Water Sorption in Amorphous Poly(ethylene terephthalate)

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ABSTRACT: The water sorption characteristics of poly(ethylene terephthalate) (PET) amorphous samples of 250 μ m thickness have been studied at various temperatures in a saturated atmosphere. Concerning diffusivity, one can distinguish the following two domains characterized by distinct values of the activation energy: $E_D \approx 36$ kJ mol⁻¹ at T > 100°C, and $E_D \approx 42$ kJ mol⁻¹ at T < 60°C, with a relatively wide (60–100°C) intermediary domain linked to the glass transition of the polymer. The crystallization of this latter occurs in the time scale of diffusion above 80°C but doesn't change the Fickian character of sorption curves. The equilibrium concentration m_{∞} is an increasing function of temperature, but the solubility coefficient S decreases sharply with this latter, with the apparent enthalpy of dissolution ΔH_s being of the order of -28 kJ mol⁻¹ at T < 80°C and -45 kJ mol⁻¹ at T > 80°C. Density measurements in the wet and dry states suggest that water is almost entirely dissolved in the amorphous matrix at T < 80°C but forms partially a separated phase at T > 80°C. Microvoiding can be attributed to crystallization-induced demixing. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1131–1137, 1999

Key words: water sorption; amorphous; poly(ethylene terephthalate); equilibrium concentrations; diffusivity; solubility; crystallization

INTRODUCTION

It is well known that water-polymer interactions play a great role in the ageing of polycondensates, for instance in the ageing of polycarbonate^{1,2} or tridimensional polyesters.^{3,4} This polymer family is characterized by its moderate hydrophilicity (for the polymers free of hydrogen bonding groups, such as polyterephthalates, polycarbonate, unsaturated polyesters, the equilibrium concentration in saturated conditions is typically lower than 2% by weight) and by the fact that the equilibrium concentration is an increasing function of the temperature (typically, $(1/m_{\infty})(\Delta m_{\infty}/\Delta T)$ is of the order of 10^{-4} K^{-1,5} with $\Delta m_{\infty}/m_{\infty}$ being the relative mass gain at equilibrium). The present article is devoted to poly(ethylene terephthalate) (PET). There were only few published works on PET–water physical interactions. Ravens and Ward⁶ studied the water sorption at ambient temperature and showed that the equilibrium mass fraction m_{∞} varies with the relative hygrometry (RH) and with the polymer crystallinity ratio X_c according to $m_{\infty} = (125 \pm 30)10^{-4} HR(1 - X_c)$.

The equilibrium concentration is almost temperature-independent in the 20-150 °C range and does not significantly depend of the chain ends concentration for a crystallized sample. Lasoski and Cobbs⁷ also showed that the water solubility at 39.5 °C is a linear decreasing function of the crystallinity ratio.

Concerning diffusivity, it is generally observed that its temperature dependence can be modelled by the Fick's law^{8,9} and that it obeys the Arrhenius law. The reported values of the activation energy of the diffusion coefficient noticeably differ, however, from 36.2^8 to 58.2 kJ mol^{-1.9}

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Water plasticizes the amorphous phase of PET, which leads to a decrease of the glass transition temperature T_g from about 80°C in a dry state to about 57°C in a saturated state.^{10–14} Significant changes of the beta transition around -120°C have been also observed by thermally stimulated depolarization current measurements.¹⁵ All these changes of the molecular mobility could have consequences on the water transport kinetics, but there are not, to our knowledge, detailed studies on sorption or diffusion mechanisms and kinetics.

The present article is focused on the sorption behavior of amorphous PET in the $0-100^{\circ}$ C temperature interval. Particular attention will be paid to eventual discontinuities linked to the glass transition temperature in the temperature dependence of the diffusivity and to the physical state of water into the polymer matrix.

EXPERIMENTAL

Material

A PET amorphous foil (number-average molar mass, 13.3 kg mol⁻¹; thickness, 250 μ m; glass transition temperature in dry state, 76°C; density, 1.345 g cm⁻³), supplied by Rhône-Poulenc (CRIT Av. des frères Perret BP 62 69192 Saint-Fons, France), was used without purification (except drying) in this study. Its reference state was obtained by drying at 50°C under vacuum until constant weight.

