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Measurement of the limiting fictive temperature over five decades of cooling and heating rates

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ABSTRACT

The fictive temperature (T_f) was defined by Tool in the 1940s as a measure of glassy structure. T_f is generally measured on heating and can be calculated from the enthalpy overshoot in calorimetric studies using a method developed by Moynihan. Prior work has demonstrated that the limiting fictive temperature (T_f') is similar to T_g (measured on cooling) and depends on the cooling rate in a manner consistent with the Williams–Landel–Ferry (WLF) relationship. Theoretically, the limiting fictive temperature should not depend on heating rate, but this has been experimentally verified only for a very limited range of heating rates. Here, rapid-scanning chip calorimetry and conventional differential scanning calorimetry (DSC) are combined to investigate T_f' for polystyrene over a broad range of heating rates ranging from 0.017 to 3000 K/s after cooling at different rates. The results show that T_f' depends on cooling rate following the WLF equation. On the other hand, T_f' is not a function of heating rate, consistent with theoretical predictions, in spite of the change in the magnitude and placement of the enthalpy overshoot.

1. Introduction

The glass transition temperature, T_g, is an important property of glass-forming materials and often defines temperature ranges for application and processing. By definition, T_g is a measure of the temperature range where vitrification occurs on cooling from the liquid state, and it is often taken as the midpoint of this range and defined as the intersection of the extrapolated glass and liquid lines made on cooling [1–3]. Since the transition is a kinetic rather than dynamic process, T_g depends on the rate of cooling following the well-known Williams–Landel–Ferry (WLF) [4] and Vogel–Fulcher–Tammann (VFT) [5–7] behavior.

On the other hand, the fictive temperature, T_f, is generally measured on heating and was introduced by Tool [8] as a measure of glass structure or the distance of a glass from its equilibrium state. In enthalpy space, T_f is defined as the intersection of the glass and liquid lines obtained on heating, which depends on cooling rate (q), as shown in Fig. 1. The glass lines move to lower enthalpies (and lower volumes) as the cooling rate decreases due to the increased time for relaxation; on heating, as shown, the enthalpy for the lowest cooling rates overshoots the liquid line resulting in a maximum or peak in the heat capacity. The overshoot observed on heating is well understood [3], and the overshoot increases as the ratio of the heating rate to the preceding cooling rate increases.

In the case of an unaged glass, T_f is termed the limiting fictive temperature T_f'. The importance of T_f' is its equivalence to T_g [9–12]. Due to instrumental limitations, early researchers performed calorimetric measurements only on heating, and thus, often referred to T_f' as T_g [13,14]. The measurement of T_g has become further confused by industrial practices [1], such as ASTM E 1356-08 [15], which defines various glass transition temperatures, including an extrapolated end temperature and inflection temperature. As indicated in the schematic Fig. 1, there can be significant differences between T_f' and the position of the enthalpy overshoot. Furthermore, because of the kinetics associated with the glass transition, the devitrification transition measured on heating depends on the heating rate, leading researchers to incorrectly assert that T_g depends on the heating rate. In fact, neither T_g nor T_f' should theoretically depend on heating rate. Rather, both should only depend on the cooling rate – and this dependence on cooling rate has been verified [9–12]. However, the lack of a dependence of T_f' on heating rate has been investigated only for a limited range of heating rates from 5 to 40 K/min [11]. Here, we extend such measurements to a much broader range of heating and cooling rates to verify the dependence of T_f' on these variables. In particular, we study a high molecular weight polystyrene with both conventional and Flash DSC using heating rates ranging from 0.017 to 3000 K/s, over five decades, after cooling at rates ranging

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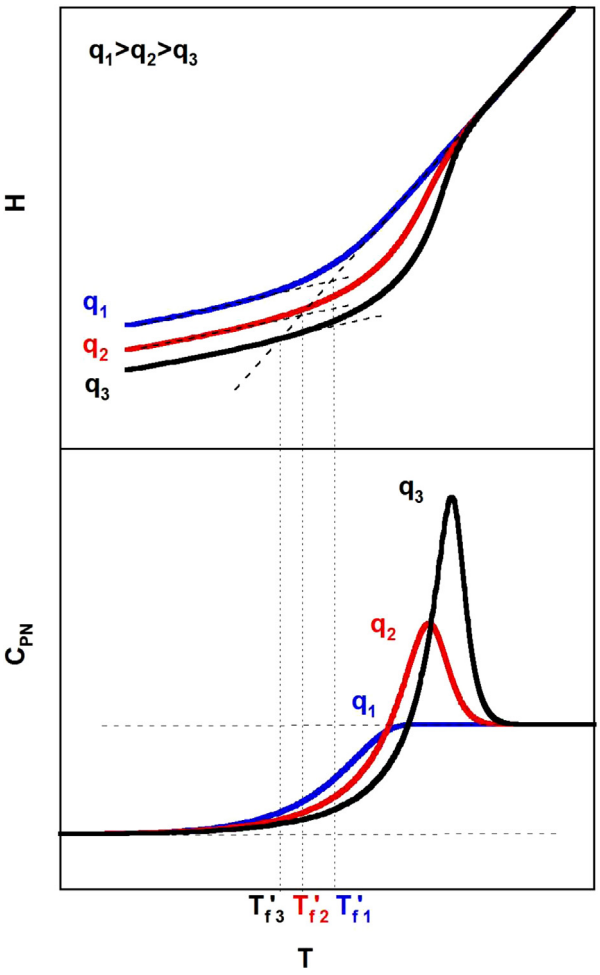

Fig. 1. Schematic plot of the enthalpy (H) and normalized heating capacity (C_{PN}) versus temperature when heating at the same rate after cooling at different rates, q_1, q_2, q_3, respectively, where $q_1 > q_2 > q_3$. The limiting fictive temperature is determined from the intersection of the glass and liquid lines resulting in $T_f'_1 > T_f'_2 > T_f'_3$ in spite of the overshoot shift to higher temperatures for lower q values. Volume and thermal expansivity plots are analogues.

over nearly six decades from 0.0017 to 1000 K/s. The dependence of the limiting fictive temperature on cooling rate and its independence on heating rate are confirmed and discussed.

