Humid Aging of Polyetherimide. II. Consequences of Water Absorption on Thermomechanical Properties

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ABSTRACT: The water sorption characteristics of aromatic polyetherimide (ULTEM 1000) were determined at various temperatures ranging from 20 to 100°C, and reported in the first part of this article. In the second part of this article the consequences of water absorption on the physical and thermomechanical properties by differential scanning calorimetry (DSC), dynamical mechanical thermal analysis (DMTA), and Tensile testing are studied. It was found that water plasticizes the polymer but the T_g depletion (for an almost constant water content) increases with the exposure temperature. The β dissipation band is decreased and shifted to low temperature. Despite a slight decrease of the yield stress linked to plasticization, the ductility decreases indicating that water absorption favors a new, presumably localized, yielding process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1445–1451, 2000

Key words: polyetherimide; glass transition temperature; plasticization; tensile properties

INTRODUCTION

This work deals with the humid ageing of aromatic polyetherimide of the ULTEM 1000 type. The characteristics of water sorption for this material were previously determined.[1] It was found that the equilibrium water concentration increased slightly with temperature (1.39% at 20°C, 1.50% at 100°C), which can be attributed to a heat of dissolution H_s in the order of -43 kJ $\cdot$ mol^{-1}. The coefficient of diffusion D varied from about 10^{-12} m$^2 \cdot$ s^{-1} at 20°C to about $16 \cdot 10^{-12}$ m$^2 \cdot$ s^{-1} at 100°C with an activation energy E_D of 43 kJ $\cdot$ mol^{-1}. Diffusion was Fickian, and was presumably kinetically governed by the dissociation of the polymer–water complex.[1]

The aim of the present article is to study the consequences of water absorption on certain physical properties: glass transition temperature, tensile properties, and viscoelastic behavior.

NMR measurements will be used to check possible heterogenous distribution of water within the polymer matrix.

EXPERIMENTAL

The polyetherimide under study (ULTEM 1000 supplied by General Electric) displays the following characteristics: number-average molar mass: 20 kg $\cdot$ mol^{-1} (viscosimetry); glass transition temperature T_g = 217°C (DSC); β transition temperature T_β = 110°C (DMTA 1 Hz); and density: 1270 kg $\cdot$ m^{-3}.

Injection-molded plaques of 3-mm thickness under pressure of 1000–1200 bars and temperature of 370–410°C for about 5 min, were used in this study.

Sorption tests were performed in thermostated (± 0.1°C) distilled water baths at temperatures ranging from 20 to 100°C. The samples were weighed on an analytical balance to determine the mass fraction of absorbed water.

Table I Variation of the Glass Transition Temperature, T_g, with the Equilibrium Water Mass Fraction w_∞

T (°C)	20	30	40	50	60	70	80	90	100
% w_∞	1.39	1.40	1.41	1.40	1.43	1.44	1.47	1.49	1.50
T_g (°C)	201.8	201.6	200.9	200.1	199.9	198.3	196.5	197.0	189.3

Differential scanning calorimetry measurements (DSC) were performed on a NETZSCH apparatus using high-pressure capsules to avoid water loss by evaporation. The scanning rate was $10 \text{ K} \cdot \text{min}^{-1}$. Dynamical mechanical thermal analysis measurements (DMTA) were performed on a Polymer Laboratories MK II apparatus in the sample cantilever configuration in the -140 to $+250$°C temperature range; 0.1 to 30 Hz frequency range at $4 \text{ K} \cdot \text{min}^{-1}$ scanning rate in single frequency mode and $0.5 \text{ K} \cdot \text{min}^{-1}$ in multifrequency mode. The sample size was $10 \times 12 \times 3$ mm.

In the conditions under study, it can be shown that the measurement time (a few hours) is lower than the characteristic time of water diffusion (a few days). It can thus be assumed that the water loss is negligible in a first approximation.

Mechanical testing was performed in a Instron series IX machine with a 10-kN cell. The measurements were made at 20°C, 0.02 s^{-1} strain rate on dog bone samples of 3*10 mm section with a calibrated length of 8 mm.

