Characteristic temperatures of enthalpy relaxation in glass

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ABSTRACT: Relationships between characteristic temperatures of glass relaxation are studied by performing annealing and calorimetric experiments on a hyperquenched glass. The $T_g$ measured directly by a calorimeter at 10 K/min is identical to that indirectly estimated by fitting the viscosity data to a viscosity model.

Introduction

Every liquid in equilibrium has a unique dependence of relaxation time on temperature. As the glass transition is approached, the relaxation process of a liquid becomes non-exponential and non-linear [1]. Below the glass transition temperature ($T_g$), this becomes particularly striking. In glass science the dynamics, thermodynamics, and structure between different glass systems are often compared directly over a large range of temperature. But, it is only meaningful to make such a comparison at a universal, characteristic temperature or at temperatures scaled by characteristic features are well distinguished between various liquids by using the fragility concept that is based on the $T_g/T$ dependence of relaxation time [2]. $T_g$ is the most useful, characteristic, dynamic temperature of a liquid. However, the way to determine $T_g$ has not been fully unified in glass literature. This paper will illustrate a well-defined calorimetric method to obtain the $T_g$ values that well agree with those derived by fitting viscosity data to a viscosity model. The method may be used as a unified way to determine $T_g$ of glasses. This paper will discuss the relationships between various characteristic temperatures of enthalpy relaxation in a hyperquenched glass based on means of differential scanning calorimetric (DSC) measurements. This paper will compare the pre-endotherm of a hyperquenched, annealed glass with the real glass transition concerning their physical origins. Such comparison benefits a final solution about one of the most controversial, important issues in glass science, namely, glass transition of water.

Experimental

To determine the characteristic temperatures of glass and liquids, two types of experiments are chosen: 1) hyperquench-anneal-DSC scan; 2) viscometric and DSC measurements. Two types of glasses were used for this study. The first type of experiment was performed on an industrial, basalt-like iron-rich aluminosilicate glass. The basalt-like glass was hyperquenched ($\sim 10^6$ K/s) [3], annealed at 723 K for 55 days, and scanned by DSC at 10 K/min. The second type of experiments was done on 21 inorganic glasses (19 silicate and 2 phosphate glasses), the chemical composition of which are given in [4-6]. From the viscosity data, the $T_g$ values were obtained by means of a viscosity model described in [3,7]. From the DSC data, the onset $T_{g,\text{DSC}}$ was obtained directly by the DSC (see Fig. 1). Subsequently, the correlation between the thermodynamic $T_{g,\text{DSC}}$ (determined by DSC) and the dynamic $T_{g,\text{visc}}$ (determined by viscometer) was established. Such correlation is useful for defining a unified procedure to determine a standard $T_g$.

Results and Discussion

Figure 1a shows the typical enthalpy relaxation of a hyperquenched basaltic glass, which is manifested by the excess heat capacity ($C_{p,\text{exc}}$) as a function of temperature. $C_{p,\text{exc}}(T)$ is determined by subtracting the heat capacity for the first upscan, $C_p$, from the heat capacity for the second upscan, $C_p^2$. The second upscan is regarded as the standard upscan since both the heating and the prior cooling rates are 10 K/min. The $T_g$ determined at 10 K/min by DSC coincides with the temperature at the viscosity of $10^{12}$ Pa s (see the last paragraph of this section). From a viscosity model described in [7], $T_g$ is the temperature at $10^{12}$ Pa s. The $T_g$ measured at 10 K/min corresponds to an average relaxation time close to 100 s [8].

As shown in Fig. 1a, the fictive temperature $T_f$ can be determined by using the enthalpy-matching method, the detailed description of which is given in [3,9,10]. Here $T_f$ refers to the temperature at which the excess enthalpy is frozen-in the glass upon cooling. The value of $T_f$ is dependent on which property of glass is concerned [11]. $T_f$ begins to decrease when the glass is reheated to a certain temperature, i.e. the onset temperature $T_{g,\text{f}}$ of release of the enthalpy stored in the glass by hyperquenching at $10^6$ K/s. The excess enthalpy (see the hatched area in Fig. 1a) is due to the arrest of the excited configurational states. The most excited states are so unstable that only a very low temperature $T_{f}$ (well below $T_g$), i.e. a very small kinetic energy $k_BT_{f}$ where $k_B$ is the Boltzmann constant, can bring them to an energy level corresponding to the real temperature. The value of the characteristic $T_f$ is determined by that of the characteristic $T_g$. The higher $T_f$ is, the lower is $T_g$. The dependence of $T_f$ on $T_g$ involves two situations. First, when a liquid is cooled at a rate higher than the standard rate of 10 K/min, $T_f$ is higher than $T_g$. Second, when a liquid is cooled at 10 K/min, $T_f$ and $T_g$ will merge to the same value equal to $T_g$. However, when a liquid is cooled at a rate below 10 K/min, $T_f$ will not exist, since no energy release takes place. Instead, an enhancement of the $T_g$-endotherm would occur, i.e. a deficient heat capacity...
would exist in the glass transition region, and therefore $T_f$ should be lower than $T_g$. Finally, an important question remains: whether there are limiting values for both $T_g$ and $T_f$.

