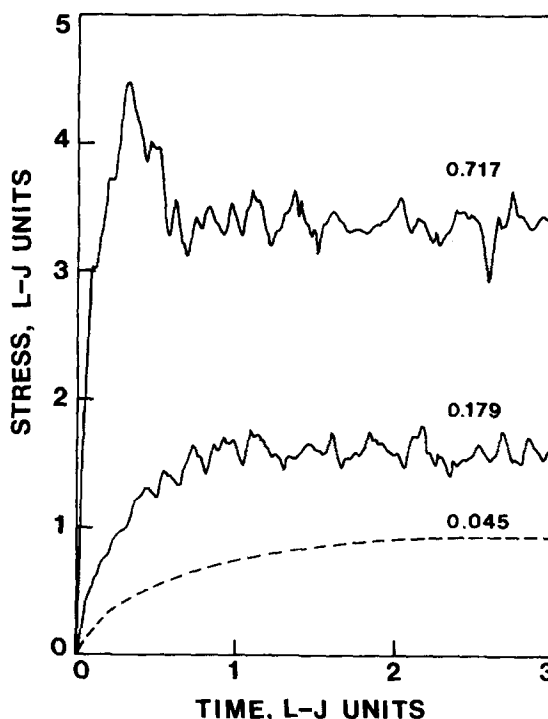

FIG. 1. Results from molecular dynamics calculations. Shear stress vs time for the shear strain rates shown at the right, switched on at time zero. Note the stress overshoot at the upper strain rate. (See Ref. 2 for details.)

standard reference material for viscosity issued by the National Bureau of Standards.[6] Its Newtonian viscosity has been measured at great length, its stability against devitrification, immiscibility, and evaporation in air at high temperatures and its homogeneity have been established through numerous tests.[6-8]

The experiment which we present is conducted differently from that of Li and Uhlmann, and is designed to reproduce the conditions of the MD calculations. The experiment is conducted at constant strain rate rather than constant stress or applied load. While these conditions are interchangeable when the material is exhibiting Newtonian behavior, they are not equivalent when the response is nonlinear. Constant strain-rate experiments were performed because they allow a detailed study of the nonlinear behavior before the onset of material failure.

I. EXPERIMENT

Measurements were conducted on oxide glass fibers whose composition is shown in Table I. Fibers were made by hand drawing from the molten glass at 1150°C, and had diameters of 0.1–1 mm with a variation for each fiber of less than 5%. Much effort was expended to avoid contact with the surface of the fiber in the test furnace and to use freshly drawn fibers; therefore, the surface is expected to have had a smooth (fire) polish. Fiber diameters were measured after the tests to avoid damaging the surface.

Each tested fiber was inserted through a furnace 12 cm long with a narrow central channel and was attached to a stationary fixture at the bottom end and to a movable load cell at the top end. See Fig. 2 for a schematic of the fiber and furnace arrangement. The furnace was designed to yield a relatively constant temperature over most of its length (± 3°C over 90 mm) and to drop rapidly in temperature at each end (ΔT of at least 20°C in the first 6 mm, thus allowing for a rise in viscosity of one decade, then a much more rapid drop for increasing distance beyond the furnace). This guaranteed a constant, well-defined hot zone. At selected temperatures, the fiber was elongated at a constant rate while the resulting force was measured. The measurements were conducted at all the different strain rates studied before the temperature was changed.

Since the length of hot fiber was fixed by the furnace, this resulted in a constant applied strain rate. The fiber diameter was reduced as its total length increased; therefore it was necessary to calculate a correction for the steady-state cross-sectional area reduction. Steady state refers to the condition where the cross-sectional area decreases uniformly over the entire hot length of the fiber. This is selected to differentiate

TABLE I. [a] Glass composition.

