JOURNAL OF CHEMICAL PHYSICS VOLUME 111, NUMBER 20 22 NOVEMBER 1999

Creep of selenium near the glass temperature

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(Received 1 July 1999; accepted 26 August 1999)

Creep experiments were carried out on amorphous selenium (Se) at temperatures in the vicinity of the glass temperature. The recoverable compliance lacks a plateau, indicating Se chains are too short to form an entanglement network. The measured compliance function was thermorheological complex, even after subtraction of the glassy level and normalizing by the steady state compliance. The temperature dependence determined from the viscosity was in accord with previous viscosity data, although weaker than the near-Arrhenius dependence deduced from the stress relaxation of Se. Based on a comparison to other, small-molecule glass-formers, the dynamic fragility calculated from the viscosity was larger than expected from Se's thermodynamic fragility (i.e., steepness of the normalized Kauzmann curve). In contrast, although polypropylene (PP) is substantially more dynamically fragile than Se, PP is less thermodynamic fragile. Thus, when compared to either small-molecule liquids or polymers, Se exhibits a disconnect between dynamic and thermodynamic measures of fragility. © *1999 American Institute of Physics.* [S0021-9606(99)50144-X]

I. INTRODUCTION

The slowing of the dynamics when liquids are cooled to their glass temperature has profound effects on both the relaxation behavior and thermodynamic properties. These changes can be analyzed using the ''fragility'' scheme, which for thermodynamics makes use of the Kauzmann plot,[1,2] while for dynamic properties it is usually based on a T_g-normalized Arrhenius plot of relaxation time or viscosity.[3–6]

For polymers, fragility has been related to the local chemical structure, in particular the manner in which local structure governs steric and polar interactions among neighboring chain segments.[7–18] Smooth, compact, symmetrical chains exhibit ''strong'' (i.e., less temperature-sensitive) relaxation behavior, while more fragile polymers tend to have rigid backbones, sterically hindering pendant groups or polar associations. Such correlations of temperature dependence with the degree of intermolecular cooperativity engendered by the molecular structure suggest that ''cooperativity plot'' may be a more appropriate term than fragility for the semilogarithmic plots of relaxation time or viscosity versus T_g/T.[8,18]

For small molecule glass-formers, the steepness of fragility curves has been analyzed in terms of the topology of a liquid's potential energy hypersurface. According to this interpretation, fragility is governed by the rapidity with which entropy generation drives a liquid up the energy landscape.[3–5,19–22] The energy landscape model implies a fundamental connection between relaxation properties and thermodynamics.[1,2,23,24] Effort has been made to extend the landscape model to polymers,[25] although Angell[26,27] has suggested that intramolecular interactions unique to chain molecules introduce difficulties to this approach. Indeed, recent mechanical and dielectric relaxation data show the model to be deficient in describing results for polymers.[7,28–33]

Herein we examine the creep behavior of selenium. The amorphous state of Se is commonly believed to be a mixture of chain molecules and eight-member rings, the concentration of the latter estimated to range from 40%[34] to near zero (the very existence of Se rings has been questioned).[35,36] Given its propensity to form chains, Se bridges the gap between small molecule liquids and polymers, and thus examination of its fragility is timely.

II. EXPERIMENT

The amorphous selenium (from Johnson Mathey, having a purity of 99.999%) was used as received. Torsional creep and recovery experiments were carried out in a magnetic bearing apparatus,[37] using a parallel plate geometry. For most measurements, Se pellets were heated in the instrument to above 220 °C to effect melting, and then shaped into a cylinder (6.4 mm diameter) between the platens. As an alternate method, verified to give equivalent results, 3.2 Se rods were molded prior to being placed in the rheometer. For this method, selenium was heated to 450 °C in a test tube. A Teflon tube was inserted into a glass capillary, and this assembly pressed into the molten Se. The rod, about 3 mm long, was removed and allowed to cool in air.

For the creep experiments, a constant torque in the range from 10^{-6} to 10^{-3} NM, depending on temperature, was employed, with linearity of the response affirmed for all measurements. Temperature control was ±0.1 °C, with about 3 h required for thermal equilibration.