To appreciate the sample porosity by ^{129}Xe NMR and the possible heterogeneous water distribution by D_2O NMR, we used a Bruker MSL 360 apparatus. (i) ^{129}Xe NMR: the samples were first wiped and introduced in the NMR cavity containing ^{129}Xe. The spectra were recorded on the NMR apparatus at a 99.29 MHz with pulses of 17.5 μs, the temperature being 295 K.[2] (ii) D_2O NMR: the same apparatus as for Xe was used, but at operating frequency of 55 MHz.

RESULTS AND DISCUSSION

Glass Transition Temperature

The values of glass transition temperature T_g determined by DSC are listed in Table I with the corresponding equilibrium water mass fractions w_∞. We can observe that T_g decreases with the exposure temperature, and thus, the T_g depletion ΔT_g increases from 15 K (at 20°C) to 28 K (at 100°C). This variation indicates that water has a

significant plasticizing effect on PEI. Is the totality of sorbed water involved in this effect?

Two plasticization theories were tested to try to answer to this question; both need the knowledge of the glass transition temperature T_{gs} of water, which is close to 120 K.[3,4]

Theory 1: according to Kelley and Bueche, one can write from free volume considerations[5]:

$$T_g = \frac{(1 - \varphi)\alpha_p T_{gp} + \varphi \alpha_s T_{gs}}{(1 - \varphi)\alpha_p + \varphi \alpha_s} \quad (1)$$

with p and s are relative respectively to polymer and water, φ is the volume fraction of water, and α is the coefficient of free volume expansion.

Assuming the validity of the Simha-Boyer rule,[7] this relationship would simplify to:

$$\frac{1}{T_g} = \frac{1}{T_{gp}} + \varphi\left(\frac{1}{T_{gs}} - \frac{1}{T_{gp}}\right)$$

One can write that $\varphi \sim \rho \cdot w$ where ρ is the polymer density; it comes, thus:

$$\frac{1}{T_g} = \frac{1}{T_{gp}} + Aw$$

where

$$A = 8 \cdot 10^{-3} \text{ K}^{-1} \quad \text{and} \quad 1/T_{gp} = 2.04 \cdot 10^{-3}$$

It comes $T_g = 465$ K for $w = 1.39\%$ against 475 K experimental value (20°C exposure); and $T_g = 463$ K for $w = 1.50\%$ against 462 K experimental value (100°C exposure).

It thus appears that the free volume theory predicts well the good order of magnitude of T_g in the wet state, but does not predict the T_g variation with the exposure temperature. This latter can be expressed as follows from the Kelley-Bueche relationship:
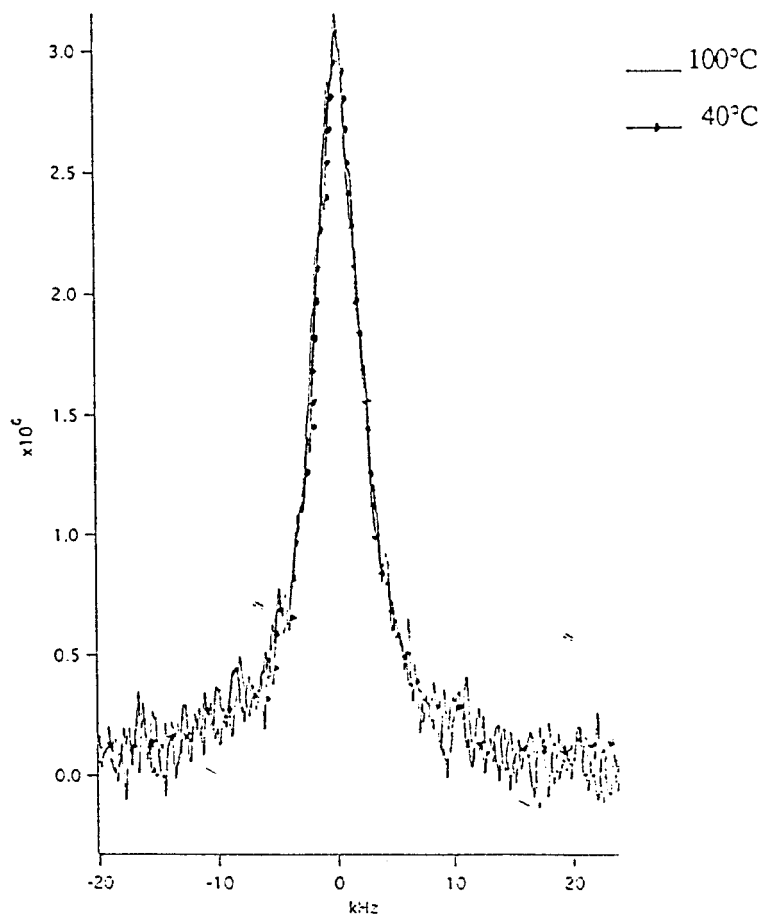
Figure 1 D_2O NMR spectra of the saturated samples at 40 and 100°C.