SiO_2	70.5%	Sb_2O_3	1.1%
K_2O	7.7%	SO_3	0.2%
Na_2O	8.7%	Al_2O_3, Fe_2O_3	0.2%
CaO	11.6%		

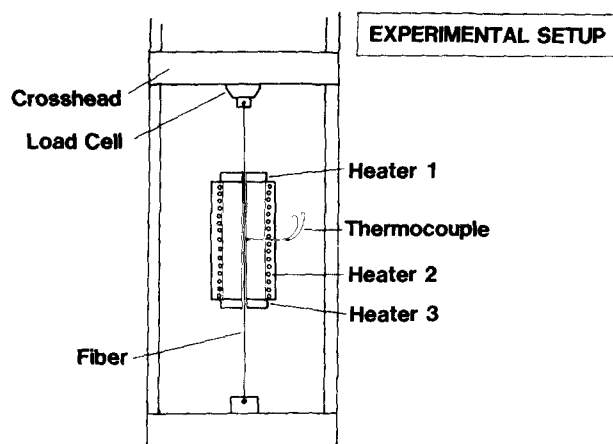[a]This glass is known as NBS-710 Viscosity Standard.

FIG. 2. Details of the furnace and load cell assemblies. The end heaters, 1 and 3, were adjusted to obtain a uniform temperature in the furnace.

it from localized necking which we shall discuss later. An exact solution to the steady-state correction is

$$A(t) = A_0 e^{-\dot{\epsilon}(t - t_0)}, \tag{1}$$

where A_0 is the area at t_0 and $\dot{\epsilon}$ is the strain rate. The validity of this correction was verified by the measurement of the expected Newtonian viscosity at low strain rates before and after substantial elongation at high strain rates. Using this area correction, plots of the variation of developed stress with time were obtained for different applied constant strain rates. A typical dependence of stress on strain rate is shown in Fig. 3. Note the linear region at low strain rates, and the pseudoplastic deviation at higher strain rates. The apparent viscosity η was calculated as follows:

$$\eta = \frac{1}{3}\frac{\sigma}{\dot{\epsilon}}, \tag{2}$$

where σ is the developed stress.[9] Figure 4 shows the temperature dependence of the Newtonian viscosity measured at low strain rates.
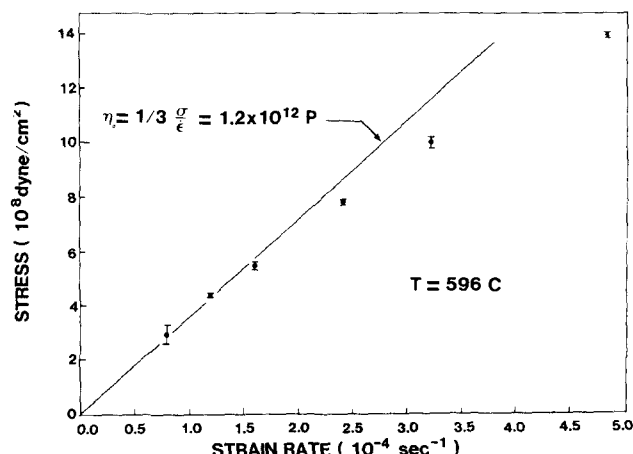

FIG. 3. Variation of stress vs strain rate for the soda-lime-silica glass. The deviation from Newtonian behavior is clearly seen for strain rates above $1.5 \times 10^{-4} s^{-1}$.

FIG. 4. Newtonian Viscosity of the measured soda-lime-silica glass.

FIG. 6. Measured viscosity vs time for the strain rates shown, switched on at time zero. The dashed line is the Newtonian value.

II. DISCUSSION
A. Experimental results

A study of the nonlinear behavior of this glass and a comparison with the Lennard-Jones, molecular dynamics experiments are best effected by looking at the time dependence of the apparent viscosity for a given applied constant strain rate. Figures 5 and 6 show the non-Newtonian behavior for two different temperatures. The onset of nonlinear behavior occurs at higher strain rates for higher temperatures and lower viscosities. The slow increase in viscosity to its Newtonian value, η_0, at the low strain rates corresponds to shear relaxation effects in the glass, and the time to reach the steady-state, Newtonian behavior is proportional to the average shear relaxation time, $\tau_0 = \eta_0/G$, where G is the instantaneous shear modulus.

