Aging of the Secondary Relaxation to Probe Structural Relaxation in the Glassy State

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The importance of glass formation and the glass transition is linked to their universality, embracing many classes of materials: metallic, inorganic, and organic. There is no agreement on what drives this phenomenon; moreover, experiments are challenging due to the nonequilibrium nature of the glassy state. We present a new approach that provides information about the very slow structural relaxation in the glassy state and reveals the important role of the secondary relaxation. Structural (α) relaxation times for glassy polyvinylethylene were determined from changes in the properties of the secondary process during physical aging. These α-relaxation times exceed 3 years, making them inaccessible via direct measurement.

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Despite the long history of glass making, the underlying physics remains an unsolved problem, without any consensus on the microscopic origin of the slowing of the dynamics during supercooling. Time constants of liquids increase by ten decades or more, culminating in the glassy state. The nonequilibrium nature of the glass presents special difficulties, since the physical properties depend on the thermodynamic path and also change during physical aging (the slow evolution of the glass toward equilibrium). Different cooling rates or formation pressures result in glasses with different properties [1], with subsequent aging times varying from seconds to many centuries. Aging is also a practical issue for thermoplastic polymers since it can cause properties to vary over their service life.

The temperature dependence of the structural dynamics can be described by a diverging equation such as the Vogel-Fulcher-Tamman (VFT) relation [2]:

$$\tau_\alpha(T) = \tau_\infty \exp\left[\frac{B}{T - T_0}\right], \tag{1}$$

where τ_∞, the high temperature limit of the α-relaxation time τ_α, T_0, the Vogel temperature, and B are all constants. In the glassy state τ_α is sometimes smaller than expected from Eq. (1) [3–5]. An equation proposed for the glassy dynamics is [6]

$$\tau_\alpha(T, T_f) = \tau_\infty \exp\left[\frac{B}{T(1 - T_0/T_f)}\right], \tag{2}$$

where B, τ_∞, and T_0 are the same liquid-state VFT parameters, and T_f is the fictive temperature, defined as the temperature at which the observed nonequilibrium properties would be the equilibrium values; at equilibrium $T_f = T$. Sufficiently below the glass transition temperature, T_f becomes constant and Eq. (2) assumes the Arrhenius form, $\tau_\alpha(T, T_f) = \tau_\infty \exp[E_\alpha(T_f)/T]$ with the activation enthalpy $E_\alpha = RB/(1 - T_0/T_f)$, where R is the gas constant [7]. Equation (2) equates to an equation [8,9] commonly used to describe the dynamics of glasses [10].

Since many physical properties are affected by glass formation, many techniques are used to study it; however, only a few can follow the dynamics over a broad frequency range. One such method is dielectric spectroscopy (DS), which can cover more than 10 decades. Most DS studies of physical aging involved measurement of the α relaxation close to the glass transition [11–21]; a few measured the effect of aging on secondary relaxations below T_g [22,23]. In this work, we employ a different approach in which the behavior of the secondary process below T_g is used to probe the otherwise inaccessible α process. This is somewhat similar to the method proposed by Lunkenheimer *et al.* [14,24,25]; however, their study was limited to measurements of the equilibrium liquid. They found that τ_α was in good agreement with a VFT fit to data obtained well above T_g. Since these experiments [14,24,25] were carried out in the vicinity of T_g [$\tau_\alpha(T_g) = 10^2$ s], there was some overlap of the α and secondary relaxations. As a result, the observed changes in permittivity were due largely to a decrease in amplitude and a shift of the α peak to lower frequency during aging. In the experimental conditions of our work, the permittivity of 1 polybutadiene (or polyvinylethylene, PVE) is unaffected by changes in the α relaxation, since the two processes are well separated at temperatures below $T_g (= 271.7$ K).

The permittivity was measured using an Andeen Hagerling 2700A able to measure loss tangents as low as 1.5×10^{-8}. The sample was contained between two gold-coated metal plates (without spacers to allow dimensional changes during aging). The capacitor assembly was kept under a vacuum in a helium cryostat, with temperature stability better than 0.2 K over the duration of the experiments. Figure 1 shows ε'' at $T = 256.3$ K at different aging times for PVE cooled from above T_g at a constant rate of 2 K/min. Note that only the β relaxation is present in

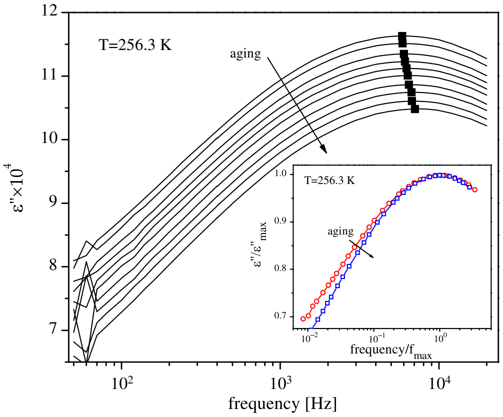

FIG. 1 (color online). Dielectric loss spectra of PVE at $T = 256.3$ K for different aging times up to over 11 days (lowest curve). The sample had been cooled from above T_g at 2 K/ min. During aging the amplitude of the loss decreases and the peak frequency, $1/2\pi\tau_\alpha$, (solid squares) increases. In the insert are the spectra for the shortest and longest t_{ag} superposed to show the narrowing (on both sides of the peak) with aging.