$$\frac{T_g}{T_{gp}} = 1 - \rho w \frac{\alpha_s}{\alpha_p}\left(1 - \frac{T_{gs}}{T_{gp}}\right)$$

where

$$\rho = 1.2831 \text{ g} \cdot \text{cm}^{-3}$$

Remarking that $\rho(1 - T_{gs}/T_{gp}) \approx 1$, one obtains:

$$\frac{1}{T_{gp}}\frac{dT_g}{dw} \approx -\frac{\alpha_s}{\alpha_p}.$$

According to the Simha-Boyer rule:

$$\frac{\alpha_s}{\alpha_p} \approx \frac{T_{gp}}{T_{gs}} \approx 4,$$

so that one expects:

$$\frac{1}{T_{gp}}\frac{dT_g}{dw} \approx -4,$$

against -19 experimental value.

It is clear that there is an unexpected effect of the exposure temperature: water absorbed at 100°C seems to be more efficient in plasticization than water absorbed at 20°C.

Theory 2: from thermodynamical considerations, Couchman[8] showed that:

$$\ln T_g = \frac{(1 - w)\Delta C_{pp}T_{gp} + w\Delta C_{ps}T_{gs}}{(1 - w)\Delta C_{pp} + w\Delta C_{ps}}$$

where ΔC_p is the difference between the heat capacities in rubbery and glassy states.

Using the same approximations as in theory 1, one obtains:

$$\frac{\ln T_g}{\ln T_{gp}} \approx 1 - w\frac{\Delta C_{ps}}{\Delta C_{pp}}\left(1 - \frac{\ln T_{gs}}{\ln T_{gp}}\right) = 1 - qw$$
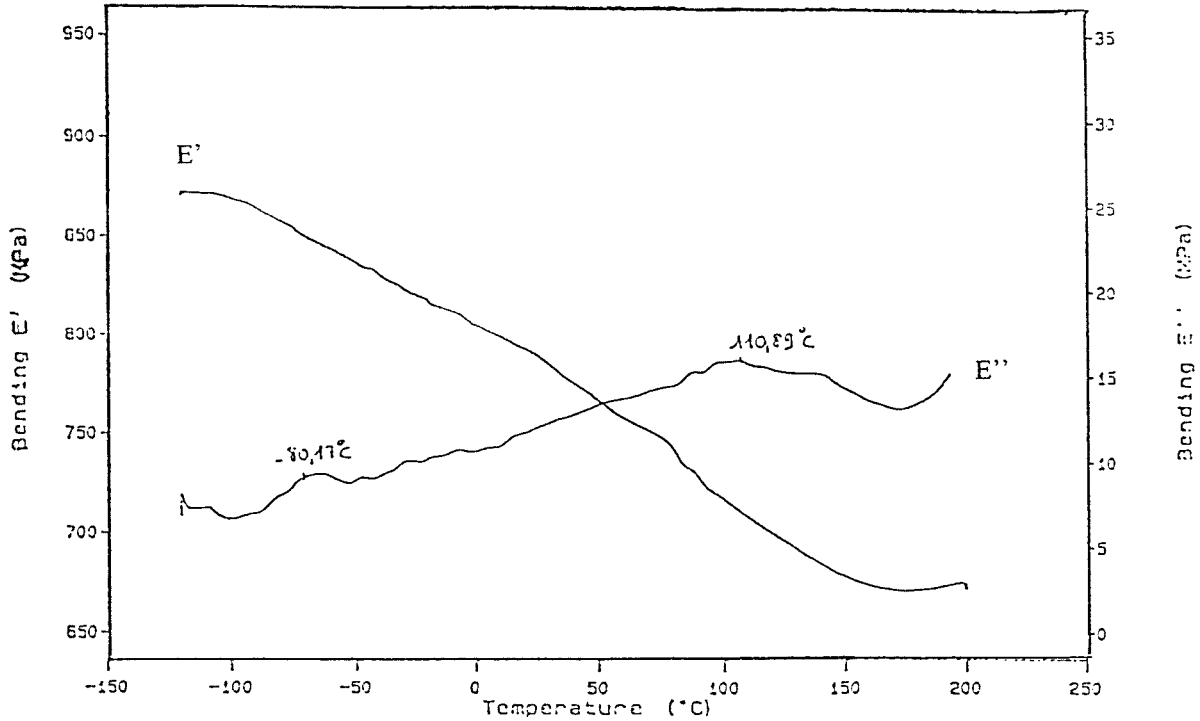
where

