

Communication: Effect of density on the physical aging of pressure-densified polymethylmethacrylate

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(Received 12 July 2017; accepted 23 August 2017; published online 6 September 2017)

The rate of physical aging of glassy polymethylmethacrylate (PMMA), followed from the change in the secondary relaxation with aging, is found to be independent of the density, the latter controlled by the pressure during glass formation. Thus, the aging behavior of the secondary relaxation is the same whether the glass is more compacted or less dense than the corresponding equilibrium liquid. This equivalence in aging of glasses formed under different pressures indicates that local packing is the dominant variable governing the glassy dynamics. The fact that pressure densification yields different glass structures is at odds with a model for non-associated materials having dynamic properties exhibited by PMMA, such as density scaling of the relaxation time and isochronal superposition of the relaxation dispersion. [<http://dx.doi.org/10.1063/1.4995567>]

The properties of liquids cannot be completely characterized without measurements of their dependence on both pressure and temperature, and in particular, the behavior under pressure has provided many insights into the phenomena associated with glass formation.¹ A prominent example is the correlation of various properties with the time scale of molecular motions, as observed under isochronal conditions. In these studies, the primary relaxation time, τ_α , is maintained constant through simultaneous control of pressure and temperature,² with consequent invariance for many liquids of the dynamic correlation length,^{3,4} the shape of the relaxation dispersion (“isochronal superpositioning”),^{5,6} the dynamic crossover,^{7,8} and for a few cases, the melting line.⁹ An interpretation of isochronal invariance of properties comes from molecular dynamics (MD) simulations, which have shown that for a certain class of materials, the behavior, including τ , is governed by the existence of isomorphs.^{10–12} Isomorphs are state points for which various properties are constant in reduced units. In MD simulations, isomorphs are identified from correlation between equilibrium fluctuations of the virial pressure and the potential energy.¹³ The usual experimental manifestations of isomorph state points are isochronal superpositioning,^{5,6} expressed as invariance of the Kohlrausch stretch exponent at constant relaxation time

$$\beta = f(\tau), \quad (1)$$

in which f is a function, and the density scaling relation (Ref. 1 and the references therein)

$$\tau = g(TV^\gamma), \quad (2)$$

in which V is the specific volume, γ is a material constant, and g is a function. All non-associated liquids and polymers tested to date conform to Eqs. (1) and (2).^{1,14}

A property predicted for materials having isomorphs that has not received experimental attention concerns the behavior

in the glassy state. Isomorph theory predicts that for a jump of the equilibrium liquid to an out-of-equilibrium glass, the effective (fictive) temperature depends only on the final density.¹⁵ Moreover, since the pressure-dependent glass transition temperature is an isomorph state point,¹² a transition to any common state point (same T and P) is predicted to yield identical behavior. Thus, the density and ensuing physical aging of an isomorph material are expected to be independent of the pressure during vitrification.¹⁶ This includes forming a glass by application of pressure to the equilibrium liquid (a process referred to as “pressure densification”^{17,18}); isomorph liquids cannot be pressure densified.

In this paper, we describe measurements on a low molecular weight polymethylmethacrylate (PMMA), a polymer that exhibits isochronal superpositioning [Eq. (1)] and conforms to density scaling [Eq. (2) with $\gamma = 1.9$].¹⁹ Since these are properties of isomorph materials, the expectation is that the structure and behavior of glassy PMMA should be independent of the pressure during glass formation, that is, it cannot be pressure densified. We find this not to be the case—the density of the glass is an increasing function of the pressure applied to the liquid while forming the glass. Depending on the magnitude of the vitrification pressure, we obtain (after release of the pressure) glassy PMMA that is either less than, equal to, or more dense than the corresponding liquid. This means that physical aging involves either negative, zero, or positive changes in mean volume as the glass evolves to equilibrium; however, the dielectric strength and relaxation time of the secondary dynamics decrease during aging, irrespective of the sign or magnitude of the volume change. Evidently, the properties of the secondary relaxation do not depend on the average density.

The oligomeric PMMA ($M_w = 1970$ D; polydispersity = 1.15) was purchased from Polymer Standards Service and used as received. The dielectric permittivity was measured with a Novocontrol Alpha analyzer. The sample cell consisted of two parallel plates with a 55 mm Teflon spacer (geometric capacitance = 30.4 pF), encapsulated in a flexible barrier to

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isolate it from the pressure transmitting fluid (silicon oil). The apparatus for dielectric measurements was a high pressure vessel from Harwood, Inc., containing the dielectric cell surrounded by the pressurizing fluid; an environmental chamber (Tenney, Inc.) for temperature control; and a hydraulic system to generate the pressure. The last consisted of two pumps (Superpressure and Enerpac from Newport Scientific), in combination with an intensifier (Harwood Eng.), which enabled pressures up to 1.4 GPa. The pressure was measured with both a transducer (Sensotec) and a pressure gauge (Heise).

