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Ageing of polyamide 11 in acid solutions

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The ageing of polyamide 11 (PA11) in water has been studied in the 53–210°C temperature range, in media of pH 0, 2, 4 and 7, for sample thickness ranging from 0.5 to 2 mm. Ageing can be described as a succession of two stages. The first one corresponds to the physical absorption of water until equilibrium. During this stage, chemical degradation is insignificant. The second stage corresponds to the polymer hydrolysis where rate increases with temperature and solution acidity. However, the rate decreases with thickness, thereby indicating that degradation is diffusion controlled. A comparison of gravimetric (weight gain due to the reaction of water with polymer) and steric exclusion chromatography data indicates that most of the hydrolysis events occur at chain ends, and causes the accumulation of monomer and oligomers in the matrix. The presence of these groups can be detected by differential scanning calorimetry. Viscoelastic spectra reveal only a small plasticization effect from water absorption, implying that the monomer has a very poor plasticizing effect on PA11. Also, degradation is probably homogeneous at the scale of amorphous domains (no splitting of the transitions). Finally, cracks appear only in the superficial layers as a result of the large scale heterogeneity which results from the diffusion control of degradation kinetics. Embrittlement in these layers is presumably linked to the degradation of the entanglement network in the amorphous phase. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polyamide 11; water sorption; hydrolysis)

INTRODUCTION

Fundamentally, the process of amide hydrolytic splitting into acid and amide is well known, but in the case of polyamides (PAs) and more generally hydrolysable polycondensates, there is a series of possible obstacles in kinetic modelling. The first type of difficulty can come from diffusion control of the hydrolysis kinetics. The water transport properties in polyamides have been extensively studied[1–5]. Heterogeneities on a large scale (degradation gradients linked to diffusion controlled kinetics), or on a small scale (presence of water clusters as established in the case of PA6 for water mass fractions up to 4%[4–6]) can complicate kinetic studies. In the case of PA12, the tendency of water to aggregate is high[3].

The second type of difficulty can be linked to heterogeneities at the macromolecular scale, e.g. to no random chain scission. In the case of linear polycondensates[7–12], molar mass measurements such as steric exclusion chromatography (s.e.c.) can bring up interesting elements of discussion on the homogeneity/heterogeneity of the reaction from polydispersity considerations. In contrast, viscosimetric measurements made on dilute solutions give only average values, from which the degree of heterogeneity of the reaction cannot be appreciated. In the case of PA6, for instance, a noticeable monomer yield has been observed[3], which indicates that degradation is not a random process.

Gravimetric determinations are often used when molar mass determinations are impossible, for instance in the area of networks[13,14], but they also yield interesting complementary information, for instance on the release of short molecules resulting from close hydrolytic chain scissions. This process is generally diffusion controlled, but it is strongly accelerated when cracking occurs. An example of kinetic modelling of mass changes due to the hydrolysis of a semicrystalline polymer (PET) has been recently reported[15].

Surprisingly, we did not find any published work about high molecular weight polyamide 11 (PA11) exposing to acid solutions at moderate temperatures (i.e. $T \leq 120°C$). The aim of this work, based on the experimental study of molar mass and weight changes at various temperatures is to gain further understanding of the chemical ageing of PA11 during immersion in acid solutions.

EXPERIMENTAL

Materials and solutions

PA11 BESNO TL grade, with $T_m = 190°C$ and $d = 1.03\ g\,cm^{-3}$ was provided by ATOCHEM. Pellets of neat PA11 were vacuum dried at 80°C during 8 h. Samples were then moulded at 220°C, 10 MPa during 30 min and slowly cooled at $5°C\,min^{-1}$ to form plaques 0.5–2 mm thick.

