# Timescales in physical ageing of poly(vinyl acetate)

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## ABSTRACT

A study of physical ageing of poly(vinyl acetate), PVAc, in the $T_g$-region has been carried out. Two different experimental techniques were used, dynamic mechanical thermal analysis (DMTA) in shear mode and dilatometry. Measurements were carried out for both temperature down- and up-jumps. The influence of the mechanical stimulation in the DMTA has been considered. Timescales for volumetric and mechanical evolutions have been compared, and ageing rates, $\mu$, have been calculated.

## INTRODUCTION

The non-equilibrium behaviour of the glassy state, and thus the structural relaxation of the glass, has important consequences for the stability of polymer properties.

The correlation between structural relaxation and quasistatic linear viscoelastic behaviour, e.g. creep and stress relaxation, has been in the mainstream of physical ageing for many years, and especially since the work of Struik[1].

On the other hand, the evolution of dynamic mechanical properties has been much less explained. It is well-known that the various viscoelastic functions are inter-related[2], and in principle any viscoelastic test completely characterises the material. With dynamic mechanical thermal analysis (DMTA), however, storage and loss properties are measured directly and can be analysed separately, also higher frequencies permit a closer approach to the unrelaxed values of compliance and modulus.

## EXPERIMENTAL

Specimens were made from poly(vinyl acetate), PVAc, ( Mowilith 50, Hoechst AG).

Bekkedahl type dilatometer (mercury- in-glass) was manufactured following ASTM Standard D864-52 and Kovacs' remarks on filling procedures[3]; it was next used to monitor the volumetric response of the material.

DMTA measurements in torsion mode were carried out using the Rheometrics Dynamic Analyzer (RDA 2). Dynamic measurements were carried out during physical ageing, at selected times. Frequencies of 0.0314 Hz, 0.1 Hz, 0.314 Hz, 1 Hz, 3.14 Hz and 10 Hz were used. The strain was 0.1 %.

## RESULTS

The glass transition, $T_g$, was determined using the dilatometer to be 33 °C at a cooling rate of -0.075 °C/min. In the case of calorimetrically determined glas transition, and particularly where the influence of fast relaxation is significant, the fictive temerature[4], $T_f$, is an alternative to $T_g$. By using a Mettler DSC 30 apparatus $T_f$ (for the ageing time=0) was found to be 43.8 °C. The main transition was determined using the shear loss modulus peak (represented in Fig. 1) to be 42.1 °C.

A few temperature down-jumps from an initial equilibrium state at 40 °C, similarly to the "groupe élémentaire" 1a described by Kovacs[5] were measured. The isothermal contraction data are shown in Fig. 2. Prior to the temperature up-jump the sample was

annealed in the dilatometer at 32.5 °C for the time required to reach voluminal equilibrium (approx. 50 hours).

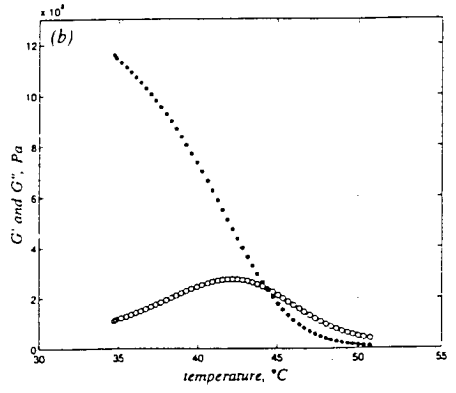


Fig. 1. Shear loss modulus ( o) and storage modulus (•) vs. temperature in a cooling sweep (-0.1 °C/min) for PVAc at the standard frequency of 1 Hz. Strain was 0.1 %.

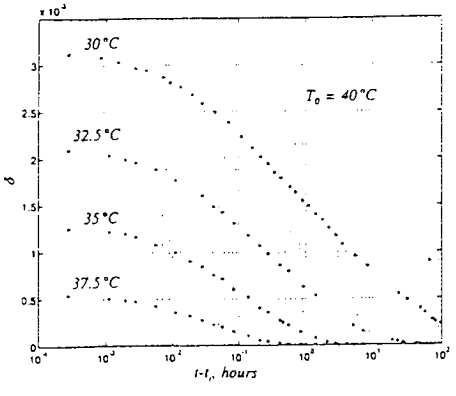


Fig. 2. Isothermal contraction of PVAc at different temperatures T (indicated on the plots), after down-jumps from equilibrium at $T_0$=40 °C. Volume is normalized as the relative departure from equilibrium, $\delta=(V-V_\infty)/V_\infty$, where $V_\infty$ denotes the equilibrium value. Time is measured from $t_i$, where $t_i$ is the time required for thermal stabilization and was 40 s.