Exposure and Gravimetric Study

The samples were exposed in a thermostated $(\pm 0.1^{\circ}\text{C})$ bath of distilled water at temperatures ranging from 0 to 100°C. They were periodically wiped and weighed with a laboratory analytical balance having a relative precision of 10^{-4} . It is noteworthy that weighing is made at ambient temperature and takes a few minutes, whereas the characteristic time of water diffusion at this temperature, for samples of such thickness, is about 6 h (see below). It can be thus considered in a first approach that water loss by evaporation during weighing is negligible.

Density Measurements

The density was determined by flotation in heptane-carbon tetrachloride mixtures using standard graduated vessels for volumetric chemical titration. The measurements were made in ther-



Figure 1 Sorption's curves of water in PET at 0, 20, 60, 80, and 100°C (100% R.H.).

mostated room (20°C, 20% RH). Solvents of analytical grade were used. In these conditions, this method can be considered accurate at the third decimal place.

Differential Scanning Calorimetry

The DSC thermograms were recorded at a 20 K min⁻¹ scanning rate. The temperature range was 50–280°C. The heat of crystallization H_c (data from the first heating) was determined by graphical integration of the exothermic peak above T_{g} .

RESULTS AND DISCUSSION

Diffusion

The sorption curves displayed an horizontal asymptote, indicating the existence of an equilibrium, at least at short term (see below). The corresponding mass uptake m_{∞} was determined, and the reduced water concentration $w = m_t/m_{\infty}$, with m_t being the mass uptake at time t, was plotted against the square root of time (Fig. 1). The curves display a linear part in the $0 \le w \le 0.6$ interval, except for the exposure at 0°C, where the absorption curves displayed an unexpected inflection point. These results can be thus summarized as follows: water diffusion in amorphous PET is Fickian or pseudoFickian in the $20-100^{\circ}$ C temperature range.

The diffusion coefficient D was determined using the following well-known relationship:

$$\frac{dw}{d(\sqrt{t})} = \frac{4}{L} \sqrt{\frac{D}{\pi}}$$

Т (К)	$m_{_\infty} imes 10^3 \ ({ m g~g})$	$D imes 10^{12} \ ({ m m}^2 \ { m s}^{-1})$	t_D (min)	t_c (min)	$d_h \ ({ m g~cm^{-3}})$	$d_d \ ({ m g~cm^{-3}})$
293	5.5	0.5	380		1.348	1.345
303	6.5	1.4	150			
313	7.7	1.6	130			
323	10.7	2.5	80		1.349	1.351
333	11.6	4.9	40	3000	1.346	1.349
343	12.9	8.3	25	1000	1.343	1.345
353	14.5	20	10	55	1.348	1.348
363	15.5	42	5		1.379	1.373
373	14.6	130	2	4	1.382	1.374

Table I Equilibrium Concentration (m_{∞}) , Diffusion Coefficient D, Characteristic Time of Diffusion (t_D) , Characteristic Time of Crystallization t_C , Density in Wet State (d_h) , and After Drying (d_d) Versus Temperature

where $dw/d\sqrt{t}$ is the slope of the initial (linear) part of the curves in Figure 1, and *L* is the sample thickness.

The values of D are listed in Table I. They increase with the temperature. An Arrhenius graph of D values is shown in Figure 2. The plot displays a significant curvature, indicating that the temperature effect on water diffusivity in PET, in the 20–100°C temperature range, does not obey the Arrhenius law. The results of Schmalz and Grundke,⁸ obtained at higher temperatures (100–200°C) on a crystallized PET sample, were plotted on the same figure. These results call for the following comments.