Immersion of PA11 samples was performed in solutions with different acidities. Solutions with pH = 0 were obtained with 1 N HCl. Three other solutions were

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prepared by dilution in 1 l distilled water under the following conditions: pH 2 (1.68): 12.7 g potassium tetraoxalate; pH 4: 10.12 g potassium hydrogenphthalate; pH 7 (6.88): 3.402 g potassium dihydrogenphosphate and 3.549 g disodium hydrogenphosphate.

Differential scanning calorimetry (d.s.c.)

A Perkin-Elmer DSC7 calorimeter was used. Polymer samples of 5 mg were placed in crimped aluminium pans, with a hole for nitrogen circulation to prevent oxidative degradation. A new sample was used for each measurement and a minimum of three runs were performed. The rate of heating and cooling was 20°C min^{-1}. The sample was heated up to 260°C, held for 10 min, cooled to 30°C and heated again to 260°C.

Steric exclusion chromatography (s.e.c.)

S.e.c. measurements were performed with a Waters 150C apparatus composed by a supply of benzoic alcohol eluant, two columns (PLgel 10 μm crosslinked polystyrene) and a differential refractometer. The flow rate was 1 ml min^{-1}. The concentration of polymer solutions was fixed at 0.5 wt% and dissolution was made at 130°C. Universal calibration was made with three different standard polymers: polystyrene, polytetrahydrofuran and polyoxyethylene.

Differential mechanical thermal analysis (d.m.t.a.)

Measurements of dynamic mechanical properties as a function of temperature were made with a Polymer Laboratories d.m.t.a. Bending small bars as a single cantilever was performed at an oscillation frequency of 1 Hz and the sample temperature is controlled in the range −150 to 100°C by a temperature programmer (4°C min^{-1}). D.m.t.a. data were obtained on dried samples (2 days at 80°C).

RESULTS AND DISCUSSION

Short term water absorption

Samples (2 mm thick) were dried for 2 days at 80°C under vacuum and weighed before their isothermal immersion in water at pH 7. The immersion temperatures (53, 70, 80, 90, 100, and 120°C) were above the glass transition temperature (T_g) of wet PA11 (45°C). The weight W_t of the samples was determined at various exposure times t and the relative weight gain $M(t) = 100\,[(W_t - W_0)W_0]$ was calculated. $M(t)$ is plotted vs normalized time $\sqrt{t}/L$ (L being the sample thickness) in *Figures 1a* and *1b*.

For temperatures lower than 90°C, it was seen that the desorption and absorption kinetics are identical. The curves of *Figure 1a* reveal that water absorption is a Fickian process characterized by a constant coefficient of diffusion, D and an equilibrium saturation concentration $M(\infty)$, and obeying the following relationship[16]:

$$M(t) = M(\infty)\left[1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left(-\frac{D_t}{L^2}\pi^2(2n+1)^2\right)\right] \qquad (1)$$

For temperatures above 90°C, it is noteworthy that a weight loss process is superimposed to water sorption. It can be attributed to the extraction of low molecular weight compounds, e.g. free monomer. The same type of behaviour was observed for PA6[17]. Assuming an additive behaviour, this can be written:

