Journal of Non-Crystalline Solids 357 (2011) 414–418

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Isobaric and isothermal glass transition of PMMA: pressure-volume-temperature experiments and modelling predictions

Luigi Grassia *, Alberto D'Amore

Department of Aerospace and Mechanical Engineering, The Second University of Naples, Aversa (CE), Italy

ARTICLE INFO

Article history:
Received 7 May 2010
Received in revised form 27 July 2010
Available online 25 August 2010

Keywords:
Glass transition;
Relaxation time;
PVT behaviour;
Amorphous polymers

ABSTRACT

The scaling law for relaxation times, recently proposed by Casalini and Roland, is utilized in the framework of KAHR (Kovacs, Aklonis, Hutchinson, and Ramos) phenomenological theory. With this approach it is shown that the pressure, volume, and temperature (PVT) data obtained on Poly(methyl-methacrylate) (PMMA) can be reliably predicted, in the region of the alpha-relaxation, by using only two fitting parameters, namely: the relaxation time in the reference state, τ_g, and the fractional exponent, β, that describes the dispersion of the alpha-relaxation.

1. Introduction

Under isobaric conditions the supercooled metastable state of a liquid can be obtained via rapid cooling from equilibrium conditions. The reduction in temperature is accompanied by a progressive slowing down of diffusive motions, until their virtual arrest. Vitrification implies that the material behaves as a solid over typical laboratory timescales, the glass preserving a disordered, liquid-like microscopic structure [1–4]. Operationally the glass transition temperature, T_g, depends on the timescale, since the glass formation is a kinetic process. T_g can be defined as the temperature at which the relaxation timescale is of the order of the experimental time window. On the other hand, glass can be obtained by isothermal compression, which makes clear that the volume (or the pressure), along with the temperature, plays an important role in the slowing down of molecular motions [2–5]. Thus, the functional form of the relaxation time should contain both the temperature and the volume dependence [2–5]. Accordingly Casalini and Roland [2–4] proposed the following scaling law for the relaxation time:

$$\tau(T,V) = \Im(TV^{\gamma}) \tag{1}$$

where $\Im$ is an unknown function and γ a material-dependent constant. This scaling property has been verified for over forty materials using different techniques, with the parameter $\gamma<8.5$ [2–4,6].

Recently, Casalini and Roland [6,7] discussed how the scaling properties can be derived from the temperature, T, and the volume, V, dependencies of the entropy, and using the Avramov model [8] derived the following expression for the $\tau(T, V)$ dependence [6,7,9]:

$$\tau(T,V) = \tau_0 \exp\left[\left(\frac{A}{TV^{\gamma}}\right)^{\phi}\right] \tag{2}$$

where τ_0, A, ϕ, and γ are constants. Eq. (2) satisfies the scaling law expressed by Eq. (1) and gives a good description of experimental data over a broad dynamic range [6,7,9].

In literature two main phenomenological models have been utilized in order to predict the behaviour of glass forming materials, namely the Kalroush, Aklonis, Hutchinson, and Ramos (KAHR) model [10,11] and the Tool–Narayanaswamy–Moynihan (TNM) model [15–17]. These theories are both capable of capturing the nonlinearity and memory effect of structural relaxation. Despite the fact that the parameters of KAHR and TNM theories are strongly correlated (their use is really equivalent under isobaric conditions) the KAHR theory accounts explicitly for the pressure and represents a more viable formalism to describe the PVT behaviour under arbitrary temperature and/or pressure histories [12–14]. For completeness, it should be mentioned that the parameters in the KAHR theory still suffer some lack of physical meaning due to the arbitrary dependence of relaxation time on temperature, pressure, and dimensionless volume [12–14].

2. Methods

The equation that describes the volume relaxation kinetics in the presence of an arbitrary temperature and pressure history reads [10–14]:

$$V = V_e + V_e \int_0^{\xi} \left[-\left(\alpha_e - \alpha_g\right)\frac{dT}{d\xi'} - \left(k_e - k_g\right)\frac{dP}{d\xi'}\right] M\left(\xi - \xi'\right) d\xi' \tag{3}$$

---

* Corresponding author.
E-mail address: luigi.grassia@unina2.it (L. Grassia).

0022-3093/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2010.07.055

where the suffix g and e indicate the glassy and the liquid/equilibrium state, respectively, α is the isobaric thermal expansion coefficient, k is the isothermal compressibility, and M is the memory function defined as follows:

$$M(\xi) = \exp\left[-\left(\xi/\tau_g\right)^{\beta}\right] \tag{4}$$

where τ_g is the relaxation time in the reference state, β is the fractional exponent that describes the dispersion of the alpha-relaxation and ξ is the reduced time defined as follows:

$$\xi = \int_0^t \frac{\tau_g dt'}{\tau} \tag{5}$$

where t is the time and τ the relaxation time.

Here, the expression proposed by Casalini and Roland [6,7,9] is utilized as the functional form of the relaxation time in the KAHR (Kovacs, Aklonis, Hutchinson and Ramos) model [10,11] that predicts the volume relaxation kinetics under arbitrary pressure and temperature histories [10–14]. In particular the relaxation time, τ, has been expressed by Eq. (2), which can be rewritten in terms of the isochoric fragility, m_V, defined as [2]:

$$m_V = \left.\frac{\partial \log\tau}{\partial\left(T_g/T\right)}\right|_{T_g, V = \mathrm{cost}}. \tag{6}$$

From Eqs. (2) and (6) it follows that the parameter A is directly correlated to m_V, according to the following equation

$$m_V = \phi\left(\frac{A}{T_g V_g^{\gamma}}\right)^{\phi}\frac{1}{\ln 10} \tag{7}$$

where T_g and V_g are the temperature and the specific volume at the glass transition. Consequently, Eq. (2) can be rewritten as:

$$\ln\tau = \ln\tau_0 + \frac{m_V \ln 10}{\phi}\left(\frac{T_g V_g^{\gamma}}{T V^{\gamma}}\right)^{\phi}. \tag{8}$$

