

## 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 ( $\alpha$ ) relaxation times for glassy polyvinylethylene were determined from changes in the properties of the secondary process during physical aging. These  $\alpha$ -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]:

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

where  $\tau_{\infty}$ , the high temperature limit of the  $\alpha$ -relaxation time  $\tau_{\alpha}$ ,  $T_0$ , the Vogel temperature, and  $B$  are all constants. In the glassy state  $\tau_{\alpha}$  is sometimes smaller than expected from Eq. (1) [3–5]. An equation proposed for the glassy dynamics is [6]

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

where  $B$ ,  $\tau_{\infty}$ , 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  $\alpha$  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  $\alpha$  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  $\tau_{\alpha}$  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  $\alpha$  and secondary relaxations. As a result, the observed changes in permittivity were due largely to a decrease in amplitude and a shift of the  $\alpha$  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  $\alpha$  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  $1.5 \times 10^{-8}$ . 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  $\epsilon''$  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  $\beta$  relaxation is present in

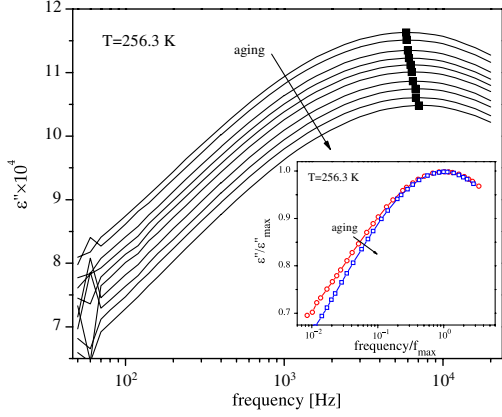


FIG. 1 (color online). Dielectric loss spectra of PVE at  $T = 256.3$  K for different aging times up to over 11 days (lowest curve). The sample had been cooled from above  $T_g$  at 2 K/min. During aging the amplitude of the loss decreases and the peak frequency,  $1/2\pi\tau_\alpha$ , (solid squares) 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.

these spectra. During aging the  $\beta$  relaxation decreases in amplitude and moves to higher frequency (the maximum of the peak is denoted with a solid symbol). The  $\beta$  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  $\beta$  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

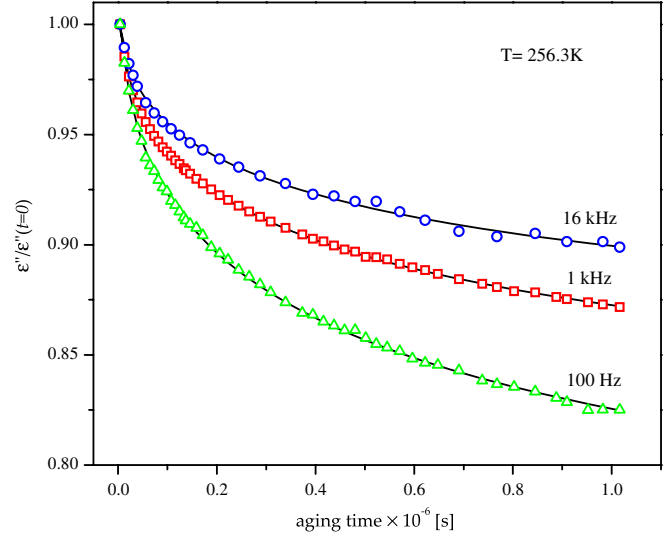


FIG. 2 (color online). Dielectric loss vs aging time for three different frequencies. The ordinate values are normalized by the loss at  $t_{ag} = 0$ . The decrease of  $\varepsilon''$  was fit to Eq. (3) (solid lines). All three curves can be described with the same time constant; i.e.,  $\tau_{ag}$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

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  $\beta$  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:

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

where  $\varepsilon''_{eq}(\tilde{f}) \equiv \varepsilon''(\tilde{f}, t_{ag} \rightarrow \infty)$  is the equilibrium value,  $\Delta\varepsilon''(\tilde{f}, t_{ag})$  is the change in  $\varepsilon''$  during the aging ( $=\varepsilon''(\tilde{f}, t_{ag} = 0) - \varepsilon''_{eq}(\tilde{f})$ ),  $\beta_{ag}$  is the stretching exponent, and  $\tau_{ag}$  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  $\tau_{ag}$  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  $\alpha$ -relaxation function close to  $T_g$ . This assumption of constant  $\beta_{ag}$  stems from the idea that the evolution towards equilibrium is driven by structural relaxation, with the following general behavior of the equilibrium stretch exponent  $\beta_{KWW}$ : At high tem-

peratures with  $\tau_\alpha \leq 10^{-9}$  s,  $\beta_{KWW}$  is close to unity (exponential decay). On lowering the temperature so that  $\tau_\alpha \sim 10^{-6}$  s,  $\beta_{KWW}$  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  $\tau_{ag}$ , our analysis is independent of the chosen frequency. This supports the idea that spectral changes due to a direct contribution from the  $\alpha$  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.

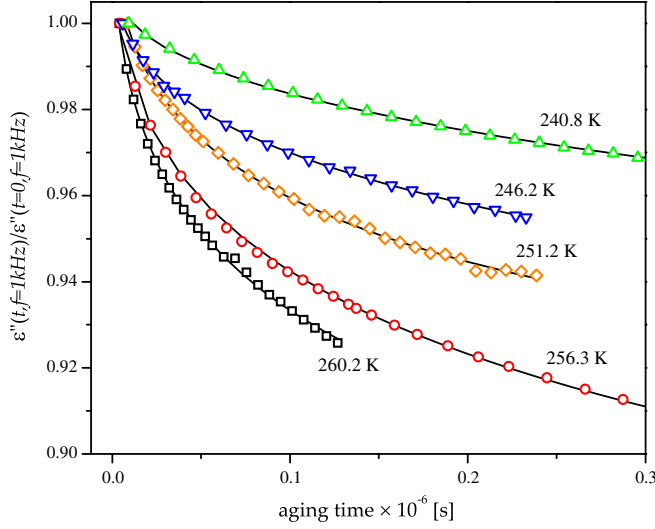


FIG. 3 (color online). Dielectric loss at  $f = 1$  kHz vs aging time for PVE at five temperatures. The ordinate values are normalized to the value at  $t_{\text{ag}} = 0$ . The solid line is the fit to Eq. (3).  $\tau_{\text{ag}}$  increases with the decrease of aging temperature; the values of  $\tau_{\text{ag}}$  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  $\beta_{\text{ag}} = 0.4$ . The values of the decay time  $\tau_{\text{ag}}$  versus inverse temperature are shown in Fig. 4 (solid triangles). These  $\tau_{\text{ag}}$  are much larger than  $\tau_{\alpha}$  measured

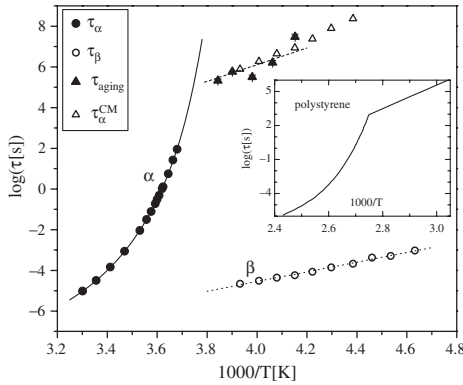


FIG. 4. Relaxation times for the  $\alpha$  and  $\beta$  processes, along with the aging decay time  $\tau_{\text{ag}}$  and the  $\tau_{\alpha}$  calculated from  $\tau_{\alpha}^{\text{CM}}$ .  $\tau_{\text{ag}}$  has the same behavior as  $\tau_{\alpha}^{\text{CM}}$ , consistent with the former being a measure of  $\tau_{\alpha}$  in the glassy state. The solid line is a fit to Eq. (1) of  $\tau_{\alpha}$  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  $\tau_{\text{ag}}$  for  $T_f = 267.0 \pm 0.3$  K, with the other parameters fixed to their values for the VFT fit of  $\tau_{\alpha}$ . The dotted line is the fit of  $\tau_{\beta}$  to the Arrhenius equation, with  $E_{\beta} = 45.6 \pm 1.2$  kJ mol $^{-1}$  and  $\log(\tau_{\infty\beta}/\text{s}) = -14.1 \pm 0.3$ . The inset shows  $\tau_{\alpha}$  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].