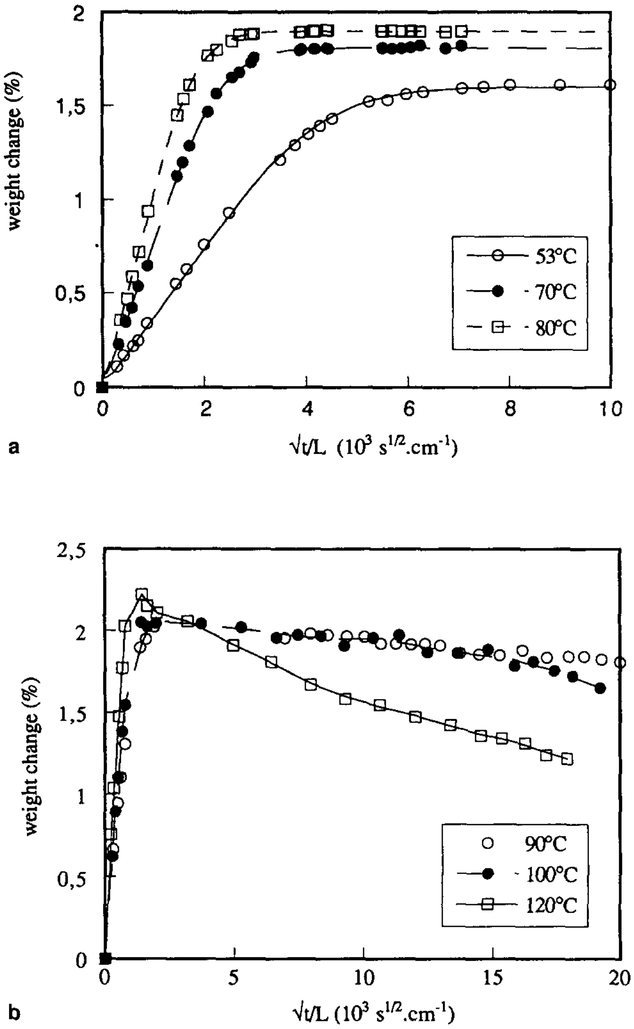

Figure 1 Fickian's water absorption at pH 7 for PA11 (L = 2 mm) (a) between 53 and 80°C and (b) between 90 and 120°C

$$M(t) = M(\infty)\left[1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left(-\frac{Dt}{L^2}\pi^2(2n+1)^2\right)\right] - M(ext)\left[-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+a)^2} \times \exp\left(-\frac{D_{\mathrm{ext}}t}{L^2}\pi^2(2n+1)^2\right)\right] \qquad (2)$$

where D_{ext} and $M(ext)$ are the coefficient of diffusion and the total quantity of the low molecular weight compounds inside the polyamide, respectively.

Arrhenius plots of D and $M(\infty)$ are presented in *Figure 2*. The experimental values obtained for D, D_{ext}, $M(\infty)$ and $M(ext)$ are listed in *Table 1*. It appears that the temperature variations $M(\infty)$ and D can be modelled

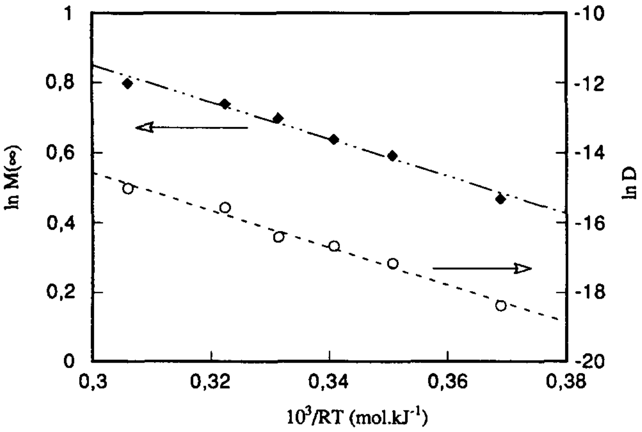

Figure 2 Arrhenius plots for the diffusion and the solubility coefficients

Table 1 D and $M(\infty)$ values for the temperatures under study

Temperature (°C)	53	70	80	90	100	120
$10^{-12} D$ ($m^2 s^{-1}$)	1.0	3.5	5.7	7.5	19	32
$M(\infty)$	1.60	1.81	1.90	2.01	2.01	2.23

