Structural Recovery of a Single Polystyrene Thin Film using Flash DSC at Low Aging Temperatures

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Abstract

The structural recovery of a single polystyrene thin film is studied using flash differential scanning calorimetry (DSC) for aging temperatures ranging from 50.5 to 100.5 °C and for aging times of up to 18,000 s (300 min). A high fictive temperature glass with $T_f' = 117.0 \pm 0.5$ °C, obtained after cooling at 1000 K/s, is employed in this study. Structural recovery is investigated by monitoring the evolution of the fictive temperature, T_f , which initially remains unchanged and then decreases smoothly and approximately linearly with logarithmic aging time. Equilibrium is reached when $T_f = T_a$ at the highest aging temperatures. The length of the initial plateau is longer for the lower aging temperatures and is related to the increase in the relaxation time with decreasing temperature along the glass line, increasing approximately one decade for every 21 K. This temperature dependence yields a normalized apparent activation energy (E_a/R) of approximately 13 kK for the mobility along the glass line. On the other hand, the apparent activation energy for the mobility along the liquid line is 102 kK.

Introduction

Glasses evolve spontaneously toward equilibrium in a process known as structural recovery. [1-4] A good understanding of structural recovery is essential for predicting the time-dependent behavior for glassy materials, particularly if long time service is needed, for example, in the aerospace industry. The fictive temperature (T_f), first introduced by Tool, can be used to monitor the evolution of the glass structure during structural recovery. [5] Generally, the fictive temperature is measured on heating and defined as the intersection of the extrapolated liquid and glass lines. In addition, the limiting fictive temperature, [6-8] T_f' or T_{fg} , is the fictive temperature of an unaged glass, and it approximately equals the glass transition temperature, T_g . [6-8]

Most structural recovery studies in the literature [1,2,5,9-15] show that the enthalpy or the volume decreases smoothly as structural recovery proceeds until the material reaches equilibrium density, where the fictive temperature equals the aging temperature (T_a). However, several calorimetric studies report that the extrapolated liquid line is not reached when equilibrium is achieved. [16-19] Cowie and coworkers studied the structural recovery of poly(methyl methacrylate) by conventional differential scanning calorimetry (DSC) and found that the value of the enthalpy loss at equilibrium (ΔH_{∞}) obtained by fitting the Cowie-Ferguson model to the experimental data was lower than expected based on extrapolation of the liquid line; however, their model has been criticized by others. [9,10] Simon and coworkers [18] also reported that the expected liquid line is not reached at equilibrium in a germanium selenide glass system especially at high germanium content. Andreozzi et al. also reported that the extrapolated liquid line is not reached at equilibrium for a high molecular weight PMMA because of the chain entanglement and topological constraints. [19]

In addition to studies showing that the extrapolated liquid line is not reached when evolution stops, several recent studies also report that the evolution of properties is not smooth during the aging process. The work from Cangialosi et al. [20] shows an intermediate plateau at aging temperatures as high as $T_g - 6K$ for three polystyrene samples with different molecular weights, [20] and they attributed this intermediate aging plateau to the existence of two relaxation mechanisms. Furthermore, another study [21] showed that for the arsenic selenide glass system, several plateaus were observed during structural recovery over 27 years at room temperature. These two studies certainly contradict the results from the classic volume recovery experiments performed by Kovacs, [1] as well as the majority of volume and enthalpy recovery studies in which equilibrium is reached; [1,2,5,9-15] all of these latter works report a monotonically decreasing departure from equilibrium with increasing logarithm of aging time with equilibrium reached at the extrapolated liquid line. Thus, one of our aims here is to further examine this issue in structural recovery study using fast scanning calorimetry.

Although enthalpy recovery has been studied using conventional calorimetry for several decades, the method has limitations. First, the range of aging temperatures is constrained at the high end to temperatures very near or below the nominal value of the glass transition temperature (i.e., T_g as measured on cooling at 10 K/min). In addition, the initial stage of the structural recovery process has not been well investigated due to limitations of the experimental response time, which are related to the lack of sensitivity for the conventional DSC and the possible existence of thermal gradients in relatively large samples. On the other hand, Dyre and coworkers [22] successfully detected aging behavior at times as short as 0.1 s using custom-built dielectric spectroscopy with a Peltier element for rapid temperature control, but due to a limited experimental temperature window, only the linear response can be measured with that instrument.

