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PII: S0032-3861(97)10034-9

Polymer Vol. 39 No. 18, pp. 4393–4397, 1998
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0032-3861/98/$19.00+0.00

Physical ageing in poly(vinyl acetate) — 3. Structural relaxation and its effect on the stress relaxation modulus

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(Received 4 April 1997; revised 28 July 1997; accepted 13 August 1997)

The extent of physical ageing of a sample of poly(vinyl acetate) (PVAc) has been determined by measuring the shear stress relaxation at three temperatures below the glass transition. The data obtained after various ageing times could be superimposed by shifts along the log time axis using the characteristic mechanical relaxation time as shift factor. A comparison of these ageing time shift factors with enthalpy and volume data already established for the same sample indicates that the mechanical properties of PVAc reach equilibrium before either the volume or enthalpy. These results are compared with those of others and for the case where dynamic mechanical methods are used to obtain shift factors. The possibility of interrelating ageing measurements using different physical properties is discussed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: poly(vinyl acetate); physical ageing; relaxation modulus)

INTRODUCTION

Polymer glasses formed by rapid cooling preserve the liquid state structure which was in thermal equilibrium at the glass transition temperature (T_g) and which is frozen in on vitrification. At temperatures not too far below its T_g a polymer will undergo slow changes with time as this structure relaxes towards its appropriate equilibrium state. This underlying relaxation is manifest by changes in physical properties such as specific volume and enthalpy, and in mechanical and dielectric responses. To all and any of these changes the term physical ageing may be applied.

The precise nature of the underlying structural changes is as yet unclear, although a generally acceptable picture would involve a reduction in the fraction of bonds flexed into high energy conformations, usually *gauche*, through localised conformational transitions, and a decay in the excess free volume or hole fraction. In the condensed phase the rate of structural change will respond to local kinetic constraints imposed by interactions between individual molecular components. For example, a *gauche* to *trans* conformational transition will encounter not only the intrinsic bond rotation barrier but also matrix constraints, requiring that all such motions become highly correlated. An analysis of structure relaxation according to a model involving vacancy-mediated displacements wherein only units immediately adjacent to vacancies (holes or defects) can move has been presented by Mazur[1]. The configurational relaxation function $\phi(t)$ resulting from this analysis resembles, at appropriate packing densities, the empirical Kohlrausch–Williams–Watts (KWW) function

$$\phi(t) = 1 - \exp[-(t/\tau)^{\beta}] \qquad (1)$$

where $0 < \beta < 1$ and τ is an average characteristic relaxation time.

Structural relaxation has been studied by dilatometry[2–4] and calorimetry[5–9], and experimentally the relaxation of these two macroscopic properties is found to be both nonexponential and nonlinear. The data from such investigations are well fitted by expressions of the KWW form in which various expressions for the relaxation time τ have been employed, derived variously from generalised Arrhenius behaviour[10,11], free volume concepts[12] or configurational entropy considerations[13,14]. Phenomenologically, τ is allowed to depend on the instantaneous structure of the relaxing glass through its fictive temperature. Reviews of the various models and approaches are to be found in the literature[15–19]. At the present time there appears no possibility of obtaining rates of structural relaxation directly and so all models are of necessity restricted to describing the observable temporal changes of a chosen physical property.

The successful use of polymers, especially in high performance applications, requires a knowledge of such time-dependent behaviour. For example, if dimensional stability is of prime importance then the rate of change of volume with time may be an important performance limiting factor. Reliable correlations between the rates of ageing shown by different physical properties would also be attractive, allowing the possibility of testing one (convenient) time-dependent response and thereby predicting the future behaviour of another. Where information is available (see below) it appears that the kinetic parameters describing the time dependence of different macroscopic properties of the same material, e.g. enthalpy and volume, are generally dissimilar, notwithstanding that these result from the same molecular mechanism.