As the strain rate is increased, three significant effects can be observed. First, the apparent viscosity approaches a steady-state value for long times. This steady-state, apparent viscosity decreases with increasing strain rate. Second, there is a short-time overshoot of this steady-state value during the shear relaxation period. Third, the slower shear relaxation
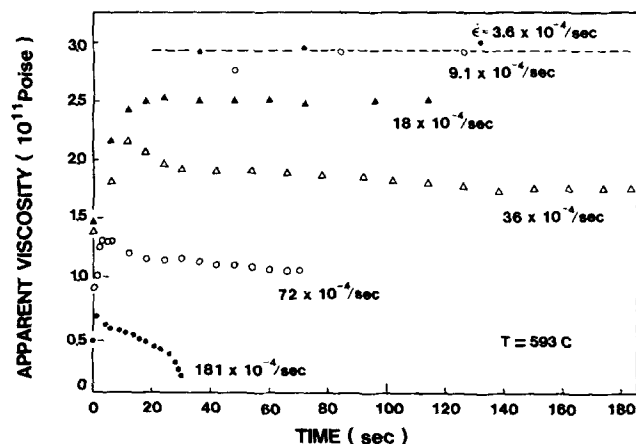
processes appear to be short circuited by a faster process which leads to the lowered viscosity. These results are qualitatively identical to the behavior of Lennard-Jones spheres in the MD experiment (Fig. 1). This process appears to be a structural breakdown mechanism and occurs at earlier times for increased strain rates (i.e., compare the curves with $\dot{\epsilon} = 72 \times 10^{-4}$/s and 18×10^{-4}/s in Fig. 5). It appears that the high strain rates cause a breakdown of the glass structure which in turn allows stress relaxation to occur by the faster available mechanisms rather than the sum of all relaxation mechanisms. Because the Newtonian shear relaxation processes and the structural breakdown processes have different relaxation times and amplitudes, there is an overshoot in the apparent viscosity.

Each set of tests shown on Figs. 5 and 6 was conducted on a single fiber. The measurements gave the same steady-state viscosity values at each given $\dot{\epsilon}$, whether the measurements were made following a higher or a lower $\dot{\epsilon}$. Therefore, the steady-state viscosity values appear to be independent of past history. In each figure, the highest $\dot{\epsilon}$ value corresponds to a failure of the fiber. In Fig. 5 the viscosity appears to be approaching steady state when failure occurs.

B. Heating effects

It is apparent that the observed nonlinear behavior of the silicate glass fibers is similar to the behavior of the Lennard-Jones glass. Before a discussion of similarities and differences between these two results, it is necessary to establish that test conditions were similar. For example, in the MD experiments, the temperature was maintained constant. Therefore it is necessary to determine whether the silicate glass fibers were heated above the furnace temperature at the higher strain rates, and whether the heating, if present, would be sufficient to cause the decrease that was observed in the viscosity. For example, the drop in observed viscosity at 563°C from the Newtonian value of 3.2×10^{12}P to the pseudo-plastic value of 1.1×10^{12}P (at the strain rate of $7.2 \times 10^{-4} s^{-1}$) corresponds to a temperature increase of 10°C.
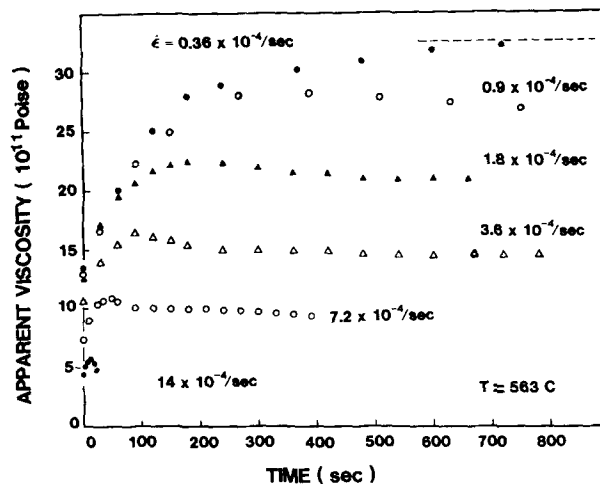

FIG. 5. Measured viscosity vs time for the strain rates shown, switched on at time zero. The dashed line is the Newtonian value.