Figure 2   Viscoelastic spectrum of virgin PEI.

$$q = \frac{\Delta C_{ps}}{\Delta C_{pp}} \left(1 - \frac{\ln T_{gs}}{\ln T_{gp}} \right)$$

where q is expected to be temperature independent, whereas experimentally it increases from 0.36 at 20°C to 0.45 at 90°C, and then it drops to 0.62 at 100°C. The average value of q (~ 0.4) corresponds to:

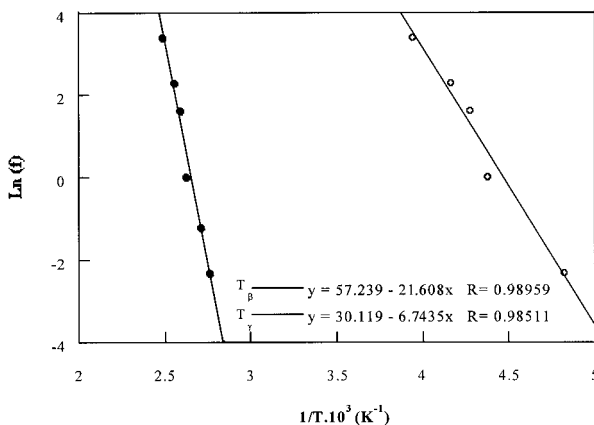$$\frac{\Delta C_{ps}}{\Delta C_{pp}} \sim \frac{0.4}{0.227} \sim 1.76.$$

Figure 3   Arrhenius plot of the β and γ transitions.

ΔC_{pp} is of the order of 0.4 J · g^{-1} K^{-1}; ΔC_{ps} is of the order of 1–2 J · g^{-1} K^{-1}.[9,10]

The value of $(\Delta C_{ps})/(\Delta C_{pp})$ is significantly higher than the one found from experimental results.

The following conclusions can be draft from the above results. (a) Both free volume and thermodynamical approaches of plasticization gave a relatively good prediction of the average effect of water on T_g of PEI; however, the free volume gave better results than the thermodynamical approach. (b) Neither free volume nor thermodynamical approach could explain the effect of temperature exposure on T_g decreasing. As a matter of fact, they predicted insignificant differences between low ($\sim$ 20°C) and high (90–100°C) temperature exposure, although plasticization effects were noticeably higher at high than at low temperature. (c) The hypothesis of hydrolysis or any other chemical effect can be discarded because molar mass changes become measurable only above 180°C in the time scale under consideration.