DMTA measurements of physical ageing for G' and G" were made following the same thermal histories as for the volumetric measurements. Results for the temperature down-jump from 40 °C to 35 °C are presented in Fig. 3. It can be seen, as has been reported by other authors (e.g. Kovacs et al.[6]), that the storage modulus G' increases monotonically after a temperature down-jump (and decreases after a temperature up-jump, not shown here). For the loss modulus G" the opposite takes place (not shown here).

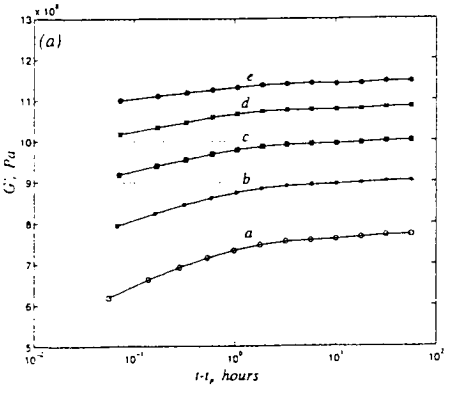


Fig. 3. Evolution during physical ageing of the storage modulus, G' for PVAc after a temperature down-jump from 40 °C to 35 °C. Frequencies: a-0.0314 Hz, b-0.1 Hz, c-0.314 Hz, d-1 Hz, e-3.14 Hz. Strain was 0.1 %.

## DISCUSSION and CONCLUSIONS

A comparison between volumetric evolution following a temperature down-jump and the evolution of dynamic mechanical properties shows that it is the external volume that equilibrates first (for example compare plot "35 °C" of Fig. 2 with plots of Fig. 3). This behaviour was representative and the same took place in case of the loss modulus, G", and for another temperature down-jump (from 40 °C to 32.5 °C). For the temperature up-jump the opposite took place, that is the

dynamic mechanical properties equilibrated earlier than external volume.

For the purpose of further analysis here the ageing rate, μ, was calculated. Ageing rate (defined by Struik[1]) is generally close to unity for the creep experiment for amorphous polymers just below the glass transition temperature. Here the ageing rate was calculated as:

$$\mu = -\frac{d\log a}{d\log (t_e/t_{er})},$$

where log a is the shift factor and was obtained by constructing isochronals from plots of the type represented in Fig. 3, and next shifting isochronals horizontally. The results are shown in Fig. 4.

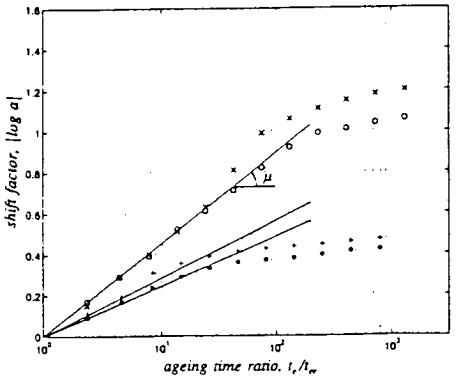


Fig. 4. Plot of log(shift factor) vs. log(ageing time ratio) evaluated from the frequency dependence of shear moduli G' and G" for the temperature down-jump 40-35 °C: G'-(•) and G"-(+), together with down-jump 40-32.5 °C: G'-(o) and G"-(x). The slope indicates the ageing rate, μ.

The ageing rates measured by dynamic mechanical thermal analysis (DMTA) in the $T_g$-region, are significantly less than unity (see Table 1). The ageing rates are lower for the ageing temperature of 35 °C compared to the temperature of 32.5 °C. We interpret the low ageing rate as resulting from mechanical stimulation used for DMTA. This rejuvenation effect appears to be possible at small strains in the region of high dissipation, affecting the timescales and ageing rates.

Table 1. Ageing rates, μ, measured by G' and G".

| quench | property | |
|---|---|---|
| | G'(ω) | G"(ω) |
| 40°C/35°C | 0.23* | 0.27* |
| 40°C/32.5°C | 0.44* | 0.44* |
| 32.5°C/36.2°C | -0.65** | -0.85** |

*) frequencies 0.0314 Hz to 3.14 Hz
**) frequencies 0.1 Hz to 10 Hz

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