

# Water Sorption in Polyamide-Imide Films and its Effect on Dielectric Loss

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## Synopsis

Water sorption and diffusion has been measured in polyamide-imide over a range of temperature and relative humidities. The results are compared to those obtained on Kapton and discussed in terms of chemical differences between these two materials. Changes in dielectric loss during hydrothermal aging under 85°C and 85% RH have been measured. These changes are correlated to the water sorption kinetics.

## INTRODUCTION

Polyimides are well recognized as a class of highly thermostable polymers and many applications in mechanics, electronics, and space have been developed. However, their widespread use is limited due to some difficulties in their processability: poor flow characteristics<sup>1</sup> and insolubility in commercially available solvents.<sup>2,3</sup> To overcome these problems, some copolymers have been proposed in particular, polyimides-coamides,<sup>2-5</sup> which can be linear, soluble, and also stable in contrast to polyamic acid solutions.<sup>6</sup> This class of polymers seems to be a good compromise between thermostability and processability. However, due to the amide group, they are expected to be more sensitive to humidity. The aim of this paper is to determine the effects of water sorption on thin films of polyamide-imide (PAI) (thickness < 5  $\mu\text{m}$ ) on the short- and long-term electrical properties.

As far as Kapton is concerned, published results report that water sorption mechanism obeys Henry's law at low water content. A clustering phenomena limit the absorption at high concentration of sorbed water.<sup>7,8</sup> The first part of this paper is concerned with the absorption and diffusion of water molecules in thin polyamide-imide films. The experimental parameters are temperature and relative humidity (RH). In the second part, the effect of water absorption on ac electrical properties will be investigated. The frequency dependence of dielectric loss as a function of time has been recorded to examine the effect of water molecules on relaxation phenomena and ionic transport.

## SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The PAI resin used in this study is the Nolyimid 32 (Rhône-Poulenc). Formulae of PAI and Kapton (Du Pont), appear in Figure 1(a) and 1(b). Thin PAI films were prepared by spin coating on silicon wafers or on aluminized glasses. The curing process is done in two steps: prebake at 130°C for 30 min

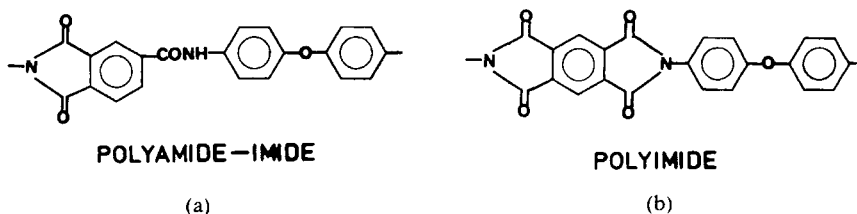


Fig. 1. (a) Polyamide-imide; (b) Kapton polyimide.

followed by a final curing at 350°C for 60 min. *N*-methyl pyrrolidone, which is the solvent used for the synthesis, is eliminated during the second step as shown from TGA analysis.<sup>9</sup>

Water absorption experiments were carried out on 5  $\mu\text{m}$  thick films spin-coated on a silicon wafer. Each sample was then divided in several elements 3  $\times$  1 cm to compare the effects of different experimental conditions. These elements are placed in a chamber in which humidity and temperature are controlled in the ranges 1–96% RH and 90°C. A Dupont 902 moisture analyzer for solids measured the water absorption.

Dielectric loss measurements were carried out on 3  $\mu\text{m}$  thick films spin-coated on aluminum-metalized glass substrate. An upper aluminum electrode was thermally evaporated on the polymer film. The surface of the upper electrode was 0.3 cm<sup>2</sup> to allow a convenient diffusion of water molecules into the polymer film. A General Radio impedance bridge allowed the measurement of the complex permittivity in the range 12 Hz–100 kHz.

## RESULTS AND DISCUSSION

### Water Absorption on PIA Films

Figure 2 shows the variation of the equilibrium water concentration in the sample as a function of relative humidity at 60°C. All the samples were virgin before humidity exposure and all originated from the same silicon wafer. The characteristic  $C = f(\text{RH})$  obtained on PIA films follows Henry's law similar to that reported by Sacher and Susko<sup>10</sup> for various polyimides. Our value of sorbed water concentration is always higher than that of polyimides.<sup>7</sup> This may be due to the polar amide groups which are favorable sites for water absorption. As in the case of Kapton,<sup>11</sup> the  $C$  values were practically temperature-independent in the range of temperatures studied.

