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The effect of physical aging on the rates of cold crystallization of poly(ethylene terephthalate)

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Abstract

The effect of physical aging and de-aging on cold crystallization rates of polyethylene terephthalate, (PET) has been investigated by differential scanning calorimetry (DSC). Storage of amorphous PET below the glass transition increases the rates of subsequent cold crystallization on heating above the glass transition temperature, T_g, and the increase in rate depends on the extent of physical aging which has developed. Various effects, from the development of primary nuclei on storage to a general decrease of the fictive temperature, have been considered. Both SEM and hot stage light microscopy of the bulk crystallizing specimens show that physical aging increased the number of spherulites present in the sample. De-aging, by heating aged specimens to higher temperatures but below T_g, was observed to reduce the extent of physical aging and the increase in the rates of crystallization closely followed the residual extent of aging.

Keywords: Physical aging; De-aging, Cold crystallization

1. Introduction

Volume relaxation studies [1–3] have revealed that on cooling a liquid, without the onset of crystallization, to a temperature below the glass transition temperature (T_g) it is no longer in thermal equilibrium with temperature and pressure. However, as the mobility of the chain segments is not zero, equilibrium will be achieved at a rate that is dependent on the storage temperature. This relaxation process has been called physical aging and as it is accompanied by a change in material and mechanical properties [4–6], it is of considerable commercial importance.

There has been some argument as to whether these changes due to physical aging can persist above T_g and for example change the rates and mechanism of crystallization. Harget and Siegmann [7] using small-angle X-ray scattering (SAXS) to detect structural changes in PET on aging found that the crystallites produced on subsequent heating were more densely packed and the crystallization developed more rapidly in aged PET specimens than unaged ones. Results from both WAXS and LAXS indicated that aging amorphous PET increased the structural order of the glass. Aharoni [8] interpreted this ordering to an increase in the packing of the molecular chains and the production of a more uniform segment density. Yeh and Geil [9] observed the formation of these ordered domains using transmission electron microscopy. These domains had a nodular structure of about 75 Å in diameter. However, Lowe [10] reported that these nodular structures were an artifact of electron beam damage of the specimen. Vittoria et al. [11,12] also described the existence of ordered domains within glasses, which formed during aging and grew with aging time.

In explaining the change in thermodynamic functions such as enthalpy, free volume towards equilibrium on aging, Kovacs et al. [13–15] suggested some form of structural rearrangements may happen within the glass. Recently, Mcgonigle et al. [16] reported that physical aging altered the rates of cold crystallization of PET and they invoked two competitive mechanism to explain these effect—one of molecular ordering and the other of reduced chain segmental mobility on physical aging. Accordingly, short-term aging accelerated the subsequent crystallization, while long-term aging retarded it.

Ito et al. [17] observed that changes occurred in the IR spectrum of PET on aging, and they attributed these to changes in chain conformation. Qian et al. [18] explained the conformational change on aging to a type of inter-chain cohesion with local parallel alignment of neighboring chain segments. They considered that cohesional entanglements

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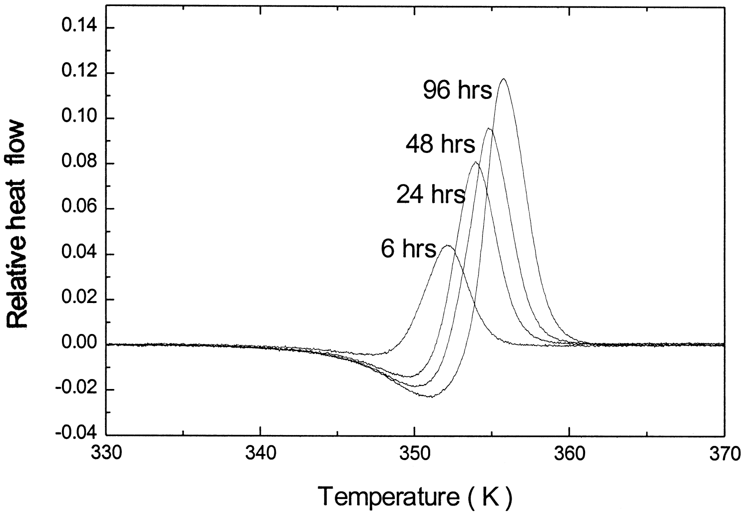

Fig. 1. The evolution of physical aging with time.

produced were the precursor to nucleation and increased rate of crystallization. A similar study has been made by Hay et al. [19] and the changes in conformation of the methylene sequence on aging were attributed to that which occurred normally in the liquid state on cooling and that they were not on account of the development of ordered domains.

The conformational and structural changes that occur during the aging of amorphous glasses still remain a subject of speculation and controversy.

De-aging appears to be an alternative method of resolving some of this controversy. This phenomenon is considered to be the reverse of aging and has been widely discussed by Kovacs et al. [20], Wright [21], Struik [4] and Behrens and Hodge [22]. It is generally considered that physical aging is thermally reversible such that heating to higher temperatures destroys the aging that developed at the lower temperature. The rate of reversal of the aging appears to be related to the temperature increase and the temperature to which the sample is heated. Generally de-aging occurs rapidly but below the glass transition is accompanied by the sample re-aging at this increased temperature.

The paper aims to confirm that the extent of physical aging and subsequent de-aging have an effect on the rate of crystallization of PET above T_g. Attention has also been paid to the nucleation density on crystallization and whether it is altered by aging as this would imply the formation of ordered domains that persist in the liquid up to the crystallization temperature.