In the previous papers of this series[20,21] we presented data

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on the enthalpy (H) and volume (V) ageing of the same sample of poly(vinyl acetate) (PVAc) and it was concluded that comparisons of ageing rates based on the values of kinetic parameters (e.g. τ values) derived from different modelling approaches can lead to conflicting answers to the question of which of the two properties is relaxing the faster. For PVAc the normalised extent of enthalpy loss was found to lag behind the normalised volume contraction at two of the temperatures studied, but to precede it slightly at the third. The rate of enthalpy loss dH/dt, however, was found to be greater than dV/dt over three decades of time t (min) at all the temperatures studied.

A link between the rates of ageing of different physical properties has been proposed by Moynihan and his coworkers[22,23] using an order parameter model such that, for any property X,

$$\frac{dX}{dt} = \sum_{i=1}^{N} \frac{\partial X}{\partial Z_i} \frac{dZ_i}{dt} \tag{2}$$

For the rate of enthalpy ageing equation (2) is written with $X = H$, and for the rate of volume ageing with $X = V$.

Order parameters are more conceptual than they are precisely defined, but intuitively one would identify the number of flexed bonds or the number of holes as order parameters and so, from the model described by Mazur[1], the rates of change of the Z_i might be expected to follow equation (1). In the preceding publication[21] a first-order treatment using only a single order parameter, the hole fraction h, along with the volume and enthalpy partial derivatives $\partial V/\partial h$ and $\partial H/\partial h$, all calculated from the Simha–Somcynsky equation of state[24], failed to describe adequately the relative enthalpy and volume ageing rates which were found experimentally for PVAc. It was concluded that a predictive correlation between these rates could not be established on this simple basis and, in order to describe the experimental behaviour, at least one further order parameter must be incorporated into the summations of equation (2).

In this paper we turn to the effect of ageing on mechanical properties. On ageing a quenched polymer below T_g the volume and enthalpy recovery described above is accompanied by changes in the viscoelastic response. Struik observed[25] that, when mechanical deformations are small, creep curves obtained at different ageing times could be superimposed by a shift along the time axis, thus establishing a time–ageing-time superposition principle similar to time–temperature superposition. The values of the ageing time shift factor depend on the ageing time in a nonlinear manner, eventually approaching an equilibrium value when the mechanical response becomes invariant with time.

The relationship between the rate of volume or enthalpy relaxation and that of the accompanying mechanical relaxation has been studied by a number of workers. Roe and Millman[26] examined polystyrene and concluded that equilibrium in creep was attained after enthalpic equilibrium by about an order of magnitude. Echeverria and her coworkers[27] question their analysis and report data on poly(etherimide) from which they suggest that the time scales for mechanical and enthalpic equilibrium are the same, at least in this polymer. Mijovic and Ho[28] have adopted the Narayanaswamy[11] model as a basis for comparing enthalpy and stress relaxation ageing times in poly(methyl methacrylate), poly(styrene-*co*-acrylonitrile) and their blends. Their approach is of limited utility, however, since it sets out to optimise a single set of model parameters to describe both viscoelastic response and enthalpy. As such it provides only an empirical 'enforced' link between these properties, and not surprisingly concludes that enthalpy and stress-relaxation relaxation times are comparable.

Pérez and his coworkers[29] have developed a description of ageing using a model in which density fluctuations are frozen at T_g and which includes a diffusion process that presents strong correlation effects. As a first approximation, they find that a single set of model parameters can account for the ageing behaviour of poly(methyl methacrylate), but that there is a significant difference in the characteristic times associated with the different techniques used such that $\tau_{\text{mechanical relaxation}} < \tau_V < \tau_H$. This sequence has been reported by Petrie[30] also, and by Sasabe and Moynihan[31] who additionally included electric polarisation in their study of relaxations in PVAc, concluding that the characteristic dielectric relaxation time also is less than those of the enthalpy and volume. However, these latter workers' conclusions are based on data garnered from different literature sources, and so perhaps the work by McKenna's group[17,32] at NIST provides a more direct comparative example of mechanical and thermodynamic ageing, using a torsional dilatometer in which the volume and relaxation modulus of a model epoxy network were measured concurrently. Their results indicate that mechanical relaxation is complete prior to volume equilibration for ageing under temperature down-jump conditions. In this present contribution we present data which is also directly comparable, and discuss the results of stress relaxation measurements made using the same sample of PVAc as was employed for measurements of the enthalpy loss and volume contraction due to ageing at three common temperatures below T_g.