The measurement of the water concentration  $C$  as a function of time gives some informations on the water diffusion mechanism. A typical curve is shown on Figure 3. At low concentration a linear variation of  $C$  vs.  $t^{1/2}$  is observed. For  $t > 60$  min, the curve tends to an asymptotic value. According to Barrie et al.<sup>8</sup> this non-Fickian behaviour is generally attributed to relaxation processes sensitive to the presence of water. Also a clustering of water molecules can appear in the polymer limiting the diffusion of further molecules. The diffusion coefficient  $D$  can be expressed as a function of the concentration of

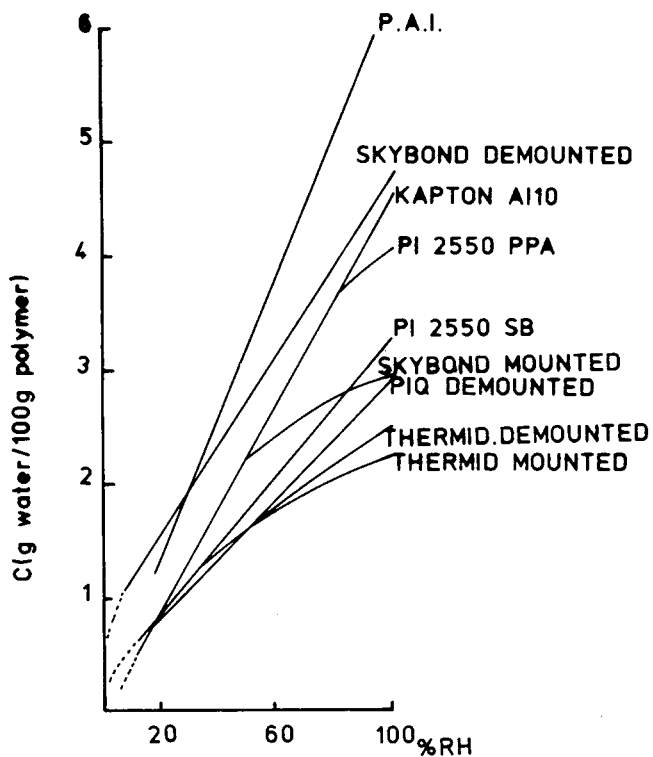


Fig. 2. Henry's law plots from various polyimides from Ref. 10 and for PAI (upper curve).

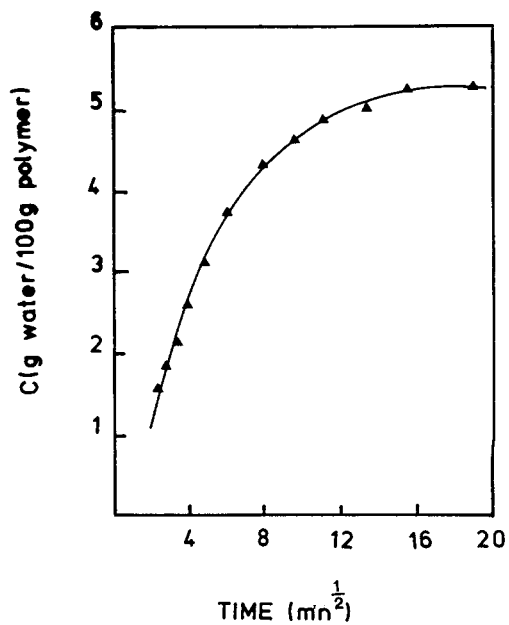


Fig. 3. Sorption kinetics run for 5 m PAI at 40°C and 60% RH.

