

Humid Aging of Polyetherimide. I. Water Sorption Characteristics

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ABSTRACT: The sorption and desorption kinetics of water into polyetherimide (ULTEM 1000) were studied at various temperatures ranging from 20 to 100°C. The water equilibrium concentration increases slightly with temperature from 1.39% (by weight) at 20°C to 1.50% at 100°C. The solubility coefficient, S , calculated from these data, and the water vapor pressure decrease with temperature. The calculated heat of dissolution H_s is close to -43 kJ mol^{-1} , which explains the low effect of temperature on the equilibrium concentration. The diffusion coefficient, D , varies from about $1.10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ at 20°C to about $16.10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ at 100°C. The apparent activation energy of diffusion, E_D , and the heat of dissolution, H_s , of water in the polymer have opposite values (respectively, $+43$ and $-42 \text{ kJ} \cdot \text{mol}^{-1}$). From this observation and a comparison of these data with water diffusion characteristics in other glassy polar polymers, it is hypothesized that the transport rate of water is kinetically controlled by the dissociation of water-polymer complexes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1439–1444, 2000

Key words: polyetherimide; water sorption; solubility; diffusion

INTRODUCTION

Aromatic polyimides display interesting engineering properties linked to their high glass transition temperature (T_g). They can, however, undergo “humid aging” because they are capable to absorb typically 1 to 6% by weight of water at equilibrium in saturated atmosphere or in immersion. Water can induce plasticization¹ and sometimes hydrolysis.^{2,3} Swelling can be a problem because it induces stresses or simply dimensional changes. Most of the polyimides have in common with amine crosslinked epoxies the fact that the equilibrium concentration of water is almost temperature independent.¹ Diffusion coefficients are often in the $10^{-12 \pm 1} \text{ m}^2 \cdot \text{s}^{-1}$ range between 20 and 100°C. However, sorption curves can reveal the existence of non Fickian anomalies.⁴

Despite their high industrial interest, thermoplastic polyetherimides⁵ have not been widely studied from the point of view of water absorption, probably because the first experimental studies showed that they display a relatively low hydrophilicity compared to the other members of the polyimide family. Values close to 1.5% were, for instance, reported for the equilibrium mass gain in saturated conditions.⁶ As it will be shown in the second part of this article, such water concentrations are, however, sufficient to induce significant changes of the mechanical behavior. This is the reason why it was interesting to us to study in detail the water absorption in PEI samples in the 20–100°C temperature interval, in saturated conditions.

EXPERIMENTAL

Material

The material examined in this study was a thermoplastic polyetherimide (Ultem 1000) supplied

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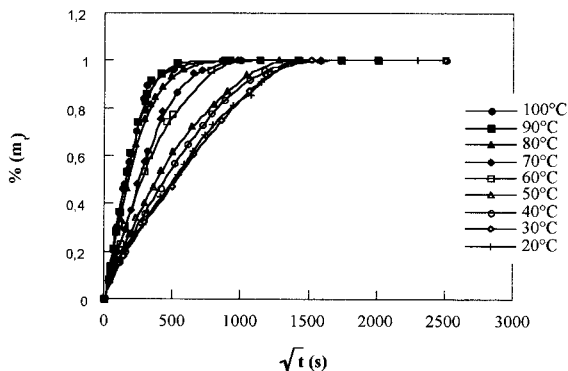


Figure 1 Sorption curves of water in PEI from 20 to 100°C (100% R.H.).

by General Electric (number-average molar mass $20 \text{ kg} \cdot \text{mol}^{-1}$, glass transition temperature in dry state 217°C , density 1.27). All the experiments were made in ISO/1 injection-molded tensile bars (3-mm thickness under pressure of 1000–1200 bars and temperature of $370\text{--}410^\circ\text{C}$ for about 5 min).

Exposure and Gravimetric Study

Sorption Tests

After drying at 50°C under vacuum (-760 mmHg) until constant weight, the samples were exposed in a thermostated ($\pm 0.1^\circ\text{C}$) bath of distilled water at temperatures ranging between 20 and 100°C . They were periodically weighed with an electronic microbalance (METTLER Mark 3) whose relative accuracy was 10^{-4} (g/g) .

Desorption Tests

The saturated samples were placed in a dry oven at the same temperatures as the sorption tests, and periodically weighed until constant weight.

