Dynamic shear measurements of ageing rate for poly(vinyl acetate) in the T_g-region

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ABSTRACT

The influence of the mechanical stimulation in shear dynamic mechanical analysis (DMA) on the physical ageing rate for poly(vinyl acetate), PVAc, has been further analysed. The previously reported ageing results below T_g (e.g. Delin et al.[1]) have been extended to lower temperatures. The ageing rate, μ, has been measured and analysed using G' modulus data for different strains and various loading sequencies.

INTRODUCTION

It is well known that all structure related properties of glasses change with time following a given thermal history. This process is referred to in literature as physical ageing (Struik[2]). A study on physical ageing of poly(vinyl acetate), PVAc, has been carried out and selected results have been reported elsewhere (Delin et al.[1]). In the above study it was shown that dynamic shear mechanical properties and external volume recovery take place on different timescales, following temperature down-jumps from equilibrium at 40 °C to ageing temperatures of 32.5 °C and 35 °C, for PVAc. Physical ageing rate, μ, as explained in the above paper, was calculated at the two mentioned temperatures (and at a temperature of 36.2 °C after an up-jump). A possibility of the ageing rates becoming affected by the torsional oscillations used by the mechanical spectrometer was postulated, taking into account the rather low μ values measured using DMA. In the present work, the ageing rate is analysed more in detail, using the same material and experimental set up as in the previous work.

Specimens were made from PVAc (Mowilith 50, Hoechst AG). DMA measurements in torsion mode were carried out using the Rheometrics Dynamic Analyzer (RDA 2). The samples were mounted in the RDA apparatus using torsion rectangular fixtures supplied by the manufacturer and were held in place using special clamps designed to overcome the problem of sample distortion in the clamped region during the experiments (Delin et al.[3]). The glass transition temperature, T_g, was determined dilatometrically to be 32.3 °C at a cooling rate of -0.075 °C/min. Also, using a well established DSC procedure, the glass temperature, T_g, was measured following cooling rates similar to the ones used during quenching, although at a standard temperature up-scan of +10 °C/min. This measured glass temperature was found to be 43.8 °C.

The interest in ageing rates derives from the currently held mainstream discussions about physical ageing in polymer glasses, in general, and about the influence of straining on ageing, in particular. The results and arguments have been excellently summarized by McKenna[4] who shows the demarcation line between the "classical" picture of ageing given by Struik and some "non-classical" recent ageing experiments. Our previous study on timescales indicates, similarly as postulated by McKenna in a great number of his works, that the effects of structure on the structural (volume) recovery response needs not be the same as for the viscoelastic response. In our study we have used dynamic mechanical properties to analyse this behaviour. For small strains in the linear viscoelastic region, we found that the mechanical evolution is slower (longer timescale) than the volumetric recovery (shorter timescale), after a temperature down-jump. However, a question here remains how do the "loading-unloading" sequences and thus energy transfered to the sample distort the timescales in the process of measuring them.

In the following, we show an investigation of the ageing rate, μ, using different strains. Clearly, at very small strains the strain energy transfered to the sample is greatly reduced and consequently the effect on ageing as measured by the ageing rate should be less pronounced. We believe this is relevant to the previously described timescales (Delin[1]) and to the general observation that actual relaxation processes in polymers occur on many different timescales. Another point of interest comes from the fact that the described effects are relevant to the frequently used DMA characterization technique.

INFLUENCE OF STRAIN AMPLITUDE

Previously (e.g. Delin et al. [1]) ageing results for PVAc at 35 °C and 32.5 °C have been analysed. In the present work, further results at 30 °C and 27.5 °C are shown. Strain amplitudes of 0.01%, 0.05%, 0.1% and 0.2% were applied. The storage and loss moduli, G' and G'', respectively, were measured for five frequencies (0.0314, 0.1, 0.314, 1, 3.14 Hz) equally spaced on the logarithmic frequency scale. In some cases a frequency of 10 Hz was also used. Acquisition of data during ageing was carried out in the following manner. At a given ageing time, a frequency sweep starting with the lowest frequency (0.0314Hz) and ending with the highest frequency (normally 3.14 Hz), with no time intervals between the individual frequency points, was carried out. This procedure was repeated starting from an early ageing time between 0.05 h to 0.1 h and continued for about 100 h. The total time of the frequency sweep (loading time) was kept at less than 0.1 ageing time.