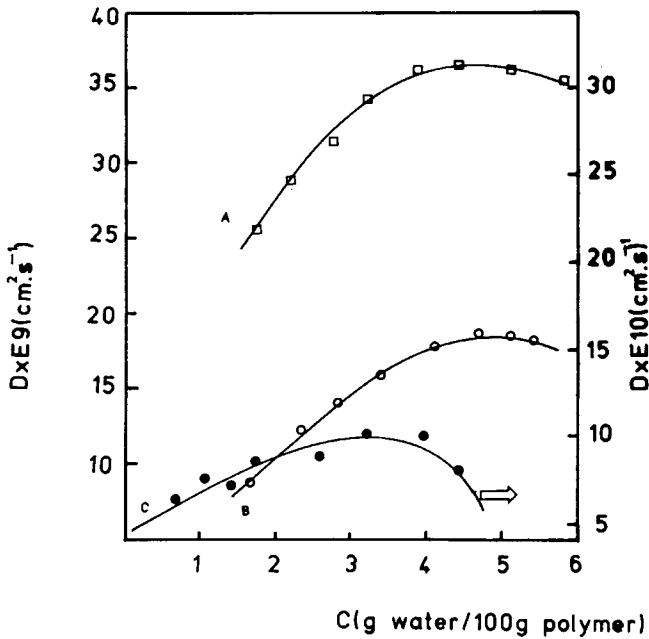


Fig. 4. Average concentration dependent diffusion coefficient  $D$  estimated from sorption kinetics: (a)  $5 \mu\text{m}$  PAI films at  $60^\circ\text{C}$ ; (b)  $5 \mu\text{m}$  PAI films at  $40^\circ\text{C}$ ; (c)  $0.3 \text{ mil}$  Kapton films at  $30^\circ\text{C}$  from Yang et al.<sup>7</sup>

the sorbed water. For the flux of water one may write<sup>12</sup>

$$F = -\mu C \frac{dW}{dx} = -\mu RT \left( \frac{\partial \ln a}{\partial \ln C} \right) \frac{dC}{dx} \quad (1)$$

where  $F$  is the flux of water molecules in the polymer layer,  $\mu$  is the intrinsic mobility of absorbed water,  $C$  is the total concentration of absorbed water,  $W$  is the chemical potential, and  $a$  the thermodynamic activity. Finally the flux of water is given by

$$F = -D(c) \frac{\partial C}{\partial x} \quad (2)$$

where  $D$  is Fick's coefficient.

Equation (2) shows that  $D$  is a function of the overall absorbed water. Physically this dependence comes from the variation of the intrinsic mobility or from the thermodynamic activity which are sensitive to any change in the free volume or solvation of hydrogen bonds. From the linear part of the  $C-t$  curve, it is possible to calculate the diffusion coefficient  $D$ .<sup>13</sup> Figure 4 shows the variation of the average value of  $D$  as a function of the water concentration. These variations are sensitive to the temperature. The maximum is  $3.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at  $C = 4.1\%$  and  $60^\circ\text{C}$  (curve a) and decreases down to  $1.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at  $C = 4.7\%$  and  $40^\circ\text{C}$  (curve b). In curve c are the results from Yang et al.<sup>14</sup> on Kapton. Barrie et al.<sup>8</sup> also report similar results on

bismaleimide resins. Comparing these results, we find again that PAI films are weaker than polyimide: For comparable thickness and temperature, the diffusion coefficient is about 1 order of magnitude higher for PAI films. The shape of the  $D-C$  curve can be interpreted considering that, among the overall sorbed molecules, one part is moving through the film and the other one is trapped in some particular sites of the macromolecular chain. Rewriting eq. (2), taking into account this two different behaviours, it becomes<sup>12</sup>

$$D(C) = D_m(C) \cdot \frac{\partial C_m}{\partial C} \quad (3)$$

where the suffix  $m$  refers to mobile molecules.

While the proportion of water immobilized increased with concentration, then  $C_m/C$  and hence  $D(C)$  decrease with increasing concentration. Hydrogen bonds or clustering effects are two processes able to fix the water molecules. For PAI and Kapton as well, the maximum of the total concentration occurs at about 4% of water in the polymer in the range 30–40°C.

#### Dielectric Losses

Dielectric constant and dielectric losses of PAI films were measured while the samples were in the chamber under 85°C and 85% RH. The time of exposure ranged from 1 to 1000 h. Figure 5 represents the dielectric loss as a function of frequency for different times of exposure. There is a rapid change during the first hour of exposure followed by a slower evolution. This behavior