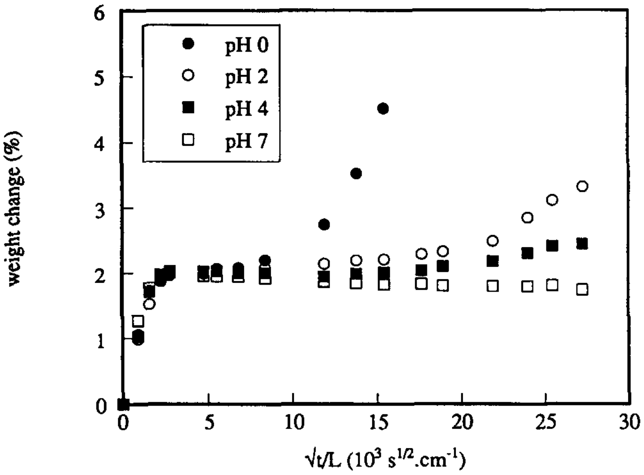

Figure 3 Water absorption for PA11 ($L = 0.6$ mm) at 90°C as a function of the solution acidity

by an Arrhenius law, according to:

$$M(\infty) = M(\infty, 0)\exp\left(-\frac{\Delta H_S}{RT}\right) \qquad (3)$$

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \qquad (4)$$

where ΔH_S is the mixing enthalpy and E_D is the activation energy of the diffusion process. We found $\Delta H_S = 4.5$ and $E_D = 55.1\,\text{kJ mol}^{-1}$. These values agree reasonably well with literature values relative to various polyamides[18–20].

On the other hand, by considering that about 2 wt% water is absorbed at saturation, it can be calculated that $M(\infty)$ corresponds to about 1 mol H_2O per 4 mol of amide groups in amorphous PA11 (the crystalline phase corresponds to around 20% by weight and is considered impermeable to H_2O).

Similar experiments in acid solutions at $T = 90°C$ are illustrated in *Figure 3* ($L = 0.6$ mm and pH = 7, 4 or 2) and *Figure 4* ($L = 0.5$, 1, 1.5 or 2 mm and pH = 2). Concerning the short term behaviour, it clearly appears that it is independent of the solution acidity. D and $M(\infty)$ do not significantly vary with pH. Strictly speaking, this indicates only that ionic species present in the bath are characterized by a low solubility or by a diffusivity in PA11 at least one order of magnitude lower than water molecules, or by both characteristics at the same time.

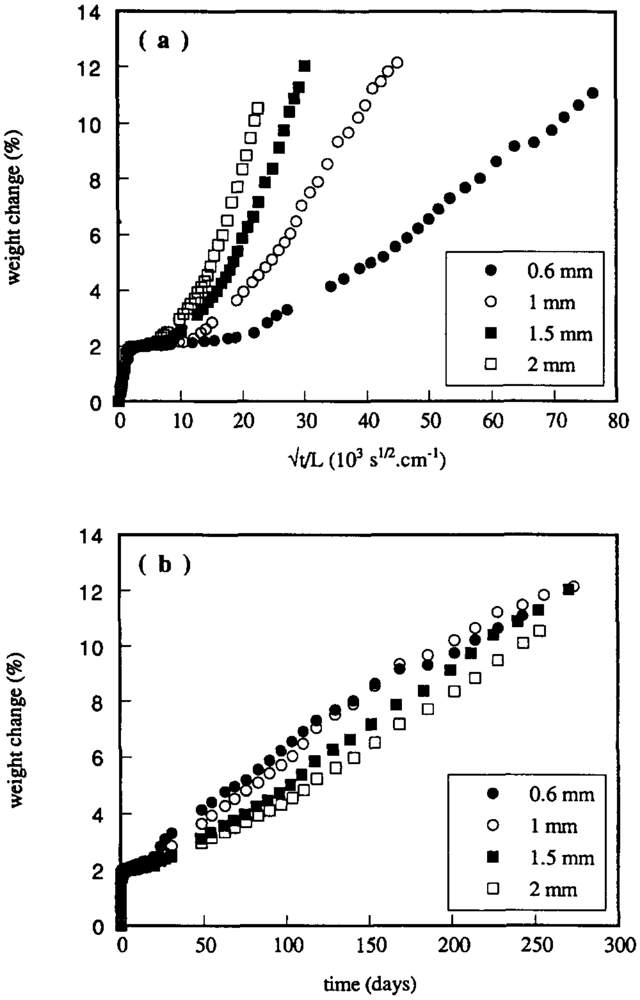

Figure 4 Water absorption for PA11 at 90°C and pH 2 as a function of the sample thickness; (a) vs $\sqrt{t}/L$ and (b) vs time