EXPERIMENTAL

The characteristics of the sample of PVAc have been reported previously[20]. Torsional stress relaxation measurements were carried out using a moulded PVAc bar (40 mm × 20 mm × 2 mm). Prior to measurements this was dried overnight in a vacuum oven above its T_g. Torsional relaxation measurements were carried out in an air thermostat and, in order to exclude moisture during measurements, the air was predried and maintained at a slight overpressure within the apparatus. The sample bar was mounted vertically, clamped at the top end to a moveable torsion arm and at the bottom to an air bearing pivoted arm in contact with a Baldwin Messtechnik HBM Q11 force transducer. Prior to ageing, the PVAc was annealed *in situ* at $T_g + 30$ K for 15 min. To minimise ageing effects as the sample was brought to the ageing temperature it was first quenched to around $T_g - 50$ K by the introduction of cold dried nitrogen gas into the sample enclosure. The nitrogen flow was then turned off and replaced by the dried air at the desired ageing temperature.

An instantaneous displacement of 0.0167 radians was applied through the upper torsion arm after consecutive ageing intervals t_{a1}, t_{a2}, t_{a3} ... and data collected over acquisition periods of t_1, t_2, t_3 ..., after which the torsional displacement was removed. The t_i were always less than one-tenth of the ageing intervals t_{ai} and the intervals between the t_{ai} were sufficient to allow complete recovery. The relaxation modulus as a function of acquisition time, $G(t)$, was evaluated using the form factor for a bar of rectangular cross-section in torsion (b) and allowing for the displacement of the transducer head itself on application of a stress from

$$G(t) = \frac{9.1V(t)}{b\theta_{\mathrm{act}}} \quad (3)$$

where $V(t)$ is the output of the transducer and θ_{act} the correct torsional displacement.

RESULTS AND DISCUSSION

Figure 1 shows examples of the relaxation modulus data $G(t)$ obtained at different ageing times for an ageing temperature of 303 K. The result of ageing is to shift the curves to longer times, an effect well documented by Struik[25], and each curve was found to be well fitted by the Booij and Palmen equation[33] which describes isothermal short-time stress relaxation in glassy polymers as

$$G(t) = G_0(t/\tau_r)^{0.006}\exp[-(t/\tau_r)^{0.4}] \quad (4)$$

where τ_r is a characteristic mechanical relaxation time which is a function of both temperature and ageing time. Isothermally, τ_r acts as an effective time–ageing-time shift factor, as can be seen from the master curves shown in *Figure 2* in which the horizontal shift factor (a) is defined by

$$\log a = \log \tau_r - \log \tau_{r0} \quad (5)$$

where the subscript 0 refers to the reference curve. *Table 1* lists the values of log τ_r and log G_0 obtained from ageing experiments at three temperatures below the calorimetric glass transition (315 K) for this sample of PVAc[20]. The parameter G_0, which approximates to the short-time plateau value of the relaxation modulus, does not appear to vary in any uniform manner with ageing time, at least within the reproducibility of our present experiments.