Pressure-volume-temperature (PVT) measurements were carried out using a Gnomix apparatus, on a $\sim 1 \text{ cm}^3$ cylindrical sample formed under vacuum. Temperature was changed at a rate of 0.5 K/min. After pressure changes, data collection commenced within several minutes after the sample temperature stabilized.

The pressure densification method consists of applying pressure to the equilibrium liquid, followed by cooling through the glass transition temperature. The pressure on the glass is then released, so that the temperature and pressure of the material are the same as for the material cooled through T_g at low pressure. Invariably the former is found to have higher density,¹⁷ with a metric for the pressure densification defined from the relative volume change¹⁶

$$\delta = \frac{V_N(P_0) - V_D(P_0)}{V_N(P_0) - V_D(P_1)} \quad (3)$$

in which V_N and V_D are the specific volumes for respective vitrification at low (P_0) and high (P_1) pressures. Representative results for PMMA are shown in Fig. 1. Note that after release of the pressure, the glass prepared at 200 MPa has a specific volume that is equal to or less than the value for the extrapolated liquid, depending on temperature. This is contrary to the glass prepared at low pressure, which is less dense. Pressure densification also broadens the glass transition toward lower temperature, consistent with a more disordered structure.

As seen in Fig. 2, the density is an increasing function of the pressure during glass formation. At the highest vitrification pressure, the glass is 2% denser than when formed at the lowest P . After release of the pressure, the volume increases but the material remains significantly denser than the ordinary glass, that is, $\delta > 0$ (Fig. 1). Over the range of vitrification pressures herein (25–200 MPa), δ varied from $\sim 6\%$ to 29%, which falls in the range of literature results for other polymers.^{20–22} That PMMA can be pressure densified is at odds with its conformance to isochronal superpositioning [Eq. (1)] and density scaling [Eq. (2)].¹⁹

The practical motivation for pressure densification is the expectation that properties can be obtained that will differ from those of an ordinary glass. For example, it has been shown that the mechanical modulus²³ and yield strength,²⁴ as well as the structure seen in small angle X-ray scattering,²⁵ are affected by the pressure during glass formation. In this work, the property of interest is the structural relaxation time, which generally is too long below T_g to be measured directly. However, we have shown that the changes in the Johari-Goldstein (JG) secondary

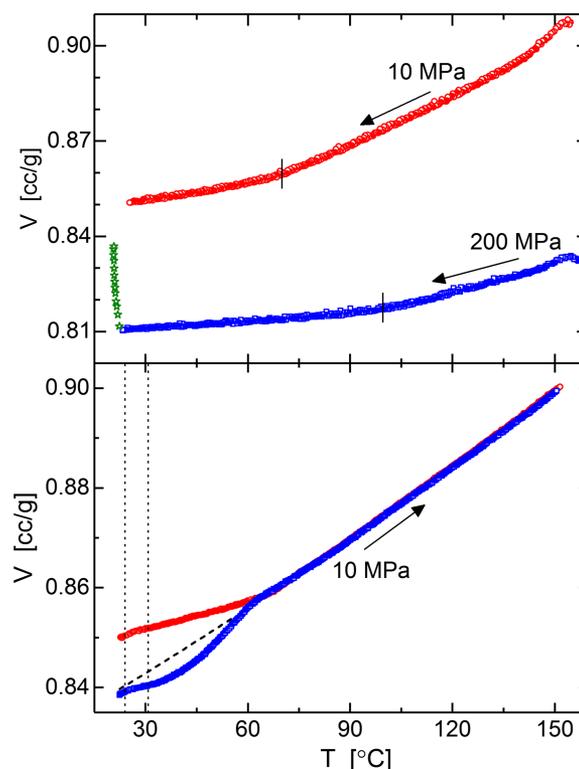


FIG. 1. (Upper panel) Specific volume during cooling at low and high pressures; vertical data (stars) measured after reduction of pressure from 200 to 10 MPa. Vertical tic marks denote the glass transition temperature. (Lower) Subsequent heating curves at low pressure. Dashed line is the extrapolation of the specific volume for the equilibrium liquid. Vertical dotted lines signify the temperatures at which the low pressure, physical aging was carried out.

relaxation are governed by τ_α .²⁶ Thus, as aging proceeds, the JG relaxation time, τ_{JG} , decreases, with a concomitant reduction in dielectric strength, $\Delta\epsilon_{JG}$. The assumption of the analysis is that physical aging governs these changes, which occur on a time scale corresponding to τ_α .

