



Effect of the initial stage of annealing on modeling of enthalpy relaxation in a hyperquenched glass



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ABSTRACT

One of the major challenges in glass relaxation study is to establish a universal model describing the enthalpy relaxation in both the hyperquenched glass (HQG) (i.e., far from equilibrium) and the partially annealed hyperquenched glass (AHQG). In particular, the detailed features of the enthalpy relaxation in both HQG and AHQG during the initial stage of both the sub- T_g and above- T_g annealing cannot be captured by the existing models. In this Letter we show that the combination of a modified stretched exponential equation [M. Peyron, et al., J. Magn. Reson. Series A 118 (1996) 214] and the recently proposed composite relaxation function [L. Hornboell, et al., Chem. Phys. Lett. 1-3 (2010) 37] is a reasonable approach for describing those features. In addition, our modeling results imply that the structural heterogeneity plays a crucial role in relaxation of HQG.

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1. Introduction

One hallmark of glassy dynamics is that the dramatic slowing-down takes place without noticeable change in static structure when a liquid approaches its glass transition temperature T_g [1–4]. During the slowing-down process, the glass falls out of thermodynamic equilibrium and conserves a structural state corresponding to a higher fictive temperature T_f [5], i.e., the glass structure is frozen at a higher temperature. One of the most intriguing phenomena, namely, structural relaxation, will occur upon re-heating. A straightforward experiment for exploring the structural relaxation is to anneal the hyperquenched glass (HQG) (cooled at $>10^5$ K/s) at temperatures below T_g , i.e., sub- T_g annealing. Subsequently, the differential scanning calorimetry (DSC) scans are performed to detect the enthalpy response in the annealed sample. Upon partial sub- T_g annealing, the enthalpy trapped in the HQG glass is released, and the resulting glass is referred to as the partially annealed hyperquenched glasses (AHQG). The loss of the enthalpy during sub- T_g annealing can be detected by a subsequent DSC upscan. However, in studying the enthalpy relaxation of the quenched saccharides by isothermal microcalorimetry, it is found that the stretched parameter β of the Kohlrausch–William–Watts equation (KWW) for the annealing process was smaller than that of a modified stretched exponential (MSE) determined from the DSC data [6]. The main reason could be that some subtle relaxations occurring

during annealing were ignored in determining the enthalpy recovery by the subsequent DSC upscan [6]. The underestimate of the enthalpy variation during the DSC upscan should be avoided, and this is important for developing a universal model describing enthalpy relaxation of HQG and AHQG.

The temperature dependence of the isobaric heat capacity (C_p) of the HQG is manifested as a broadly distributed energy release peak below the offset temperature of the glass transition. The peak broadness is determined by the structural and energetic heterogeneity in glass [7]. The spatially heterogeneous dynamics has been revealed in the supercooled liquids [3,4] and its characteristic length scale increases when a liquid is cooled down to T_g [8–11]. Experimentally, it is found that the pressure dependence of structural relaxation time is related to the heterogeneity length [12]. The heterogeneous version of the Tool–Narayanaswamy–Moynihan (TNM) model [13] can be used to fit the C_p data of DSC up-scans for As_2Se_3 obtained at different cooling rates. The fitting quality of the TNM model is higher than that of the standard homogeneous TNM model [14–16]. Despite substantial progress in studying structural relaxation of the HQG and AHQG [7,17,18], a universal model for describing the enthalpy relaxation of these glasses is still lacking, and the complex dynamics has not been fully understood [19]. For instance, we have not answered the following questions. How does the relaxation rate change during annealing? Is the enthalpy decay function capable of describing the enthalpy evolution? In this work we attempt to answer these questions.

We firstly investigate the influence of the initial stage, i.e., the first few minutes, of the sub- T_g annealing on the enthalpy relaxation of a basaltic HQG. Then we demonstrate that none of the existing models, e.g., the empirical Kohlrausch–William–Watts (KWW) equation [20,21]

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and the newly proposed composite relaxation function (CRF) [19], are sufficiently precise for describing the evolution of the excess enthalpy during the initial stage of annealing below T_g in HQG. The excess enthalpy evolution during the initial annealing is inherently multi-exponential in character since it is affected by several factors, e.g., its heterogeneous structure, T_f , annealing temperature (T_a), the heating rate used from room temperature to T_a and so on. Hence, it is crucial to understand the initial annealing and to develop a scheme for describing the enthalpy relaxation of HQG and AHQG. For this purpose, we combine a modified stretched equation (MSE) with CRF model. With this combined scheme, we model the C_p patterns of the AHQG as a function of temperature, especially for the HQG annealed above T_g (super- T_g annealing).

2. Experimental

The HQG used experimentally for this study are basaltic glass fibers with the chemical composition (in wt.%): 40.6SiO₂, 20.8Al₂O₃, 1.6TiO₂, 7.1FeO, 13.6CaO, 11.4MgO, 1.6Na₂O, 0.8K₂O, and 0.3P₂O₅. The glass fibers were hyperquenched at about 10⁶ K/s during the spinning process [22–24]. The reference glass was obtained by annealing the HQG from the same batch at T_g for 1 hour and then cooled down naturally inside the furnace. The ‘reference glass’ is considered to have released all excess enthalpy during T_g annealing.