The advantage of the flash DSC for structural recovery studies is the extended time and temperature window which allows measurements to be made at times as short as 0.01 s and at temperatures as high as 15 K above the nominal glass transition temperature. [23] In this study, we extend the aging temperatures to as low as 50 K below the nominal T_g with structural recovery behavior investigated for more than 6 decades in time. Although similar experiments could theoretically be performed in a conventional DSC, they have not been accomplished because the timescales of experiments would have to be orders of magnitude longer in order to achieve data of similar quality.

Methodology

A monodisperse polystyrene (Sigma-Aldrich, $M_n = 1,998,000$ g/mol, PDI = 1.02) was used in this study. The preparation of flash DSC sample has been described previously, [23] but pertinent details are reiterated for the sake of clarity. A film of 1.1 μm (as determined by AFM in tapping mode) was prepared by spincoating polystyrene from toluene (99.999% purity, Sigma-Aldrich) using 2.0 wt % concentration on freshly-cleaved mica substrates. The film was separated from the mica using the water floating technique and annealed 24 hours in an ambient environment followed by another 24 hours in a vacuum oven at 50 °C. A sample of $\sim 0.35 \times 0.35$ mm was cut from the film and transferred to the center of the sensor chip using a hair pen. A layer of Krytox oil (DuPontTM, $T_g = -63.2$ °C) was put between the sensor chip and the film to enhance the thermal conductivity. The polystyrene is stable in the Krytox oil based on measurements in our laboratory over the course of several months. [24,25]

A Mettler Telodo Flash DSC with freon intercooler was employed with nitrogen purge. For aging experiments, the sample was first held at 190 °C for 6 s to erase the previous thermal

history. The film was then quenched to a specified aging temperature ranging from 50.5 to 100.5 °C, aged for a specified time from 0 to 18,000 s, and then cooled to 30 °C. A subsequent heating scan from 30 to 190 °C at 600 K/s gives the scan for the aged sample, from which the fictive temperature is calculated. The sample was then cooled from 190 °C to 30 °C and heated at 600 K/s in the absence of aging to yield a scan for the unaged sample. The scan for the unaged sample provides an internal reference for the sample, and provides a long liquid line on the heating scan to ensure accuracy of the fictive temperature calculation. [26,27]

The fictive temperature, T_f , is calculated from the heating scan using Moynihan's method [28]:

$$\int_{T_f}^{T \gg T_g} (C_{pl} - C_{pg}) dT = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{pg}) dT \quad (1)$$

where C_{pl} is the liquid heat capacity, C_{pg} is the glass heat capacity, and C_p is the heat capacity of the sample. This method strongly relies on drawing an unbiased liquid line especially when a large overshoot is present. [26,27,29] Thus, each heating scan was superposed (away from the enthalpy overshoot and transition region) with the subsequent scan of an unaged sample performed on heating directly after cooling at 1000 K/s, with superposition determined by minimizing χ^2 . A consistent liquid line can then be obtained to calculate the T_f values by integration which reduces error, especially for long aging times and large enthalpy overshoots. [26,27,29] For selected aging times below 600 s, multiple runs were made for reproducibility purposes; the average difference between the fictive temperatures for different runs performed for the same aging history is less than 0.4 K and the maximum difference is 1.2 K.

The chip sensor was subjected to preconditioning and correction following the protocol provided by manufacturer. The temperature calibration was corrected by - 0.34 K after

measuring the limiting fictive temperature at cooling rates ranging from 0.1 to 1000 K/s and matching these to prior results obtained from our laboratory. [23,26,27] For those prior results, temperature had been calibrated by placing a piece of indium on the top of the sample. [23,27] For the isothermal aging temperature calibration, the melting point of indium was measured as a function of the heating rates (β); the change of the melting points then was plotted versus heating rate and fit linearly to obtain the extrapolated melting point in the isothermal condition at 0 K/s. [23,27] The aging temperatures reported are the values after the calibration, with the actual isothermal temperature being 0.5 K higher than the program temperature.

