Characteristic temperatures of enthalpy relaxation in glass

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Yue, Yuanzheng

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Yuanzheng Yue
Aalborg University, Section of Chemistry, Sohngaardsholmsvej 57, Aalborg, Denmark. Fax: +45 9635 0558; Tel: +45 9635 8522; E-mail: yy@bio.aau.dk

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 temperatures, e.g. usually by T_g. For instance, the dynamic 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 (~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 $T_{g,DSC}$ was obtained directly by the DSC (see Fig. 1). Subquently, the correlation between the thermodynamic $T_{g,DSC}$ (determined by DSC) and the dynamic T_g,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 ($C_{p,exc}$) as a function of temperature. $C_{p,exc}(T)$ is determined by subtracting the heat capacity for the first upscan, C_{p1}, from the heat capacity for the second upscan, C_{p2} . 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 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_z 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_z (well below T_g), i.e. a very small kinetic energy k_bT_z 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_z is determined by that of the characteristic T_f. The higher T_f is, the lower is T_z. The dependence of T_z on T_f 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_z. Second, when a liquid is cooled at 10 K/min, T_f and T_z will merge to the same value equal to T_g. However, when a liquid is cooled at a rate below 10 K/min, T_z 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_z and T_f.

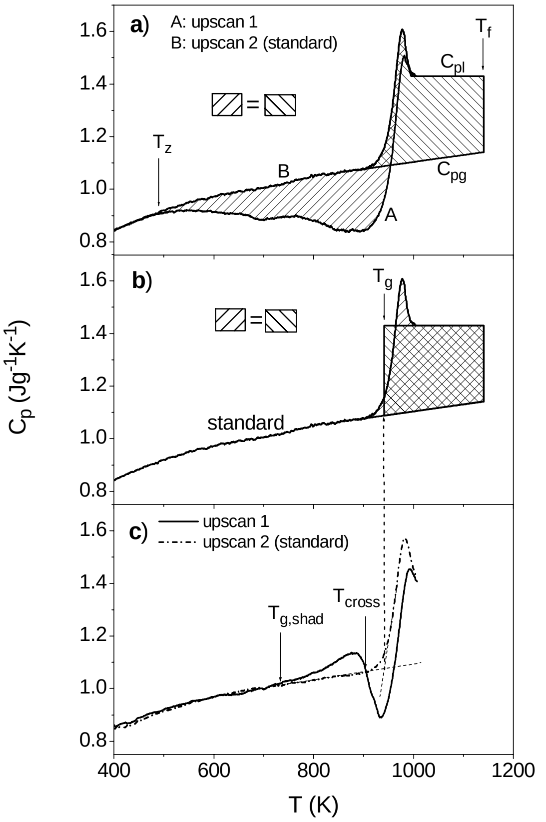

Figure 1: Determination of various characteristic temperatures for glass dynamics for both the hyperquenched and the annealed, hyperquenched, basaltic glasses. **a)** Determination of a fictive temperature (T_f) by using the energy-matching method, and the onset temperature (T_z) of energy release for a hyperquenched state [9,10]. C_{pl} is the heat capacity of the liquid, whereas C_{pg} is the heat capacity of the glassy state; **b)** The high temperature region of figure 2 which includes the left borderline (the line for determining T_g) and the right borderline (the line for determining T_f). The way of placing the left borderline was described in Ref. [1]. **c)** The difference between the onset temperature of the annealing-induced pre-endotherm, i.e. the 'shadow' glass temperatures ($T_{g,shad}$) [14] and the real glass transition temperature (T_g) for the glass that was first hyperquenched, and annealed at 723 K for 55 days. T_{cross} is the distinction temperature between the pre-endotherm and the energy release exotherm. The heating and cooling rates in DSC measurements are 10 K/min. The vertical dashed line illustrates the correspondence between the two T_g values determined by the two methods.

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_{pg} 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.

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 (α) relaxation process upon cooling or speeding-up of the α 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.

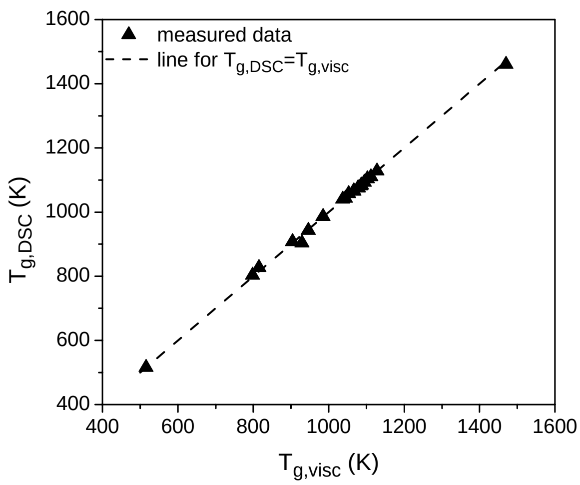

Figure 2: Comparison between the glass transition temperatures measured by a DSC, $T_{g,DSC}$, and those obtained from the fit of viscosity data to Eq (1), $T_{g,visc}$, for 21 inorganic glasses [4-6].

The T_g can be derived by fitting the viscosity-temperature data to the equation: $\log \eta = A+B(T_g/T)^F$, where A=-1.5, B=13.5, A+B=12, and F is the fragility index. From this equation, the T_g corresponds to the viscosity of 10^{12} Pa s, and hence is denominated in Fig. 2 as $T_{g,visc}$. 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 $T_{g,visc}$ 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 $T_{g,visc}= T_{g,DSC}$ 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_z) of the energy release is determined by the fictive temperature of hyperquenched glasses. T_z decreases with increasing T_g. However, it is unclear whether there is limiting values for both T_z 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 dowscan 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.

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