A lower limit to the rate of heat loss from a fiber can be calculated using the radiative heat transfer coefficient, H, defined for small temperature differences between the fiber and the furnace as

$$H = 4eST^3,$$ (3)

where e is the glass emissivity, S is the Stefan-Boltzmann constant, and T is the absolute temperature. The rate of heat loss dQ/dt is then given by

$$dQ/dt = HA_s\Delta T,$$ (4)

where A_s is the surface area of the fiber in the furnace and ΔT is the temperature difference between the fiber and the furnace. Using $S = 5.67 \times 10^{-8} \text{J/s·m}^2\text{·K}^4$, $T = 836$ K, and $e = 0.9$ we calculated a value for $H = 1.2 \times 10^2 \text{J/K·m}^2\text{·s}$. This value is an underestimate of the total heat transfer coefficient since only radiative mechanisms have been considered. Paek and Kurkjian[10] have estimated H from cooling rate measurements made on glass fibers with similar dimensions as those tested here. Their estimate yielded $H = 2.9 \times 10^2 \text{J/K·m}^2\text{·s}$ which is consistent with our calculation.

A calculation of the rate of doing work on the fiber was made to determine an upper limit on any resulting temperature rise. The rate of doing work is

$$dW/dt = \sigma\dot{\epsilon}V,$$ (5)

where V is the volume of the fiber given by $1\cdot A(t)$. Under steady-state conditions the maximum rate of heat input due to conversion of all the work to heat was calculated to be $3.37 \times 10^{-4} \text{J/s}$. Since the surface area of the fiber in the furnace was approximately 1 cm^2 the largest temperature rise that could be supported considering only radiative heat loss is less than 0.03°C. This is far below the value of 10°C necessary to cause the observed nonlinear behavior. Therefore, we can reasonably conclude that the nonlinear behavior of the glass during these experiments was not a result of localized heating of the fiber, and the test does duplicate the isothermal conditions of the MD experiments.

C. Mechanism

During the MD experiments, it is possible to arrest the system and examine its structure. The examinations of systems having undergone extensive nonlinear behavior showed definite structural changes indicative of a layering effect for planar shear. The layers appear to form almost parallel to the shear planes with a small angular deviation from the shear direction. The angles decrease with increasing shear rates.[2] Real glasses may also be suddenly frozen by rapid cooling to temperatures below the glass transition temperature. However, structural examinations of real glasses on the molecular level are difficult and cannot be made directly. Therefore, we have not yet attempted to gather structural correspondence for the nonlinear behavior.

It is possible however, to discuss the nonlinear behavior of real, inorganic glasses by comparison with MD results. The reduced steady-state viscosity (apparent viscosity divided by Newtonian viscosity, η/η_0) can be plotted versus stress or versus reduced strain rate (strain rate times the Newtoni-

an average relaxation time, $\dot{\epsilon}\tau_0$) for each temperature. In both instances, the data reduce to the same general shape, although it appears to us that the reduction with reduced strain rate is better. Both inorganic glass experiments and the MD data follow the same general behavior.

The decrease in viscosity with increasing strain rate results from an asymptotic approach of the sustained steady-state stress to a maximum value (σ_{limit}) at very high strain rates. The existence of a limit in the sustainable steady-state stress indicates that if the system is placed under a stress greater than the limit, steady-state conditions cannot be maintained and catastrophic failure ensues. This stress limit, therefore, can be interpreted as the actual cohesive strength of the material. This result shows a unique and valuable feature of the non-Newtonian viscosity studies, since the actual cohesive strength of the material is obtained here without a need to fracture the material.

A calculation of the limiting stress requires some extrapolation of the data to very high shear rates. In this task, we rely on the similarity between the measurements conducted on the soda-lime silica glass and the MD calculations on the Lennard-Jones glass. The normalized viscosity of both systems reduces to the same curve when the shear rate is normalized through the function $\dot{\epsilon}\tau_0/\alpha$, where α is an adjustable parameter. The value of α is found to be 0.0063 for the soda-lime silica glass, 0.0053 for the rubidium silicate glass, and 0.077 for the Lennard-Jones glass. Reduced in this fashion, all data follow the same behavior, independent of temperature and composition as shown in Fig. 7.

The falloff in reduced viscosity at increasing strain rates thus appears to result from dynamic changes in the structure of the material which accompany the large applied strain rates. Reduction of this data from different temperatures on the same glass by use of the average Newtonian shear relaxation time indicates that the structural rearrangement is controlled by the shear flow processes in the glass.