One possible explanation would be that only a fraction of the absorbed water, depending on temperature (increasing with temperature), would be dissolved in the polymer, and hence, active in plasticization, the remaining fraction being clus-
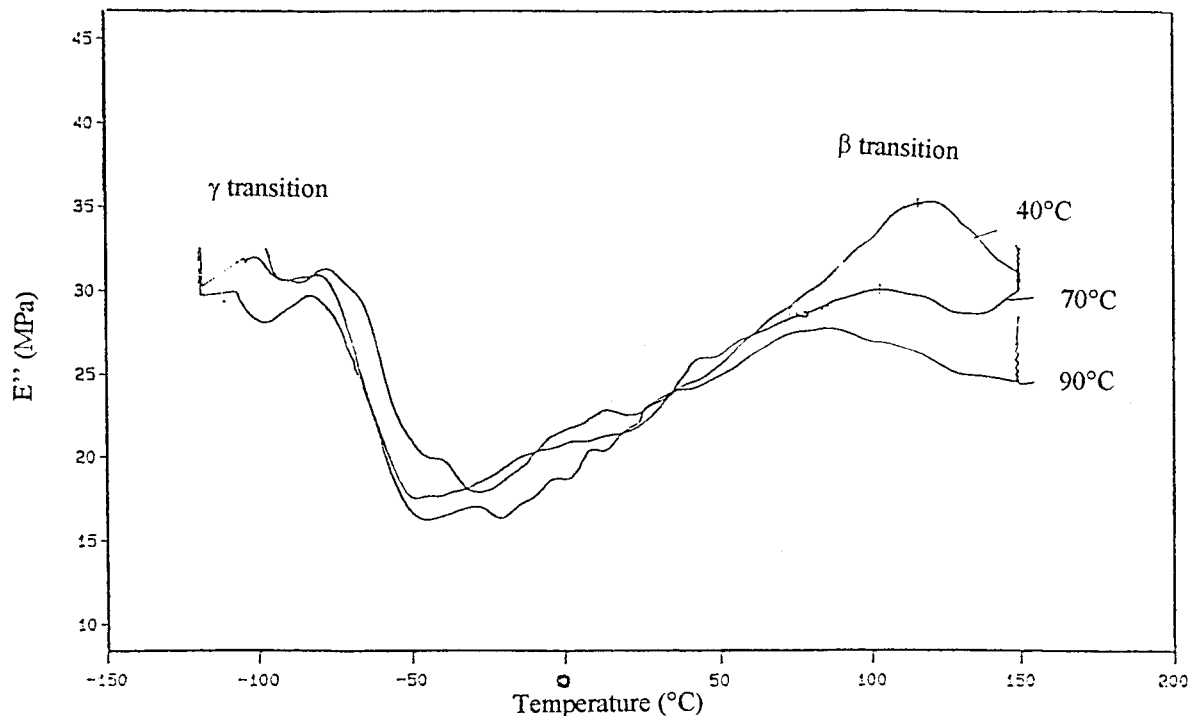
Figure 4 Viscoelastic spectra of the saturated samples at 40, 70, and 90°C.

tered. However, there are many experimental arguments against this hypothesis.[1] NMR measurements in this study confirmed these observations. First, Xenon NMR reveals the absence of porosity on aged samples (thus, there was no cavitation linked to water–polymer phase separation).

D_2O NMR measurements reveal the absence of free water eventually demixed from the polymer (no sharp component in the spectrum, the broad component is linked to water molecules immobilized in the macromolecular network by hydrogen bonds) (Fig. 1).

On redrying, the samples recover the initial T_g value: 216–218°C, which indicates that the water effects on T_g are fully reversible.

It thus seems reasonable to assume that PEI plasticization results from two distinct mechanisms: one classical mechanism, which predominates and which would be well predicted by the (simplified) free volume theory, and one nonclassical mechanism, which takes a more and more important part as the exposure temperature increases.

Viscoelastic Properties

The viscoelastic behavior of virgin PEI in the glassy state revealed two secondary transitions (Fig. 2). The γ transition (−78°C at 1 Hz, activa-

tion energy 56 kJ · mol^{-1}), which is attributed to the rotation of phenylene groups, and the β transition (107°C at 1 Hz, activation energy 180 kJ · mol^{-1}) (Fig. 3), which is characteristic of aromatic polyimides, and has been attributed to a motion of the benzimide group. The effects of water absorption are illustrated in Figure 4 in which the spectra, taken at 1 Hz of samples exposed at 40, 70, and 90°C, are presented. A noticeable decrease of the amplitude of the β dissipation band and its shift towards low temperatures can be observed, both changes being marked as the exposure temperature increases.