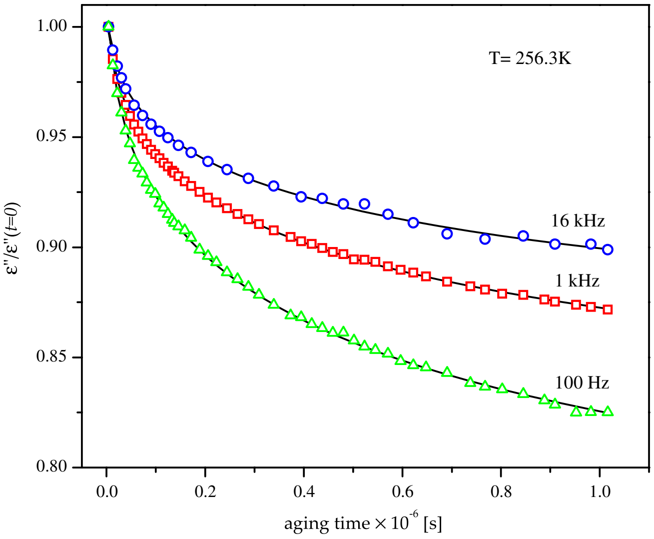

FIG. 2 (color online). Dielectric loss vs aging time for three different frequencies. The ordinate values are normalized by the loss at $t_{ag} = 0$. The decrease of ε'' was fit to Eq. (3) (solid lines). All three curves can be described with the same time constant; i.e., τ_{ag} is independent of the chosen frequency, since the dominant effect is the decrease of the β-relaxation intensity.

these spectra. During aging the β relaxation decreases in amplitude and moves to higher frequency (the maximum of the peak is denoted with a solid symbol). The β peak becomes narrower on both the high and low frequency sides, as shown in the insert to Fig. 1. Similar results have been reported for molecular glass formers [22,23,26]. The anomalous speeding up of the β relaxation during aging is the subject of a recent publication, in which the effect of different routes to vitrification was discussed in terms of the changes in the distribution of the local (microscopic) density [27]. We argued therein that the aging behavior can be interpreted in terms of a decrease of the local density fluctuations, which governs the amplitude of the Johari–Goldstein (JG) motion (i.e., the average angle of orientation). These changes can be rationalized in terms of the change of the local potential.

The focus of this Letter is the variation at a fixed frequency of the permittivity with aging time t_{ag}. From the data in Fig. 1, it is evident that the major effect of aging on the β relaxation is a change of amplitude. Figure 2 shows the dielectric loss $\varepsilon''(\tilde{f}, t_{ag})$ at three fixed frequencies $\tilde{f}$ (above and below f_{max}) as a function of aging time, each normalized by the initial values $\varepsilon''(\tilde{f}, t_{ag} = 0)$. The $\varepsilon''(\tilde{f}, t_{ag})$ clearly deviate from simple exponential decay; we find that a stretched exponential function gives a good description of the data:

$$\frac{\varepsilon''(\tilde{f}, t_{ag})}{\varepsilon''(\tilde{f}, t_{ag}=0)} = \left\{\Delta\varepsilon''(\tilde{f}, t_{ag})\exp\left[-\left(\frac{t_{ag}}{\tau_{ag}}\right)^{\beta_{ag}}\right] + \varepsilon''_{eq}(\tilde{f})\right\}\Big/\varepsilon''(\tilde{f}, t_{ag}=0), \tag{3}$$