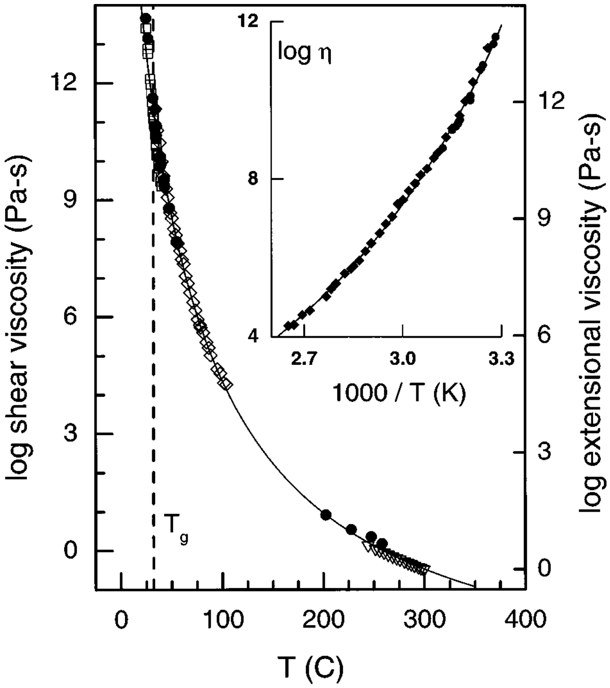

FIG. 1. Se shear viscosity (●) measured by creep herein and from Ref. 38 (◇) and 39 (△), along with elongational viscosities (□) reported by Stephens (Ref. 45). To allow comparison, the ordinate scale for the latter has been shifted by a factor of log 3, corresponding to Trouton's rule (Ref. 47). Data are absent from the intermediate temperature range ($55<T$(C)<200) because of crystallization. The vertical dashed line indicates the dilatometric glass temperature. The inset includes only shear viscosities obtained at lower temperatures, along with the VFTH curve corresponding to the parameters listed in Table I.

III. RESULTS

A. Viscosity

Shear viscosities, measured from the creep compliance when a terminal velocity is achieved,

$$\eta = \lim_{t\to\infty} \frac{dt}{dJ(t)}, \tag{1}$$

are shown in Fig. 1, along with data from the literature.[38,39] At temperatures beyond 55 °C, crystallization of the Se precludes measurements until the melting point is approached. Near T_m (=221.1 °C under equilibrium conditions),[40] crystallization is sufficiently slow that the creep of amorphous Se can be measured. The curve through the shear viscosity data for low temperatures and at higher temperatures, up to 258 °C, represents the VFTH (or Vogel) equation[41]

$$\eta = \eta_0 \exp \frac{B}{T - T_0}. \tag{2}$$

Interestingly, although the data encompass two distinct ranges, it can be described fairly well by a single VFTH equation. Generally, the temperature dependence of relaxation properties undergoes a change at a temperature above T_g.[42] Whether Se is exceptional in this regard is difficult to judge, given the absence, due to crystallization, of data over a substantial temperature interval.

TABLE I. Results for selenium.

η_0 (Pa-s) [Eq. (2)]	B [Eq. (2)]	T_∞ (K) [Eq. (2)]	T_g [a] (K)	ΔS_g [b] (JK^{-1} mole^{-1})	T_m [c] (K)	ΔS_m [b] (JK^{-1} mole^{-1})
146	2264	236	305	6.80	494	12.5

[a] Reference 43
[b] Reference 64.
[c] Reference 40.

The inset to Fig. 1 is an Arrhenius plot of the shear viscosities for temperatures in the vicinity of the glass temperature, T_g. The latter is 32.0 °C, as measured by dilatometry at 0.2 deg/min cooling.[43] This compares to $T_g = 30.3$ °C, obtained by slow calorimetry.[44] The fit to Eq. (2) of the data over this limited range yields the parameters listed in Table I.

