

Effect of Crystallinity on the Kinetics of Liquid Absorption into Poly(ethylene terephthalate)

ADEOLA V. POPOOLA

Department of Chemistry, Federal University of Technology, P.M.B. 704, Akure, Ondo-State, Nigeria

SYNOPSIS

Drawn poly(ethylene terephthalate) fibres (D.R. 5 : 1) were treated unrestrained in dimethylformamide and benzaldehyde at 100°C for varying amounts of time. A rapid diffusion of liquids into the polymer occurred, the latter experiencing considerable retention of the absorbed liquids at 60°C. The increase in chain mobility brought about by both the liquids absorbed and the liquid-induced crystallisation that followed allowed orientation strains existing in the polymer structure to be relieved. This brought about a 20% shrinkage in the polymer and a change in its overall geometry. Subsequently, a sharp drop occurred in the level of liquid retention within the polymer signifying expulsion of liquids from the crystallising domains and ultimately a levelling off (equilibrium) in the weight retention kinetics.

However, precrystallisation of the fibres at 200°C for 3 h using dry hot air prior to liquid treatment study at 100°C and retention at 60°C, led to a linear increase in the amount of liquid retained in the polymer as a function of time until an equilibrium was established. The essential feature of the latter liquid retention kinetic is that a plot of the amount of relative liquid retained, that is M_t/M_∞ as a function of square root of time, (\sqrt{t}) agrees with Fick's standard diffusion process. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a readily crystallisable polymer especially if produced by rapid cooling from the melt in which case an essentially amorphous and glassy polymer material results. Appreciable crystallisation of the polymer during the rapid cooling is not allowed because the time necessary for it greatly exceeds that required to quench the polymer melt to the glassy state. Even when an oriented semicrystalline polymer is obtained following strain or thermal effects on the amorphous polymer, further crystallisation by heat or liquid treatment is readily achievable.^{1,2} The crystallisation usually obtained as a result of either thermal or chemical energy on the polymer leads to modifications of both the structure and properties of the polymer. This has been well studied in recent years.^{3,4} In thermal crystallisation, exposure of the polymer to heat energy leads to a sigmoidal kinetic

when the amount of crystallinity induced is shown as a function of time for a particular temperature (thermal annealing). This is not so for chemically induced crystallisation where the crystallinity induced has been found to increase with time of treatment to an equilibrium value at a given temperature (see Figs. 1, 2). The presence of certain interactive liquids within the amorphous phase of the polymer will depress both the crystalline melting temperature and the glass-transition temperature (T_m and T_g) of the polymer leading to a reorganisation of the chain molecules within this domain into more perfect arrangement. Usually, the T_g is depressed to a greater extent than the T_m resulting in a large $T_m - T_g$ °C that will further facilitate the crystallisation process within this crystallisable domain.⁵

Liquid sorption into polymer is a diffusion-controlled process with both the rates of the liquid uptake by the polymer as well as the crystallisation accompanying it being temperature dependent leading to an overall classical Fickian diffusion.⁶⁻⁸ The fact that the crystallisation process accompanies the liquid sorption into PET has been shown

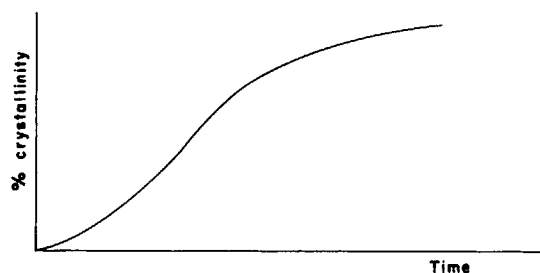


Figure 1 A typical crystallisation kinetic profile for thermally annealed PET fibre.

to affect both the level of absorption and kinetic of the latter resulting in a marked deviation from Fickian mechanism. There is an increase in chain mobility brought about by the lowering of the T_g of the polymer and the induced crystallisation process that follows. This allows the orientation strain existing in the polymer structure to be relieved, shrinkage of the polymer (particularly if fibrous) occurs, and subsequent change in the geometry of the structure that will affect the level of liquid uptake. In fact, a decrease in the level of liquid uptake with time with increasing crystallisation of a methanol-swollen PET was observed by Zacchmann.⁹ Also in a recent mathematical model proposed for diffusion with induced crystallisation in PET, the same deviation was recognised.¹⁰

While most of the previous work on liquid interaction with PET involved absorption into the polymer, a slightly different technique has been used in the present study, the objective of which is to establish the effects of thermally induced crystallinity on liquid retention within the polymer. Liquid absorption into the polymer was carried out at 100°C for varying times using dimethylformamide (DMF) and benzaldehyde as low molecular weight interactive liquids. Following the absorption exercise, the amount of each liquid retained at 60°C was then studied. The result obtained was compared with those of fibres annealed at 200°C prior to liquid treatment to evaluate the influence of the thermally induced crystallinity on the kinetic of the liquid retention process.