Density Measurements

The density was determined by flotation in heptane-carbon tetrachloride mixtures. The measurements were made in a thermostated room (20°C , 20% R.H.). Solvents of analytical grade were used. Under these conditions, this method can be considered accurate to the third decimal place. The density being expressed in $\text{g} \cdot \text{cm}^{-3}$.

Differential Scanning Calorimetry (DSC)

The D.S.C. thermograms were recorded at $10 \text{ K} \cdot \text{min}^{-1}$ scanning rate. We have used the high-

pressure crucibles for the analysis of the samples damps to avoid the evaporation of the water.

Nuclear Magnetic Resonance (NMR)

The samples were stored in D_2O ; the surfaces were wiped before the samples were introduced in the NMR tube. The spectra were recorded with a Bruker MSL 360 (55 MHz) apparatus at 22°C .

RESULTS

The sorption and desorption curves are presented, respectively, in Figures 1 and 2. After drying, the samples, the PEI reached their initial weight. Thus, the process can be considered reversible within experimental uncertainties. The equilibrium water mass gain m_∞ is of the order of 1.5% (Table I). The densities d_o (dry state) and d_∞ (saturated state) of PEI determined at 20°C are also given in Table I. Two extreme hypotheses about densities were considered. (a) Polymer and water volumes are additive. In this case:

$$\frac{1}{d_a} = \frac{w}{d_w} + \frac{1-w}{d_o} \quad (\text{with } d_o = 1.27 \text{ g} \cdot \text{cm}^{-3}) \quad (1)$$

where d_a is the theoretical value in saturated state according to hypothesis (a),

$$w = \frac{m_\infty}{100 + m_\infty}$$

is the equilibrium water mass fraction, and d_w is the water density. (b) Water is entirely absorbed into initially present microvoids "free volume." Then:

$$d_b = d_o(1 + m_\infty) \quad (2)$$

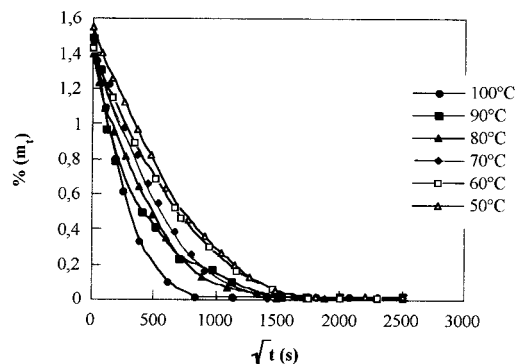


Figure 2 Desorption curves of water in PEI.

Table I Theoretical (d_a , d_b) and Experimental (d_∞) Densities, Equilibrium Concentration (m_∞), Diffusion Coefficient of Sorption (D), Diffusion Coefficient of Desorption (D'), and Solubility Coefficient (S)

T (°C)	d_a (g · cm ⁻³)	d_b (g · cm ⁻³)	Saturate d_∞ (g · cm ⁻³)	$m_\infty \cdot 10^2$ (g/g)	$S \cdot 10^8$ (mol · cm ⁻³ · Pa ⁻¹)	$D \cdot 10^{12}$ (m ² · s ⁻¹)	$D' \cdot 10^{12}$ (m ² · s ⁻¹)
20	1.2781	1.3009	1.2963	1.39	42.96	0.97	/
30	1.2780	1.3011	1.2963	1.40	23.78	1.21	/
40	1.2779	1.3012	1.2973	1.41	13.79	1.65	1.52
50	1.2780	1.3011	1.2977	1.40	8.19	2.29	2.05
60	1.2779	1.3014	1.2979	1.43	5.18	4.28	4.13
70	1.2779	1.3016	1.2985	1.44	3.33	6.12	5.57
80	1.2778	1.3019	1.2987	1.47	2.24	13.22	12.32
90	1.2777	1.3022	1.2990	1.49	1.53	14.37	14.09
100	1.2777	1.3023	1.2992	1.50	1.07	16.37	15.87

where d_b is the theoretical density according to hypothesis (b).

The values of d_a and d_b are listed in Table I. It clearly appears that the experimental value d_∞ is closer to d_b than to d_a . It thus seemed to us interesting to check the presence of free water molecules from wide-band NMR measurements. The results (Fig. 3) clearly indicated that most of the water molecules are linked to the polymer: no clustering was detected. Furthermore, the differential scanning calorimetry thermograms showed the absence of the crystallization/melting peaks of water.

