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Physical ageing in poly(ethylene terephthalate)—its influence on cold crystallisation

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Abstract

The relationship between the crystallisation behaviour and physical ageing history of poly(ethylene terephthalate) is reported. It is shown that short term ageing can enhance the subsequent rate of crystallisation, but longer ageing times can retard the crystallisation process. It is suggested that physical ageing favours the formation of ordered domains. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Physical ageing; Cold crystallisation

1. Introduction

Physical ageing is the process whereby amorphous materials in the glassy state approach a state of thermodynamic equilibrium [1]. This process can be detected through the time evolution of thermodynamic properties such as specific volume or enthalpy, as well as mechanical, dielectric or other physical properties [2].

Amorphous polymers such as atactic polystyrene, PS, have been studied intensively and the physical ageing process attributed to a free volume controlled event. The rate at which the ageing process occurs is directly related to the difference between the glass transition temperature (T_g) and ageing temperature (T_a). Poly(ethylene terephthalate), PET, is a semi-crystalline polymer susceptible to physical ageing effects when stored below its T_g. The morphology of 'amorphous' PET has been shown to contain paracrystalline type order [3] resulting from the alignment of molecular segments in the structure. The parallel alignment of molecules is enhanced by the planarity of the benzene rings in the molecular backbone. Consequently, physical ageing in amorphous PET is likely to be subject to constraints on the motion and conformational distribution imposed by the generation of these micro crystallites.

There is a general view that physical ageing is associated with the onset of glass formation and the restricted mobility of chain segments [4]. Earlier works speculated that ageing of glassy materials favoured the formation of ''ordered domains'' where the polymer chains were conformationally more ordered [3,5–8]. Studies using X-ray diffraction and electron microscopy have provided evidence for such increases in local order. For example, in glassy PET, Yeh and Geil [3] observed ''ball-like structures'' possessing a paracrystalline-type order which move, aggregate and align to produce structures of around 75 Å during annealing near or below T_g. More recently, using a microhardness technique, Baltá-Callleja et al. [9] observed a hardening of PET upon physical ageing, which they visualised as a nucleation mechanism. They ascribed ageing to local molecular motions that result in molecular ordering. One suggested mechanism was the parallelisation of the aromatic rings in the structure that would account for both a decrease in segmental mobility and molecular ordering. Work by Vittoria et al. on isotactic PS [10] and PET [11] also favours the suggestion of ordered domains which subsequently act as nuclei of crystallisation upon heating above the T_g. Thus the rate of crystallisation of samples aged below T_g is increased relative to the unaged samples. However, Hay and co-workers [12] maintain that there is *no* evidence of crystalline domains developing during the physical ageing process. Nevertheless, the notion of the formation of ordered domains upon ageing is particularly of interest in crystallisable polymers such as PET as possible sites for nucleation may already exist in the microstructure. For

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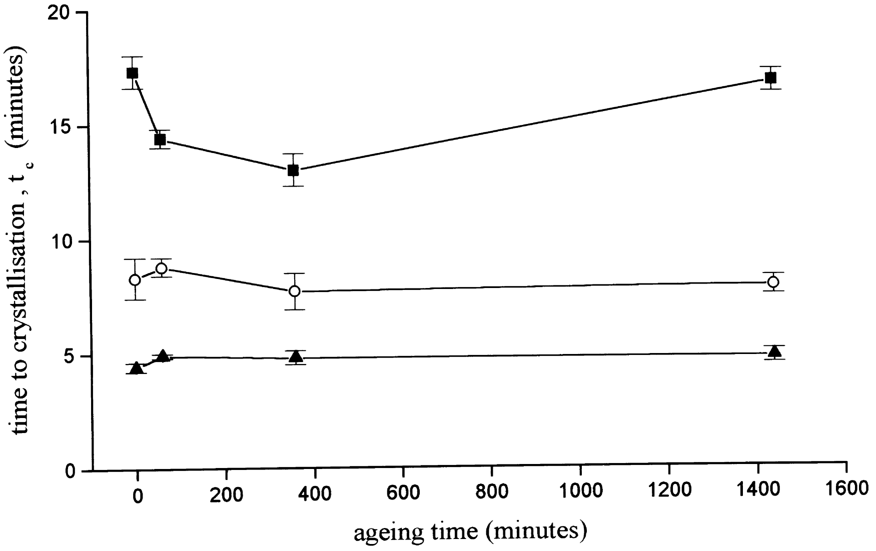