2. Experimental

Commercial PET was supplied by ICI Ltd in sheet form. Its viscosity average molecular weight was16 kg mol^{-1} and polydispersity 2.2. PET was dried in vacuum at 100°C for 12 h before use. Disc specimens, 3.0 mm in diameter and 1.5 mm thick, were cut from the dried sheet and sealed in aluminum pans for DSC measurements. They were melted at 280°C for 3 min and rapidly quenched in liquid nitrogen to produce amorphous samples. Rectangular SEM specimens, $6 \times 6 \times 0.8$ mm^3 were cut from amorphous plaques, moulded at 290°C and 20 MN m^{-2} pressure for 3 min in a hydraulic press and quenched in ice/water. The same procedure was used to prepare 40–60 μm thick films for use in a polarized light microscopy and DETA. These specimens were amorphous as measured by density and to WAXS.

A Perkin–Elmer differential scanning calorimeter, model DSC-2, interfaced to a PC, was used to measure the thermal properties of PET. The temperature of the calorimeter was calibrated from the m. pt. of zone-refined stearic acid and 99.999% indium. The thermal response of the calorimeter was calibrated from the enthalpy of fusion of indium. Isothermal experiments were carried out in DSC by heating the samples at 160°C min^{-1} from the storage temperature to a predetermined crystallization temperature, T_c. Measurement of the rate of heat evolved was continued until crystallization was complete. Dynamic scans were carried out by heating from room temperature to 280°C at 10°C min^{-1}. All DSC experiments were repeated with fresh samples to check reproducibility.

A dielectric thermal analyzer, DETA, from Polymer Laboratories Ltd, was used to characterize the extent of physical aging in the PET samples. The DETA was equipped with parallel electrodes placed in a thermostat furnace and used to follow the change in dielectric constant, ϵ' with applied frequency, time and temperature. To ensure good electrical contact between the electrodes and specimens, both sides of the specimens were sputtered with a thin layer of gold using an Emitech Coater, model K550.

The morphology of the PET specimens were examined by scanning electron microscopy, Model Jeol 5410. Potassium hydroxide/methanol solution was used to etch the surface and reveal the spherulites. By controlling the concentration

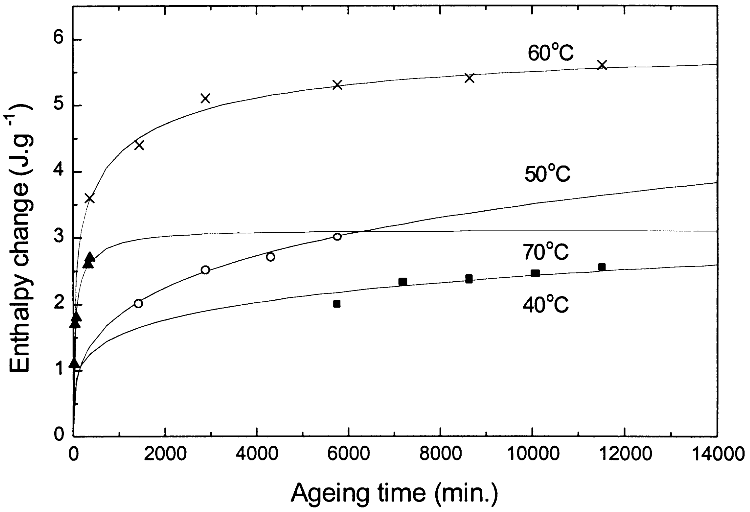

Fig. 2. The change in enthalpy of the glass with time at various aging temperatures.

of etchant and etching time, amorphous region was selectively removed; and the crystalline regions exposed on the surface of the specimen. The specimens were coated with gold and a silver paint adhesive was used to make electrical contact with a metal holder. This reduced charging-up effects on exposure of the specimens to the electron beam.

Direct observations of the development of crystalline regions were made using a polarized light microscope (Leitz Dialux Pol.) with a Linkam hot stage (TH600) and temperature controller (PR600). The heating rate from ambient to the crystallization temperature was 90°C min^{-1}. Image analyses were carried out with a Leica Quantimet 500 and a Nikon light microscope on the spherulitic size distribution. Aging of the specimens was carried out in ovens controlled to ±0.1°C.

3. Results

3.1. Development of physical aging

DSC was used to measure the extent of relaxation towards equilibrium as a function of storage time from the progressive increase in the endothermic peak on heating aged samples through the glass transition. Fig. 1 shows the development of physical aging with time for a sample aged at 60°C. Similar results were obtained at 40, 50 and 70°C. The endotherms were measured by subtracting the thermal response of the quenched glass from that of the aged samples between two fixed temperatures as suggested by Savill and Richardson [23]. As aging developed, the endothermic peak increased in size and shifted to higher temperatures.

Table 1
Parameters for enthalpy relaxation of PET in physical aging

Parameters	Temperature (°C)			
	40	50	60	70
ΔH_∞ (J g^{-1})	18.0	13.6	5.9	3.1
τ (min)	1.0×10^8	5.0×10^5	4.5×10^2	71
β	0.21	0.31	0.32	0.39
$t_{1/2}$ (min)	1.7×10^7	1.5×10^5	1.42×10^2	27

The enthalpy change, ΔH_t at time t, was related to the extent of relaxation, ϕ_t, by Cowie and Ferguson's relationship [24], i.e.

$$\Delta H_t = \Delta H_\infty (1 - \phi_t) \tag{1}$$

where ΔH_∞ is the enthalpy change at equilibrium.

