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Physical aging in a hyperquenched glass

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We report experimental data on the enthalpy relaxation of a hyperquenched silicate glass subjected to long-time aging (annealing) below the glass-transition temperature (T_g). The relaxation of a hyperquenched glass substantially differs from that of a normally cooled glass. Two mechanisms govern the relaxation of a hyperquenched glass. During relaxation of the first hyperquenched, and afterward aged glass, a relaxation endotherm occurs followed by an exotherm. This is reflected by the occurrence of crossover. By increasing the aging temperature and time, the endotherm becomes more pronounced, while the exotherm gradually disappears. The consequence of this is the shift of the crossover point to higher temperature. The relaxation of the hyperquenched glass at $0.66T_g$ with the aging time is highly nonexponential. © 2002 American Institute of Physics.

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A thin fiberglass formed with a high drawing speed is a typical hyperquenched glass. A fiberglass is an important material for communication technologies and for advanced structural composites, because of its extraordinary mechanical and optical performance compared to a bulk glass with the same chemical composition.^{1–6} The fictive temperature (T_f) of a hyperquenched glass substantially exceeds that of a “normally cooled” glass.^{7–11} The term “normally cooled glass” refers here to a glass cooled with the rate 0.167 K/s that is conventionally used for determination of the glass transition temperature (T_g). The cooling rate is a crucial factor in determining T_f , the parameter that characterizes the difference between the structure and properties of hyperquenched and normally cooled glasses.^{7–11} In this work, the hyperquenching of 10^6 K/s is reached by the fiber spinning process that results in a high fictive temperature, $T_f = 1.23T_g = 1155$ K.⁷ Substantial progress has so far been made in exploring the structural relaxation of normally cooled inorganic nonmetallic bulk glasses. Some inspiring results have recently been achieved also on the relaxation of hyperquenched glasses.^{8–11} However, the relaxation behavior of a hyperquenched glass below T_g is understood to much less extent than that of normally cooled glasses. In particular, the thermodynamic consequences of physical aging in a hyperquenched inorganic nonmetallic glass below T_g remain unknown. This work contributes to the better understanding of the energy landscape of glass-forming liquids.

Physical aging exerts a strong and complex impact on properties of glasses.^{12,13} Substantial work has been done on physical aging in polymer glasses.^{12,13} However, similar investigations have not been carried out on hyperquenched inorganic fiberglasses. To reveal the mechanisms of physical aging and to correlate with structural features of the glass under consideration, we perform systematic calorimetric experiments on a fiberglass aged for various times at temperatures between $0.5T_g$ and T_g . The enthalpy relaxation is demonstrated on both aged and nonaged hyperquenched fiberglasses. The energy release of a fiberglass has important

implications for topographical rearrangement of its structure and for the distribution of bonding strengths in a glass. The knowledge about the dependence of the energy release on both aging temperature and time is crucial for clarifying the influence of physical aging on the mechanical and optical properties of hyperquenched glasses.

The fibers used for this study were drawn from a basaltic melt with the composition 49.3 SiO₂, 15.6 Al₂O₃, 1.8 TiO₂, 11.7 FeO, 10.4 CaO, 6.6 MgO, 3.9 Na₂O, and 0.7 K₂O (wt%) in the temperature range from 1473 to 1573 K by using a cascade technique.¹⁴ The average diameter of the fibers is 3.5 μm. Aging of the fibers is performed in air at various temperatures for various times. Figure 1 shows the rate of the energy release of the fiber samples, $d\Delta E/dT$, as function of temperature T . The energy release per Kelvin per gram sample is $d\Delta E/dT = C_{p2} - C_{p1}$, where $\Delta E(T)$ is the total excess energy released during heating to a given temperature, and C_{p1} and C_{p2} are the heat capacities measured on the first and second runs of differential scanning calorimetry (DSC) upscans, respectively (see the inset of Fig. 1). In