Results

Typical flash DSC heating scans as a function of aging time after isothermal aging at 100.5 °C are shown in Figure 1 (a) for the high fictive temperature glass obtained by cooling at 1000 K/s. The enthalpy overshoot shifts to higher temperatures and grows in magnitude with increasing aging time because higher temperatures are needed to regain the equilibrium liquid line as the sample's molecular mobility decreases. Even at the shortest aging time of 0.01 s, the scan for the aged sample shows discernable difference from the scan for the unaged sample, indicating that the response time of the Flash DSC is shorter than 0.01 s and that the instrument can effectively investigate aging behavior at very short aging times. At long aging times, the heating scans after isothermal aging for 6,000 s and 18,000 s superpose within experimental error, indicating that the completion of aging is achieved. In addition, the data superpose well in glass and liquid regions away from the overshoot, and this is critical for accurate calculation of the fictive temperatures. The evolution of fictive temperature calculated from heating scans of Figure 1 (a)

during aging is shown in Figure 1 (b). The fictive temperature evolves from the unaged limiting fictive temperature T_f' (117.0 °C) to the aging temperature T_a (100.5 °C).

The heating scans and corresponding fictive temperatures are plotted in Figure 2 (a) and (b) for aging at the much lower aging temperature of 60.5 °C. Here, the enthalpy overshoot remains unchanged for several decades in time before it starts to grow in magnitude and shift to higher temperatures. Thus, the fictive temperature in Figure 2 (b) shows an initial plateau where T_f is constant and equal to T_f' (117.0 °C) before it begins to decrease. Since, the Flash DSC response time is shorter than 0.01 s, this initial plateau is a measure of the relaxation time along the glass line.

The aging temperature range is extended to study the effect of aging temperature in Figure 3 where now we plot the departure from equilibrium, $T_f - T_a$, versus the logarithm of the aging time for the high fictive temperature glass. The departure from equilibrium evolves from the initial value of $T_f' - T_a$ towards zero as the aging time increases. For all aging temperatures, the evolution of departure is smooth without any intermediate plateau, the latter of which was observed by Cangialosi and coworkers for several polystyrenes near their nominal T_g . [20] At the highest aging temperature of 100.5 °C, T_f evolves to T_a within the error of the measurements, indicating that the equilibrium state is reached at long times. In addition, the times required to reach equilibrium at these temperatures are also consistent with findings from conventional DSC for polystyrene. [9,11,23]

At short aging times, an initial plateau is observed at each aging temperature in Figure 3 where no aging occurs, indicating that the instrument response time is shorter than the initial relaxation time of the sample as mentioned previously. The plateau length increases as the aging temperature decreases, indicating that the molecular mobility along the glass line at $T_f' =$

117.0 °C decreases with decreasing temperature. The length of the initial plateau is a measure of the relaxation time along the glass line. We define the induction time (t_{ind}) as the time at which the fictive temperature begins to evolve; the value of t_{ind} is obtained from the intersection of the average initial fictive temperature value with a linear fit to the data over approximately three decades after the initial drop. The induction time increases with decreasing aging temperature, consistent with other works [1,30,31], although in those works, the induction time ranges from 150 s to 1 day, whereas with the Flash DSC, the induction time ranges from 0.01 s to 5 s. It should be noted that the induction time is unrelated to the instrumental delay time (5.5 ms for the Flash DSC) and it is unrelated to the time scale for cooling both in other work [30] and in the present work (where cooling takes < 0.15 s). Indeed, an induction time is a characteristic of aging behavior [1,30-33]. The diagonal line in Figure 3 indicates the aging temperature dependence of the induction time, with a slope of approximately 21 K/decade (0.05 decade/K). This temperature dependence is related to the apparent activation energy along the glass line, i.e., at constant T_f .

The temperature dependence of the relaxation time along the glass line can also be obtained by aging time-temperature superposition of the data at constant T_f [34-36]. The reduced curve, shown in Figure 4, is obtained by shifting T_f values horizontally along the log time axis, taking 100.5 °C as a reference curve; the data at each aging temperature are well superposed. For the highest two aging temperatures, the T_f values deviate from the reduced curve at $T_f = T_a$ at long times, indicating that equilibrium is reached. The natural logarithm of the shift factors, used to reduce the data are plotted vs inverse temperature in Figure 5 to obtain the apparent activation energy along the glass line from the slope. Also shown is the natural logarithm of induction time vs reciprocal temperature. The resulting apparent activation energies (E_a/R) are 13.1 ± 0.9 kK