The Kohlrausch–Williams–Watts [25–26] equation was used to relate ϕ_t, to time, t,

$$\phi_t = \exp(-(t/\tau)^\beta) \tag{2}$$

τ is the average relaxation time, and β is a measure of the width of the underlying relaxation spectrum of the aging process. The combined equation,

$$\Delta H_t = \Delta H_\infty (1 - \exp(-(t/\tau)^\beta)) \tag{3}$$

shows the development of ΔH_t with time, see Fig. 2. A non-linear least-square fitting procedure was used to determine ΔH_∞; τ; β and the half-life of the relaxation process, $t_{1/2}$. The values are tabulated in Table 1 and best fit curves are shown with the experimental results in Fig. 2. The half-life of the relaxation, $t_{1/2}$, increased with decreasing aging temperature, and appeared to follow an Arrhenius relationship with an activation enthalpy of 470 ± 20 kJ mol^{-1}. This is in good agreement with a previously reported value [27].

3.2. The effect of physical aging on isothermal crystallization rates

PET specimens aged at 40 and 60°C for different periods of time were subsequently crystallized at 110, 115 and 120°C. In DSC thermograms, the maximum rates of crystallization

Table 2
The Avrami rate parameters

Temperature, T_c (°C)		Avrami index n (±0.2)	Half-life $t_{1/2}$ (min)	Nucleation density N (Nuclei/m^3)	Rate Constant Z (min^{-3})	Linear growth rate g (m/min)
110	Un-aged	2.6	38.4	1.1×10^{13}	1.2×10^{-5}	6.4×10^{-7}
	Aged	2.7	28.0	3.2×10^{13}	3.1×10^{-5}	6.2×10^{-7}
115	Un-aged	2.5	19.9	9.6×10^{12}	8.8×10^{-5}	1.3×10^{-6}
	Aged	2.7	13.2	3.0×10^{13}	3.0×10^{-4}	1.3×10^{-6}
120	Un-aged	2.5	9.93	9.2×10^{12}	7.0×10^{-4}	2.6×10^{-6}
	Aged	2.6	6.67	2.8×10^{13}	2.3×10^{-3}	2.7×10^{-6}

shifted to shorter times with increasing aging time and aging temperature. Samples aged at 60°C with small under cooling from the T_g, appeared to be affected more than samples aged at 40°C but the changes were consistent with the extent of aging which had developed within the specimens.

The isothermal crystallization rates were analyzed using the Avrami [28,29] equation such that,

$$1 - X_t = \exp(-Zt^n) \tag{4}$$

Relating the fractional crystallinity, X_t, to time, t, a composite rate constant, Z, and the Avrami exponent, n. The value of n is characteristic of the crystallization mechanism [30] and Z includes both nucleation density and growth rate constants. The rate parameters for aged and quenched samples are listed in Table 2. Crystallization half-life were used as a measure of the rate of crystallization and is shown in Fig. 3 as a function of the aging time and temperature. Aging clearly leads to faster crystallization rates.

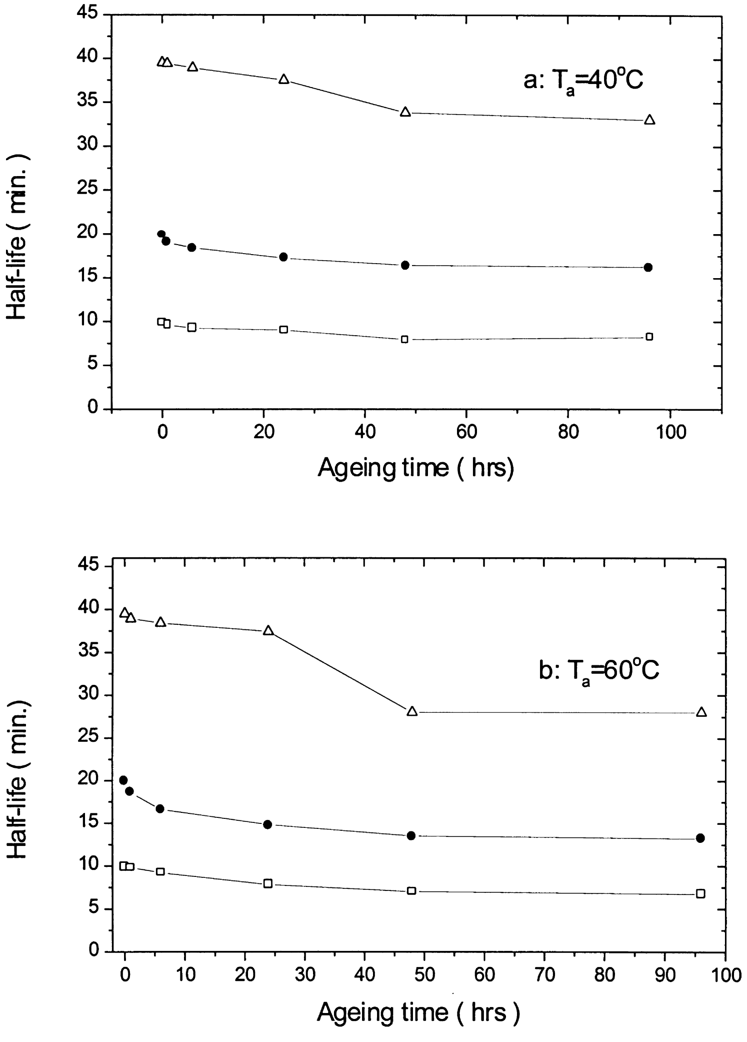

Fig. 3. The effect of aging on the crystallization half-lives.