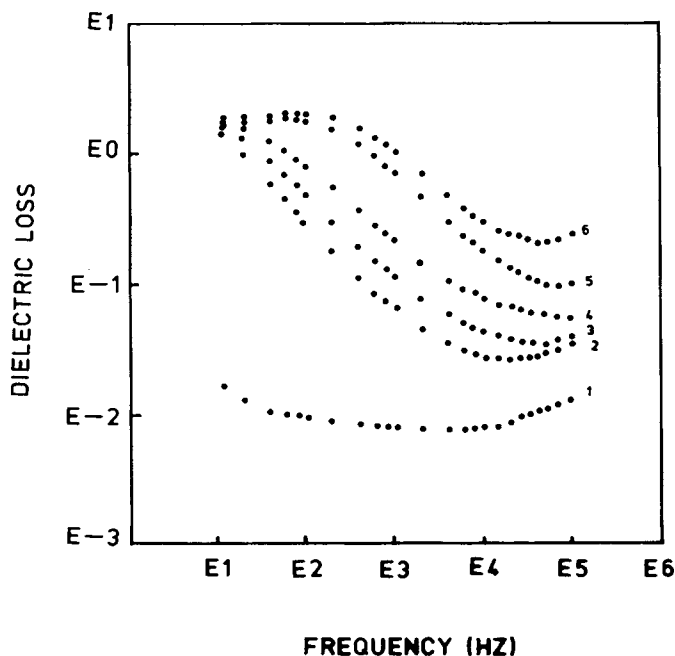


Fig. 5. Dielectric loss vs. frequency of 3  $\mu\text{m}$  PAI films: (1) 85°C; (2–6) 85°C and 85% HR under 3, 24, 100, 500, and 1000 h of exposure, respectively.

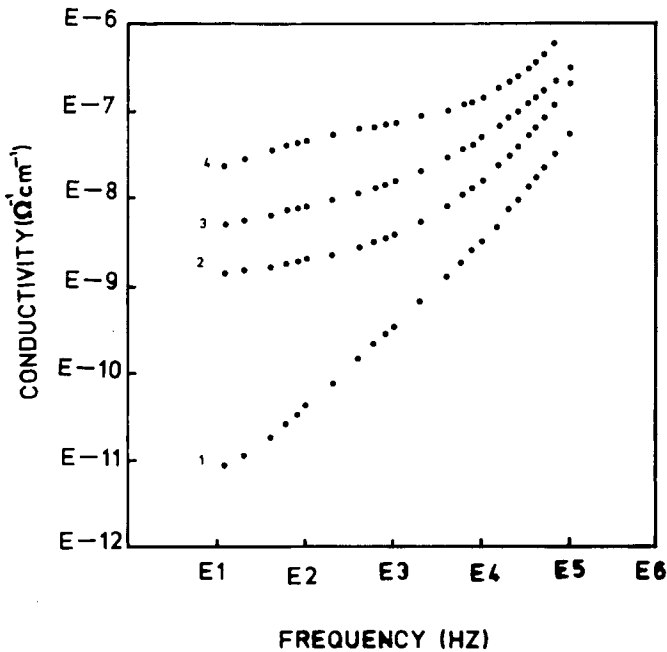


Fig. 6. Conductivity vs. frequency of 3  $\mu\text{m}$  PAI films: (1) 85°C; (2-4) 85°C, 85% RH during 3, 100, and 1000 h, respectively.

is comparable to the change of water concentration (Fig. 3). It must be noted that a temperature of 85°C and 0% RH do not change significantly the dielectric loss, although it is not quite clear if bonded water gives rise to losses or if they induce losses due to a plasticization of the polymer. A strong correlation between water content and loss has very often been reported.<sup>15-19</sup>

From Figure 5, it is clear that the change in dielectric loss occurs mainly in the low frequency range (10-500 Hz). On the other hand, if the conductivity is plotted vs. frequency (Fig. 6), one can observe the effect on the dc component of the conductivity up to 1 kHz as the time of exposure to RH increases. Comparing the size of the water molecule and the mean intermolecular distance between polymer chains, it is reasonable to expect an ionic conductivity coming from nonbonded water. The experimentally measured loss is the sum of the true dielectric contribution and the contribution of the dc conductivity according to the equations

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{\sigma}{\omega \epsilon'} \quad (4)$$

and

$$\begin{aligned} \epsilon'' &= \frac{\sigma}{\omega} = \frac{\sigma_{ac}}{\omega} + \frac{\sigma_{dc}}{\omega} \\ \epsilon'' &= \epsilon''_{ac} + \frac{\sigma_{dc}}{\omega} \end{aligned} \quad (5)$$