Elongational viscosities, η_E, have been reported for selenium,[45] and are included in Fig. 1. The elongational viscosity is related to the shear viscosity according to[46]

$$\eta_E = 2(1+\mu)\eta, \tag{3}$$

where μ is Poisson's ratio. For an incompressible material, this gives Trouton's rule,[47] $\eta_E = 3\eta$. The η_E in Fig. 1 are indeed threefold larger than the shear viscosities (to allow for comparison, the ordinate scale on the right-hand side of Fig. 1 has been scaled by a factor of log 3), suggesting $\mu = 1/2$. This is not always the case for temperatures near and below T_g.[48] Böhmer and Angell[49] reported different time dependences for Se undergoing shear versus bulk (volume) relaxation, which indicates a time-dependence for μ near T_g.[50]

B. Temperature dependence

From the deformation after removal of the stress, the recoverable compliance, $J_r(t)$,

$$J_r(t) = J(t) - \frac{t}{\eta}, \tag{4}$$

was obtained (Fig. 2). As apparent from the value of $J_r(t)$ at longer times, these curves can not be reduced to a master curve by time–temperature superpositioning. We can attempt to superimpose the recovery data by subtracting the glassy compliance ($J_g = 3.6\times10^{-10}$ Pa^{-1}), which is sensibly independent of temperature, and then normalizing at each temperature by the steady-state compliance,

$$J_s = \lim_{t\to\infty} J_r(t). \tag{5}$$

However, these normalized recoverable compliance curves are also thermorheologically complex (Fig. 3). Consequently, the temperature-dependence of Se cannot be assessed from $J_r(t)$. We employ the viscosity data for this purpose.

A common method of characterizing the temperature-dependence of the viscosity or relaxation time is from the steepness of a T_g-normalized Arrhenius plot. The slope at T_g of this curve is referred to as the fragility, or steepness index,

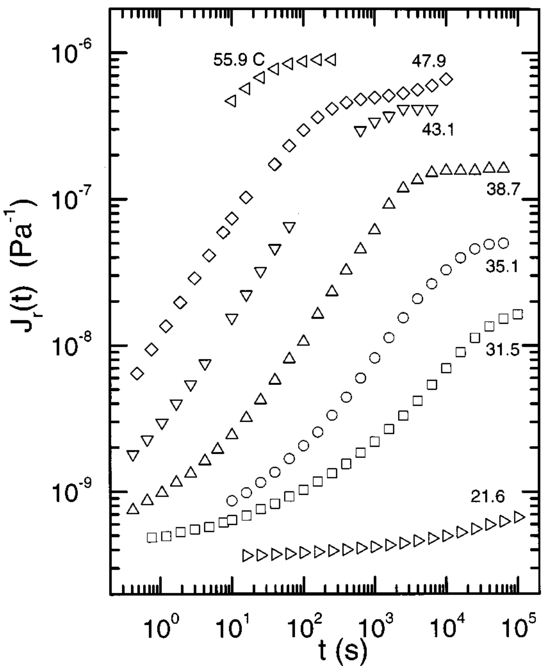

FIG. 2. Recoverable compliance of Se measured at the indicated temperatures (Celsius).

$$m=\left.\frac{d\log(\eta)}{d(T_g/T)}\right|_{T=T_g}. \tag{6}$$

The shear viscosities in the inset of Fig. 1 are displayed in T_g-normalized form in Fig. 4. In terms of the VFTH parameters, fragility is given by[6]

$$m=\frac{B}{\ln(10)T_g}\times(1-T_\infty/T_g)^{-2}, \tag{7}$$

which yields $m=62$ for Se.