1. Water diffusion kinetics apparently obey the Arrhenius law at both extremities of the temperature range under consideration, as follows:



Figure 2 Arrhenius plot of diffusion rate including the results of Schmalz and Grundke⁸ and our own results.

$$D = D_0 \exp{-rac{E_D}{RT}}$$

with $D_0 = 7.2 \ 10^{-6} \ \mathrm{m}^2 \ \mathrm{s}^{-1}$, and $E_D = 36 \ \mathrm{kJ} \ \mathrm{mol}^{-1}$ at $T > 100 \ \mathrm{^oC}$, $D_0 = 1.6 \ 10^{-5} \ \mathrm{m}^2 \ \mathrm{s}^{-1}$, and $E_D = 42 \ \mathrm{kJ} \ \mathrm{mol}^{-1}$ at $T < 60 \ \mathrm{^oC}$. The difference between activation energies can be attributed to the change of physical state of the amorphous phase, which is rubbery above 100 \ \mathrm{^oC} and glassy below 60 \ \mathrm{^oC}. The difference between preexponential factors can be partly attributed to the difference in diffusion mechanisms but also presumably to the difference in amorphous phase volume fraction, higher in our samples than in Schmalz and Grundke ones.

- 2. There is a transition zone between 60°C (corresponding practically to the glass transition temperature of amorphous PET plasticized by water in its equilibrium concentration) and 100°C. The bad junction between both curves at 100°C is obviously due to the difference in crystallinity ratio X_c , with the value of D being, as expected, higher for the amorphous than for the crystallized sample.
- 3. The fact that the diffusion remains apparently Fickian in the 60–100°C temperature interval is somewhat surprising since the following two types of complications are expected: first, the amorphous phase is rubbery on this side and glassy beyond the diffusion front, a situation often responsible for non-Fickian diffusion kinetics¹⁶;



Figure 3 $H_c = f[(Ln(t)]$ curves after various exposure times (t) at constant temperature 60, 70 and 80°C.

second, crystallization occurs in the time scale of diffusion.

To establish it, we have determined a characteristic time of crystallization t_c as follows. The crystallization exotherm was recorded after various exposure times at constant temperature, by differential scanning calorimetry (DSC) at 20 K \min^{-1} . The crystallization enthalpy H_c was plotted against logarithm of exposure time. The characteristic time of crystallization t_c was defined as the abscissa of the inflection point in $H_c = f(Lnt)$ curves. Some examples of these curves are shown in Figure 3. Approximate values of t_c are given in Table I. The characteristic time of diffusion t_D was determined from the following relationship: $t_D = L^2/D$ (L is the sample thickness). As can be seen, t_c becomes of the order of t_D or lower above 80°C. In other words, crystallization occurs at an appreciable extent during the transient of water sorption above 80°C. According to Michaels, $^{17} D$ is expected to decrease when the crystallinity ratio X_c increases, as follows: $D \sim D_a(1 - X_c)$, where D_a would be the diffusion coefficient in the amorphous phase. Despite that, water diffusion remains apparently Fickian in the 80–100°C interval, probably because the crystallization effects are compensated by other ones (see below).

Equilibrium Concentration

The values of the equilibrium mass fraction m_{∞} are listed in Table I and are plotted against temperature in Figure 4. The curve is sigmoïdal and suggests, as precedingly found for diffusivity, the existence of two regimes separated by a transition zone covering the temperature interval between the wet glass transition $T_{gh} \approx 60$ °C and the dry glass transition $T_{gd} \approx 80$ °C.

In the glassy state regime ($\theta < 60^{\circ}$ C), the equilibrium concentration is an increasing function of temperature; whereas in the rubbery regime ($\theta > 80^{\circ}$ C), the equilibrium water concentration is almost temperature-independent.

The solubility coefficient S was calculated from the following relationship:

$$S = \frac{m_{\infty} \times d_h}{18p} \pmod{\operatorname{cm}^{-3} \operatorname{Pa}^{-1}}$$

where d_h is the density of the sample in the humid state, and p is the water vapor pressure at the temperature under consideration.

S values range from $4.27 \ 10^{-7}$ at 0°C to 1.11 $10^{-8} \text{ mol cm}^{-3} \text{ Pa}^{-1}$ at 100°C. The corresponding Arrhenius plot is shown in Figure 5 and calls for the following comments.