Detailed examination of short time relaxation data can show a response to ageing[34], as discussed by Struik[25], but more pertinent here is the time evolution of the mechanical response as reflected by the shift parameter log a, which is compared directly with the extent of ageing as shown by the volume and enthalpy changes already established for this sample[20,21]. *Figure 3*, which shows these three sets of data as a function of log ageing time at 303 K, strongly suggests that the mechanical response reaches its equilibrium value before both the enthalpy and the volume at this temperature. A clearer representation of this effect can be seen in *Figures 4 and 5* in which log a has been plotted against the normalised departure (δ_X) from equilibrium at all three

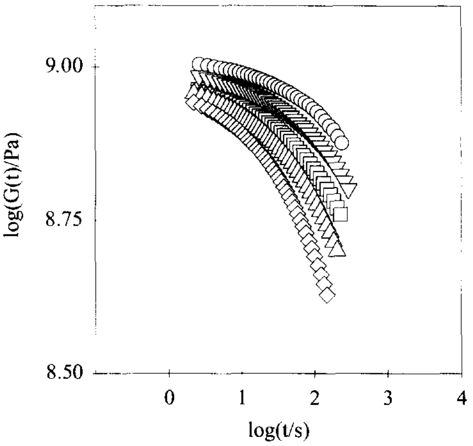

Figure 1 Stress relaxation modulus $G(t)$ for PVAc at 303 K after different ageing times: 30 min (◇); 60 min (△); 90 min (□); 120 min (▽); 990 min (○)

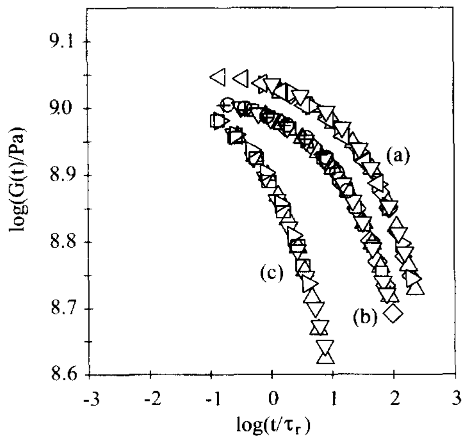

Figure 2 Master curves for PVAc obtained by time–ageing-time superposition. For clarity, approximately only one in five data points per ageing time run are shown compared with *Figure 1*. (a) 298 K curve: 30 min (◇); 60 min (△); 120 min (▽); 240 min (▷); 1350 min (◁). (b) 303 K curve: 30 min (◇); 60 min (△); 90 min (□); 120 min (▽); 990 min (○); 1170 min (+). (c) 308 K curve: 60 min (△); 120 min (▽); 240 min (▷); 1250 min (□)

Table 1 Values of log G_0 and the characteristic relaxation times τ_r for PVAc after various ageing times (t_a) at three ageing temperatures

T (K)	t_a (min)	log (G_0 (Pa))	log (τ_r (s))
298	30	9.15	2.57[a]
	60	9.15	2.76
	120	9.14	3.03
	240	9.11	3.36
	1350	9.12	3.63
303	30	9.04	2.25[a]
	60	9.03	2.63
	90	9.07	2.92
	120	9.00	3.11
	990	9.11	3.14
	1170	9.07	3.21
308	60	9.09	0.80[a]
	120	9.07	0.97
	180	9.04	0.97
	240	8.97	1.07
	1250	8.98	1.25

[a] Values of τ_{r0} used to calculate values of log a shown in *Figures 3–5*

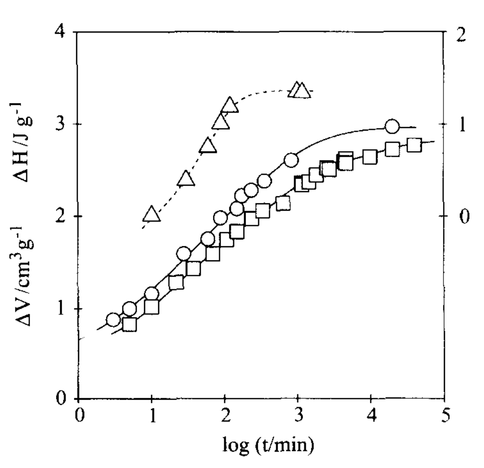

Figure 3 Enthalpy (○) and volume (□) changes for ageing of PVAc at 303 K, taken from Cowie *et al.*[20,21], and shift factor log a (△) as a function of ageing time