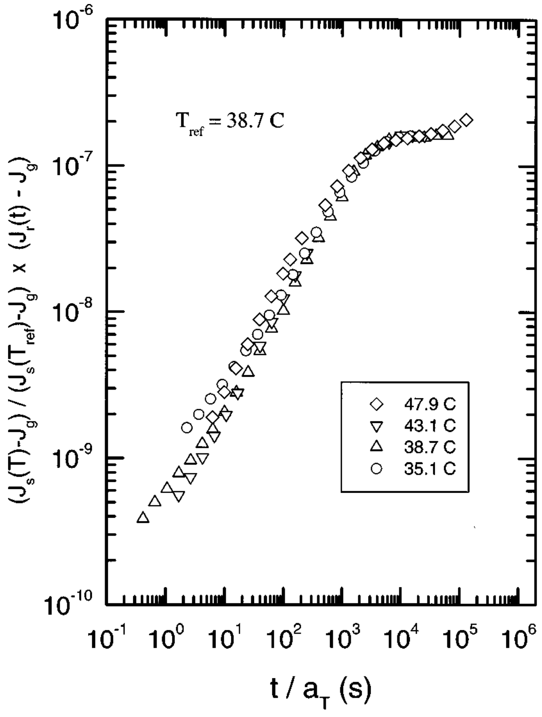

FIG. 3. Recoverable compliance of Se, normalized by the steady-state compliance after subtraction of the glassy compliance. The data nevertheless fail to superpose.

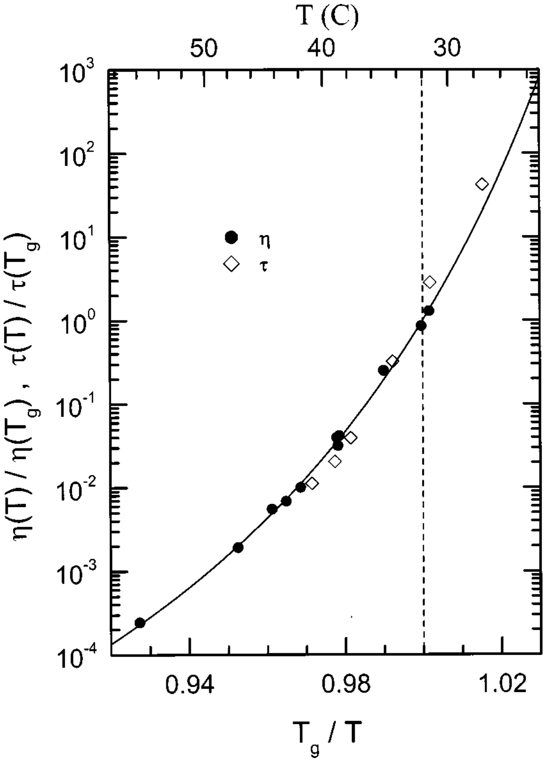

FIG. 4. T_g-normalized Arrhenius plots of the shear viscosities (●) and mechanical relaxation times (◇) of selenium (the latter taken from Ref. 49), both quantities normalized by their value at the glass temperature. The solid line is the fit of Eq. (2) to the viscosity data.

Böhmer and Angell[49] measured stress relaxation of amorphous selenium at temperatures within the range of those in Fig. 1. Beyond the usual α-relaxation at short times, the modulus function showed a second relaxation process at longer times, presumed to involve long-range motions of Se chains.[49] The shape of the mechanical spectrum changed with temperature. This thermorheological complexity, consistent with the behavior of the compliance curves in Fig. 3, was ascribed to a temperature-dependent ring/chain equilibrium. The chain structure of Se is reported to be favored with increasing temperature,[36,51,52] although Lucovsky[35] has argued against any substantial ring population in Se.

A step change in stress observed at intermediate temperatures gives rise to a plateau in the relaxation modulus. The mechanical spectrum of high polymers exhibits a distinct rubbery plateau, due to a transient network of chain entanglements; however, there is no such plateau in the recoverable compliance of Se (Fig. 2). The contribution of viscous deformation to the mechanical response can produce a plateau in the modulus; thus, the latter does not necessarily indicate the existence of entangled chains.[53] This complication is avoided in the compliance function [e.g., Eq. (7)], since contributions to the deformation are additive in the strain,[54,55] so that viscous flow can be eliminated, either mathematically or by a creep recovery experiment. The lack

TABLE II. Thermodynamic and dynamic fragilities.

