Physical ageing in glassy polymers. An i.r. spectroscopic investigation of poly(ethylene terephthalate)

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The progress of physical ageing has been followed spectroscopically in thin films of polyethylene terephthalate, stress relieved to eliminate the effect of orientation. The changes observed are ascribed to the temperature dependent conformational changes of liquids interrupted by the onset of the glass formation. On physical ageing, there is progressive relaxation of the glass, determined by the temperature, towards the equilibrium conformation as defined by extrapolation of the liquid temperature dependence, and there is no necessity to assume structure formation within the glass to account for the spectroscopic changes. Physical ageing has no effect on the subsequent rate of crystallization at temperatures above the glass transition. Heating above the glass transition immediately eliminated physical ageing effects.

Keywords Ageing; glass transition; crystallization; infra-red spectrum; thermal analysis; calorimetry

INTRODUCTION

There have been several reports on the formation of ordered domains within glassy materials during physical ageing[1-5] and these domains have been observed to grow with ageing time. Ageing has also been observed to increase the rate of subsequent crystallization on heating to temperatures above the glass transition[4,6], consistent with the formation of stable nuclei. Yeh[7] has proposed a folded chain fringed micelle model for these ordered domains and Geil[8] has suggested that amorphous polymers consist of nematic liquid-like domains with extended chain order, while Aharoni[9] contends that the chains are densely packed with uniform segment packing.

In contrast, Flory[10] has listed the evidence for chains in a polymer melt having a random coil conformation, as evident from low angle neutron scattering studies. Recently, Lowe[11] has reported that the nodular domains observed on electron microscopic examination of thin polymer films are artefacts of electron beam damage. Super-nodular structures, 20–100 nm in diameter, observed on the surface are not associated with physical ageing since they do not increase in size, and were a feature of surface topography only.

Petrie[12], and others[13], have related observed changes in thermodynamic and mechanical properties to a relaxation process associated with the kinetic nature of the glass formation from the liquid, and the trend towards equilibrium as defined by the super-cooled liquid.

Ito *et al.*[14] have observed a change in the i.r. spectrum of polyethylene terephthalate with physical ageing which could be interpreted as indicative of structural changes occurring within the glass. This has been reconsidered in terms of similar changes observed during recrystallization for comparison.

EXPERIMENTAL

I.r. spectra of PET were measured on a Perkin-Elmer model 21 i.r. Spectraphotometer in a heated cell which could be heated to 470 K and controlled to ±2 K, by adjusting the voltage. The cell has been described elsewhere[15].

30 Micron films were moulded between aluminium foil, coated with silicone oil for rapid release, at 550 K for 2 min. They were rapidly quenched by immersing in ice/water. Films were amorphous, by density and by d.s.c. analysis, and exhibited no decrease in viscosity over original moulding powder. These moulded sheets were stress relieved by heating for several hours above the glass transition temperature to eliminate orientations which altered i.r. spectra. No measurable amounts of crystallization developed in this treatment.

A differential scanning calorimeter, d.s.c., Perkin-Elmer model 2, was used to characterize the glass transition and the heat capacity–temperature dependence of the quenched, aged and crystalline PET. 25 mg samples encased in aluminium pans were used at various heating rates. The calorimeter was calibrated with indium, and benzoic and stearic acids, as described elsewhere[16].