However, the Avrami exponent, n was not observed to change and within the experimental error was 2.6 ± 0.2, consistent with the growth and impingement of heterogeneously nucleated spherulites, for which $n = 3.0$.

Since there was no change in crystallization mechanism, the observed increase in rate on aging can only be attributed to an increase in nucleation density or spherulitic growth rate.

Samples which had been aged at 40, 50, 60 and 70°C for different periods of time were also heated at 10°C min^{-1} through the glass transition until they crystallized. The changes that occurred, as measured by DSC, can be seen in Fig. 4. An endothermic process, attributed to enthalpic relaxation, is seen superimposed on the glass transition followed by an exotherm due to crystallization. With increasing aging there was a slight shift in the observed endotherms to lower temperature but this was only apparent with a high extents of aging. The temperature corresponding to the maximum rate of crystallization shows the shift and although it was consistent with the crystallization rate increasing with increasing extent of aging the trend is not as marked as in the isothermal crystallization studies, when a heating rate of 160°C min^{-1} was used.

Samples, aged at 40°C for less than 96 h, exhibited a pre-transition endotherm, as can be seen in Fig. 4a, and the subsequent maximum rate of crystallization showed little or no change with aging. Similarly samples aged at 50 and 60°C for short times did not show any increase in the rate of crystallization over that of quenched material. The difference between isothermal and dynamic rate studies is the heating rate between T_a and T_c, i.e. 160 and 10°C min^{-1}, respectively, and the slower rate of heating enabled the aging process to be reversed. Nevertheless, aging at higher temperatures and to a high degree of conversion appeared to increase the rate of dynamic crystallization.

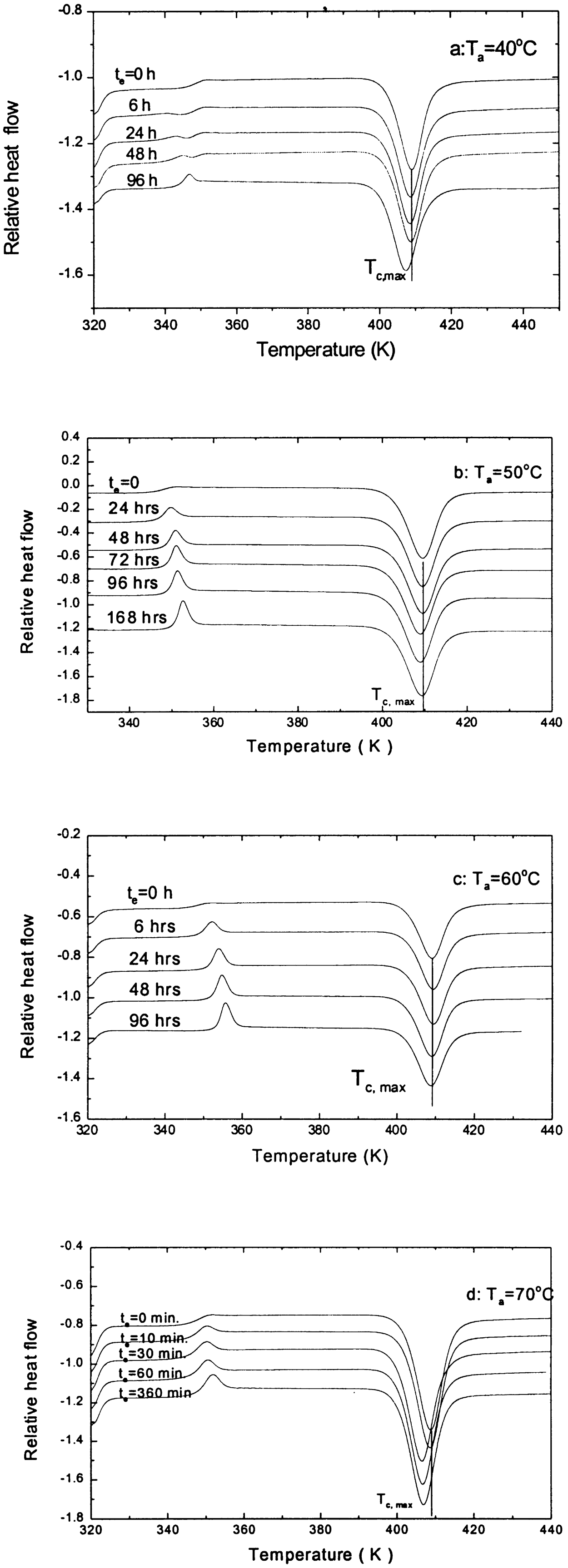

Fig. 4. The effect of aging on the dynamic crystallization of PET.

3.3. The effect of physical aging on the glass transition temperature

According to Richardson [31] the properties of a glass are not uniquely determined by temperature and pressure but are influenced by history and so the T_g changes during aging. Using the procedure adopted by Richardson and Savill [32] the T_g values during aging were measured. The T_g of amorphous PET was found to be 74°C, and it decreased with extent of aging, see Fig. 5, depending on temperature and time. At the highest aging temperature, 70°C, aging proceeded rapidly and the T_g shifted to the aging temperature, T_a, as equilibrium was achieved. At the lowest aging temperature, 40°C, T_g decreased so slowly that it never reached close to the value of T_a. The overall trend was for T_g to decrease with aging time but the extent of the decrease increased with the under-cooling from T_g.