It was then assumed that water was entirely dissolved into the PEI matrix and the solubility

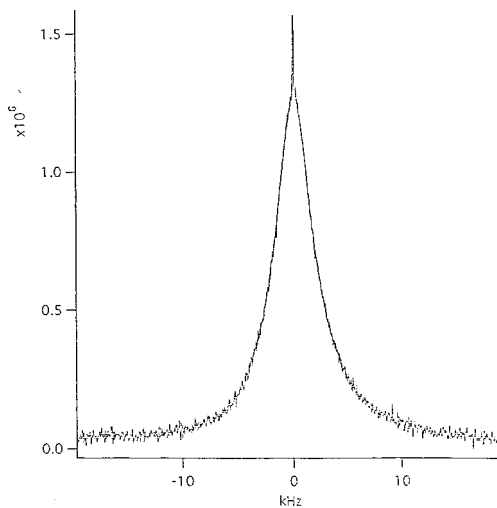
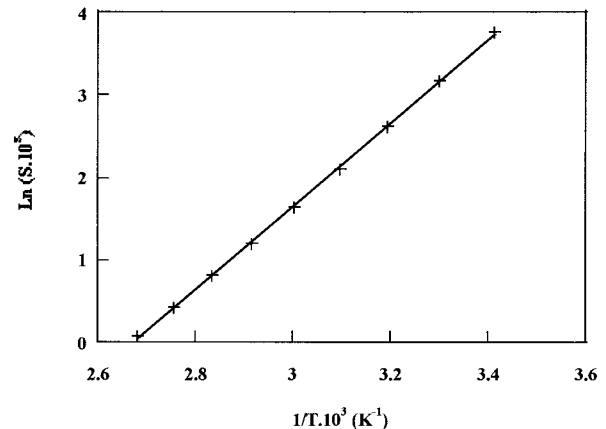
coefficient S was determined from the following relationship¹⁰:

$$S = \frac{10}{18} \frac{w d_\infty}{p} \quad (3)$$

where p is the water vapor pressure. The values of S are given in Table I. S decreases rapidly with temperature, and obeys the Arrhenius law (Fig. 4):

$$S = S_o \exp\left(-\frac{H_s}{RT}\right) \quad (4)$$

Because the equilibrium mass fraction varies only slowly with temperature, H_s can be estimated as follows. (i) One can assume that in the temperature interval (20–100°C) under consider-


Figure 3 NMR spectra of the saturated samples at 100°C.

Figure 4 Arrhenius plot of the solubility.

ation, the water vapor pressure p obeys to the Arrhenius law:

$$p = p_o \exp\left(-\frac{H_p}{RT}\right) \quad (5)$$

(with $\text{Ln } p_o = 25.345$ and $H_p/R = 5149$ K, i.e.; $H_p \sim 43$ kJ · mol⁻¹). (ii) w and d_∞ vary slowly with temperature. In a first approximation one can take, $w \sim m_\infty$. The variation of m_∞ and d_∞ can be approximated by both a linear (expansion) and Arrhenius law:

$$x_2 = x_1[1 + \alpha(T_2 - T_1)] \quad (x \text{ being } m_\infty \text{ or } d_\infty) \quad (6)$$

$$\begin{aligned} x_2 &= x_1 \exp\left[-\frac{H_x}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \\ &\approx x_1\left[1 + \frac{H_x}{RT_1T_2}(T_2 - T_1)\right] \end{aligned} \quad (7)$$

with $T_1 = 293$ K and $T_2 = 373$ K (temperatures of the sorption tests).

Both relationships are equivalent provided that:

$$\alpha = \frac{H_x}{RT_1T_2} \quad (8)$$

with $H_x = H_{m_\infty}$ or H_{d_∞} .

Then one can write, according to the definition of the solubility, and because:

$$\begin{aligned} m_\infty &= m_o \exp\left(-\frac{H_{m_\infty}}{RT}\right) \\ d_\infty &= d_o \exp\left(-\frac{H_{d_\infty}}{RT}\right) \end{aligned}$$

Thus,

$$\frac{H_s}{R} = \frac{H_{m_\infty}}{R} + \frac{H_{d_\infty}}{R} - \frac{H_p}{R} \quad (9)$$

where H_m or H_{m_∞} and H_d or H_{d_∞} are the respective apparent activation energies of m_∞ and d_∞ [indeed, this approach is only valid in the case of small temperature variation of m_∞ and d_∞ , where the approximation of eq. (7) is valid as in the case under study].

α is the expansion coefficient, which is approximately $(2.5 \pm 1.0) 10^{-4}$ for most of the glassy polymers.