Fig. 1. Time to crystallisation (t_c) against ageing time for PET aged at 40°C with crystallisation temperatures (T_{crys}) of 110°C (■), 115°C (○) and 120°C (▲).

example, infrared spectroscopic studies such as those of Hay and coworkers [12] have shown that two distinctive conformers can co-exist in completely amorphous PET samples at ambient conditions through internal rotation of the O–CH_2–CH_2–O moiety: the *gauche* (G) conformation constitutes a large fraction of the amorphous phase, and the extended *trans* (T) conformers are distributed within the amorphous phase as localised regions of order and less ordered regions. Cole et al. [13] estimate that in amorphous PET, the ethylene glycol segment exists as about 10% *trans* and 90% *gauche* isomers.

As part of a larger study on the physical ageing of PET, we have re-examined the effect of physical ageing upon the cold crystallisation of PET. Particular emphasis was placed on the relationship between physical ageing and the crystallisation behaviour of PET as studied by DSC to examine whether or not physical ageing promotes the existence of ordered domains. In this article we report that under certain conditions ageing does indeed increase the rate of subsequent crystallisation, but that in other circumstances it retards crystallisation.

2. Experimental

2.1. Materials

A commercial grade of PET (Laser +) with an intrinsic viscosity of 0.809 dl g^{-1} was supplied by ICI Polyester and used in this study. The samples were melt cast amorphous films (230 μm), which were prepared for the ageing experiments by annealing above the melt temperature for 2 min followed by a direct quench in liquid nitrogen. No crystallinity was incorporated by this process.

2.2. Differential scanning calorimetry (DSC)

Samples of ca. 8 mg were sealed in aluminium pans and the thermal properties measured using a Du Pont 910 DSC. Indium was used to calibrate the instrument and a nitrogen atmosphere was used to prevent oxidative degradation of the samples. Ageing of the samples were conducted in air-controlled ovens at the appropriate ageing temperature, T_a. Two types of experiment were conducted: *isothermal* experiments and *dynamic* experiments. In the isothermal runs, the samples were quickly ramped from below the ageing temperature to the appropriate crystallisation temperature and the time to the peak of the crystallisation exotherm, t_c recorded. The second type of experiment (dynamic) involved heating the samples in the DSC from 40 to 300°C at 10°C per minute, noting the glass transition (T_g) and cold crystallisation exotherm peak temperature, T_p. All DSC experiments were conducted in triplicate. As an operational definition, T_g for the unaged and 40°C samples was defined as the temperature at which the specific heat was midway between that of the glass and the fluid. For all other samples, T_g was more readily defined experimentally in terms of the enthalpic recovery peak. Both values are known to shift to higher temperatures as ageing proceeds, and can thus be used as a measure of the extent of ageing.

2.3. Dielectric spectroscopy

Dielectric measurements were performed using the Strathdow dielectric spectrometer, which has been detailed previously [14]. Silver electrodes were coated onto the samples to provide maximum electrical contact. Samples were then equilibrated at the desired ageing temperature and dielectric spectra recorded over the frequency range 0.01–65 × 10^5 Hz at specified intervals. Temperature

