When this equation is used recursively, it determines $[\alpha]_i$ in terms of $\{w_j, {}^jM_1, {}^jM_2, ..., {}^jM_{\alpha-1}\}_{j=1...N_c}$.

For completeness we also note that

$$[\alpha]_i = \frac{[\alpha + 1]_i}{[\alpha + 1]_i + \sum_{\substack{j=1 \\ j\neq i}}^{N_c} ({}^iM_\alpha/{}^jM_\alpha)[\alpha + 1]_j} \tag{B.16}$$

This result can be obtained by similar reasoning using

$$(\alpha) = (\alpha + 1)/M_\alpha \tag{B.17}$$

Equation B.17 follows from eq B.12 and the general result

$$\langle M^{\gamma+\mu}\rangle_\alpha = \langle M^\gamma\rangle_\alpha \cdot \langle M^\mu\rangle_{\alpha+\gamma} \tag{B.18}$$

with $\gamma = 1$ and $\mu = -1$. Equation B.18 can be derived from eq B.11 and B.4.

These results generalize those given by Friedman and Porter.[18]

Appendix C

We demonstrate that the viscosity-average molecular weight M_v is less than the weight-average molecular weight M_w for any molecular weight distribution w_M.

The argument is based on the Holder inequality[21]

$$\sum_i |a_ib_i| \leq (\sum_i |a_i|^\lambda)^{1/\lambda}(\sum_i |b_i|^\mu)^{1/\mu} \tag{C.1}$$

where $\lambda, \mu > 1$ such that $\lambda^{-1} + \mu^{-1} = 1$, and on the definition of M_v, namely

$$M_v{}^q = \sum_M w_M M^q \tag{C.2}$$

where w_M denotes the weight fraction at M and q depends on the polymer–solvent interaction. Equation C.2 also defines M_w if q is replaced by unity. So when $q > 1$, we let $\lambda = q$, $a_M = w_M{}^{1/\lambda}M$, and $b_M = w_M{}^{1/\mu}$ and substitute in eq C.1 to obtain $M_v \geq M_w$. If $q < 1$, we put $\lambda = 1/q$, $a_M = w_M{}^{1/\lambda}M^{1/\lambda}$, and $b_M = w_M{}^{1/\mu}$ to obtain $M_v \leq M_w$. Usually[22] one has $0.5 < q < 0.8$ and thus $M_v \leq M_w$.

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Predicting the Shift in Viscoelastic Response Caused by Physical Aging of Glassy Polymers[†]

Robert R. Lagasse and John G. Curro*

Sandia National Laboratories, Albuquerque, New Mexico 87185. *Received April 16, 1982*

ABSTRACT: Measurements of the specific volume of a poly(vinyl acetate) glass during isothermal annealing at 25 and 30 °C are analyzed theoretically to predict the shift in the time scale of viscoelastic response. These predictions agree with direct measurements of the change in the viscoelastic shift factor of the poly(vinyl acetate) at those temperatures. Both the volume and shift factor measurements were taken from literature reports of Kovacs, Stratton, and Ferry. Our predictive method is based on an extension into the glassy state of Simha and Somcynsky's theory for the equation of state of polymeric liquids. Analysis of the volume changes with that theory yields a time-dependent fraction of free volume. This free volume fraction is then substituted into the Doolittle equation to predict the shift in viscoelastic response. Our method had been tested previously with measurements on an isothermally annealed poly(methyl methacrylate) glass, but we consider the present test with the poly(vinyl acetate) results to be more rigorous.

Introduction

It is well-known that polymer glasses prepared by cooling from the liquid state exhibit spontaneous changes in certain physical properties.[1] For example, isothermal annealing causes a change in their specific volume and a shift in the time scale of their viscoelastic response. Predicting the time shift in viscoelastic response from measurements of the volume change is the subject of this work.

Recently, the present authors and R. Simha proposed[2] that a theoretical equation of state for amorphous polymers[3] could be utilized to make the prediction. In particular, we analyzed volume changes with that theory to yield a time-dependent fraction of unoccupied volume. This free volume fraction was then substituted into the Doolittle equation to predict the shift in viscoelastic response. The results of our analysis agreed with some viscoelastic measurements[4] taken during annealing of a

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poly(methyl methacrylate) (PMMA) glass at 25 °C. For testing our predictive method, these measurements had two deficiencies. First, they did not include all the data needed to determine the parameters in our analysis. To determine these parameters, we[2] had to resort to other measurements obtained at much higher temperatures on a different sample of PMMA. Second, the application of our analysis to annealing of PMMA at 25 °C might be questioned. At 25 °C, the viscoelastic response of PMMA is dominated by local motion of a side chain.[5] We felt[6] that our analysis might be more valid at temperatures closer to the glass temperature (T_g = 110 °C for PMMA), where the viscoelastic response is dominated by large-scale, main-chain motions.