So that, according to eq. (8), in the range $T_1 = 293$ K to $T_2 = 373$ K:

$$\frac{H_{d_\infty}}{R} \approx -(27 \pm 11) \text{ K}$$

Here, the equilibrium mass fraction varied from 1.39% at 20°C to 1.50% at 100°C, so that:

$$\frac{1}{m_\infty} \frac{\Delta m_\infty}{\Delta T} \approx (9.8910^{-4}) \text{ K}^{-1} \text{ and } \frac{H_{m_\infty}}{R} \approx 108 \text{ K}$$

Equation (9) thus gives:

$$\frac{H_s}{R} \approx 5068 \pm 11 \text{ K}^{-1}.$$

So that $H_s = -42$ kJ · mol⁻¹.

H_s is directly linked to the strength of polymer–water bonds. As it will be shown, its value is important data in the discussion of sorption and, perhaps, diffusion mechanisms.

Diffusion

The sorption curves are linear in $t^{1/2}$ in their initial part ($0 \leq m_t \leq 0.6 m_\infty$), showing that the diffusion process is Fickian.

The coefficient of diffusion D was determined from the classical relationship:

$$D = \frac{\pi}{16} \left(\frac{m}{m_\infty}\right)^2 \frac{L^2}{t} \quad \text{for } m_t \leq 0.6 m_\infty \quad (10)$$

where m_t is the mass uptake at time t for a sample of thickness L .

The corresponding values of the diffusion coefficient are given in Table I for the sorption (D) and desorption (D') curves. D' is slightly lower for desorption than for sorption (D), similar to the results found by Iler and al.⁷ in the case of poly-pyromellitimide Kapton. The difference, which is less than 10%, could be attributed to a small concentration dependence of the diffusivity.

D increases with temperature, and obeys the Arrhenius law (Fig. 5); thus, the diffusion of water into PEI can be considered Arrhenian in a first approach. The apparent activation energy would then be: $E_D \approx 43$ kJ · mol⁻¹.

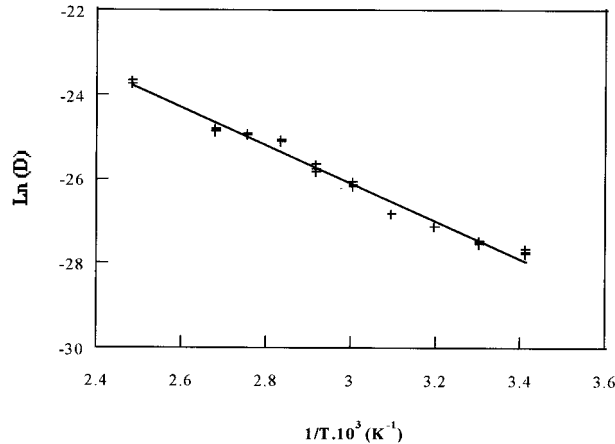


Figure 5 Arrhenius plot of the diffusivity.

DISCUSSION

Empirical relationships establish a link between the heat of dissolution H_s and the cohesive properties of the penetrant, for instance^{8,9}:

$$\frac{H_s}{R} \approx a - bT_{LJ} \quad (11)$$

where $a \sim 1000$ and $b \sim 10$ are constants, independent of the polymer structure, and T_{LJ} is the Lennard-Jones temperature of the penetrant. The T_{LJ} for water is 809 K¹⁰, so that H_s/R takes a high negative value characteristic of a highly exothermic dissolution.

The value obtained experimentally: $H_s/R \approx -5068$ K, is lower than the values predicted by eq. (11) ($H_s/R \approx -6400$ to -8800 K), but the trend is correct and the fact that H_s/R takes a value close to the one found for other polyimides¹¹, does not result, in our opinion, from a coincidence. The fact that the equilibrium water concentration m_∞ is temperature independent thus results from the fact that the temperature effect on the solubility S almost exactly equilibrates the temperature effect on water pressure. In other words, from eq. (9) and neglecting in a first approach the temperature effect on density ($H_{d_\infty}/H_{m_\infty} < 30\%$), one can write:

$$H_{m_\infty} \sim H_s + H_p$$

Because it is experimentally observed in PEI that $H_{m_\infty} \sim 0$ (m_∞ practically temperature independent), it becomes: $H_s \sim -H_p$.

It is noteworthy that H_m can be positive as, for instance, in polycarbonate¹² and polyesters,¹³ or negative, as in certain epoxies of relatively high hydrophilicity,¹⁴ depending on whether H_p is higher or lower than the absolute value of H_s .