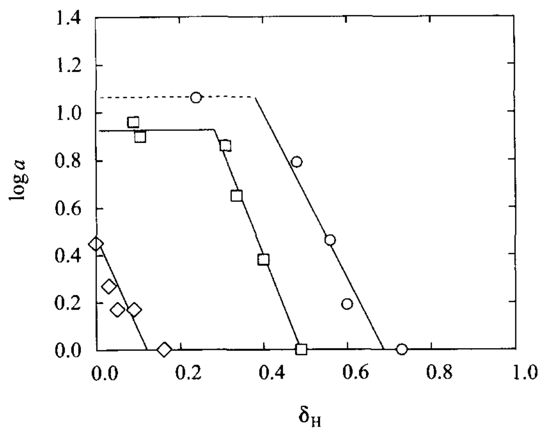

Figure 4 log *a versus* departure from enthalpy equilibrium δ_H: 298 K (○); 303 K (□); 308 K (◇)

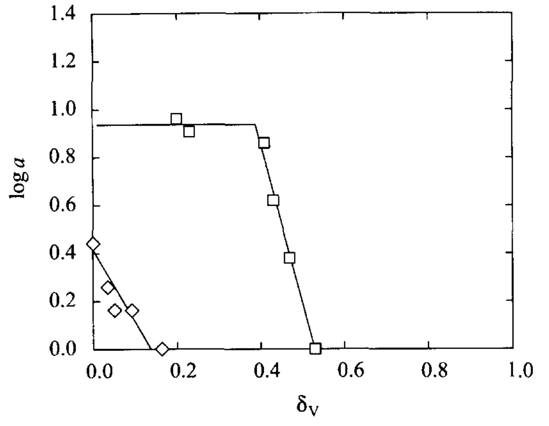

Figure 5 log *a versus* departure from volume equilibrium δ_V: 303 K (□); 308 K (◇)

temperatures studied, where

$$\delta_X(t) = 1 - \frac{\Delta X(t)}{\Delta X_\infty} \qquad (6)$$

ΔX is the change in volume V or enthalpy H and ΔX_∞ is the equilibrium value of that parameter. The behaviour at 298 K and 303 K is such that we may conclude that the shift factor attains a constant value while the sample volume and the sample enthalpy are still greater than their respective equilibrium values ($\delta = 0$). At the highest temperature examined, 303 K, this effect is not clear, or is absent.

The accepted relationship between free volume and ageing is due to Struik[25]. He reasoned that since the temperature-dependent free volume of a polymer above T_g has no effect on the shape of a relaxation response but only on its position, so then below T_g the time-dependent free volume of a glass will also dictate position, but now on the ageing time scale. The results we show in *Figure 4* are similar to those of McKenna and his coworkers[32] who also found that mechanical equilibrium was attained before volume equilibrium (and hence before free volume equilibrium), leading these workers to suggest that such a rationalisation of the time–ageing-time superposition cannot be so confidently based on free volume arguments as was previously assumed. In fact, *Figure 4* is in direct contradiction to the correlation between viscoelastic shift factors and free volume presented by Lagasse and Curro[35] for PVAc. These investigators calculated that the mechanical state of the system does *not* come to equilibrium prior to the volume by employing the Simha and Somcynsky[24] equation of state to calculate time-dependent free volume $f(t)$ from Kovacs's volume measurements[37], and then inserted this into the Doolittle equation

$$\ln a(t) = B[f(t)^{-1} - f_0^{-1}] \qquad (7)$$

where B is a constant and f_0 the reference state. Within the Simha–Somcynsky theory f is essentially a linear function of the total volume and so equation (7), if applied to the volume data in *Figure 3*, would predict eventual mechanical equilibrium at least approx. 2 orders of magnitude later than is actually observed. A similar form of equation (7) has been employed by others[34,37] who also presuppose that mechanical response changes are linked to volume relaxation and that the shape of a log a curve reflects directly how long it takes for f to approach f_0, in essence that mechanical equilibrium and volume equilibrium should take place on the same time scale.