3.4. The effect of aging on nucleation density

Crystalline PET samples were viewed by SEM after etching. This revealed the underlying spherulitic texture of the

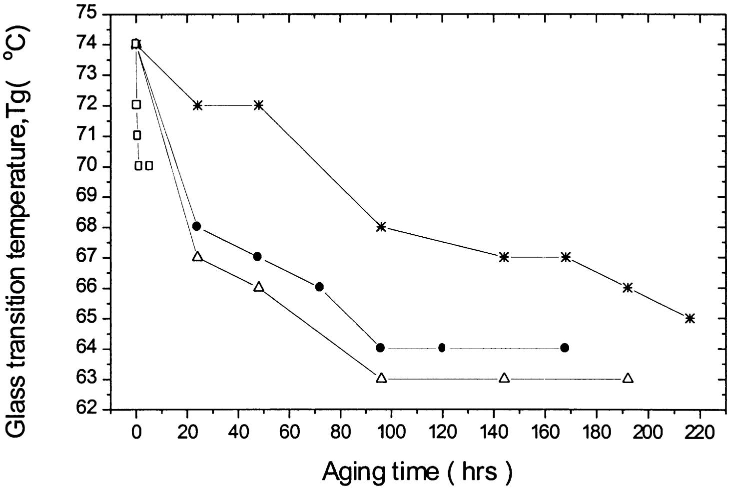

Fig. 5. The decrease of the glass transition temperature with aging.

specimens, see Fig. 6. In order to determine the effect of aging, identical heating and cooling profiles were adopted for the aged and quenched specimens and the samples were crystallized under same conditions. The average size of the spherulites was much smaller in the aged specimens as well as being dependent on the crystallization temperature, see Fig. 6. Aged samples formed more spherulites than the quenched samples, by a factor of 3, in agreement with the increase of crystallization rate on aging. Since the composite rate constant, z, incorporates nucleation density and growth rate, the change in nucleation density alone is sufficient to account for the increase in overall crystallization rate, see Table 2. It would appear that the crystal growth is also unaltered by aging.

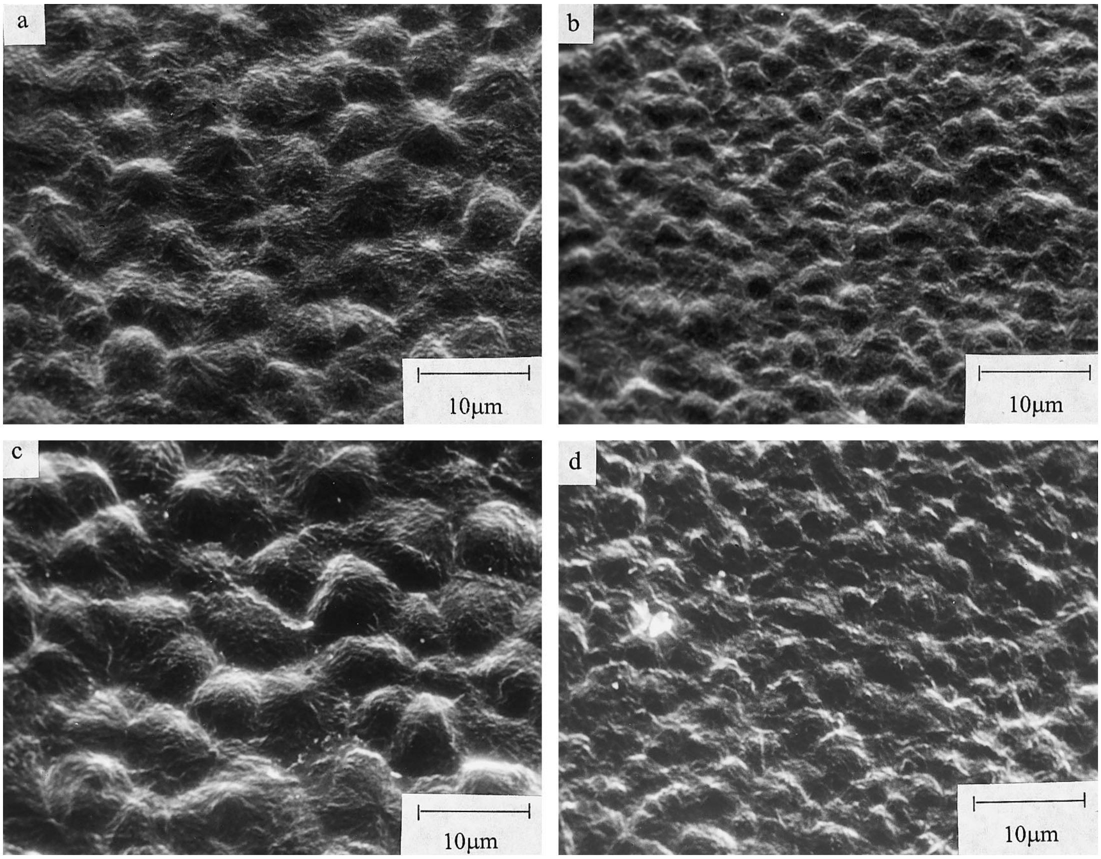

Fig. 6. Electron micrographs of etched crystalline PET samples.