and 13.0 ± 0.5 kK from the aging time-temperature superposition and induction time, respectively. Our results are consistent with Struik's rule of thumb that the relaxation time along the glass line changes less than 2 to 3 orders of magnitude on decreasing temperature, [37] as well as the activation energies at constant T_f reported by McKenna [35] and Simon [36], for poly(ethylene naphthalate) and poly(ether imide) respectively, of 12.6 and 15.0 kK. In addition, E_a/R along the glass line (at constant T_f) is expected to be related to $x\Delta H/R$ in the Tool-Narayanan-Moynihan (TNM) model of structural recovery [38-40], where x is the nonlinearity parameter and $\Delta H/R$ is the apparent activation energy in the equilibrium state. Using an inflectional analysis method aimed at obtaining the parameter x , [41] Malek and coworkers also obtained a temperature dependence of the relaxation time in the glassy state for As_2Se_3 glass of $E_a/R = 23.3$ kK [42].

A relaxation map for all of the data obtained from this study and our previous study of aging at higher temperatures [23] is constructed in Figure 6. Three timescales are plotted: the time required to reach equilibrium (t_∞), the average relaxation time, and the induction time. The time required to reach equilibrium (t_∞) was obtained for each aging temperature by fitting the ($T_f - T_a$) data close to equilibrium using the Kohlrausch-William-Watts (KWW) function [43,44] and then using equation [11]:

$$t_\infty = \tau_o \left[\ln \left(\frac{T_f' - T_a}{T_{f\infty} - T_a} \right) \right]^{-\frac{1}{\beta}} \quad (2)$$

where the relaxation time τ_o and the nonexponential parameter β are the KWW fitting parameters, and $T_f' - T_a$ is the initial departure from the equilibrium temperature. The time required to reach

equilibrium t_{∞} is defined as the time when $T_f - T_a = \delta_{H\infty}/\Delta C_p = 0.035$ K, taking the enthalpy departure at equilibrium, $\delta_{H\infty} = 0.01$ J/g, as in other work [11] and the step change of heat capacity, ΔC_p , to be the fixed value of 0.29 J/(g·K) [27]. The times to reach equilibrium (t_{∞}) are shown as solid circles for data from Flash DSC. Their temperature dependence (over the temperature range where equilibrium is reached for the Flash DSC data) is well described by the William-Landel-Ferry (WLF) [45] temperature dependence found for the cooling rate dependence of T_f' [23]:

$$\log t_{\infty} = -\frac{C_1(T - T_{go})}{C_2 + (T - T_{go})} + 3.4 \quad (3)$$

where WLF constants C_1 and C_2 are 16.3 ± 2.5 and 51.4 ± 9.7 K, respectively, and $T_{go} = 374.65$ K (corresponding to reference cooling rate q_0 of 0.167 K/s). At lower temperatures, one expects that the time required to reach equilibrium will deviate from this WLF temperature dependence, as we have found in previous works [8,9,11,34,46-50].

Also plotted on the relaxation map is the average relaxation time at T_g (τ). The relationship between the average relaxation time and the cooling rate (q) can be derived from an effective time scale for cooling using time-temperature superposition ideas; i.e., the relaxation time at some reference temperature T_{ref} is related to that at temperature T by the apparent activation energy E_a in the liquid state:

$$t(T_{ref}) = t(T) \exp\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (4)$$

Using this idea, the effective time scale for cooling to T_g can be obtained by integrating over the temperature range of cooling (T_o to T_g):

$$t(T_g) = \frac{1}{q} \int_{T_o}^{T_g} \exp\left(-\frac{E_a}{R} \frac{1}{T}\right) \frac{dT}{T_g} \quad (5)$$