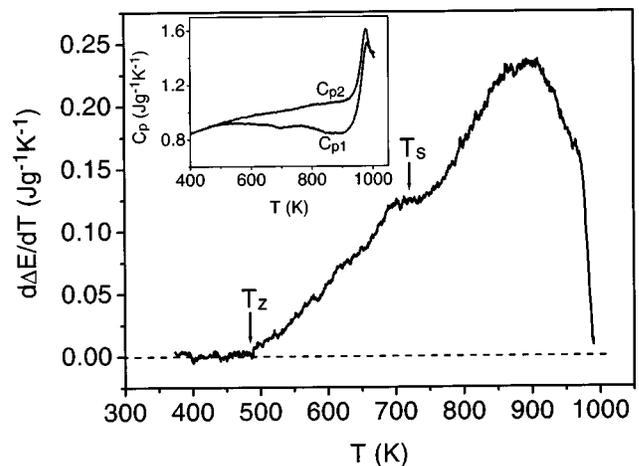


FIG. 1. The rate of energy release during heating, $d\Delta E/dT$, as function of temperature T , which is the difference between the heat capacity (C_{p2}) measured by the second upscan and that by the first upscan (C_{p1}), that is, $C_{p2} - C_{p1}$. Both heating and cooling rates used in the DSC measurements are 0.167 K/s. The inset: The C_{p2} and C_{p1} curves.

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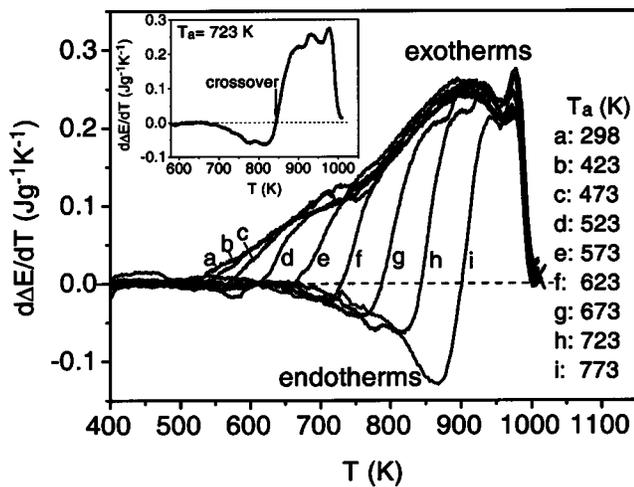


FIG. 2. The rate of energy release, $d\Delta E/dT$, of fibers aged for eight days at different temperatures (T_a). The heating rate is 0.333 K/s and the cooling rate is 0.167 K/s. Inset: The rate of energy release, $d\Delta E/dT$, of fibers aged for eight days at $T_a = 723$ K, showing the crossover temperature.

this letter, $d\Delta E/dT$ is treated as the rate of energy release from a fiberglass, because of the relation $d\Delta E/dT = d\Delta E/(Q_h dt)$, where Q_h is a constant heating rate.⁷ The heat capacities of the samples were measured using the DSC apparatus Netzsch STA 449C. The sample was subjected to two upscans. T_g was found to be 944 K from the C_p curve of the second upscan with the heating rate 0.167 K/s. Before the second upscan, any sample was cooled at 0.167 K/s. DSC measurements on aged samples were performed with the heating rate 0.333 K/s and the cooling rate 0.167 K/s. The total energy stored during fiber forming, ΔE_{tot} , is calculated by integrating $d\Delta E/dT$ over the entire temperature range of the measurement. The energy release function $d\Delta E/dT(T)$ implicitly exhibits the distribution of the stored energy over all configurational coordinates. The existence of the shoulder suggests two overlapping domains of relaxation mechanisms below T_g .

Two important characteristic temperatures are identified in Fig. 1. The first is the onset temperature ($T_z = 0.52T_g$), at which the enthalpy starts to release, meaning, that the fictive temperature begins to drop. The second is the “shoulder” temperature ($T_s = 0.72T_g$), which implies an overlap of two relaxation processes of a fiberglass. The distribution of $d\Delta E/dT$ over T is not symmetric, and a long tail is observed at the lower temperature range above T_z . Figure 2 illustrates the effect of aging temperature on the relaxation behavior of the fiberglass for the aging time of eight days. When increasing the aging temperature (T_a), the exotherm is gradually reduced from the left- to the right-hand side, until it totally disappears, i.e., the left-hand side foot of the exotherm shifts to higher temperatures. During the aging process, the structural configuration with a higher energy is transformed into that with a lower energy. The aging temperature determines the extent of changes in the structural configuration. The vibrational excitation energy required for the change in the structural configuration depends on its energy level. All configurational states approach the energy level corresponding to the aging temperature. The shift of the left-hand side foot of the exotherm to higher temperatures is due to the fact that more and more low-energy basins of the energy landscape