In the present work, we have tested our predictive method on some measurements[7,8] taken on a poly(vinyl acetate) (PVAc) glass during annealing at temperatures within 10 °C of its T_g. Since the annealing temperatures are closer to T_g, these data are believed to be more suitable for testing our method than were the PMMA data. Moreover, we were able to determine the parameters in our analysis using experimental results obtained[7,8] near the annealing temperatures on the same sample of PVAc. Another reason for testing our method with PVAc results is to determine its generality for different polymers.

Summary of Predictive Method

Our analysis is based on an extension into the glassy state of the theory of Simha and Somcynsky[3] for the equation of state of polymeric liquids. In this theory, each of the repeat units of a chain is confined to a cell lying on a lattice, but empty cells are also allowed. For the case of equilibrium liquids at a given pressure, minimization of the free energy defines the fraction of unoccupied cells as a function of a reduced temperature $\tilde{T}$:

$$f = f(\tilde{T}) \tag{1}$$

where the reducing temperature is denoted by T^*:

$$\tilde{T} = T/T^* \tag{2}$$

Evaluation of eq 1 requires simultaneous solution of two transcendental equations, eq 12 and 13 in ref 2. For nonequilibrium glasses, eq 1 is not valid since the free energy is not minimized. Instead, a value for the time-dependent f is chosen so as to account for the volume observed during isothermal annealing. In particular, the fraction of unoccupied cells is computed from the time-dependent volume using eq 12 of ref 2, a transcendental equation having the following form:

$$f(t) = f(\tilde{T},\tilde{V}(t)) \tag{3}$$

Here, $\tilde{V}$ is the volume reduced by a parameter V^*, as in eq 2, and the pressure is assumed to be low, i.e., atmospheric. Finally, the shift in viscoelastic response during annealing of the glass can be computed by substituting $f(t)$ into the Doolittle equation:[9]

$$\ln a(t) = B[f^{-1}(t) - f_0^{-1}] \tag{4}$$

The term $a(t)$ is the factor by which all the viscoelastic relaxation times differ relative to those in a reference state, which is signified by the subscript 0. B is a parameter that can be determined independently from measurements on the equilibrium liquid.

Predicted Shift Factors

The change in the viscoelastic shift factor during isothermal annealing of PVAc glasses at 25 °C and at 30 °C was predicted from volume measurements obtained by Kovacs and co-workers.[7,8] The reducing parameters T^* and V^* in the Simha–Somcynsky theory were evaluated from equilibrium volumes over the range 33–57 °C. These results were calculated from the equilibrium volume at 35 °C and the thermal expansion coefficient that are listed in Table I. Analysis of these data by the conventional method[10] yielded V^* = 0.813 86 cm³/g and T^* = 9471 K, which are very close to the parameters cited by Simha and Wilson[10] for PVAc.

Table I
Experimental Results for the Poly(vinyl acetate) Sample

parameter	source
$V_e(35\ ^\circ C) = 0.8445\ cm^3/g$	ref 7, Figure 15
$V_e^{-1}(dV_e/dT) = 6.9 \times 10^{-4}\ K^{-1}$	ref 7, p 159
$b = 7.36 \times 10^{-4}$	ref 8, Table VII
$t_0 = 0.53$ min	ref 8, Figure 15
$t_m = 10\ 500$ min	ref 8, Figure 15

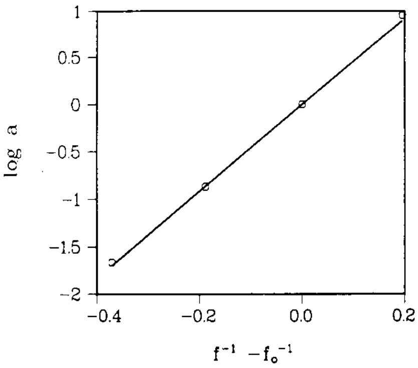

Figure 1. Determination of parameter B by fitting to eq 4 measurements[7] of the viscoelastic shift factor for poly(vinyl acetate) glasses at volumetric equilibrium. For the four temperatures of interest (33, 35, 37, and 39 °C), the free volume fraction f was computed with eq 1. The reference state, denoted by subscript 0, was volumetric equilibrium at 35 °C.

The remaining parameter, B in eq 4, was evaluated using measurements[7] of the shift factor for PVAc glasses at volumetric equilibrium over the temperature range 33–39 °C. Since the glasses were at equilibrium, their free volume fractions could be computed with eq 1 and 2. A plot of these equilibrium values of a and f, shown in Figure 1, yielded B = 10.5. Although this is considerably higher than the value of 1.0 proposed in the literature,[9] it is nevertheless consistent with our particular definition of the free volume fraction.