The functional dependence of the decrease in normalized viscosity can be obtained from an equation based on the concept of a limiting stress used by Bair and Winer to discuss similar behavior for highly viscous organic lubricants.[11] The equation was derived by Montrose using semi-empirical arguments.[12] The equation yields a simple relationship between reduced viscosity and the normalized strain rate funtion, $\dot{\epsilon}\tau_0/\alpha$:

$$\frac{\eta}{\eta_0} = \frac{1}{1 + \dot{\epsilon}\tau_0/\alpha},$$ (6)

where the factor α is found to be the ratio of the maximum stress sustained by the system and the instantaneous shear modulus of the glass, σ_{limit}/G. The fit of this equation to the data is also shown in Fig. 7.

σ_{limit} is the maximum stress developed in the system under steady-state conditions as the strain rate goes to infinity without material failure. Therefore, σ_{limit} represents the actual cohesive strength of the material. This actual cohesive strength is interpreted as the maximum stress sustainable by the material when the stress is applied at a rate slower than the effective relaxation time of the glass. Its existence suggests that when viscous or plastic flow occurs under an in-
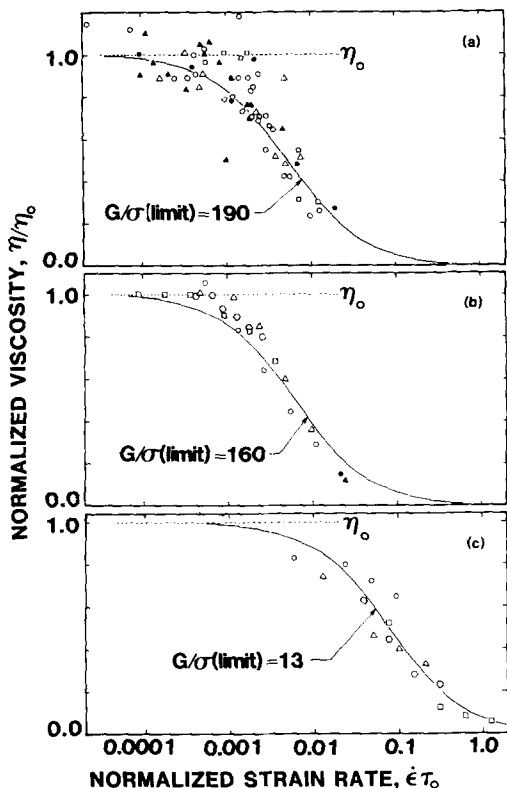
FIG. 7. Plots of viscosity reduced by the Newtonian value vs normalized strain rates, $\dot{\epsilon}\tau_0$, for various temperatures. The solid line represents Eq. (6) and shows how a reduction of the strain rate by the single parameter of G/σ_{limit} can fit the data from three totally different materials: (a) Rubidium-silicate data from Li and Uhlmann (see Ref. 5) analyzed by the method presented in this paper. The temperatures are as follows: open circles = 528°C, solid triangles = 555°C, open triangles = 536°C, squares = 501°C, solid circles = 480°C. (b) Soda-lime-silica glass whose measurement is described here. The temperatures are as follows: circles = 563°C, diamonds = 574°C, triangles = 593°C, and squares = 596°C. The two solid points are estimates of viscosity before failure. (c) Molecular dynamics calculations on a Lennard-Jones glass. (See Ref. 2.) Here different densities are used to represent different thermodynamic states. The densities are in terms of the triple point density, ρ_T: circles = $1\rho_T$, triangles = $1.1\rho_T$, diamonds = $1.2\rho_T$, and squares = $1.5\rho_T$.

creasing tensile or shear stress, there is a stress value where steady-state flow cannot be sustained and the material fractures at the point where the stress is applied. In the case of loaded fibers, this result suggests that as the diameter of the fiber undergoes localized necking, a point is reached when $\sigma_{applied} > \sigma_{limit}$ and fracture occurs, rather than continued necking of the fiber.