Fig. 1c shows another characteristic temperature, i.e. the so-called shadow glass temperature $T_{g,shad}$, which is the onset temperature of the pre-endotherm. The $T_{g,shad}$ is fundamentally different from the real glass transition temperature ($T_g$) regarding their physical sources. The former is a consequence of annealing and is attributed to the energetic and structural heterogeneity of glass. The pre-endotherm is a manifestation of the non-exponential nature of glass relaxation. The $T_{g,shad}$ is associated with a local process. By contrast, the real glass transition is a consequence of the slowing-down of the main ($\alpha$) relaxation process upon cooling or speeding-up of the $\alpha$ relaxation process upon heating. During the real glass transition, a dramatic change in the configurational entropy occurs during heating. The size of the cooperative rearrangement region rapidly increases when the temperature is lowered towards the glass transition [12]. Knowledge of the fundamental differences between the shadow and real glass transition is essential for a better understanding the evolvement of both thermodynamics and dynamics of hyperquenched glasses during annealing. This also provides information on the energy landscape of supercooled liquids [13]. In particular, the recognition of the difference between $T_{g,shad}$ and $T_g$ leads to further clarification of the glass transition behaviour of glassy water [14]. However, the glass transition of water is still one of the most important and controversial issues in glass science. One of the main challenges is that the glass transition of water cannot be probed directly by a DSC. The features of the $T_{g,shad}$ will be discussed in detail in separate papers [14-17]. The pre-endotherm shows a recovery feature under certain annealing and DSC-scan conditions [17]. Fig. 1b shows a crossover temperature $T_{cross}$ between the pre-endotherm and the energy release exotherm, which depends on the annealing temperature and time. The pre-endotherm only takes place when the glass is first hyperquenched and then partly annealed.

![Figure 1: Determination of various characteristic temperatures for glass dynamics for both the hyperquenched and the annealed, hyperquenched, basaltic glasses.](image)

Fig. 1b demonstrates a well-known area-matching method to determine $T_g$ [1], which proves to be accurate. By comparing with Fig. 1c, it is noticed that the $T_g$ determined coincides well with the onset glass transition temperature, at which the line extrapolated from the $C_p$ curve is intercepted with the line extrapolated from the rapid rising curve of $C_p$. Such a coincidence is seen to be a general finding for the inorganic glasses so far measured by DSC.

![Figure 2: Comparison between the glass transition temperatures measured by a DSC, $T_{g,DSC}$, and those obtained from the fit of viscosity data to Eq (1), $T_{g,visc}$, for 21 inorganic glasses [4-6].](image)
and hence is denominated in Fig. 2 as $T_{g,\text{visc}}$. As shown in Fig. 2, the $T_g$ is determined as the onset temperature of the rapid $C_p$ increase, i.e. the cross point between the two extrapolated lines (see the dotted lines), and is hence denominated as $T_{g,DSC}$. Both the $T_{g,\text{visc}}$ and the $T_{g,DSC}$ values, of 21 inorganic glasses (2 phosphate [5] and 19 silicate systems [4,5]) have been plotted in Fig. 2. The figure shows an excellent agreement, i.e. the relation $T_{g,\text{visc}}=T_{g,DSC}$ is valid. This indicates that it is reasonable to determine $T_g$ by using the DSC heating and the prior cooling rates of 10 K/min. This means that the real $T_g$ should be measured at the DSC upscan and the prior downscan rates of 10 K/min, which corresponds to the viscosity of $10^{12}$ Pa s. Such $T_g$ should be used for scaling the temperature in fragility plot.

**Summaries**

The onset temperature ($T_o$) of the energy release is determined by the fictive temperature of hyperquenched glasses. $T_o$ decreases with increasing $T_g$. However, it is unclear whether there is limiting values for both $T_o$ and $T_g$. The onset $T_g$, at which $C_p$ rapidly increases, coincides with the $T_g$ estimated by Moynihan’s area-matching method. The origin of the onset temperature of the pre-endotherm or the shadow glass temperature is fundamentally different from that of the real glass transition temperature. The glass transition temperatures $T_g$ estimated by fitting the viscosity-temperature data to a viscosity model agrees excellently with those directly estimated by a DSC at the upscan and downscan rates of 10 K/min. This suggests that the $T_g$ should be measured at 10 K/min and then can be used for constructing the fragility plot.

**References**

6. Y. Z. Yue, unpublished data.