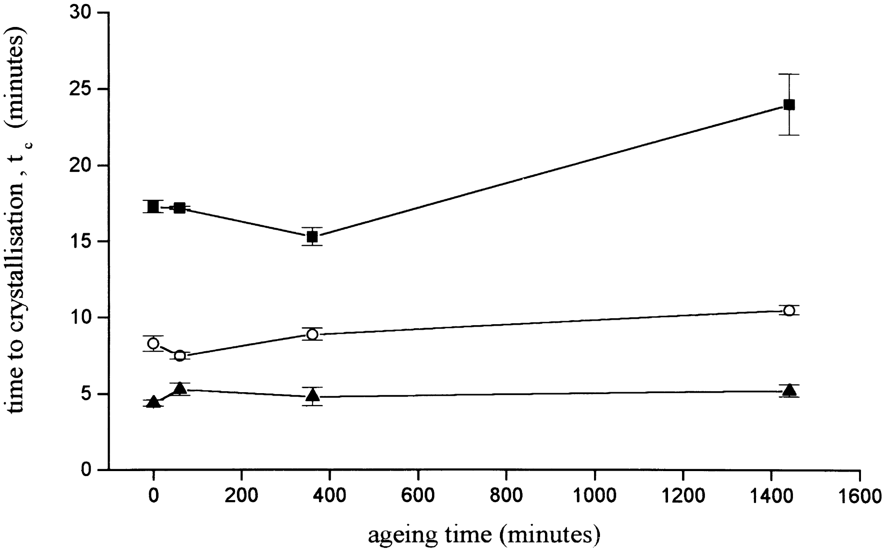

Fig. 2. Time to crystallisation (t_c) against ageing time for PET aged at 60°C with crystallisation temperatures (T_{crys}) of 110°C (■), 115°C (○) and 120°C (▲).

control for the dielectric measurements was better than ± 0.1°C.

3. Results

According to Vittoria and co-workers [10,11], if ordered domains develop during physical ageing, they provide a nucleus for subsequent crystallisation. Both our isothermal and dynamic crystallisation experiments show that the cold crystallisation process can indeed be accelerated by short term physical ageing. Surprisingly and significantly, however, longer ageing times can *retard* the crystallisation process. The isothermal results are displayed in Figs. 1 and 2 for samples aged at 40 and 60°C, and then crystallised at 110, 115 and 120°C. As expected, the crystallisation rate increases with crystallisation temperature, and at 115 and 120°C, there is little variation of t_c with ageing history. However, at 110°C, ageing at both 40 and 60°C leads first to a *reduction* in t_c followed by an *increase*. The dynamic experiments show similar trends (Fig. 3). Ageing at 40°C resulted in a significant decrease in T_p from an initial value of 152°C for the unaged PET, to a minimum value of 135°C after 24 h. Ageing at 60°C also produced a reduction in T_p, this time after just 1 h (137°C). No such reduction in T_p was observed for samples which had been aged at 70°C.

Fig. 4 shows the changes in T_g with ageing time. Within experimental error, at 40°C no changes in T_g are observed over the time-scales studied. This is in contrast to an ageing temperature of 60°C which showed a gradual increase in T_g

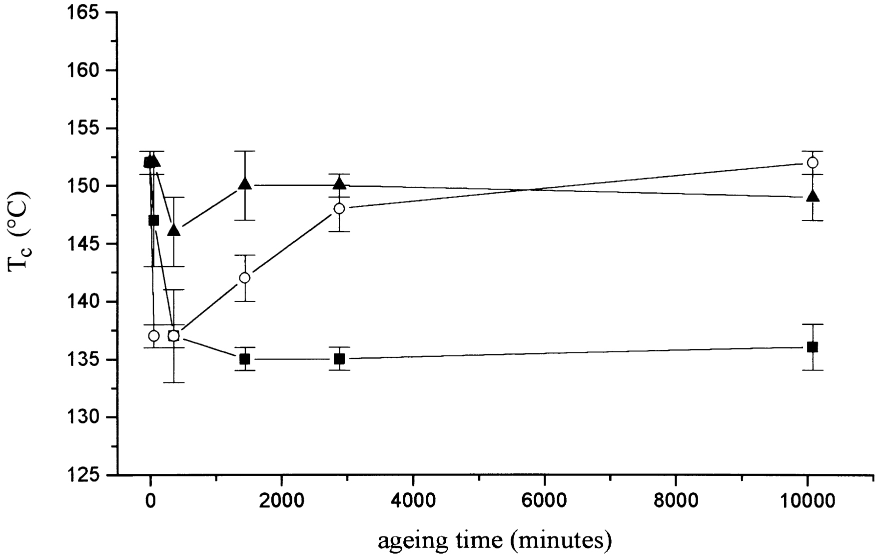

Fig. 3. Variation of T_p versus ageing time for PET aged at 40°C (■), 60°C (○) and 70°C (▲).