The apparent activation energy decreases from 180 kJ · mol^{-1} for the virgin PEI to 114 kJ · mol^{-1} for the saturated samples at 100°C.

These results could be interpreted as follows: less and less benzimide groups are involved in β motions, but the remaining are more and more mobile.

Tensile Properties

Some typical tensile curves are shown in Figure 5. They display a yield overboost of 30–40 MPa amplitude and a more or less extented plastic deformation. The maximum strain value was measurable with the used machine $\varepsilon_{R\ max} = 1.06$.

Virgin PEI

PEI saturated at 100°C
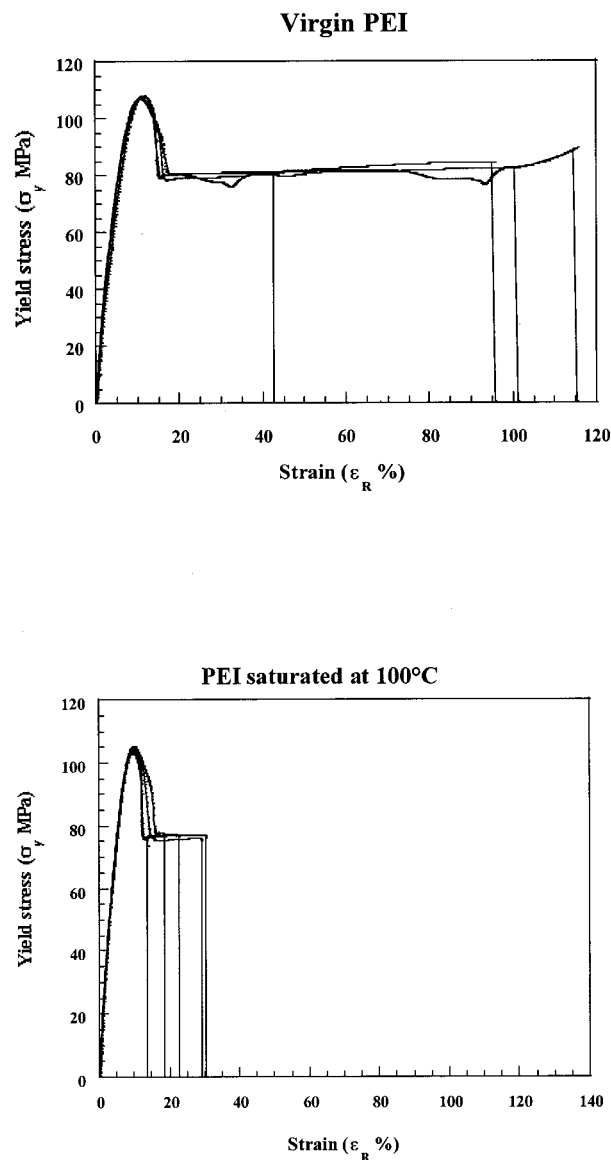
Figure 5 Tensile curves of virgin PEI and saturated samples at 100°C.

The results can be summarized as follows: (a) elastic properties: no significant change was observed; (b) yield properties: the high yield stress σ_{yh} decreases slightly from 119 to 110 ± 7 MPa at 23°C, from 103 to 97 ± 3 MPa at 60°C, and from 82 to 74 ± 4 MPa at 100°C. The same trend can be observed on the low yield stress σ_{yl}, which decreases from 80 to 75 ± 4 MPa at 23°C, from 66 to 62 ± 1 MPa at 60°C, and from 52 to 45 ± 1 MPa at 100°C.