Table 3
Time dependence of the fractional crystallinity in unaged and aged PET specimens by image analysis

Crystallization temperature (°C)	Crystallization time (min)	Crystalline area fraction (%)		
		Un-aged	Aged at 40°C for 4 days	Aged at 60°C for 4 days
130	5	13.3 ± 0.7	14.0 ± 1.0	15.0 ± 1.0
	15	21.3 ± 2.3	24.6 ± 1.4	24.8 ± 2.0
	25	25.0 ± 1.0	25.0 ± 2.0	25.7 ± 1.7
140	4	10.3 ± 0.7		19.0 ± 1.0
	10	16.3 ± 1.3	24.7 ± 2.7	24.2 ± 1.2
	25	27.3 ± 1.7	27.3 ± 1.7	27.3 ± 2.7
150	4	15.3 ± 1.7	24.0 ± 2.0	23.7 ± 1.7
	6	18.8 ± 2.2	26.3 ± 1.7	26.7 ± 2.3
	15	29.6 ± 1.4		29.3 ± 1.7
160	2	18.7 ± 1.7	23.3 ± 0.7	25.6 ± 2.6
	4	21.7 ± 2.3	25.6 ± 1.6	27.7 ± 2.7
	15	28.3 ± 1.7	29.6 ± 0.4	29.3 ± 1.3

Hot-stage polarized-light microscopy was used to study nucleation and growth characteristics of the aged specimens. The thin film specimens were aged and heated to the crystallization temperature at 90°C min^{-1}. The progress of the crystallization was followed and recorded by video but it was not possible to determine the size of spherulite quantitatively. There were too many spherulites to resolve due to the limited depth of focus. However, using image analyses, the fractional crystallinity was determined from the relative amount of birefringence developed. As can be seen from Table 3 the initial onset of crystallization developed faster in aged than quenched material but both samples achieved the same final fractional crystallinity. Again aging accelerated the development of crystallization, but it did not change the final degree of crystallinity.

Aging has been shown to be reversed on heating to temperatures above the aging temperature, but lower than T_g—a process of de-aging. If aging increase the crystallization rate then de-aging should reverse the effect. The effect of heating aged samples at 5°C above their aging temperature for different periods on the subsequent crystallization rate at 118°C can be seen in Fig. 7. Initially the half-lives increased with time up to a maximum and then decreased again. The crystallization half-lives, however, at the maximum did not returned to that of the quenched sample. Aging was not completely removed by this treatment. The initial increase in half-lives was attributed to a limited extent of de-aging, followed at a later stage by a second re-aging process occurring at this higher temperature. The subsequent crystallization rates reflected the residual degree of aging within the sample.

DETA was used to monitor the development of aging in PET from the change in dielectric constant, ϵ', with time at 55 and 60°C. The reduction in dielectric constant with time occurred over the same time scale as aging as measured by DSC, see Fig. 8. However, on heating the sample by 5 and

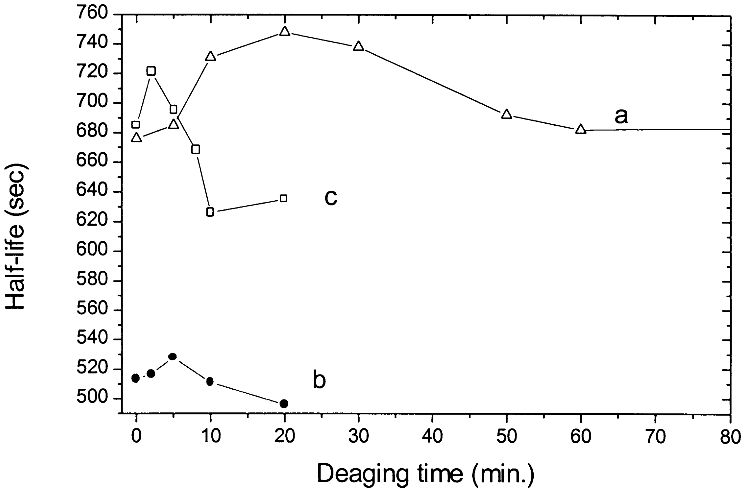

Fig. 7. The change in crystallization half-life on de-aging.

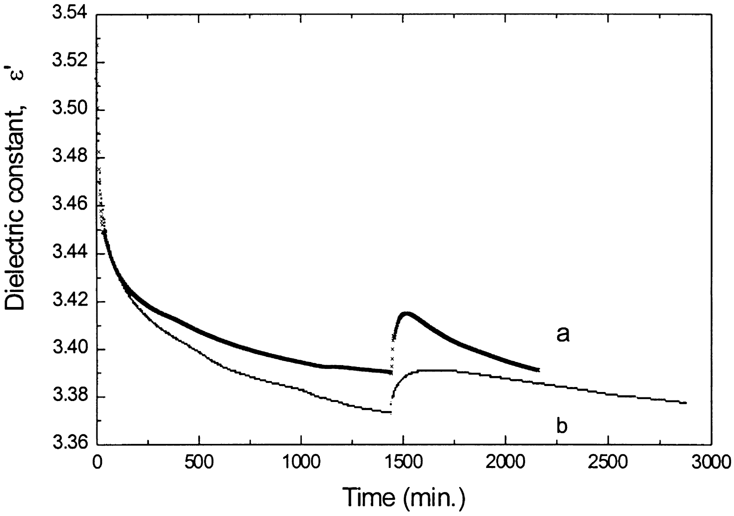

Fig. 8. The change in dielectric constant of PET on aging at T_a and de-aging at T_2.