In order to observe the course of the enthalpy relaxation during sub- T_g annealing, the DSC output as a function of time was recorded using a simultaneous thermal analyzer (NETZSCH STA 449C Jupiter, Selb (Germany)). A platinum crucible containing the HQG sample and an empty platinum crucible were placed on the sample carriers of the DSC at room temperature. Both crucibles were held for 5 min at 333 K, and then heated at 20 K/min to the annealing temperature (T_a), and kept for 0.5 hour. Afterwards, the samples were cooled down to 523 K at 20 K/min, and finally down to room temperature at a natural rate. All the measurements were performed in ambient Argon atmosphere. In this work we focus on the very initial annealing process of the samples in the DSC. In order to determine the relative extent of exothermic enthalpy relaxation during sub- T_g annealing at T_a , the DSC upscan curves of the HQG were compared with those of the so-called reference glass. Moreover, the C_p data of the AHQGs as a function of temperature were measured using the same DSC instrument through the classical three step measuring method: correction, reference material and sample [22,23].

3. Results and discussion

3.1. Experimental sub- T_g annealing results

Fig. 1(a) shows the time dependence of the DSC output of both the HQG and the reference glass (denoted as H and R respectively) at different annealing temperatures (T_a). The thermal response of the samples for each annealing experiment is shown in the inset of Fig. 1(a). In the present study, the samples were kept at T_a for 0.5 hour after the course of 20 K/min DSC upscan from room temperature to T_a . The reference glass was subjected to the same DSC isothermal holding as that of the HQG in order to overcome the inability of the DSC in recording the enthalpy response during the isothermal scanning, i.e., in determining the relative extent of exothermic enthalpy relaxation during annealing. In this study we are interested in the annealing time (t_a) dependence of the DSC output of both the HQG and the reference glass at different T_a as indicated by a green ellipse in Fig. 1(a). In order to clearly observe the t_a dependence, the DSC curves for different T_a were separately plotted in arbitrary unit as shown in Fig. 1(b). At a fixed T_a , a pronounced exothermic enthalpy response (i.e., enthalpy release) is observed in the DSC curve denoted as H, particularly within the first few minutes. The enthalpy release only occurs if T_a is lower than T_g .

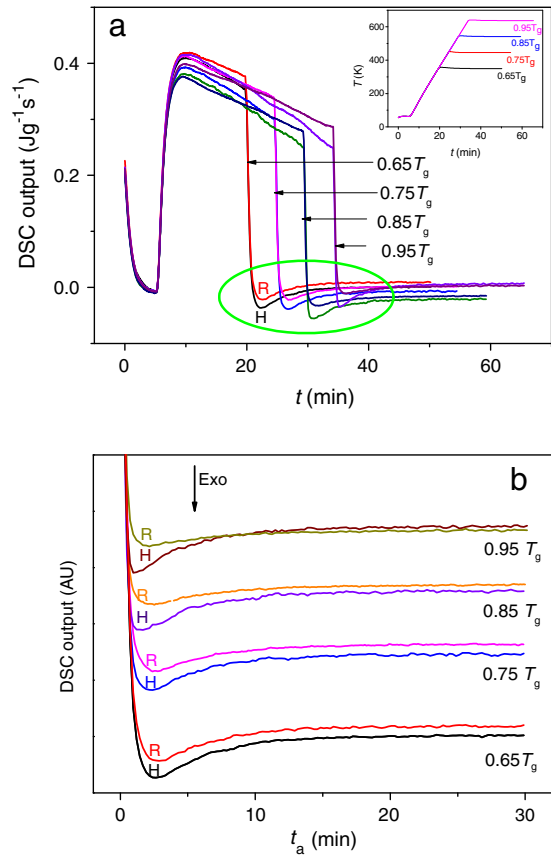


Fig. 1. (a) DSC output of both the basaltic HQG and the reference glass evolved with time under different T_a ($0.65T_g$, $0.75T_g$, $0.85T_g$ and $0.95T_g$). Here H and R stand for the basaltic HQG and the reference glass, respectively. The reference glass refers to the HQG which was annealed at T_g for 1 hour. The upper DSC curve of each T_a is for the reference glass while the lower one is for the HQG. Inset: The temperature evolution as a function of time for each T_a . (b) DSC output (arbitrary units) versus t_a during isothermal annealing (indicated by a green ellipse in (a)).

3.2. The KWW equation and CRF

The physics of the enthalpy relaxation in HQG and AHQG is so complicated that an efficient universal model for describing the enthalpy relaxation of HQG upon both dynamic heating and static annealing has not been established despite some progress has been made, e.g., the CRF model has been recently proposed [19]. However, the CRF model is still not satisfying in capturing the full picture of the non-exponential enthalpy relaxation of the AHQG with any chemical compositions.

The KWW decay equation quantifying the dispersion of relaxation process is described as:

$$f(t_a) = \exp\left[-\left(\frac{t_a}{\tau}\right)^{\beta_{\text{KWW}}}\right], \quad (1)$$

where t_a is the annealing time, τ is the mean relaxation time of the non-equilibrium glass state at the annealing temperature and β_{KWW} is a relaxation time distribution parameter with a value between 0 and 1. The particular property of interest in this work is the normalized remaining excess enthalpy of a glass far from equilibrium after annealing ($\Delta H_{\text{rem}}/\Delta H_{\text{tot}} = 1 - \Delta H_{\text{rel}}/\Delta H_{\text{tot}}$), where ΔH_{rel} is the released enthalpy during isothermal holding at different T_a and it is calculated by integrating the difference of the DSC output between the HQG annealed at T_a and the reference glass over the holding time. When $T_a = T_g$, the maximum ΔH_{rel} is considered to be equal to ΔH_{tot} . The KWW equation has been used to analyze the

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