where $\varepsilon''_{eq}(\tilde{f}) \equiv \varepsilon''(\tilde{f}, t_{ag} \to \infty)$ is the equilibrium value, $\Delta\varepsilon''(\tilde{f}, t_{ag})$ is the change in ε'' during the aging $(=\varepsilon''(\tilde{f}, t_{ag} = 0) - \varepsilon''_{eq}(\tilde{f}))$, β_{ag} is the stretching exponent, and τ_{ag} is the aging (or decay) time constant. This function is very similar to that used by Leheny and Nagel [11]. The best fits of Eq. (3) are displayed in Fig. 2 as solid lines, with the fitting done simultaneously using a single value of the parameter τ_{ag} for the three sets of data. The stretching exponent was fixed at $\beta_{ag} = 0.4$, as determined from measurement of the shape of the α-relaxation function close to T_g. This assumption of constant β_{ag} stems from the idea that the evolution towards equilibrium is driven by structural relaxation, with the following general behavior of the equilibrium stretch exponent β_{KWW}: At high temperatures with $\tau_\alpha \le 10^{-9}$ s, β_{KWW} is close to unity (exponential decay). On lowering the temperature so that $\tau_\alpha \sim 10^{-6}$ s, β_{KWW} markedly decreases, attaining an almost constant value in the range $\tau_\alpha > 1$ s [28–31]. Thus, we assume that $\beta_{ag}(T < T_g) = \beta_{KWW}(T_g) = 0.4$. Since all three sets of data in Fig. 2 can be described by the same τ_{ag}, our analysis is independent of the chosen frequency. This supports the idea that spectral changes due to a direct contribution from the α process (which would be larger at lower frequency) are minimal.

Aging experiments were performed for different temperatures in the glassy state, with similar changes in the permittivity observed. For example, in Fig. 3 $\varepsilon''(\tilde{f}, t_{ag})$ at a fixed $\tilde{f} = 1$ kHz is plotted for five different temperatures.

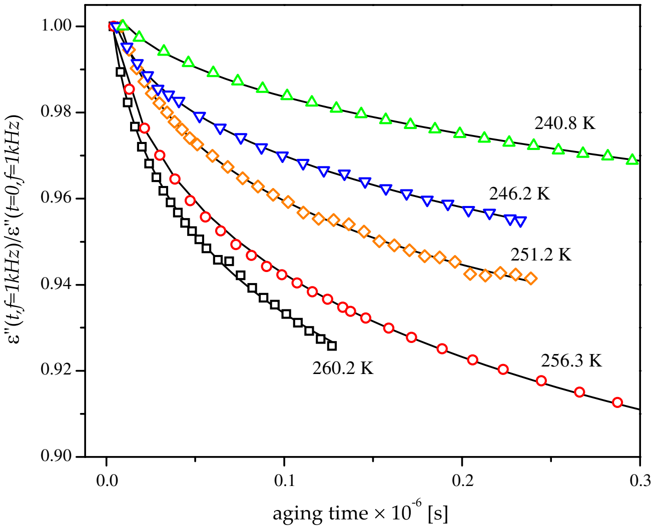

FIG. 3 (color online). Dielectric loss at $f = 1$ kHz vs aging time for PVE at five temperatures. The ordinate values are normalized to the value at $t_{ag} = 0$. The solid line is the fit to Eq. (3). τ_{ag} increases with the decrease of aging temperature; the values of τ_{ag} are shown in Fig. 4.

It is evident that at higher T the evolution towards equilibrium is faster. The solid lines are the best fits to Eq. (3) again using $\beta_{ag} = 0.4$. The values of the decay time τ_{ag} versus inverse temperature are shown in Fig. 4 (solid triangles). These τ_{ag} are much larger than τ_α measured above the glass transition and exhibit Arrhenius behavior with an activation energy smaller than that of the α relaxation at T_g. Figure 4 also shows the fit of eq. (1) to the τ_α data (fit parameters given in the caption). Using the same VFT parameters determined for τ_α in Eq. (2) (dotted line), we fit the τ_{ag} data to obtain $T_f = 267.0 \pm 0.3$ K. The behavior of τ_{ag} is therefore consistent with its identification with τ_α in the glassy state. Thus, from the change of the β relaxation with physical aging we can characterize the structural relaxation dynamics, which are too slow for direct measurement. In a previous study of physical aging by Lunkenheimer *et al.* (Ref. [14]) it was found that Eq. (3) could not describe the time dependence of $\varepsilon''(\tilde{f}, t_{ag})$ for a similar set of data just below T_g. This was attributed to the expected change of τ_{ag} during the evolution towards equilibrium (in the range of $t_{ag} = 10^2$ to 10^6 s, they found about an order of magnitude change of τ_{ag}). This issue is more significant for aging temperatures closer to T_g, where the structure of the glass becomes strongly dependent on the aging time. Although a similar evolution of τ_{ag} presumably occurs in the present case, Eq. (3) still holds because deep in the glassy state the evolution of the system is very slow. (Note that we did not sample the very short times $t_{ag} < 10^4$ s, in which the changes in τ_{ag} might no longer be negligible.) Since the same experimental protocol was used to reach the various aging temperatures well below T_g, we can assume that we are studying a glass with a given, fixed structure, consistent with the observed constant T_f [7]. Therefore, although the determined τ_{ag} do not necessarily represent equilibrium τ_α, they are isostructural values. As a test of the validity of the assumption that τ_{ag} does not appreciably change during our aging experiments, we analyzed a single curve by simultaneously fitting Eq. (3) to four different time intervals (overlapped and covering the entire range). All the parameters were taken as common for the four data sets with the exception of τ_{ag}, which was allowed to vary independently. We found that the values of τ_{ag} for the different time intervals were equivalent within the experimental error, thus confirming our assumption.