Figure 3 shows fits of stretched exponential decay functions

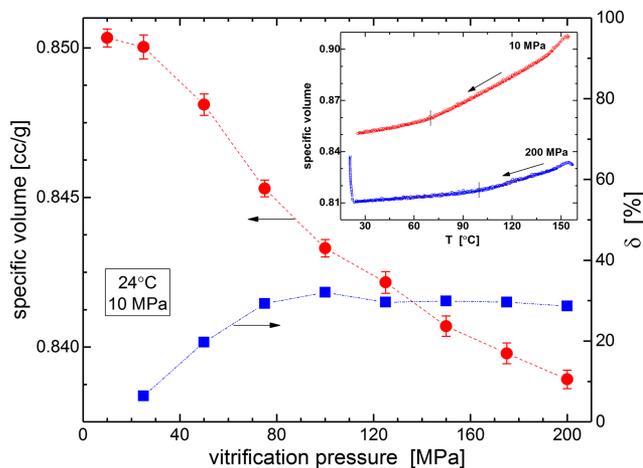


FIG. 2. Specific volume (circles) and degree of pressure densification (squares) for PMMA measured at the indicated temperature and pressure as a function of the pressure during cooling from the liquid state.

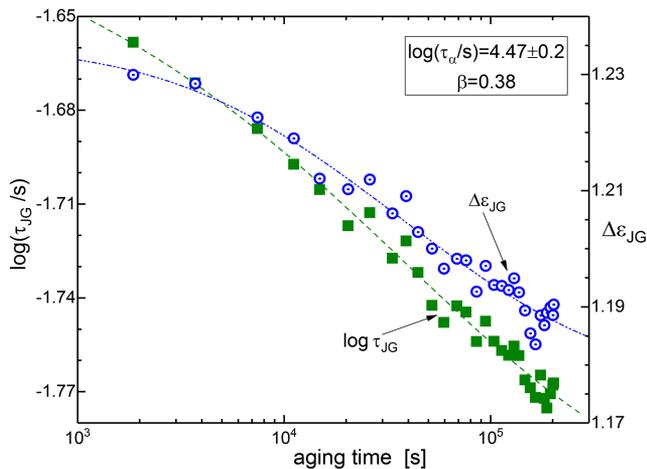


FIG. 3. Change in the JG relaxation time and dielectric strength during physical aging of glassy PMMA formed at 188 MPa. The curves are fits to Eqs. (4) and (5), respectively, using the Kohlrausch exponent measured at T_g and yielding the indicated value of the structural relaxation time.

$$\tau_{JG}(t) = \tau_{eq}^{\infty} + A \left(\exp[-t/\tau_{\alpha}]^{\beta} \right) \quad (4)$$

and

$$\Delta\epsilon_{JG}(t) = \Delta\epsilon_{eq}^{\infty} + B \left(\exp[-t/\tau_{\alpha}]^{\beta} \right) \quad (5)$$

to the respective relaxation time and dielectric strength of the JG relaxation. Here τ_{eq}^{∞} , A , $\Delta\epsilon_{eq}^{\infty}$, and B are constants. For the stretch exponent, we take the value measured at T_g (i.e., for the equilibrium liquid), $\beta = 0.38$. As an isolated variable, the densification during physical aging should increase the relaxation time (greater congestion) and the dielectric strength (more dipoles per unit volume). The opposite results reflect the influence that other factors, in particular structure and entropy, exert on the JG dynamics.^{27,28}

From the fits, we obtain the α relaxation times shown in Fig. 4. This Arrhenius plot includes data for the equilibrium liquid.²⁹ These τ_{α} can be described using an equation from the work of Hodge³⁰

$$\tau_{\alpha}(T) = \tau_{\infty} \exp \left[\frac{B}{T(1 - T_0/T_f)} \right]. \quad (6)$$

In applying Eq. (6), the fictive temperature T_f is set to unity above T_g and then becomes an adjustable parameter for fitting relaxation times in the glass. The parameters obtained for PMMA were $\log(\tau_{\infty}/s) = 10.61 \pm 0.7$, $B = 1500 \pm 200$ K, $T_0 = 291 \pm 4$ K, and $T_f = 335$ K. The temperature dependence shows the usual strongly non-Arrhenius behavior above T_g and a weaker, Arrhenius T-dependence in the glassy state.