EXPERIMENTAL

Materials

The PET fibre used in this study was supplied by Nigeria Chemical and Textile Co., Ltd., Ikorodu. They were twistless multifilament yarns. Following

spinning, they were drawn to ratio 5 : 1 and purified from spin finish before use. General purpose grades of DMF and benzaldehyde were used following distillations at their respective boiling points.

Weight Uptake and Retention Study

PET fibres weighing approximately 30 mg each were predried in a vacuum oven set at 60°C/15 mmHg for 24 h, the predetermined temperature at which liquid retention was to be studied. This was followed by further drying in a dessicator containing silica gel for another 24 h to ensure removal of moisture. The samples were then weighed and subsequently treated in the liquid contained in a 2-L culture flask for varying times of 0.5 min–3 h. At the end of each treatment, they were removed and blotted dry of surface-held liquid, pressed under standard load to ensure complete removal of unabsorbed liquids, and again dried in a vacuum oven at 60°C to constant weight. Usually drying period of 15–24 h achieved this. The amount of liquid retained was calculated in moles of liquid per kilogram of the dry fibre.

Measurement of Diffusion Coefficient

To assess the effect of the crystallisation on the diffusion process, values of the diffusion coefficients for the control and treated fibres were determined using Crank's equation.⁶ The results are shown in Table I.

Thermal Crystallisation and Measurement of Crystallinity

Fibres were annealed without tension in a vapour-bathed jacket at 200°C for 1 min and 3 h, respectively, to induce the necessary crystallinity prior to liquid treatment and retention studies at 100 and 60°C, respectively. The degree of crystallinity in-

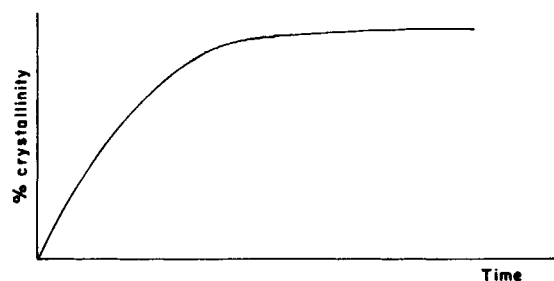


Figure 2 A typical crystallisation kinetic profile for chemically annealed PET fibre.

Table I Correlation between Crystallinity Values and Diffusion Coefficients for PET Fibres Annealed and Liquid Treated

Specimen Detail	Fibre Diameter ($\times 10^{-3}$ cm)	Crystallinity (%)	Diff. Coef., $df \times 10^{-7}$ ($\text{cm}^2 \text{s}^{-1}$)
Untreated, drawn 5 \times	1.40	7.7	0.48
Heat set, 1 min at 200°C	1.42	37.5	0.62
Heat set, 3 h at 200°C	1.70	59.0	0.71
Benz. treated for 1 h at 100°C	1.80	44.70	1.03
DMF treated for 1 h at 100°C	1.82	44.70	1.25

duced in the thermally annealed fibres was determined by the density measurement method using the appropriate conversion equation reported elsewhere.¹¹ The density of the fibres was measured by means of a density gradient column using inert liquid media comprised of *n*-heptane and carbon tetrachloride. Sample positions were read after 48 h of fibre settling and the apparent densities were calculated by linear interpolation between the positions of calibrated glass floats. The percentage crystallinity of the liquid crystallised samples were also determined following complete drying of the samples using the procedure described.

RESULTS AND DISCUSSION

The results obtained for the amounts of liquids retained in the polymer at 60°C, that is, DMF and benzaldehyde for the drawn fibre are shown in Figure 3. The corresponding crystallinity values for the drawn fibres, those treated in liquids for varying times and their diffusion coefficients are shown in Tables II and III. It is seen that the results obtained for the liquid retention in the fibres have similar characteristics. There was a rapid increase in the quantity of the liquids retained within the polymer

usually reaching maxima within 5 min of immersion followed by a slow desorption of the absorbed liquids. Equilibrium value was obtained that was higher for benzaldehyde-treated fibres than DMF-treated ones. It was also noticed that DMF diffused faster into the fibre than benzaldehyde attaining higher maximum in the liquid retention value over a shorter period, that is, while a maximum of $0.52 M \cdot \text{kg}^{-1}$ was achieved in DMF retention within 5 min of immersion, only $0.47 M \cdot \text{kg}^{-1}$ of benzaldehyde was retained over the same period. The observation of higher diffusion rate for DMF than benzaldehyde at the same temperature followed by lower equilibrium value has been interpreted in terms of the molecular size of the two liquids on the diffusion process.¹² The molecular weight values of the two liquids being ca. 73.09 g for DMF and 106.12 g for benzaldehyde, respectively. DMF being the lower molecular weight species diffuses faster into the polymer than benzaldehyde much in the same way as the desorption process. There was a deviation from Fick's standard diffusion behaviour for the fibres. The absorption of liquids into the amorphous phase of the polymer led to a lowering of its T_g evident by the increase in the chain mobility. The free volume created as a result of the chain mobility allowed orientation strains existing in the polymer structure to be relieved. This