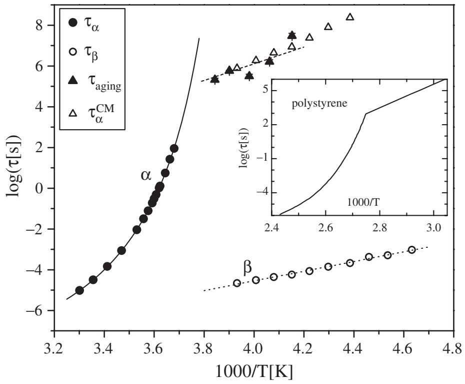

FIG. 4. Relaxation times for the α and β processes, along with the aging decay time τ_{ag} and the τ_α calculated from τ_α^{CM}. τ_{ag} has the same behavior as τ_α^{CM}, consistent with the former being a measure of τ_α in the glassy state. The solid line is a fit to Eq. (1) of τ_α using $\log(\tau_\infty) = -10.3 \pm 0.1$, $T_0 = 248.0 \pm 0.3$ K, and $B = 672 \pm 16$ K. The dotted line is the fit to Eq. (2) of the τ_{ag} for $T_f = 267.0 \pm 0.3$ K, with the other parameters fixed to their values for the VFT fit of τ_α. The dotted line is the fit of τ_β to the Arrhenius equation, with $E_\beta = 45.6 \pm 1.2$ kJ mol^{-1} and $\log(\tau_{\infty\beta}/\mathrm{s}) = -14.1 \pm 0.3$. The inset shows τ_α for polystyrene in the equilibrium liquid and glassy states (T_g indicated by the large change in slope), the latter determined from the intensity of second harmonic generation from chromophores within the polystyrene [5].

Since the only group pendant to the chain backbone of PVE is the short, inflexible vinyl moiety, the β relaxation must originate with α motion of the main chain segments (i.e., it is coupled to the conformational transitions of the chain backbone and does not involve any independent side-group motion). This type of relaxation is commonly referred as a JG process, in recognition of the pioneering work of Johari and Goldstein [32]. More recently a correlation between the JG secondary relaxation and the α relaxation has been reported [33,34]. Specifically, the separation in time between the two processes is of the same order as the separation between τ_α and the primitive (noncooperative) relaxation time τ_0 of the coupling model [35]. The latter is related to the stretch exponent β_{KWW} for the α

process according to

$$\tau_0 = \tau_\alpha{}^{\beta_{\mathrm{KWW}}} t_c{}^{1-\beta_{\mathrm{KWW}}}, \tag{4}$$

where t_c is a characteristic time (~2 ps) associated with the onset of strong intermolecular cooperativity. This correlation in turn implies that

$$\tau_\beta \cong \tau_0 \tag{5}$$

suggesting that the JG type β process functions as the precursor to the structural α relaxation. Using Eqs. (4) and (5), it is possible to predict τ_α from τ_β in the glassy state.

The τ_β and the values of the α-relaxation time calculated from the coupling model, $\tau_\alpha^{\mathrm{CM}}$, are displayed in Fig. 4, together with the experimentally measured τ_α. In the calculation, we assumed that β_{KWW} retains the value for the loss peak at T_g, $\beta_{\mathrm{KWW}} = 0.4$; as discussed above, this choice is consistent with the idea that $\beta_{\mathrm{ag}} \cong \beta_{\mathrm{KWW}}$. It can be seen that both the absolute values and the temperature dependence of $\tau_\alpha^{\mathrm{CM}}$ are in good agreement with the aging data [τ_{ag} from Eq. (3)]. These results suggest that the aging time scale is determined by structural relaxation (viz. $\tau_{\mathrm{ag}} \sim \tau_\alpha$); consequently, it is possible to use the JG relaxation as a probe of the structural dynamics in the glassy state, which otherwise is inaccessible given the magnitude of τ_α at temperatures even moderately below T_g.

The general pattern of τ_α for PVE is reproduced in prior results for polystyrene (Fig. 4 inset). These were obtained above and below T_g, the latter from the intensity of second harmonic generation from chromophores embedded in the polystyrene [5]. The VFT behavior at high temperatures changes to an Arrhenius-like response below T_g. The correspondence between the two experiments corroborates the use of aging-induced changes in the JG relaxation to follow the structural dynamics in the glassy state. The present approach has the advantage of obviating the need for adulteration of the polymer with a chromophoric dopant, thus offering a relatively simple approach to study the glassy state using DS. Our work showing that a correlation between the α and JG relaxations persists even in the glassy state confirms the importance of the JG process, supporting the view that it functions as the precursor of structural relaxation.

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