In the MD experiments, an independent measurement of σ_{limit}/G was conducted and agrees very well with the value of α obtained by fitting the nonlinear viscosity to Eq. 6.

This generalized behavior of inorganic glasses at different temperatures and composition is an encouraging basis for the development of molecular models to interpret nonlinear behavior in inorganic glasses. The strong similarities to the MD glasses indicate that the effect is indeed a result of structural rearrangements in the glasses. The parameter, α, appears to be linked to the strength of some average structural bond of the material at the temperature of measurement.

Therefore, this experiment offers a direct measurement of the cohesive strength of different glasses and a possibility for measuring its temperature dependence. The values obtained here show that both oxide glasses can only sustain stresses about 1/160 of their shear modulus, while the Lennard-Jones glasses can go up to about 1/10 of the shear modulus. This result is reasonable from structural considerations since the bonding forces in the LJ glass are spherically symmetric, while a significant portion of the bonding of the oxide glasses is dominated by the silicate structure which is covalent[4] and therefore highly directional. It is expected that these covalent bonds are much less resistant to shear stresses, since they can break by bond rotation, than are the nondirectional ionic bonds, which break by bond extension alone. Estimating a shear modulus for the soda-lime silica glass of 2.2×10^{10} Pa, based on high temperature ultrasonic sound velocity measurements, our interpretation of the reported measurements yield an actual cohesive strength of 1.4×10^8 Pa (20 Kpsi) for this glass at temperatures near 560°C, and Newtonian viscosities of 10^{10}–10^{11} Pa·s (10^{11}–10^{12} Poise).

III. SUMMARY AND CONCLUSIONS

The viscosity of a stable, soda-limit silica glass was measured at high shear rates. The results showed a non-Newtonian viscosity behavior of the pseudo-plastic type. As a function of time, the viscosity at high, constant strain rates first increased to a maximum, then decreased to a constant time-independent value, lower than the expected Newtonian viscosity. The time-independent behavior at long times yields a steady-state viscosity which is a function of the applied strain rate.

The measurements when compared to molecular dynamic calculations on a Lennard-Jones material show unexpected similarity in the time and temperature dependence of the non-Newtonian viscosity. The observed behavior also agrees with earlier work on a rubidium silicate glass. Comparison of these data indicates that the time evolution of the viscosity of the silicate glasses corresponds to that calculated for the Lennard-Jones glasses which is known to result from a structural rearrangement in the material under high deformation rates.

An examination of the combined data of the inorganic glasses and the MD glass showed that the steady-state, sustained stress under applied constant strain rates approaches a limiting stress value, σ_{limit}, for infinite strain rates. This limiting sustained stress is interpreted as the actual cohesive strength of the glass since any applied stress greater than σ_{limit} cannot be sustained under steady-state conditions and leads to catastrophic failure. The extrapolation of data using a semi-empirical model showed that σ_{limit} for the two inorganic glasses analyzed is near 1/160 times the rigid shear modulus, or approximately 20 Kpsi for the soda-lime silica glass. These results suggest a mechanism for material failure at high temperature (under conditions of plastic flow). By this mechanism, an applied shear stress greater than σ_{limit} induces initially a plastic flow reaction which changes to fracture when the structure attempts to adjust to the stressed condition. An applied shear stress lower than σ_{limit} induces a

plastic flow reaction which reaches a steady-state strain rate as the structure rearranges itself to accommodate the stress.

Note added in proof: In this paper, the distinction between the uniaxial stress measured on the fiber and its shear component which is the stress discussed in comparison with MD calculation was not clearly made. In particular, the quantity σ_{limit} is the maximum shear stress sustainable by the glass.

ACKNOWLEDGMENT

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[9] This is a commonly used definition of viscosity in the Newtonian region. The definition of viscosity in non-Newtonian regions becomes somewhat ambiguous and others[5] have suggested that $\eta = 1/3(\partial\sigma/\partial\dot{\epsilon})$ is a more appropriate definition (the two definitions are equal in the Newtonian region). The use of Eq. 2, however, allows us to plot viscosity as a function of time at fixed $\dot{\epsilon}$ and this is more useful for our fixed strain rate experiments. The use of the differential form requires data with very low scatter to calculate the viscosity with any accuracy and therefore is not used here.

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