The disparity between the apparently successful prediction of shift factors from volumetric data obtained by Lagasse and Curro and our present data, and also the findings of McKenna's group, may find reconciliation of sorts in a recent paper by Delin *et al.*[38]. They also have examined ageing in PVAc, both by dilatometry and by dynamic mechanical analysis. In down-jump experiments it is their volume which relaxes faster than the dynamic mechanical properties, the exact reverse of our own and McKenna's findings for this type of thermal history. From various arguments Delin's group propose that this contradiction is due to rejuvenation effects caused by the applied cyclic straining in the dynamic tests. If this is so, and some limited information is provided to support the premise, then yet one further complication is now interposed when one is attempting to correlate or predict ageing effects using different physical properties; i.e., quite different responses are to be expected from relaxation experiments and dynamic experiments. In this respect it should be noted that Lagasse and Curro employed *dynamic* shift factors derived separately from the work of Kovacs *et al.*[39].

Returning to the original intention of this series of papers on the physical ageing of PVAc, which was (a) to obtain enthalpic, volumetric and mechanical data using the same sample so that meaningful comparisons can be drawn and (b) to investigate the possibility of predicting one response from measurement of another, we find that the three properties change on distinctly different time scales which show different temperature effects. The different dependences of volume on temperature and enthalpy on temperature are evident from the KWW characteristic times presented in the second paper of the series[21]. A temperature-dependent change in mechanical response with respect to volume or enthalpy is apparent from the shape of the 308 K curve in *Figures 4 and 5* relative to that at the other two temperatures. The possibility of prediction thus seems elusive and there is still much to be done regarding a fuller understanding of the relaxation processes in a glass. For the moment we can do no better than to reiterate a previous conclusion[21], i.e. that comparisons between the ageing rates of different physical properties of a polymer glass lie firmly within the *experimental* discipline of kinetics.

Even so, some explanation of the trends in the ageing behaviour found for PVAc does seem preferable to none at all. It is likely that different physical properties respond to different motions which make up the underlying structural relaxation. Indeed, this is the explanation that Roe and Millman[26] proposed in 1983 when they noted that the photon correlation spectrum of polystyrene near its T_g is broad and consequently proposed that mechanical properties may respond to the whole range of frequencies but volume and enthalpy changes reflect only those modes and relaxations with longer relaxation times. A somewhat similar philosophy, the partitioning of effects among different molecular events, is inherent in equation (2) and can be used to rationalise the observed disparity[20] in volumetric and enthalpic ageing of PVAc, in particular the fact that the enthalpy continues to change after the volume has reached an equilibrium state at certain temperatures. Assume that two order parameters operate, vacant sites and the proportion of *gauche* to *trans* conformers. Although the latter must relax towards equilibrium by localised motions involving adjacent vacancies, these vacancies need not contribute to free volume but could equally well be due to density fluctuations. Conformational enthalpy therefore can continue to change after the free volume, and global volume, have equilibrated.

That the mechanical response ceases to shift prior to the attainment of volume or enthalpic equilibrium is not easily explained. If one considers packing effects as the determining factor for entanglement formation, and hence the response to mechanical relaxation probes, then it appears that beyond a certain stage of structural equilibration entanglement has reached an effective limit. Close to the equilibrium glass structure slow structural changes may, and do, still occur, but these are limited or localised to such an extent that they do not create structural architectures which affect the mechanical response. In this sense, then, the shifting of viscoelastic response with ageing appears discontinuous on free volume at some stage in structural reorganisation. McKenna *et al.*[32] express similar reservations about the direct link between free volume and viscoelastic response, but more data need to be gathered from a variety of structures to see whether the effects found in this paper are indeed general.

ACKNOWLEDGEMENTS

S. Harris gratefully acknowledges support from the SERC during the course of this study.

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