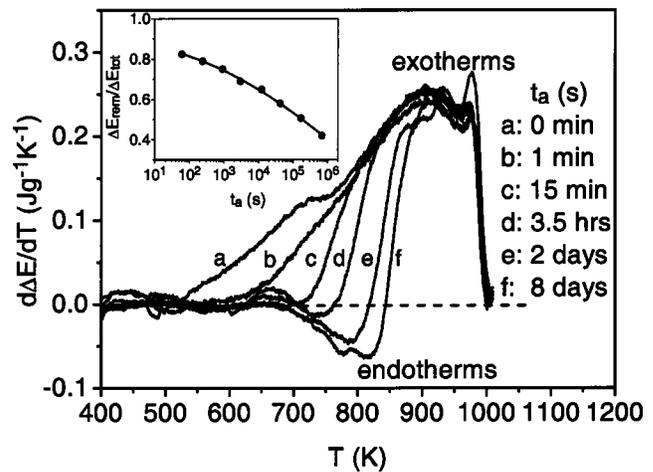


FIG. 3. The influence of aging time (Δt_a) on the energy release of fibers at $T_a = 723$ K. The heating rate is 0.333 K/s and the cooling rate is 0.167 K/s. Inset: $\Delta E_{rem}/\Delta E_{tot}$ as a function of t_a , where ΔE_{rem} is the energy remaining in the fibers after aging and ΔE_{tot} is the stored energy before aging at $T_a = 723$ K. Solid line in the inset is obtained by fitting the experimental data by the Kohlrausch–Williams–Watts equation.

are sampled by the system when increasing the aging temperature.

From Fig. 2, it is also seen that at certain temperature a relaxation endotherm occurs on the left-hand side of the exotherm. The higher the aging temperature is, the deeper and the broader the endotherms become. At the same time, the endotherm gradually shifts to higher temperatures, but at the cost of successive loss of the left-hand side part of the exotherm. In a certain range of aging temperatures, the exotherm and endotherm coexist, that leads to the occurrence of the crossover point (see the inset of Fig. 2).

Figure 3 shows the effect of aging time on the relaxation behavior of the fiberglass at the aging temperature 723 K. When the aged samples are heated from room temperature to T_g , a relaxation endotherm appears followed by an exotherm. The endotherm becomes more and more pronounced with aging time and it shifts to higher temperatures until the exothermic peak totally disappears. This implies that at aging, a structural domain of the fiberglass releases the excess energy and tends to reach the energy level corresponding to a given aging temperature. Another structural domain proceeds to lose the remaining part of the excess energy.

The aging-time dependence of the energy release rate at a constant temperature reveals that it takes a long time for all configurations to find the lowest minima, although they are subjected to the same excitation energy. This means that there exists a broad distribution of relaxation times whose width is determined by the diversity of configurational states. The endotherm becomes deeper as the aging time increases. At a given aging temperature, the density of states with high energy decreases with aging time.

The inset of Fig. 3 shows the effect of aging time on the remaining energy, ΔE_{rem} , normalized by the total energy stored during fiber forming, ΔE_{tot} . The solid line is the fit of observation by the Kohlrausch function $\Delta E_{rem}/\Delta E_{tot} = \exp[-(t/\tau)^\beta]$, where τ is the characteristic, temperature-dependent relaxation time, and $\beta \in (0,1)$ is the stretch exponent. In Fig. 3, we obtained $\beta = 0.16$ for $T_a/T_g = 0.66$, which is much lower than the β values given by other authors¹⁵ for

the energy landscape-influenced regime ($0.45 < T/T_g < 1$). The small β value could be attributed to the high fictive temperature of the fiberglass. The small β value implies a very stretched distribution of relaxation times for the aging process at 723 K.

In conclusion, two characteristic temperatures (T_z and T_s) have been identified in the relaxation process of a hyperquenched fiberglass. Relaxation of hyperquenched glasses substantially differs from that of normally cooled glass. During relaxation of the aged fiberglass, a relaxation endotherm occurs followed by an exotherm, which leads to the occurrence of the crossover point. With increasing aging temperature and time, the endotherm becomes more and more pronounced, while the exotherm gradually disappears. The consequence of this is the shift of the crossover point to higher temperature. The relaxation of the fiberglass at $0.66T_g$ exhibits a high nonexponentiality with a stretched exponent of 0.16.

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