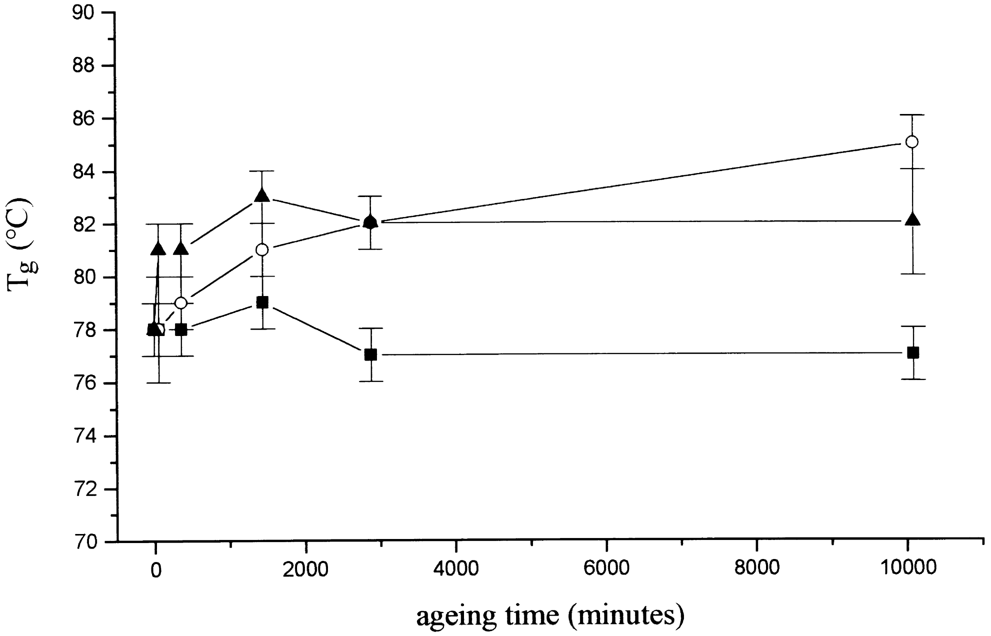

Fig. 4. Variation of T_g versus ageing time for PET aged at 40°C (■), 60°C (○) and 70°C (▲).

with further signs of increase after 168 h. At 70°C, a maximum increase in T_g is obtained after ageing for only 60 min.

By looking at the relaxation behaviour of specific molecular dipoles during ageing, it is possible to probe the changes in microscopic molecular mobility which one would expect to occur during ageing. A reduction in dielectric permittivity, ε' with ageing is attributed to a loss in dipole mobility and hence, segmental mobility of the polymer chains. In order to quantify these changes, the initial scan at each ageing temperature was taken as a reference and the reduction in ε' for each ageing time calculated at 1 Hz. It should be noted that though ε' did not change evenly over the whole frequency range, the same overall trends were observed. Plotted in Fig. 5 are the changes in ε' (1 Hz) for PET aged at 40, 60 and 70°C. Although a loss in dipole mobility is observed for all the studied temperatures, the largest, and fastest, reduction is observed at 70°C.