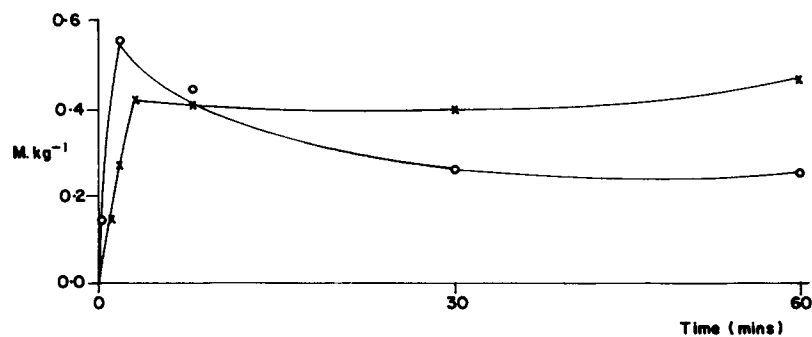


Figure 3 Retention of DMF (○ — ○) and benzaldehyde (x — x) in $M \cdot \text{kg}^{-1}$ at 60°C versus time of treatment for PET fibre D.R. 5 : 1.

brought about a shrinkage of about 20% in the length of the fibre and the accompanied crystallisation process led to expulsion of imbibed liquids from the crystallising domains as the latter arranged itself into a more perfect order. This change in the geometry was manifested in the observed marked deviation from Fick's diffusion behaviour for the fibres in Figures 3 and 4. Evidence for the crystallisation is shown in the values of the amount of crystallinity developed in the liquid-treated fibres contained in Table II. All things being equal, the occurrence of crystallisation with the liquid uptake would be expected to influence the liquid retention because those liquids trapped within the crystallising amorphous regions must be expelled to facilitate further crystallisation and rearrangement into more perfect order.

Comparing these results with those obtained for PET fibres thermally annealed prior to liquid treatment, the growth of crystals accompanying liquid intake as underlying factor for the fall in liquid retention further validated this interpretation. The liquid-retention kinetics for PET fibres that had been thermally annealed at 200°C for 1 min and 3 h prior to treatment in DMF are shown in Figure 4. Again the apparent crystallinity values for the annealed fibres are shown in Table III. Except for fibres annealed for 1 min at the stated temperature, the one annealed for 3 h showed a progressive increase in the amount of liquid retained in the polymer until an equilibrium was achieved in agreement with Figure 2. A plot of the relative weight of liquid retained as a function of the square root of time showed a linear relationship in accordance with Fick's diffusion behaviour shown in Figure 5, observed and reported by other workers.¹³⁻¹⁵ For these fibres, the crystallisation process had been completed and stable crystal growth developed by the thermal pretreatment that subsequent exposure to interactive liquids did not modify the existing crystal any longer, leaving the diffusion-controlled liquid-retention kinetic unperturbed. Previous study on DMF after-

Table II Crystallinity Values at 100°C

Time of Treatment	DMF	Benzaldehyde
30 s	42.30	41.80
1 min	44.70	44.70
5 min	44.70	44.70
30 min	44.70	44.70

Values in percentage for PET fibre D.R. 5 : 1 and liquid treated in DMF and benzaldehyde at 100°C. Control fibre = 7.7%.

Table III Crystallinity Values at 200°C

Time of Annealing	Crystallinity (%)
1 min	37.50
30 min	56.50
60 min	58.00
180 min	59.00
6 h	59.60

Values in percentage for PET fibre D.R. 5 : 1 annealed at 200°C.

treatment at 140°C of PET thermally annealed at 180°C was found to modify the structural changes resulting from the thermal treatment. However, prior heat treatment above 180°C has been found to stabilise the fibre's structure such that subsequent modification by liquid treatment was no longer possible.¹⁶

Examination of the liquid retention curves for the fibres annealed for 1 min revealed that the results were similar to those obtained for the unannealed samples. This is explained in terms of both the rate of heat-transfer and liquid-diffusion phenomena into the polymer. Gases in general are poor heat transfer media thus air annealing effects crystal growth only very slowly. It would be observed that for the thermally annealed sample at 200°C for 1 min and 3 h, crystallinity values are ca. 37.50 and 59.60, respectively compared to the value of 44.70% for 1-min treatment both for DMF and benzaldehyde treatments that in the latter two cases were also the equilibria crystallinity values. Therefore, in the sample annealed in air, the effect produced on the polymer structure, especially in terms of crystal growth, did not lead to ultimate stabilisation of the polymer morphology because of the short contact time of thermal treatment. Because similar morphological changes were brought about by both thermal and liquid treatments, however, the short thermal annealing time produced some structural changes in terms of crystal growth that was to be completed and stabilised by the subsequent liquid treatments leading to an overall liquid-retention kinetics quite reminiscent of the unannealed polymer.