RESULTS AND DISCUSSION

Films of PET were physically aged at various temperatures from 320 to 350 K and for various periods of time. The extent of ageing was followed by the decrease in the enthalpy of the glass, as measured by d.s.c., which became apparent at the glass transition temperature, see *Figure 1*, by an endothermic process. The procedures developed by Richardson and Saville[17] were adopted to measure this decrease in enthalpy from that of the ice/water quenched PET. This decrease in enthalpy

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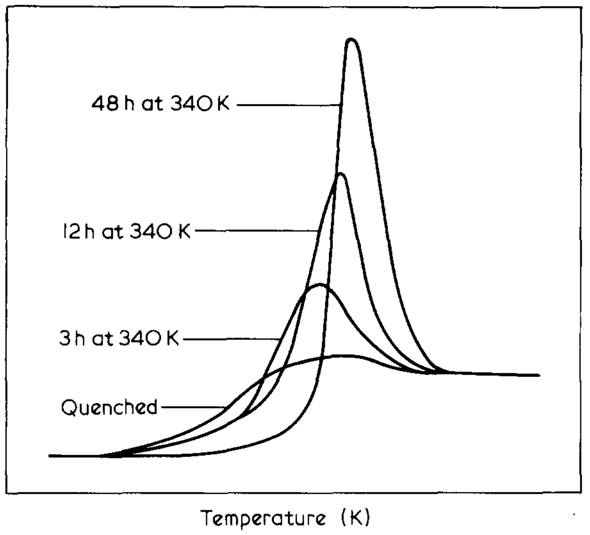

Figure 1 Effect of physical ageing period on the development of endothermic peaks at the glass transition temperature. Endothermic peaks at T_g with increasing ageing time

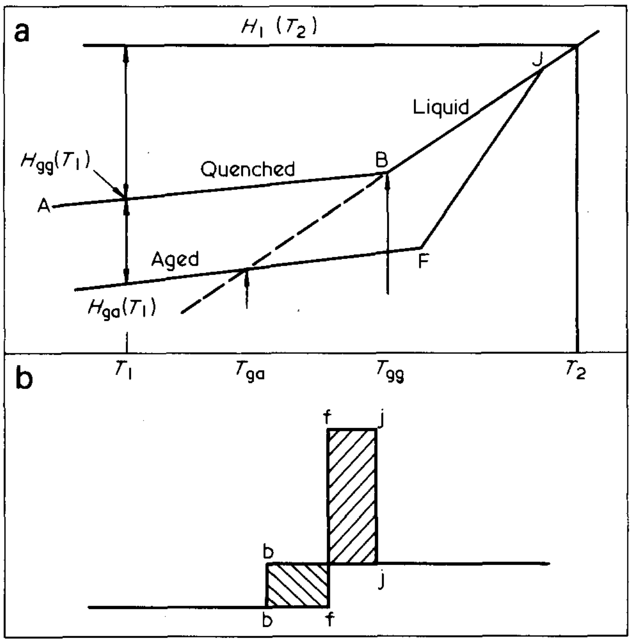

Figure 2 (a) Schematic representation of the temperature dependence of the enthalpy of quenched, physically aged and liquid PET: (b) showing how peaks arise on heat capacity curves; after Richardson (see ref 17)

($-\Delta H_A$) changed linearly with log (time) towards the equilibrium limit imposed by the restriction of the supercooled liquid, i.e.

$$-\Delta H_{\infty} = \Delta C_p \cdot \Delta T \qquad (1)$$

see *Figure 2*, in which ΔC_p is the heat capacity change between liquid and quenched glass at the glass transition temperature T_g and

$$\Delta T = T_g - T_A, \quad \text{with } T_A \text{ the ageing temperature.}$$

Linear plots of $(1-\Delta H_A/\Delta C_p \cdot \Delta T)$ against log (time) define an apparent relaxation time (τ) for the physical ageing process at which equilibrium is achieved, see *Figure 3*.