2. Methodology

Polystyrene (Sigma–Aldrich) with 1,998,000 g/mol number-average molecular weight and PDI of 1.02 is used in this study. This material has been used previously in our laboratory and its T_g behavior has been characterized [16–18].

A Mettler Toledo Flash DSC was used with a freon intercooler with nitrogen purge. The sensor support temperature (T_{ss}) was set at −100 °C. The Flash DSC sample was a 160 nm-thick polystyrene film, spin-cast from toluene (99.999% purity, Sigma–Aldrich) using a 0.91 wt% concentration. The thickness was determined by atomic force microscope (AFM, Advanced Scanning Probe Microscope XE-100) in tapping mode after making a scratch on the film supported by a glass substrate. After spincoating, the film was floated on water to separate it from the mica substrate, and then picked up with mesh wire. The sample was annealed under ambient environment for 24 h, followed by another 24 h under vacuum at 50 °C. The film was then cut to a ~0.2 mm × 0.2 mm piece under a microscope and picked up by a hair pen to transfer it on the center of the sensor chip, which contained a thin layer of Krytox oil (DuPontTM, T_g = −63.2 °C) to enhance the thermal conductivity. The Krytox oil is inert to the polystyrene sample over several months based on measurements in our laboratory [19–21]. Heating rates (β) of 3000, 1000, and 300 K/s were employed from 35 to 180 °C after cooling at five different rates from 0.1 to 1000 K/s. Three runs were performed at each heating rate to check reproducibility.

For conventional DSC, a Mettler Toledo DSC 1 with intracooler at 5 °C and a DSC 823 with freon cooler at −80 °C were employed for this study, both with nitrogen gas purge. For these studies, the polystyrene was molded to a 1 mm thick sample to ensure good thermal contact with the standard aluminum DSC pan. The sample was heated from 25 to 150 °C at four different heating rates from 0.017 to 0.5 K/s (1–30 K/min) after cooling at rates ranging from 0.0017 to 0.5 K/s (0.1–30 K/min) for the DSC 1 and after cooling at a rate of 1 K/s (60 K/min) for the DSC 823. Three runs were also conducted at each heating rate to check reproducibility.

The limiting fictive temperatures were calculated from the heating scans using Moynihan's method [14] for both Flash DSC and conventional data:

$$\int_{T_{f'}}^{T \gg T_g} (C_{pl} - C_{pg})dT = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{pg})dT \quad (1)$$

where C_{pl} and C_{pg} are the liquid and glass heat capacities, C_p is the heat capacity of the sample. The methodology is illustrated in Fig. 2 for heating rates of 3000 and 0.17 K/s from Flash and conventional DSC, respectively, both obtained after cooling at 0.1 K/s. The limiting fictive temperature T_f' is determined by equating areas A_1 and A_2 as shown in Fig. 2. The glass and liquid lines for scans with a given heating rate are well superposed far from the transition in both glass and liquid region by minimizing χ^2 (shown later). This methodology reduces the error in the limiting fictive temperature calculation because it results in a consistent liquid line for the integration, and it is especially important for curves having large enthalpy overshoots, for example, on heating after a very low cooling rate [18]. When the enthalpy overshoot is large and the T_f' value is lower than the onset of devitrification, as shown for the first heat capacity curve obtained at 3000 K/s heating rate, a

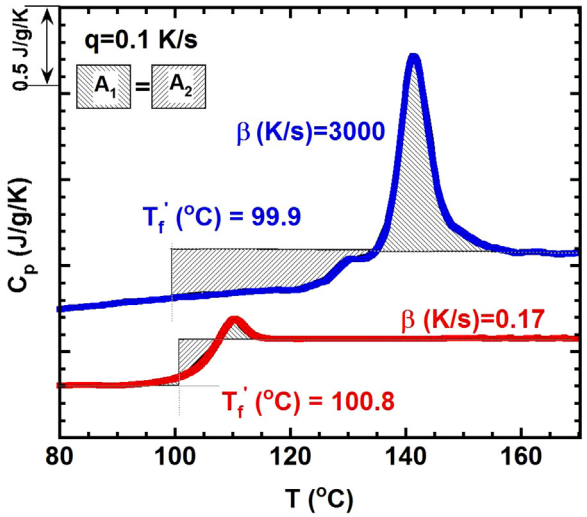

Fig. 2. Heat flow in heat capacity units for polystyrene from Flash and conventional DSC heating curves obtained at heating rates of 3000 and 0.17 K/s, respectively, after cooling at 0.1 K/s. The step change in heat capacity at 100 °C for the Flash DSC sample is assumed to be the same as that measured using conventional DSC. Curves were rotated to be horizontal in the liquid state.

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