Correlation between Crystallinity and Diffusion Coefficient

Under appropriate conditions of temperature and concentration of a diffusant, the rate of liquid uptake into a fibre is a function of the ease of penetration of the fibre by the diffusant. It is observed from Fig-

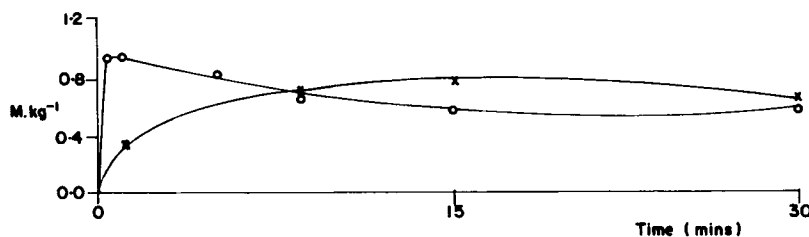


Figure 4 Retention of DMF at 60°C in $M \cdot \text{kg}^{-1}$ for PET fibre D.R. 5 : 1 annealed at 200°C for 1 min (O — O) and 3 h (x — x).

ures 3 and 4 that an initial rapid increase occurs in the amount of liquid uptake of both annealed and liquid treated fibres with the consequential increase in the degree of crystallinity as shown in Table I. This increase in the amount of liquid uptake is clearly shown in the accompanied diffusion coefficients of the treated fibres compared to the untreated control. It is observed that the increase in the liquid uptake and retention is higher for the liquid pre-treated fibres than for the annealed ones. The increase in the diffusion coefficients of the annealed and liquid treated fibres is consistent with the expected result in light of the time scale of the two separate processes of liquid absorption and crystallisation occurring. It is to be noted that in the study of liquid uptake into and retention by semicrystalline polymer, liquid assisted crystallisation is a secondary process preceded by the faster diffusion of the liquid into the polymer structure through the amorphous regions. The appreciable crystallisation process that followed the liquid uptake therefore did not inhibit

the liquid uptake that preceded it. Consequently no negative effect on the diffusion coefficients was observed. In a fibrous polymer where regions of various degrees of order ranging from amorphous to crystalline exists, the amorphous region has an *ab initio* effect on the degree of interaction of the polymer, especially with liquids as their diffusion occurs through the amorphous domains.

CONCLUSIONS

Interaction of both DMF and benzaldehyde with essentially amorphous PET led to liquid absorption and subsequent retention within the polymer. The liquid sorption was accompanied simultaneously by crystallinity induction within the polymer. The latter, the slower process of the two phenomena, was the rate limiting giving rise to an overall non-Fickian diffusion process as a result of liquid desorption from the crystallising amorphous domains. Thermal crystallisation of the polymer at high temperature for periods long enough to allow for development of stable modified structure, especially crystal growth within the polymer, followed by liquid sorption however, led to apparent Fickian observed behaviour in the liquid retention kinetic.

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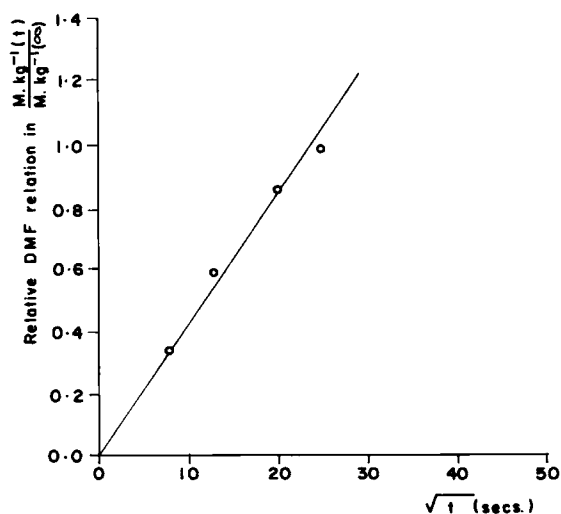


Figure 5 Relative DMF retention in $M \cdot \text{kg}^{-1}(t) / M \cdot \text{kg}^{-1}(\infty)$ at 60°C versus \sqrt{t} (s) for PET fibre, D.R. 5 : 1 annealed at 200°C for 3 h and DMF treated at 100°C.

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