Since the structure and properties of pressure densified glass differ from conventional glass,^{23,25} the aging behavior is also expected to be different. However, as shown in Fig. 4, τ_{α} for glassy PMMA, describing the time scale of the physical aging, are independent of the pressure during glass formation. [This is true within the experimental uncertainty, which derives mainly from fitting the overlapping and JG dispersions to yield β used in Eqs. (4) and (5).] The expectation is

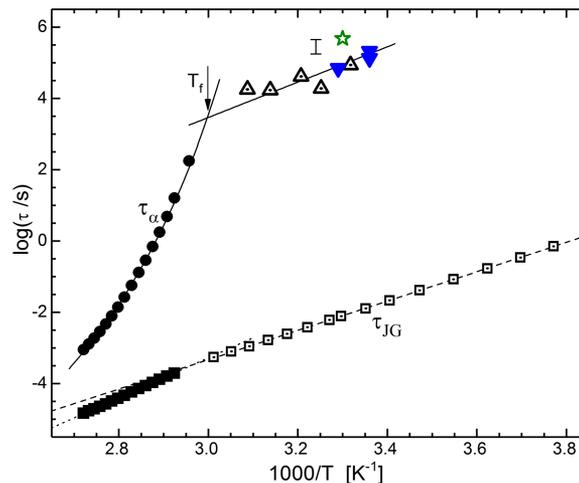


FIG. 4. Arrhenius plot of the primary and secondary relaxation times. τ_{α} above the fictive temperature (≈ 61.5 °C) and τ_{JG} (squares) measured at ambient pressure; τ_{α} below T_f obtained from the change of the JG process for PMMA vitrified at 0.1 MPa (triangles) and at higher pressures (185 and 245 MPa; inverted triangles), and from the volume change during aging at ambient pressure (star). The aging was carried out at 24.5 °C for glass formation at 185 MPa and at 24.5 °C and 31.0 °C for PMMA vitrified at 245 MPa. The curves through τ_{α} are the fit of Eq. (6) and through τ_{JG} are linear fits.

that glass-forming materials associated with isomorphs will exhibit simple aging behavior, that is, the aging will be independent of thermodynamic pathway.^{10,15} And indeed, we find that the physical aging of PMMA is independent of its density. The inconsistency is the capacity of PMMA to be pressure densified at all.

To verify τ_{α} extracted from the changes in JG properties during aging, the structural relaxation time was measured directly from the change in volume as PMMA evolves toward equilibrium (Fig. 5). This experiment included a measurement on a sample aged 4.8 years at ambient conditions. Fitting the data to Eq. (4) or (5) written in terms of V , we obtain the value included in Fig. 3. Within the experimental uncertainty, this time constant is consistent with τ_{α} deduced from the change in JG properties.

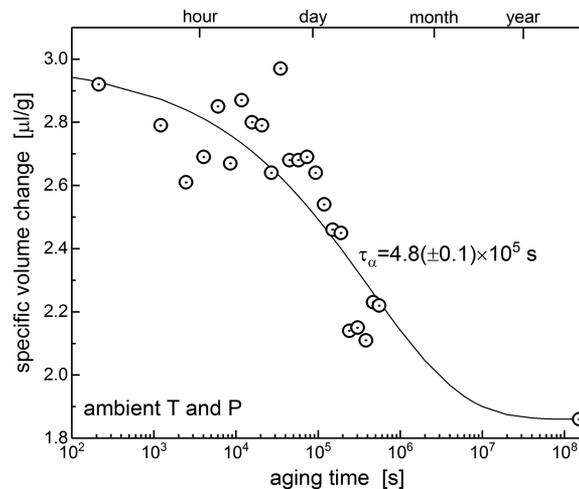


FIG. 5. Change in specific volume during physical aging of PMMA vitrified by cooling at 10 MPa.

In summary, the pressure during glass formation was adjusted herein so that after its release, PMMA had a density that was higher, lower, or equivalent to that of the extrapolated equilibrium value. Nevertheless, the structural relaxation rate of the glassy PMMA and the change of JG properties during physical aging were independent of the average density. This result is consistent with pressure densification studies in which glass was prepared having a density equal to that of the equilibrium liquid but exhibited different distributions of local volume.³¹ The average density does not govern the properties of the glass, but rather the local structure and barriers for thermal fluctuations of density are the main control parameters. A more disordered local structure leads to a lower glass transition temperature in the pressure densified polymer. We have previously shown that an asymmetric double well potential model can qualitatively reproduce physical aging behavior, with the degree of asymmetry inversely related to the fictive temperature describing the non-equilibrium structure of the glass.³²

PMMA exhibits properties of a material having isomorphs in its phase diagram; to wit, isochronal superpositioning, density scaling, and as found herein, physical aging kinetics are independent of both the conditions during glass formation and the subsequent density. Nevertheless, the density of glassy PMMA is a function of the pressure during vitrification, and since pressure densification follows an isomorphic pathway,¹⁶ this pressure dependence is unexpected. Thus, the capacity for pressure densification of PMMA indicates that the polymer has some, but not all, of the properties predicted for materials associated with isomorphs.¹² This apparent contradiction underscores the need for a better understanding of the connection between the properties of real materials and those found in MD simulations, even for relatively “simple” systems. Particularly for polymers, the properties along isomorphic pathways seem to be related to the flexibility of the polymer backbone.³³

This work was supported by the Office of Naval Research. Enlightening discussions with D. Fragiadakis are gratefully acknowledged.

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