At T < 80 °C, Arrhenius law is obeyed (within experimental incertitudes), as follows:

$$S = S_0 \exp{-rac{\Delta H_s}{RT}}$$
 with $rac{\Delta H_s}{R} = -3330$ K

At T > 80°C, the temperature interval under study is too sharp to allow an accurate determination of the enthalpy of dissolution ΔH_s , but it is clear that $|\Delta H_s|$ (rubbery) is higher than $|\Delta H_s|$ (glassy). One can tentatively estimate that, between 80 and 100°C,

$$rac{\Delta H_s}{R} \approx -5400 \ {
m K}$$

It thus appears that the water dissolution in PET is relatively highly exothermic since $\Delta H_s/R$ values range between about +1000 and -3000 K for simple gases in a wide variety of polymers. This result is not very surprising since many au-



Figure 4 Variation of equilibrium water concentration with temperature.



Figure 5 Arrhenius plot of solubility coefficient (*S*).

thors^{17–19} have found a correlation between the enthalpy of dissolution and the Lennard–Jones temperature T_{LJ} , as follows:

$$\frac{\Delta H_s}{R} = a - bT_{LJ}$$

where a is of the order of 1000 K, and b is of the order of 10.

 T_{LJ} is linked to the cohesive energy density so that water displays one of the highest values for small molecules, T_{LJ} = 809 K,²⁰ which leads to calculated values of $\Delta H_s/R$ of the order of -7000 to -10,000 K. Experimental values are lower, but the predicted trend can be considered correct.

For the authors cited above,^{17,20} ($\Delta H_s/R$) is higher in a rubbery state than in a glassy state. Here, we observe rather the opposite trend, as follows: the solubility is lower than predicted, which could be explained, at least partly, by the polymer crystallization.

In order to obtain complementary informations about the physical state of water in the polymer, we have measured the density of the samples after an exposure duration corresponding to the characteristic time t_D of diffusion (see above), in the wet state (d_h) and after drying (d_d) . The results are given in Table I. It can be seen that the relative difference between d_h and d_d is two or three times higher above than below 80°C. It seemed interesting to us to compare these values with theoretical ones calculated from two extreme hypotheses, as follows.

1. Water is entirely dissolved into the polymer and there are no strong interactions (volumes are additive). In this case:

$$rac{1}{d_{h_a}}=rac{1-m_{\infty}}{d_d}+rac{m_{\infty}}{d_w}$$

where d_{ha} is the theoretical value of the density in wet state, and d_w is the water density.

2. Water is entirely present in voids/clusters (no miscibility). In this case,

$$d_{h_b} = d_d (1 + m_\infty)$$

where d_{hb} is the density in wet state corresponding to this hypothesis.

The experimental values of d_h and the calculated values of d_{ha} and d_{hb} have been plotted against temperature in Figure 6. It appears that d_h is close to d_{ha} , although slightly higher at $T \leq 80$ °C, which is consistent with the hypothesis of complete miscibility of the PET-water system for $m \leq m_{\infty}$, but with a small volume contraction linked to the polymer-solvent interaction. At T > 80 °C, however, d_h is practically the arithmetic average of d_{ha} and d_{hb} , which could be consistent with the hypothesis of some voiding/clustering.

To confirm the existence of voids in samples exposed at high temperature, we have taken a



Figure 7 Effect of fast cooling on a saturated sample. A: starting point at equilibrium. B: final point out of equilibrium with a water concentration excess $w_A - w_B$.

sample exposed at 100°C until equilibrium, dried it until a constant weight, and then reexposed it to water at 20°C. The equilibrium mass gain was then 0.8% against 0.35% for a first exposure at 20°C. The difference is, no doubt, essentially linked to microvoiding during the exposure at 100°C.