10°C, an increase in dielectric constant was observed, followed by a slow decrease at longer times to values similar to those observed in the previously aged specimen. The initial rise in dielectric constant on heating was to slow to be attributed to the temperature rise and was due to the de-aging of the sample. It was subsequently followed by a decrease in dielectric constant at the higher temperature analogous to a re-aging process at the higher temperature. The crystallization rates studies followed the same trend with time. It was apparent that aging was not completely eliminated and the crystallization half-lives did not return to the original value of the quenched sample (i.e. 809 s at the 118°C) and similarly, the dielectric constant, ϵ', did not return to the initial value of the quenched sample. Nevertheless, the rate of crystallization is closely related to the extent of aging in the specimen.

4. Discussion

As described above, physical aging results in a decrease of the glass transition temperature by the relaxation of the chain toward equilibrium conformations but the time required to achieve equilibrium is long and dependent on the under-cooling from T_g. The reverse process of enthalpic relaxation equally is kinetic in nature, does not occur instantaneously but time is required for equilibrium to be to attained. This is apparent in DSC measurements with displacements of the observed glass transition temperature to higher values with extent of aging. Some memory of sample history is retained on heating into the liquid and the fictive temperature will be lower than sample temperature. The increased rates of crystallization in previously aged specimens we attribute to some retention of a memory of the

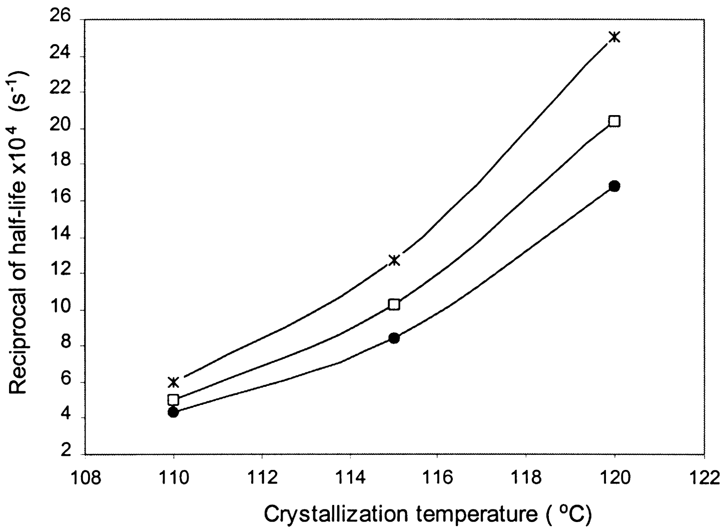

Fig. 9. Rates of crystallization against temperature for PET.

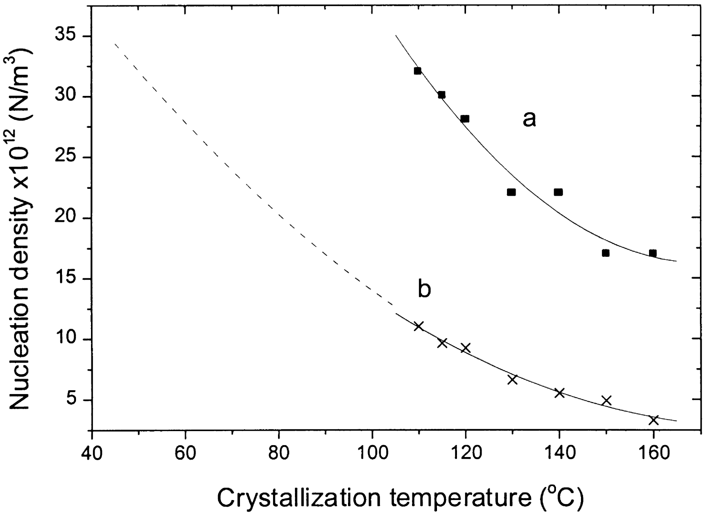

Fig. 10. The change of nucleation density with temperature.

glassy state. The increase in rates is too small to be attributed to the overall decreased in T_g. Samples aged at 60°C for 96 h have a decrease in T_g of up to 13°C and at 40°C of up to 6.5°C. However, the rates of crystallization can be superimposed on those of the quenched unaged specimen by a shift of the temperature by about 2.5 and 1.5°C, see Fig. 9. These results are also in agreement with the de-aging experiment that suggest that thermal history is largely destroyed during heating from T_a to T_c, but the extent to which it is removed will be determined by the rate of heating. The effect is greater in aged sample on heating to the crystallization temperature at 160 rather than 10°C min^{-1} because less time is available for the liquid to achieve equilibrium.

The direct effect of changing the T_g on the rate of crystal growth rate, g, was first described by Turbull-Fisher [33] but later extended to polymer crystal growth rates by Hoffman–Lauritzen [34]. The crystal growth rate, g, close to T_g is related to the crystallization temperature, T, and T_g, by

$$g = g' \exp(-\Delta E/\mathrm{R}\,(T - [T_g - 30])) \qquad (5)$$

where R is the gas constant, g' a function of temperature, but independent of T_g, and ΔE is the activation energy of viscous flow, normally taken to be 6.28 kJ g^{-1}. The crystal growth rate, g, was observed to be independent of the extent of aging, see Table 2, and the nucleation density alone is responsible for the increased rate of crystallization.