Another way to examine the structure–hydrophilicity relationship consists in considering the molar contributions of the polymer groups to water absorption. The quantity of water absorbed at equilibrium and expressed in mol water per mol of monomer unit is:

$$W = \frac{10m_\infty \cdot M}{18}$$

where m_∞ is expressed in percent, and M is the molar mass of the monomer unit, in $\text{kg} \cdot \text{mol}^{-1}$. In the case of PEI, one obtains: $W \sim 0.49$ mol water per mol of monomer unit.

The monomer unit of PEI contains two ether and two imide groups that are hydrophilic (the hydrophilicity of hydrocarbon groups can be neglected). It is not very easy to compare PEI with thermosetting polyimides, because in these polymers, the water equilibrium concentration can heavily depend on the degree of cure. For instance, in the case of polypyromellitimide Kapton, values as different as $\sim 2.6\%$,¹⁵ $\sim 3.2\%$,¹¹ and $\sim 5\%$ ¹ were reported in the 30–50°C temperature range. They correspond to values of W ranging from 0.55 to 1.05 mol/mol of monomer unit, although this latter contains two imides and only one ether.

It thus seems that in the polyimide family, the rule of molar additivity of the group contributions to water absorption¹ does not apply. The fact that Kapton is proportionally more hydrophilic than PEI could be linked to the imide concentration, which is higher in the former ($5.2 \text{ mol} \cdot \text{kg}^{-1}$) than in the latter ($3.8 \text{ mol} \cdot \text{kg}^{-1}$), and also to the water molecules, which can be doubly bonded, i.e., must be linked to two polar groups. Indeed, the probability to have a sufficiently close pair of polar groups increases with the concentration of these sites, i.e., decreases with their average distance. This hypothesis explains why only a small fraction of polar groups are capable of forming a complex with water (Fig. 6).

It is noteworthy that the apparent activation energy of diffusion E_D is practically equal to the absolute value of the heat of dissolution H_s . Furthermore, for three polymers investigated in the laboratory, there is a trend of E_D to vary in the same way as the absolute value of H_s , indepen-

dently of the mobility characteristics of the polymers (T_g , amplitude of the β dissipation band, etc.)^{12,14} (Table II).

One possible explanation of this behaviour could be that the mobility of water molecules would be governed by the dissociation of the polymer–water complexes, as illustrated by the following mechanistic scheme describing an elementary step of diffusion from the polymer site P_1 to the neighbouring polymer site P_2 :



One sees that the water–polymer interaction governs the whole diffusion process if, schematically, the lifetime of the polymer–water complex is longer than the duration of the water migration elementary step (II), this latter being presumably linked to various parameters among which are the average distance between hydrophilic sites, the “free volume,” and the polymer mobility associated to local motions.

CONCLUSION

The water equilibrium concentration m_∞ of polyetherimide is $1.45 \pm 0.05\%$ by weight in all the temperature intervals under consideration (20–100°C), which corresponds to a heat of dissolution $H_s \sim -43 \text{ kJ} \cdot \text{mol}^{-1}$. The decrease of water solubility with temperature is almost entirely compensated by the increase of saturated vapor pressure, which explains the low temperature effect on m_∞ . Water diffusion is Fickian, and its apparent activation energy E_D is equal to $-H_s$.

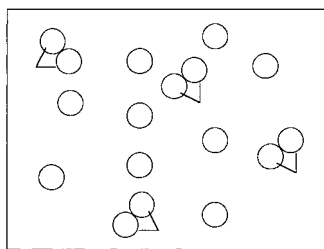


Figure 6 Schematization of the mechanism of water absorption at the molecular scale: \circ polar groups, \triangle water molecules. Water fixation can occur only on close pairs of polar groups.

Table II Activation Energy of Diffusion (H_D), Heat of Dissolution (H_s)

Material	H_D ($\text{kJ} \cdot \text{mol}^{-1}$)	$-H_s$ ($\text{kJ} \cdot \text{mol}^{-1}$)
PEI	43	42
PC	31	37
EPO	61	45

From a comparison of PEI with a less polar (PC) and a more polar (EPO) polymer glass (Table II), one can suggest that the water diffusivity in these polymers is essentially governed by the strength of the hydrogen bonds between the water molecules and the polymer polar groups. In other words, the dissociation of the polymer–water complex would be the slowest step in an elementary diffusion event.

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