Glass former	Symbol	m [Eq. (6)]	F [Eq. (10)]
salol	⋯	63[a]	0.32[a]
1,3,5-tri-α-naphthylbenzene	TNB	66[b]	0.28[c]
2-methyltetrahydorfuran	MTHF	65[a]	0.26[a]
selenium	Se	62	0.18
polypropylene	PP	137[d]	0.11[e]

[a] Reference 63.
[b] Reference 59.
[c] Reference 65.
[d] Reference 58.
[e] Reference 33.

of a plateau in $J_r(t)$ for Se (Fig. 2) does not imply the absence of chains, but only that they are too short to form an entanglement network.

Böhmer and Angell[49] reported the stress relaxation modulus for Se at short times to be well-described by the (Kohlraush–Williams–Watts) KWW function,[56,57]

$$\phi_\alpha(t) = \exp - \left(\frac{t}{\tau_\alpha} \right)^\beta, \tag{8}$$

where τ_α is the relaxation time and $\beta(\leqslant 1)$ the fractional exponent. By assuming the average relaxation times $(=\tau_\alpha \Gamma[1+1/\beta]$, where Γ is the gamma function), which are included in Fig. 4, to have an Arrhenius temperature dependence, these authors obtained an apparent activation energy, $E_a = 485\,\text{kJ/mole}$. Using the relation $m = E_a/RT_g \ln(10)$, the fragility was estimated to equal 83;[49] using Eq. (7) and their reported VFTH parameters, we obtain $m = 89$. This compares to $m = 93$ deduced from the elongation viscosities (Fig. 1), assuming Arrhenius behavior with $E_a = 544\,\text{kJ/mole}$.[45] These values are all larger than the fragility determined from the shear viscosity (Table II), which encompass a substantially broader range of temperatures.

The stretch exponent in Eq. (8) was found to vary with temperature, with $\beta = 0.6$ at T_g.[49] As first shown by Ngai and Plazek,[58] the breadth of the relaxation function usually correlates with fragility, lower beta (i.e., a broader dispersion) associated with greater fragility.[8–10,59–62] The relationship has been expressed quantitatively as[58,59]

$$m = 250(\pm 30) - 320\beta, \tag{9}$$

which for Se yields 58, consistent with the value of $m = 62$ determined from the shear viscosity.

Richert and Angell[63] have proposed a different measure of fragility, $F_{1/2}$, defined from the temperature at which the relaxation time assumes a value midway between $10^{-14}\,\text{s}$ and its value at $T_g(=100\,\text{s})$. If Eq. (2) is valid, the two quantities are related as

$$F_{1/2} = \frac{m-16}{m+16}. \tag{10}$$

In many cases, these two fragility measures agree. For Se, Angell *et al.*[20] determined $F_{1/2} = 0.52$. In light of the fact that the VTHF equation describes the Se data well over a broad range of temperatures (Fig. 1), we use Eq. (10) to deduce from $F_{1/2}$ that $m = 0.51$. This is somewhat smaller than the value of 0.62 determined directly from the viscosity data using Eq. (7).

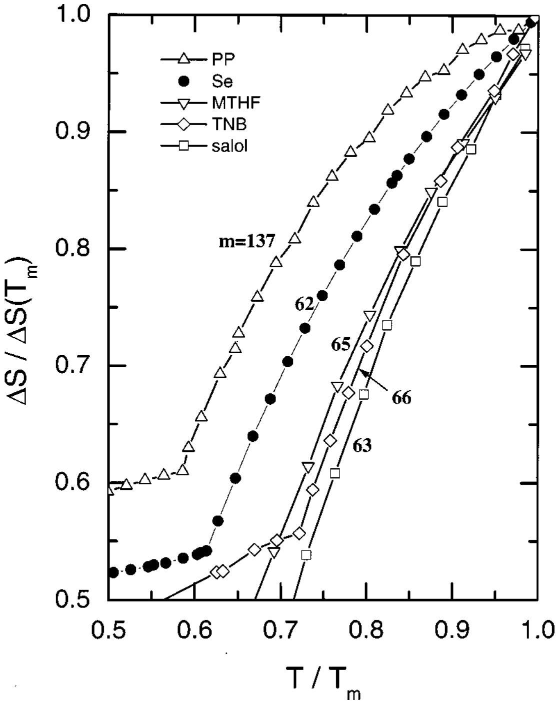

FIG. 5. Normalized Kauzmann plots for selenium and three small-molecule glass-formers having comparable dynamic fragilities (values as indicated). Also included are data for polypropylene, which has the least steep Kauzmann curve, notwithstanding that it is the most dynamically fragile.