I.r. spectra were also measured on specimens aged at various temperatures and for various periods. There was a progressive decrease in the ratio, *R*, of the intensities of two bands at 896 and 763 cm^{-1} characteristic of *gauche* and *trans* conformations of the chain. The band at 896 cm^{-1} has been assigned by Miller and Willis[18] to the methylene rocking mode of the *gauche* isomer and the band 973 cm^{-1} to the stretching mode of C–O in the ethylene glycol residue; the absorbance of the 973 cm^{-1} band changes depending on whether it is in a crystalline or amorphous region[19]. Koenig and Cornell[20] have discussed the use of the ratio of the intensities of these bands to measure chain orientation in stretched PET, and in measuring crystallinity. The ratio appeared within the limiting accuracy of the technique to change linearly with log (time) with a similar rate to that observed with the decrease in enthalpy, implying a trend towards an equilibrium conformation. Accordingly, the infra-red spectrum of a quenched PET film was measured while heated progressively from room temperature. The ratio of intensities of the two bands (*R*) in the glass increased linearly, over the limited temperature range, up to a temperature close to the d.s.c. measured T_g[8]. Thereafter, the ratio increased at a higher rate with temperature until above 370–375 K when crystallization occurred. On crystallization, the film whitened and the ratio decreased rapidly. The temperature dependence of the ratios for the quenched glass and the liquid PET are shown in *Figure 4*, along with the ratios, measured at room temperature, observed with aged specimens. It is obvious that these ratios lie within the limits of those of the quenched and supercooled liquid, obtained by extrapolating to the ageing temperature. On ageing, at a constant temperature, the ratio moves towards the extrapolated equilibrium ratio defined by the liquid ratio temperature dependence. Crystallinity has a marked effect on the ratio

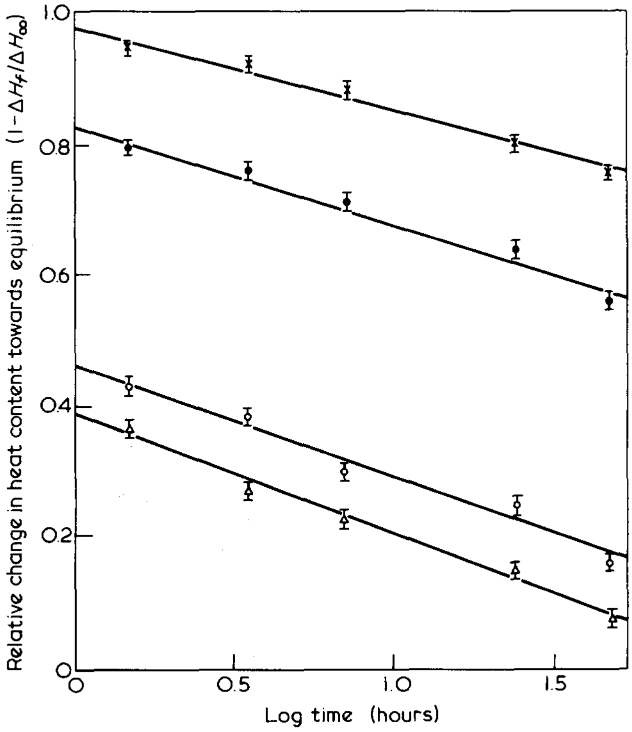

Figure 3 Relative enthalpy change with ageing period: △, aged at 344K; ○, aged at 340K; ●, aged at 333K; X, aged at 325K

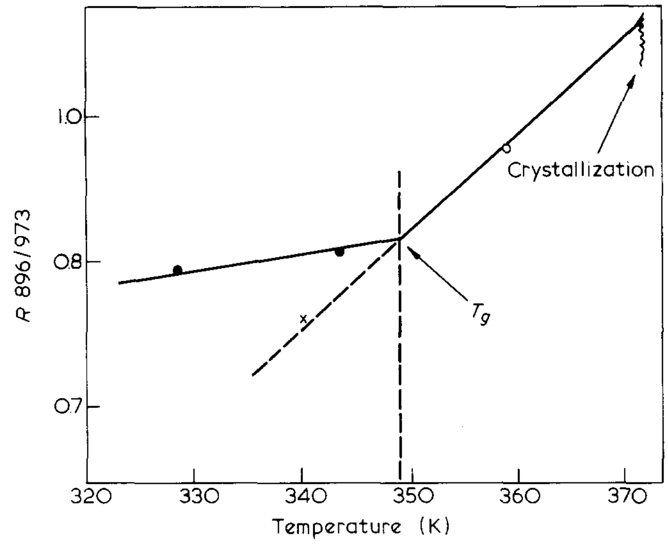

Figure 4 I.r. spectroscopic changes on physical ageing and temperature variations. $R \equiv$ Ratio of absorbance of 896 to 973 cm^{-1} bands: ●, quenched; X, aged at 340K for 48 hours; ○, above T_g