The procedure for calculating the aging rate, μ, has been described elsewhere (Delin et al.[3]). Following this procedure the ageing rates were calculated from G' data for the four previously mentioned ageing temperatures following a temperature down-jump from equilibrium at 40 °C. The results are presented in Figure 1.

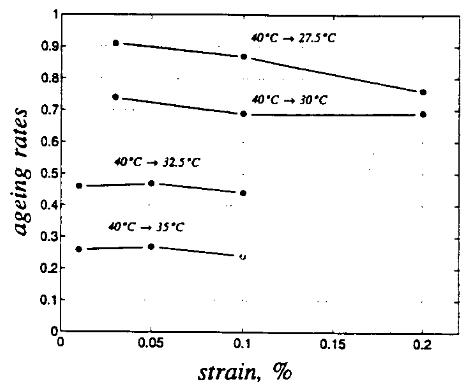

Fig. 1. The influence of strain used in DMA on the ageing rate μ, for PVAc following indicated on curves thermal histories.

As can be seen from Figure 1 there is hardly any measurable influence from the strain magnitude at temperatures close to T_g, for the applied small strains in the linear viscoelastic region. However, the effect increases with negative distance to T_g becoming obvious, although weak, at about 3 °C below the T_g. It is well known that the ageing rate should approach zero at the glass temperature, increase to unity just below T_g, and next decrease again at deeper in glass temperatures. This behaviour can be seen from the plots in

Figure 1 although the level of μ =1 has not been reached and instead the level of 0.9 has been approached. Also, lower than 27.5 °C ageing temperatures would be required to investigate the deeper in glass behaviour, however, this was outside the scope of the present study.

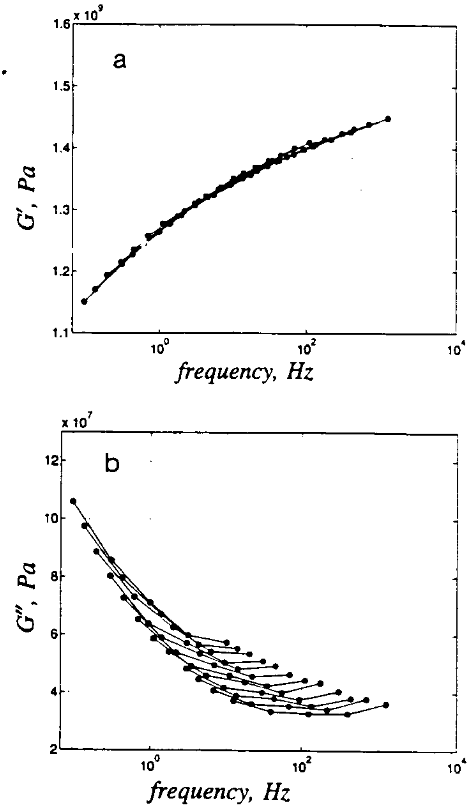

Fig. 2. Time-ageing time superposition following a 40 °C to 27.5 °C down-jump: G' modulus forms a master curve (a), while the superposition breaks down (b) for G'' modulus (the same as for G' shift factors were used). Strain was 0.2%.

The time-ageing time superposition (horizontal shifts of isochronal lines constructed from acquired data) was successfully used in this work to obtain ageing rates for the G' modulus (see Fig. 2a). An attempt to achieve the same for the loss modulus G'' was unsuccessful. The break down of G'' modulus to form a master curve is shown in Figure 2b. At the present stage we cannot explain this behaviour.

INFLUENCE OF THE LOADING SEQUENCE

As explained in the previous section five frequencies with no time interval were used to measure the ageing rate. The closeness in time at which each frequency point is taken could suggest that the procedure influences the measured ageing rate. To investigate this effect measurements of μ were carried out with two instead of five frequencies, and sequencies were introduced where frequency points were separated by 20 s from each other . No measurable influence was observed.

CONCLUSIONS

The study has provided results relevant to the understanding of physical ageing in polymer glasses (PVAc). The use of the DMA technique for measuring ageing effects in polymers has been demonstrated.

ACKNOWLEDGEMENTS

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