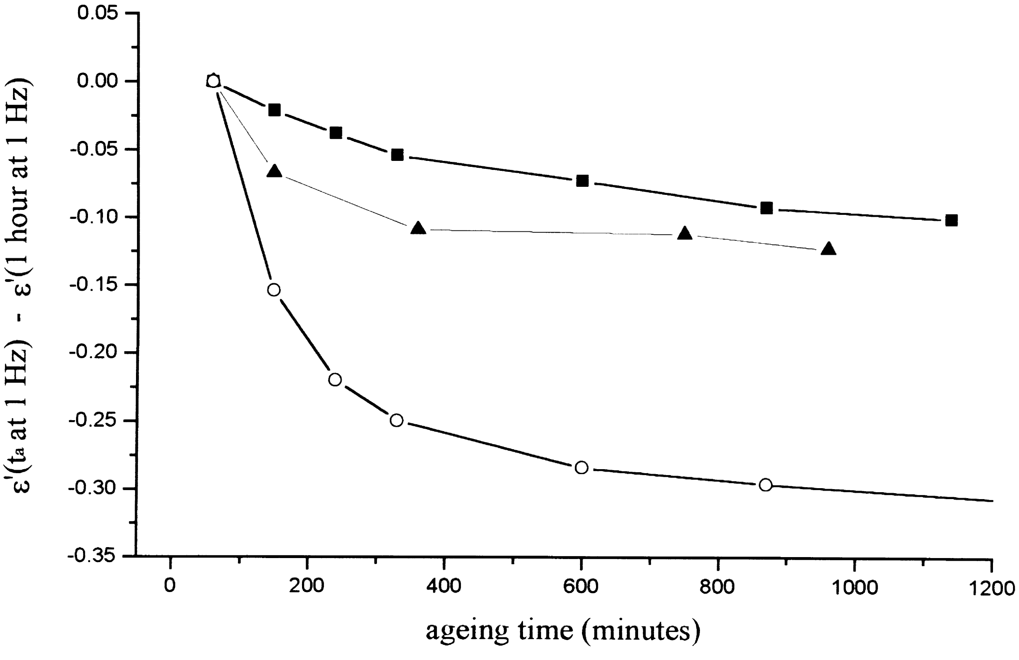

Fig. 5. Change in ε' measured at 1 Hz versus ageing time for PET aged at 40°C (■), 60°C (○) and 70°C (▲).

4. Discussion

Numerous enthalpic relaxation studies have been carried out on amorphous and semi-crystalline PET [15–20] and generally show an endothermic recovery peak which increases both in size and temperature with increasing ageing time. The increase in T_g with increased ageing time is normally attributed to a decrease in free volume in the glass during annealing [21]. Moreover, the extent of this increase in transition temperature depends not only on the ageing time, but also on the ageing temperature [21]. Our data showed the expected trends in T_g, and this, along with the dielectric permittivity data suggests that the physical ageing process is influencing cold crystallisation via both molecular ordering and reductions in chain mobility.

Consider first the T_p behaviour. Ageing at 40°C showed a decrease in T_p of 17°C after 24 h (Fig. 3). It is speculated that this reduction in T_p reflects a move towards a more ordered system upon ageing with regions of localised molecular order acting as crystallisation nuclei, consistent with the views of Vittoria et al. [10,11]. Ageing at 60°C also produced a large reduction in T_p (15°C), this time after just 1 h, as the faster ageing kinetics at this lower undercooling [1] is sufficient to produce an ordered system at a quicker rate. After 24 h, T_p gradually increased, regaining its initial value of 152°C after one week at 60°C concurrent with an increase in T_g of 8°C, indicative of a reduction in segmental mobility. Within experimental error, there is essentially no change in T_p for the samples aged at 70°C suggesting that any changes in molecular ordering or segmental mobility had occurred too quickly for changes in T_p to be measured. This is substantiated by the fact that T_g reached a maximum value after only 1 h at 70°C. Thus, the observed changes in T_p result from the opposing influence of increasing molecular order and decreasing chain mobility. The effect is most clearly observed experimentally for the samples aged at the lower temperatures, for as the dielectric data shows, at 70°C the reduction in chain mobility is both fastest and most pronounced, resulting in an ‘equilibrium’ value of T_p being achieved within the shortest experimental ageing time.

Similar conclusions can be drawn from the isothermal crystallisation studies. The sample aged at 40°C showed an initial decrease in the t_c compared with unaged PET, suggesting the presence of ordered domains which could provide a nucleus for crystallisation. At longer ageing times a gradual increase in t_c was observed, indicative of a decrease in segmental mobility. Similarly, the sample aged at 60°C and then crystallised at 110°C exhibited an initial decrease in t_c but this was not as distinctive as the sample aged at 40°C. After just 24 h at 60°C, the t_c was found to increase markedly, again reflecting a decreased chain mobility resulting from a more organised system. Physical ageing did not appear to affect the rate of crystallisation at 115 and 120°C, suggesting that these temperatures were sufficient to erase the effects of previous ageing in PET. This agrees with observations by Struik [1].

An alternative explanation for the observed behaviour can be formulated in the light of the recent proposal by Qian et al. [2,22] of the concept of ‘cohesional entanglements’ between neighbouring chains. These may or may not be identified with the regions of molecular order proposed by other workers but these cohesive regions can be conceived as acting as pinning points which will act to restrict the chain rotations associated with a molecular ordering process, leading to an increase in stress at the molecular level. Thus, the increase in cold crystallisation rate is due essentially to stress induced crystallisation. At a critical strain level, dependent on the ageing temperature, the entanglements disengage, relieving the stress and removing the stress induced component of any subsequent crystallisation process.

5. Conclusions

Clearly, our results show that physical ageing is influencing cold crystallisation via two ‘competitive’ mechanisms. The exact nature of these two opposing influences is unclear but will be subject to a more detailed scrutiny in our further study.

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