The time-dependent volume measured by Kovacs during annealing of the PVAc has been plotted (in Figure 15 of ref 8) as a dimensionless departure from the equilibrium volume V_e:

$$\delta(t) = [V(t) - V_e]/V_e \tag{5}$$

The $\delta(t)$ shown in Table II for 25 °C are readings from that plot. Fortunately, $\delta(t)$ readings for 30 °C could be verified by evaluating an empirical equation[11] that represents those results over the time range of interest:

$$\delta(t) = b \log [(t + t_m)/(t + t_0)] \tag{6}$$

The parameters b, t_m, and t_0 are listed in Table I. Evaluating eq 5 with these $\delta(t)$ results and the V_e (calculated as before) produced the $V(t)$ results listed in column 4 of Table II.

The final part of the analysis consisted of computing the time-dependent free volume fractions from eq 3 and, thence, the shift factors from eq 4. These $f(t)$ and $a(t)$ results are listed in columns 5 and 7 of Table II. The

Table II
Comparison of Measured and Predicted Shift Factors for Poly(vinyl acetate) Glasses Annealed Isothermally

T, °C	t, min	$\delta(t) \times 10^3$	$V(t)$,[a] cm^3/g	$f(t) \times 10^2$	log $a(t)$[b]	
					measd	pred
30	50	1.707	0.843 03	7.835	0.8439	0.8951
30	100	1.489	0.842 84	7.810	1.050	1.082
30	200	1.271	0.842 66	7.786	1.260	1.263
30	400	1.056	0.842 48	7.762	1.471	1.444
25	50	3.70	0.841 80	7.753	1.48	1.51
25	100	3.45	0.841 59	7.725	1.73	1.73
25	200	3.21	0.841 38	7.697	1.98	1.94
25	400	2.97	0.841 18	7.670	2.23	2.15
25	1370	2.56	0.840 84	7.625	2.68	2.50

[a] Although the fifth decimal place is uncertain, errors in the *absolute value* of $V(t)$ tend to cancel in calculating $a(t)$ from eq 4. [b] log $a(t) = 0$ for equilibrium at 35 °C.

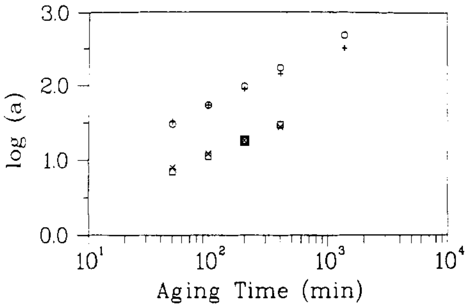

Figure 2. Comparison between viscoelastic shift factors measured[7] during isothermal aging of a poly(vinyl acetate) glass and shift factors predicted from measurements of the volume change. Open symbols represent the measurements at 25 °C (circles) and at 30 °C (squares), and the crosses represent the corresponding predictions. The reference state, where log $a = 0$, is equilibrium at 35 °C.

reference state for the shift factors is equilibrium at 35 °C.

Measured Shift Factors

Kovacs, Stratton, and Ferry[7] measured the in-phase shear modulus G', during annealing of the PVAc at 25 °C and at 30 °C. Plots of G' vs. log (frequency) over the range 4–250 Hz were shifted in the usual way to determine the time-dependent shift factors. These $a(t)$ measurements were represented[7] by the equation

$$\ln a(t) = [0.0225 + 5.3 \times 10^{-4}(T - 35) + \delta(t)]^{-1} - (0.0225)^{-1} \quad (7)$$

where T is in °C. The measured $a(t)$ from eq 7 are listed in column 6 of the table and are compared to the predicted values in Figure 2. The accuracy of our prediction is evident.

Discussion

Other methods for using $V(t)$ measurements on glasses to predict the shift in viscoelastic response are based on assumptions that are somewhat arbitrary.[2] One method[7,9] requires that the free volume fraction at equilibrium be linearly dependent on temperature and that parameter B in eq 4 equal 1.0. In fact, eq 7 was actually derived using this method, rather than a simple, empirical fit of the $a(t)$ measurements. Accordingly, our recently proposed method is no more successful in predicting the change in viscoelastic shift factor during annealing of the PVAc than is an earlier method. Nevertheless, our method does have a firmer theoretical basis and can, therefore, be expected to have a wider range of validity. This expectation is supported by our earlier analysis[2] of the annealing results on PMMA.[4] In that case, our method was successful, while all alternative methods failed. As mentioned earlier, the success of our method in predicting the PMMA results was somewhat unexpected.

Conclusions

The predictions of a recently proposed analysis[2] agree with measurements[7] of the shift in viscoelastic response during annealing of a PVAc glass. This test of our analysis is more rigorous than an earlier test that used measurements[4] on a PMMA glass.

Acknowledgment. A. J. Kovacs pointed out in a private communication that his experimental $\delta(t)$ measurements could be reproduced by evaluating eq 6.

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