C. Thermodynamics

The energy landscape model[1,2,5,22] attempts a thermodynamic interpretation of the dynamics of glass-formers. Analogous to the parameter m describing the viscosity's temperature dependence, thermodynamic fragility is reflected in the steepness of Kauzmann plots[1,2] of ΔS, the configurational entropy difference between the liquid and perfect crystal, versus T/T_m, where T_m is the equilibrium melting point. The implication is that thermodynamic fragility parallels dynamic fragility, so that the latter may even be determined from purely thermodynamic data.[1,22–24]

We test this idea in Fig. 5, which shows the Kauzmann plot for Se, based on literature values.[64] Also included are data for three small-molecule glass-formers with essentially the same fragility.[59,63] Thermodynamic data for these materials was obtained from the literature.[63,65] To allow comparison, ΔS for each glass-former was normalized by the respective excess entropy at the melting temperature.

As can be seen in Fig. 5, the normalized Kauzmann plots for the small-molecule glass-formers roughly parallel their thermodynamic fragility. This is in keeping with recent results on nonpolymeric glass-formers.[1,23,24] However, the slope of the Kauzmann curve for Se is at odds with the magnitude of its dynamic fragility. Se has the substantially lower thermodynamic fragility than the other liquids, despite having a nearly equivalent m. Of course, the fragility values deduced from other studies,[45,49] $83 \leqslant m \leqslant 89$, would make the divergence between Se and the other liquids worse.

Thermodynamic fragility can be quantified as the fractional decrease of the fusion entropy at $T/T_m = 0.8$ (Ref. 1)

$$F_{\Delta S} = 1 - \frac{\Delta S(0.8T_m)}{\Delta S(T_m)}. \tag{11}$$

Values for $F_{\Delta S}$, as well as dynamic fragility, are listed in Table II, illustrating the lack of any connection between these two properties.

Given its capacity to form chains, Se is different from other small-molecule glass-formers. Angell has pointed out that the high T_g of many polymers may be associated with higher vibrational contributions to the configurational heat capacity.[26,27] Such a dichotomy between molecular glass-formers and polymers might make it inappropriate to assess the landscape model through comparisons between them. Notwithstanding this caveat, included in Fig. 5 are data for polypropylene, a polymer for which $m = 137$.[58] Despite its very fragile behavior, normalized Kauzmann plot of PP is *less* steep than for Se, or indeed any of the other materials in Fig. 5. Clearly, no obvious relationship exists between thermodynamic and dynamic fragilities, a finding in accord with a recent analysis of data for a wide range of polymers.[33]

IV. SUMMARY

Se is of particular interest for studying the dynamical behavior of glass-formers because it is a monatomic liquid which can exist as chains; thus, Se bridges the gap between molecular glasses and polymers. Time–temperature superpositioning of creep measurements on Se fails, even after subtraction of the glassy compliance and normalizing by the steady-state recoverable compliance. This thermorheological complexity may be a consequence of the propensity of Se to form chains. Nevertheless, the viscosity can be described by a single VFTH equation over a 220 deg range of temperatures.

We have attempted to interpret the temperature dependence of the viscosity of Se using the energy landscape model, the principle appeal of which is providing a connection between thermodynamics properties and the dynamics near T_g. It has previously been shown that, while the model enjoys some success in describing the viscosity and relaxation dynamics of molecular glass-formers,[1,23,24] significant problems arise with respect to polymers.[33] From the results herein, we can conclude that this shortcoming extends to Se. A comprehensive accounting of the dynamics of glass-formers likely requires explicit consideration of other contributing factors, such as intermolecular cooperativity and the crowding coupling associated with relaxation in dense phase.

ACKNOWLEDGMENTS

The work at NRL was supported by the Office of Naval Research, and that at the University of Pittsburgh by the National Science Foundation (Grant No. 9530372).

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