σ_{yh} is linked to the thermal history through structural relaxation (physical aging)[11]; it thus seems better to consider σ_{yl} values that display less scatter. For the virgin sample, σ_{yl} varied linearly with the testing temperature (T):

$$\sigma_{yl} = 0.364(T_o - T)$$

We obtained a value of T_o equal to 513 K close to T_g (490 K). The effect of a glass transition temperature variation on σ_{yl} can be ascribed in a first approach:

$$\Delta\sigma_{yl}/\Delta T_g \sim 0.364 \ (MPa \cdot K^{-1})$$

so that $\Delta\sigma_{yl}$ is expected to vary between 5 and 10 MPa for the observed T_g depletion values.

It thus appears that yield stress values decrease slightly with water absorption, and their decrease is correlated with the T_g decrease, at least in a first approximation. There is no peculiar effect of the exposure temperature. (c) Ultimate strain ε_R: The variation of ultimate strain with exposure temperature is shown in Figure 6 for the three testing temperatures under study: 23, 60, and 100°C.

Despite the relatively high data scatter, the trends are very clear: the ultimate strain is a decreasing function of the temperature of exposure: it is generally higher than unity for the samples exposed at 20°C whatever the test temperature and it reaches about 0.2 (23°C), 0.5 (60°C), or 0.9 (100°C) for the samples exposed at 100°C.

Very typical, lozenge-shaped defects appear upon stretching of aged samples (Fig. 7). It seems that yielding becomes localized in shear bands in wet samples. The shear bands are oriented at 45° of the loading axis so that they delimitate lozenges. Rupture would result from stress concentrations in certain these areas, and the crack propagation would be influenced by shear bands, which would explain the peculiar shape of the
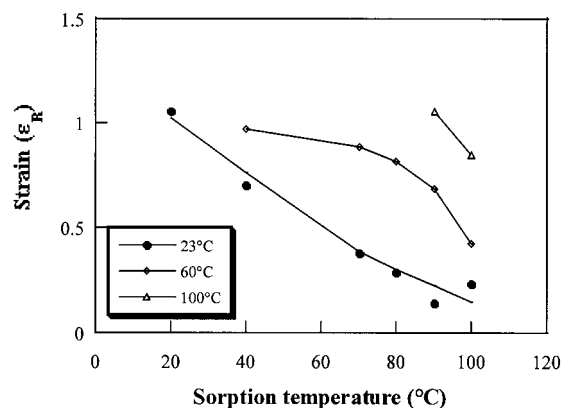
Figure 6 Variation of ε_R with exposure temperature for the three testing temperatures 23, 60, and 100°C.
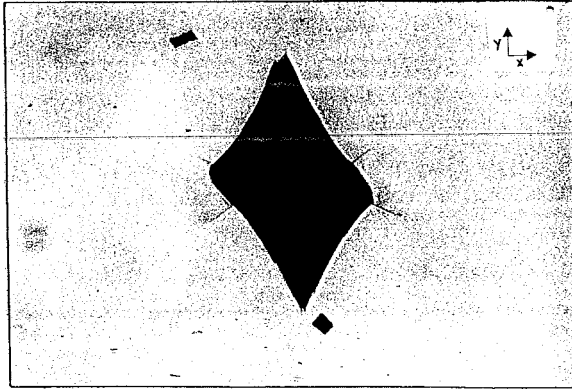
Figure 7 Lozenge-shaped defects for saturated samples at 100°C.

defects. The exact mechanism of cracking remains to establish.

CONCLUSION

The effect of water absorption on various physical properties of PEI has been studied in the 20–100°C temperature range. The glass transition temperature, T_g, decreases in a value ranging from 200°C (for sorption testing at 20°C) to 190°C (for sorption testing at 100°C), whereas the water equilibrium concentration varies only slightly between 20 and 100°C.

In the absence of water clustering or pore filling, as evidenced by NMR, it appears that there are two distinct plasticization processes: one obeys the classical free volume theories, it is temperature independent; the other, which results from an unknown mechanism, is founded at high temperature. These processes seem to affect also the β transition, which decreases in amplitude and is shifted towards low temperatures, both changes being more marked at high than at low sorption test temperatures.

Yield stress slight variations can be correlated to a T_g decrease, as theoretically expected. In contrast, ductility decreases unexpectedly as a result of the formation of lozenge-shaped defects resulting presumably from shear banding.

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