There is no analytical solution to the Arrhenius integral but approximation [51] gives the final result for the average relaxation time at T_g , as provided by Hodge [4]:

$$t = \frac{RT_g^2}{qE_a} \quad (6)$$

where E_a/R is the normalized activation energy in the liquid state, which is 102.4 kK at the nominal $T_g = 374.65$ K, [23] resulting in $E_a/RT_g^2 = 0.73$ (K^{-1}). Thus, one expects, $\log \tau = -\log q + 0.14$, where τ is the average relaxation time in s and q is the cooling rate in K/s. Using the WLF temperature dependence of T_g [23], we obtain:

$$\log \tau = -\frac{C_1(T - T_{go})}{C_2 + (T - T_{go})} + 0.94 \quad (7)$$

where the values of C_1 , C_2 , and T_{go} are the same as in equation 3, and constant is based on $\log \tau_o = -\log q_o + 0.14 = 0.94$ (for $q_o = 0.167$ K/s). Then comparing the two equations, we have $\log t_\infty = \log \tau + 2.46$, indicating that the time required to reach equilibrium at a given temperature is approximately two and a half orders of magnitude longer than the average relaxation time. The

difference in the average relaxation time τ and the time required to reach equilibrium t_∞ is expected to depend on the relaxation time distribution and to be greater for broader distributions.

In addition to the temperature dependence of the equilibrium relaxation time, the relaxation map also includes the induction times and shift factors obtained from the temperature-aging time superposition of T_f , i.e., the relaxation time along the glass line at constant T_f . The induction time has a weaker temperature dependence than the time scales in the liquid state (i.e., t and t_∞), as already discussed. Interestingly, the value of the induction time at an aging temperature of $T_{fo} = 117^\circ\text{C}$ is expected to be $10^{-2.5}$ s (based on extrapolation); this value can be compared to the average relaxation time τ of $10^{-2.8}$ s for the liquid state at $T = 117^\circ\text{C}$ (based on equation 5). Hence, it is suggested that the induction time at any aging temperature may be obtained from the equilibrium relaxation time at T_{fo} and the apparent activation energy along the glass line.

Conclusion

The structural recovery of a single polystyrene thin film is studied at aging temperatures from 50.5 to 100.5 $^\circ\text{C}$ using flash DSC for a high fictive temperature glass obtained after cooling at 1000 K/s. The departure from equilibrium, $(T_f - T_a)$, decreases smoothly and approximately linearly with logarithmic aging time without any evidence of intermediate plateaus. At short aging times, an initial plateau or induction time is observed, indicating that the aging times are shorter than the initial relaxation time in the glassy state. The length of the initial plateau increases with decreasing aging temperature, at a rate of 21 K/decade, indicating a normalized apparent activation energy along the glassy line of approximately $E_a/R = 13$ kK, in agreement with Struik's rule of thumb and the earlier works in the literature. In addition, the equilibrium relaxation time in the liquid state from both cooling rate dependence of T_f' and temperature

dependence of the time to reach equilibrium (t_{∞}) are obtained and yield a normalized apparent activation energy of 102 kK. Results are plotted in a relaxation map which indicates that the time required to reach equilibrium at a given aging temperature is several decades longer than the average relaxation time in the liquid state at that temperature.

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Figure Captions

Figure 1. Structural recovery at 100.5 °C for polystyrene cooling at 1000 K/s. a) The evolution of DSC heating curves as a function of aging time; b) The evolution of the fictive temperature with aging time.

Figure 2. Structural recovery at 60.5 °C for polystyrene cooling at 1000 K/s. a) The evolution of DSC heating curves as a function of aging time; b) The evolution of the fictive temperature with aging time.

Figure 3. The temperature departure from equilibrium, $T_f - T_a$, versus the logarithm of aging time as a function of aging temperatures from 50.5 to 100.5 °C for polystyrene after cooling at 1000 K/s. The dashed line shows the temperature dependence of the induction time.

Figure 4. The reduced curve obtained from temperature-aging time superposition of T_f vs $\log t$ data. The aging curve at 100.5 °C is taken as the reference curve. View in color for best clarity.

Figure 5. Arrhenius plot for a) induction time t_{ind} (●) and shift factor a_T (◆).

Figure 6. The relaxation map of polystyrene cooling at 1000 K/s showing the induction times t_{ind} (◆) and shift factors a_T (◇) versus temperature, as well as the times required to reach equilibrium t_∞ at 100.5 °C from this study and for higher temperatures from reference 23 by the Flash DSC (●). The red dashed line is the linear regression of induction times. The solid line is the WLF temperature dependence of the average relaxation time based on the cooling rate dependence of T_g from reference 23 (equation 7). The blue dashed line is the same WLF temperature dependence shifted 2.46 decades higher (equation 3).

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.