At the glass transition the relaxation time reduces to:

$$\ln\tau_g = \ln\tau_0 + \frac{m_V \ln 10}{\phi} \tag{9}$$

in a way that the final expression for τ is the following:

$$\ln\tau = \ln\tau_g + \frac{m_V \ln 10}{\phi}\left[\left(\frac{T_g V_g^{\gamma}}{T V^{\gamma}}\right)^{\phi} - 1\right]. \tag{10}$$

From Eqs. (3–5) and (9), the constitutive equation for the specific volume, V, takes the following final expression:

$$V = V_e + V_e \int_0^t \left[-\left(\alpha_e - \alpha_g\right)\frac{dT}{dt'} - \left(k_e - k_g\right)\frac{dP}{dt'}\right] \times \exp\left[-\left(\int_{t'}^{t} dt''/\tau_g \exp\left[\frac{m_V \ln 10}{\phi}\left[\left(\frac{T_g V_g^{\gamma}}{T V^{\gamma}}\right)^{\phi} - 1\right]\right]\right)^{\beta}\right] dt'. \tag{11}$$

3. Results and discussion

In what follows we report on a procedure that, step by step, allowed us to implement Eq. (11). It will be shown that most of the material's functions (namely, α_g, α_e, k_g, and k_e) and the material's properties (γ, m_V and ϕ) appearing in Eq. (11) can be derived directly from opportune PVT data. The remaining parameters τ_g and β rest as fitting parameters that can be evaluated minimizing the sum of squared differences between the model prediction and the experimental data. Under this perspective Eq. (11) differs substantially from the original KAHR model that required the optimization of five parameters [10–14].

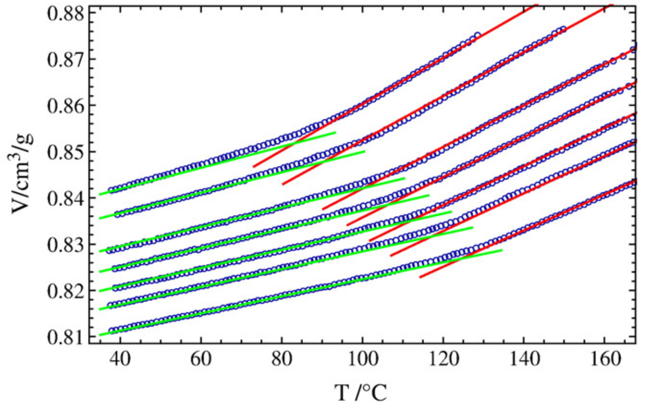

Fig. 1. Isobaric PVT data (symbols) at seven different pressures, namely 10, 30, 60, 80, 120, and 150 MPa, and at a cooling rate of 0.5 °C/min. The solid lines indicate the fit of Tait's equation above (red) and below (green) T_g. The intersections between the two families of curves yield the T_gs.

A commercially available Poly(methyl-methacrylate) (PMMA) (Sigma-Aldrich, Mw = 120.000) was chosen as the probe material. The dilatometric study was performed by using a GNOMIX pressure–volume–temperature (PVT) apparatus. PVT data were obtained in terms of specific volume change, while the absolute values were obtained by measuring the absolute value of the specific volume, using a helium picnometer, at 28 °C and ambient pressure, few minutes before introducing the sample in the PVT apparatus.

The isobaric PVT data were obtained when cooling the sample from above to below T_g at 0.5 °C/min, as reported in Fig. 1. The measurements were performed at seven different pressures, namely 10, 30, 60, 80, 120 and 150 MPa.

Tait's equation [18] is here utilized to fit the data either above or below the T_g and the results are reported in Fig. 1 as red and green lines, respectively. The fitting procedure above T_g allows obtaining the equation of state (EOS) for PMMA, i.e. the equilibrium specific volume V_e at each temperature and pressure. The isothermal compressibility, k_e, and the isobaric expansion coefficient, α_e, are calculated in analytical form ($k_e(T,P) = \frac{1}{V_e}\frac{\partial V_e}{\partial P}\big|_T$,$\alpha_e(T,P) = \frac{1}{V_e}\frac{\partial V_e}{\partial T}\big|_P$) from the EOS. The isobaric expansion coefficient in the glassy state, $\alpha_g(T,P)$, is calculated by differentiating Tait's expression for the specific volume that fits the data

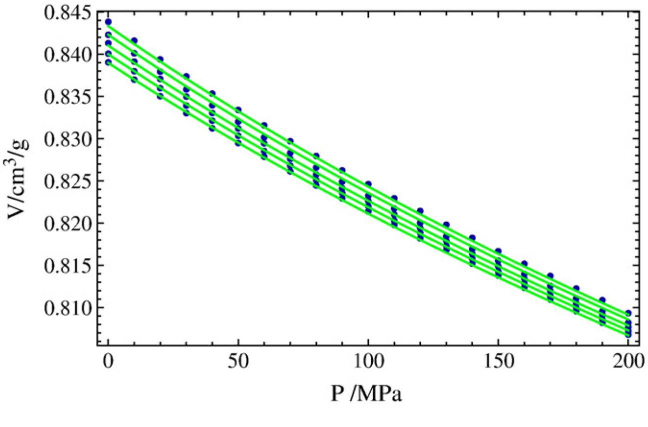

Fig. 2. Isothermal PVT data (symbols) in the glassy state at five different temperatures, namely 21, 25, 29, 34, and 39 °C. The solid lines indicate the fit of Tait's equation.