above the glass transition and exhibit Arrhenius behavior with an activation energy smaller than that of the  $\alpha$  relaxation at  $T_g$ . Figure 4 also shows the fit of eq. (1) to the  $\tau_{\alpha}$  data (fit parameters given in the caption). Using the same VFT parameters determined for  $\tau_{\alpha}$  in Eq. (2) (dotted line), we fit the  $\tau_{\text{ag}}$  data to obtain  $T_f = 267.0 \pm 0.3$  K. The behavior of  $\tau_{\text{ag}}$  is therefore consistent with its identification with  $\tau_{\alpha}$  in the glassy state. Thus, from the change of the  $\beta$  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  $\varepsilon''(\tilde{f}, t_{\text{ag}})$  for a similar set of data just below  $T_g$ . This was attributed to the expected change of  $\tau_{\text{ag}}$  during the evolution towards equilibrium (in the range of  $t_{\text{ag}} = 10^2$  to  $10^6$  s, they found about an order of magnitude change of  $\tau_{\text{ag}}$ ). 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  $\tau_{\text{ag}}$  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  $t_{\text{ag}} < 10^4$  s, in which the changes in  $\tau_{\text{ag}}$  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  $\tau_{\text{ag}}$  do not necessarily represent equilibrium  $\tau_{\alpha}$ , they are isostructural values. As a test of the validity of the assumption that  $\tau_{\text{ag}}$  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  $\tau_{\text{ag}}$ , which was allowed to vary independently. We found that the values of  $\tau_{\text{ag}}$  for the different time intervals were equivalent within the experimental error, thus confirming our assumption.

Since the only group pendant to the chain backbone of PVE is the short, inflexible vinyl moiety, the  $\beta$  relaxation must originate with  $\alpha$  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  $\alpha$  relaxation has been reported [33,34]. Specifically, the separation in time between the two processes is of the same order as the separation between  $\tau_{\alpha}$  and the primitive (non-cooperative) relaxation time  $\tau_0$  of the coupling model [35]. The latter is related to the stretch exponent  $\beta_{\text{KWW}}$  for the  $\alpha$

process according to

$$\tau_0 = \tau_\alpha \beta_{\text{KWW}} t_c^{1-\beta_{\text{KWW}}}, \quad (4)$$

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

$$\tau_\beta \cong \tau_0 \quad (5)$$

suggesting that the JG type  $\beta$  process functions as the precursor to the structural  $\alpha$  relaxation. Using Eqs. (4) and (5), it is possible to predict  $\tau_\alpha$  from  $\tau_\beta$  in the glassy state.

The  $\tau_\beta$  and the values of the  $\alpha$ -relaxation time calculated from the coupling model,  $\tau_\alpha^{\text{CM}}$ , are displayed in Fig. 4, together with the experimentally measured  $\tau_\alpha$ . In the calculation, we assumed that  $\beta_{\text{KWW}}$  retains the value for the loss peak at  $T_g$ ,  $\beta_{\text{KWW}} = 0.4$ ; as discussed above, this choice is consistent with the idea that  $\beta_{\text{ag}} \cong \beta_{\text{KWW}}$ . It can be seen that both the absolute values and the temperature dependence of  $\tau_\alpha^{\text{CM}}$  are in good agreement with the aging data [ $\tau_{\text{ag}}$  from Eq. (3)]. These results suggest that the aging time scale is determined by structural relaxation (viz.  $\tau_{\text{ag}} \sim \tau_\alpha$ ); 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  $\tau_\alpha$  at temperatures even moderately below  $T_g$ .

The general pattern of  $\tau_\alpha$  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  $\alpha$  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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