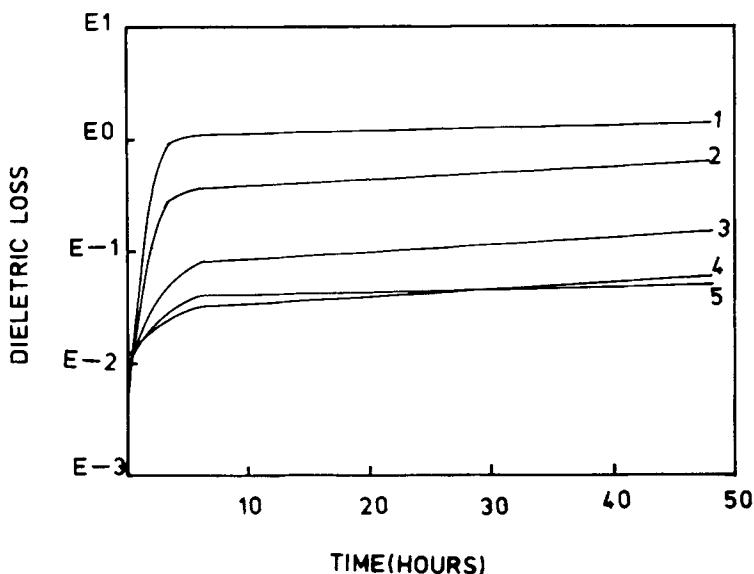


Fig. 7. Kinetics of dielectric loss of 3  $\mu\text{m}$  PAI under 85°C and 85% RH at different frequencies: (1) 20 Hz; (2) 150 Hz; (3) 1 kHz; (4) 10 kHz; (5) 100 kHz.

At low frequency the  $\sigma_{\text{dc}}/\omega$  can be the main contribution. However, in this case the slope of the curve in a log-log plot would be  $-1$ . Examination of Figure 5 does not lead to this conclusion. More likely it seems that a relaxation process appears in the range of frequency studied. The shift of the characteristics toward high frequency is in good agreement with the suggestions made by Sacher<sup>11,15</sup> on the plasticization of polyimide making easier the motion of some groups which, in turn, move the relaxation peak toward higher frequencies. Probably the same peak has been identified by Luckeshin et al.<sup>11</sup> It appears at 1 kHz at 150°C with an activation energy of 17–20 kcal/mol. A simple calculation locate this peak around 15 Hz at 85°C. It is attributed by these authors to the torsional oscillation of the diphenyl ether groups which are also present in our polymer. If this interpretation is correct, we have also to conclude that the position of the peak and presumably its activation energy not only depends on the nature of the group involved in the relaxation but also to the water content of the polymer.

In the same way that the water concentration tends to an asymptotic value as the sample is exposed to 85°C, 85% RH, the dielectric loss changes very slowly after 10 h (Fig. 7).

Thermal treatment under vacuum allows the recovery of the previous level of loss.

### CONCLUSIONS

The water content of PAI films is higher than conventional polyimides but lies in the same range. At 80% RH, the water content of Kapton is 4% against 5.2% for PAI (Fig. 1).

The absorption kinetics is 1 order of magnitude faster in PIA due to the value of the diffusion coefficient  $D$  ( $2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for PAI at 40°C against

$1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  for Kapton at  $30^\circ\text{C}$ ). Thickness of the samples were also comparable at  $5 \mu\text{m}$  for PAI and  $7.5 \mu\text{m}$  for Kapton.

From dielectric loss measurements we can conclude that both PAI and polyimides are more dielectrically lossy than polyolefines like polyethylene or polypropylene, for example. This is due to the ability of PAI and PI to absorb water. Because the water content of PAI is slightly higher than that of PI, the level of losses is also slightly higher. However, both materials exhibit losses in the same order of magnitude:  $7 \times 10^{-3}$  for PAI against  $3 \times 10^{-3}$  for Kapton at 1 kHz and room temperature.

The change in dielectric losses was important and relatively fast for PAI. When it is exposed to 85% RH, an increase of more than 1 order of magnitude was observed during the first hour of exposure. The presence of the amide group in PAI and the fact that the diffusion coefficient is much lower for Kapton probably lead to a slower evolution for Kapton. Unfortunately, to our knowledge the same kind of data does not exist for this material. The effect of water on the losses of PAI is

- (i) to shift a relaxation process toward the range 10 Hz–1 kHz at  $85^\circ\text{C}$  whereas it appears at much lower frequency
- (ii) to increase the dc conductivity which appears to be nonnegligible compared to ac conductivity after 3 h of exposure at 85% RH and  $85^\circ\text{C}$ .

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