Nucleation in PET is heterogeneous and the density of nuclei produced during crystallization increases with decreasing crystallization temperature, following an apparent exponential decay, see Fig. 10. This is the reverse temperature dependence to Eq. (5), in that the nucleation density would fall to zero as T approaches T_g-30. Nucleation on heterogeneities occurs on a range of different size particles or structural irregularities, and the progressively smaller ones become effective nuclei with increasing super-cooling from the melting point. There is a threefold increase in nucleation density on aging at 60°C and nucleation density exhibits a similar increase with decreasing temperature to that observed in the quenched material. To all intent and purpose aged material has nucleation densities more appropriate to crystallizing at lower temperatures and indeed the increased densities are consistent with nucleation having occurred in the quenched glass at about 50–70°C, i.e. at the aging temperature. This can be seen in Fig. 10 where the nucleation densities of the aged specimens have been laterally transposed on to the extrapolated temperature dependence of the quenched samples by using aging rather crystallization temperature.

It would appear that aging increases the number on crystallization nuclei in PET. Since the rate of crystallization increases with extent of aging, during all the aging and de-aging experiments, the number of nuclei must increase with extent of aging. The question remains as to whether these nuclei grow in size as well as number. Using SYNCHROTRON radiation LAXS studies were carried on PET samples that were both quenched and aged at 60°C to close to equilibrium. The collection channels used were capable of resolving structures from 20 to 150 Å. The scattering envelopes from both materials were identical and no differences were detected. It was not possible to detect any structural changes occurring during aging by this means.

5. Conclusion

Physical aging increases the rates of cold crystallization of PET not by decreasing the fictive temperature of the glass, as the crystal growth rate does not change but by increasing the nucleation density. Complete de-aging eliminates the effect and heating the aged glass at different heating rates alters the residual amount of aging and changes the subsequent crystallization rate. In the faster rates of heating there is insufficient time for the melt to attain equilibrium before the onset of crystallization. The non-equilibrium liquid then retains a memory of aging.

No evidence has been obtained from LAXS to suggest that ordered domains are present in the aged material that can act as crystal nuclei. Instead there is evidence that the changes in molecular structure which accompanies aging is reversed on heating. Certain of these structures can act as nuclei during subsequent crystallization but being thermally labile the extent to which they persist at the crystallization temperature, and act as nuclei, is dependent on thermal history. Consequently the subsequent crystallization rates of PET are dependent on sample history.

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References

[1] Vigier G, Tatibouet J. Polymer 1993;34(20):4257.
[2] Itoyama K. Polymer 1994;35(10):2117.
[3] Montserrat S, Cortes P. J Mater Sci 1995;30:1790.
[4] Struik LCE. Physical aging of amorphous polymers and other materials. Amsterdam: Elsevier, 1978.
[5] Aref-Azar A, Biddlestone F, Hay JN, Haward RN. Polymer 1983;24:1245.
[6] Kemish DJ, Hay JN. Polymer 1985;26:905.
[7] Harget PJ, Siegmann A. J Appl Phys 1972;43:4357.
[8] Aharoni SM. J Appl Poly Sci 1973;17:1507.
[9] Yeh GSY, Geil PH. J Macromol Sci Phys 1968;2:13.
[10] Lowe A. PhD thesis, University of Liverpool, 1977.
[11] Vittoria V, Petrillo E, Russo R. J Polym Sci -Phys B 1996;35:147.
[12] Bove L, D'Amello CD, Gorrasi G, Guadagno L, Vittoria V. Polym Bull 1997;38:579.
[13] Hutchinson JM, Aklonis J, Kovacs AJ. ACS Polym Prepr 1975;16:94.
[14] Hutchinson JM, Kovacs AJ. J Polym Sci, Polym Phys Ed 1976;14:1575.
[15] Kovacs AJ, Aklonis JM, Hutchinson JM, Ramos AR. J Polym Sci, Polym Phys Ed 1979;17:1079.
[16] McGonigle E-A, Daly JH, Gallagher S, Jenkins SD, Liggat JJ, Olsson I, Pethrick RA. Polymer 1999;40:4977.
[17] Ito E, Yamamoto K, Kobayashi Y. Polymer 1978;19:39.
[18] Wang Y, Shen DY, Qian RY. J Polym Sci, Polym Phys Ed 1998;36:783.
[19] Aref-Azar A, Hay JN. Polymer 1982;23:1129.
[20] Kovacs AJ. Fortschr Hochpolym Forsch 1963;3:394.
[21] Wright DC. Polymer 1976;17:77.
[22] Behrens AR, Hodge IM. Macromolecules 1982;15:756.
[23] Savill NG, Richardson MJ. Br Polym J 1979;11:123.
[24] Cowie JM, Ferguson R. Polym Commun 1986;27:258.
[25] Williams G, Watts DC. Trans Faraday Soc 1970;66:80.
[26] Williams G, Watts DC, Dev SB, North AM. Trans Faraday Soc 1977;67:1323.
[27] Aref-Azar A, Arnoux F, Biddlestone F, Hay JN. Thermochim Acta 1996;273:217.
[28] Avrami MJ. Chem Phys 1939;7:1103.
[29] Avrami MJ. Chem Phys 1940;8:212.
[30] Morgan LB. Process in polymer science, Part 1. London: Heywood, 1961 (p. 268–69).
[31] Richardson MJ, Aras L. Polymer 1989;30:2246.
[32] Richardson MJ, Savill NG. Polymer 1975;16:753.
[33] Turnull D, Fisher JG. J Chem Phys 1949;17:71.
[34] Hoffman JD, Lauritzen Jr. JI. J Res Natl Bur Std 1961;65A:297.