Table 1 Rate parameters – crystallization

Crystallization temperature (K)	Time to max. rate (min.)	Half life $t_{1/2}$ (min.)	$-\log(Z)$ (min^{-n})	n ±0.2
378	38.2	67	4.74	2.5
379	25.1	33	3.65	2.3
380	9.8	13.6	2.47	2.0
381	4.8	7.4	1.82	1.9
382	3.6	4.4	1.42	2.0

of the intensities of these bands and the change is an order of magnitude larger than that of physical ageing. Even after prolonged ageing periods, it was not possible to exceed the ratio limit imposed by the extrapolation of the liquid line.

The crystallization kinetics of PET were studied isothermally by d.s.c. on samples quenched to the crystallization temperature, in the region 375 to 385 K, from above the observed melting temperature. Crystallization rate was controlled by bulk diffusion rather than nucleation in this region. The extent of crystallization at time t, i.e. X_t, was obtained by integrating from the onset of crystallization to time t the rate of heat evolution, as outlined previously[19]. A computer interface substantially improved the quality of the integration procedure and corrected for initial cooling effects[22]. Rate parameters were determined by analysing the time dependence of the extent of crystallization using the Avrami equation, i.e.

$$-\ln(1-X_t)=Zt^n \qquad (2)$$

in which Z is a composite rate constant including nucleation and growth, and n an integer constant characteristic of the crystallization mechanism. Some rate parameters are listed in *Table 1* from which it is apparent that the crystallization rate increases with temperature consistent with segmental diffusion control. For comparison the rate parameters of physical ageing are listed, in *Table 2*, and in particular the half life of the process. Clearly there is no continuity between the two processes, in that ageing appears by extrapolation to be instantaneous at the glass transition, i.e. 350 K, while crystallization has stopped.

Table 2 Rate parameters – physical ageing

Ageing temperature	Equilibration time (hours)	Half life $t_{1/2}$ (hours)
325K	10^8	1000
333K	6×10^5	100
340K	10^3	0.5
344K	3×10^2	0.17

Also, aged specimens exhibiting large endothermic transitions at the glass transition temperature, lost these within a very short equilibration time at the glass transition temperature (~1–5 min), unlike crystallinity, which persisted to a much higher temperature, i.e. to the m.pt.

Amorphous specimens aged in the region 320–340 K for various extended periods were subsequently recrystallized at 375–385 K, but no changes were detected in the crystallization rate parameters as listed in *Table 1*. The effects of physical ageing, as measured by d.s.c., i.r. spectra, and mechanical and thermodynamic properties, were apparently destroyed by heating to the quenched glass transition temperature. Indeed, there was evidence for some reversal in the effect of physical ageing by heating the aged specimens to higher than the ageing temperature for short periods. This is in total agreement with the phenomenon of physical ageing as described and characterized by Struik[23], and also by Kovacs *et al.*[24].

CONCLUSIONS

There is no evidence from rate studies on crystallization that stable nuclei develop during physical ageing which can survive to temperatures above the glass transition temperature, and nucleate phase separation.

Infra-red spectral changes are consistent with the temperature dependent changes in chain conformation which occur in the liquid but which are slowed down by the glass forming process. The changes only reflect the kinetic nature of the glass forming process.

There is no evidence for crystalline domains developing on physical ageing other than that which can normally be associated with liquid structures.

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