The crystallinity ratio X_c is about zero before and 0.35 after exposure at 100°C. If one supposes that the true water solubility in the amorphous phase at 20°C is unchanged after exposure at 100°C, one expects that the mass fraction of water dissolved in the matrix at equilibrium in the second exposure at 20°C is

$$m_{\infty a} = m_{\infty}(1 - X_c) = 0.23\%$$

The mass fraction of water present in voids would thus be



Figure 6 Experimental (d_{exp}) and theoretical $(d_{h_a}$ and $d_{h_b})$ density versus temperature.

$$\Delta m=m_{\scriptscriptstyle \infty}-m_{\scriptscriptstyle \infty a}=0.57\%$$

To explain the voiding phenomenon, we have the following alternatives.

- 1. Voiding is linked to the positive dependence of the water equilibrium concentration with temperature.²¹ It occurs when the sample is cooled at ambient temperature, at the end of exposure, according to the scheme of Figure 7. The thermal diffusivity D_T of PET is about 10^{-7} m² s⁻¹, for example, about 100,000 times higher than the water diffusivity. Thus, when a saturated sample (point A) is rapidly cooled from T_A (equilibrium water concentration w_A) to T_B (equilibrium concentration w_B $\langle w_A \rangle$, the excess of water $(w_A - w_B)$ cannot be eliminated by evaporation or exsudation because the water diffusivity is too low. Thus, there is demixation.
- 2. Voiding is linked to crystallization. The latter leads to a reduction of the amorphous content. On the other hand, crystallization rejects water in the amorphous phase so that this latter becomes oversaturated, as shown in Figure 8.

The mass fraction Δm of water in excess relatively to equilibrium would be, for an initially amorphous sample,



Figure 8 Schema of the effect of crystallization on a saturated sample: W_A : initial water concentration at equilibrium in the amorphous sample. W_B : final water concentration in amorphous phase after crystallization.

where $m_{\infty a}$ is the equilibrium concentration of water in the amorphous phase, and X_c is the final crystallinity ratio.

Since the whole mass fraction m_{∞} is of the order of 1.5% at 90–100°C, one can write

$$m_a + \Delta m = 1.5\%$$

for example, $m_a[1 + (X_c)/(1 - X_c)] = 1.5\% \rightarrow m_a = 0.98\%$, which seems to be not unrealistic. Thus, by two independent ways (results of a second sorption test at 20°C $\rightarrow \Delta m = 0.57\%$, calculated from consideration of the crystallization effects $\rightarrow \Delta m = 0.50\%$, one finds close values of the water mass fraction in voids (which corresponds to a volume fraction of about 0.6–0.7%). This relatively good agreement between both values can be considered as a positive argument in favor of the crystallization induced demixing (hypothesis 2).

CONCLUSIONS

We have studied the water sorption in amorphous PET in the 0–100°C temperature range. Diffusion is apparently Fickian in the whole temperature range except perhaps 0°C. The diffusion coefficient D increases with temperature. Three domains can be distinguished.

- the glassy domain ($T \leq 60^{\circ}$ C), where the apparent activation energy is about 42 kJ mol⁻¹;
- the rubbery domain ($T \ge 80^{\circ}$ C), where the apparent activation energy is about 36 kJ mol⁻¹;
- A transition domain between 60 and 80°C, with both limits corresponding to the glass transition temperature of the wet (saturated) and the dry amorphous phase of PET, respectively.

It is clearly shown that, above 80°C, polymer crystallization occurs during the transiency of diffusion. The crystallinity ratio X_c increases from about 0 to about 35%, but there is no clear effect on diffusion kinetics.

The equilibrium water mass fraction varies from about 0.35% at 0°C to about 1.5% above

80°C. The solubility coefficient S decreases with temperature with an apparent activation energy (enthalpy of dissolution) $\Delta H_s \approx -28 \text{ kJ mol}^{-1}$ below 80°C and $\approx -45 \text{ kJ mol}^{-1}$ above 80°C. The fact that ΔH_s takes a relatively strong negative value is consistent with current structure–property relationships.

A detailed analysis of sample densities in wet and dry states and complementary studies of a second sorption cycle (after exposure at 100°C) indicates that demixing of the water-polymer system, presumably induced by the crystallization, is responsible for microvoiding (void volume fraction estimated to about 0.6-0.7%).

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