Long term water absorption

The kinetic curves of water absorption reveal however that another water uptake process, characterized by a longer time scale than Fickian sorption, is superimposed onto the first one. This water uptake process displays the following characteristics:

1. It is almost parabolic when plotted as function of time or reduced time ($\sqrt{t}/L$). In other words, it is not far from a zero order process (weight gain proportional to exposure time), as shown in *Figure 4*.
2. It is accelerated by an increase of pH (*Figure 3*), an increase of temperature, and a decrease of sample thickness (*Figure 4*).
3. In the temperature range ($T < 100°C$), where extraction of low molecular weight compounds is negligible, it was found to be almost completely irreversible. In

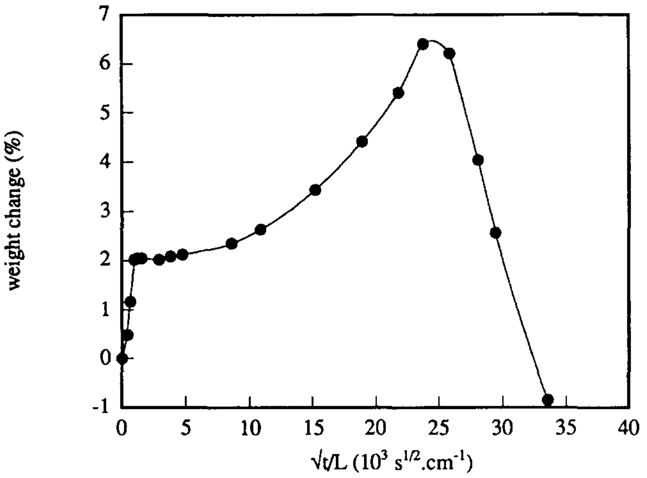

Figure 5 Water absorption for PA11 ($L = 1\,\mathrm{mm}$) at 120°C and pH 4

Table 2 Estimated hydrolysis rates from data of *Figure 4* relative to hydrolysis at 90°C in a solution of pH 2

Thickness (mm)	r (80 days) ($\mathrm{mol\,kg^{-1}\,s^{-1}}$)	r (240 days) ($\mathrm{mol\,kg^{-1}\,s^{-1}}$)
0.6	2.8×10^{-7}	3.0×10^{-7}
1	2.5×10^{-7}	3.1×10^{-7}
1.5	1.9×10^{-7}	2.9×10^{-7}
2	1.5×10^{-7}	2.7×10^{-7}

Table 3 Free water content estimated at pH 2 and 90°C as a function of the sample thickness by considering that 2 wt% water are reversibly absorbed and that 7.6 wt% have been consumed by hydrolysis

Thickness (mm)	M(t) (%)	free water (%)
0.6	10.2 ± 0.3	0.6
1	11.4 ± 0.2	1.8
1.5	11.0 ± 0.1	1.4
2	10.3 ± 0.1	0.7

other words, if we consider the time domain when $t > L^2/D$ (D being the water diffusivity), i.e. the domain in which the sorption equilibrium is characterized by $M = M(\infty)$ has been reached. If $M(t)$ is the actual weight gain for weight samples ($M(t) > M(\infty)$), $W = M(t) - M(\infty)$ is the irreversible weight gain linked to the long term process under consideration. The sample weight after drying becomes $M_d(t) = M_0 + W$ where M_0 is the initial weight in dry state.

4. In the temperature range ($T \geq 110$°C), the extraction of low molecular weight compounds becomes important after cracking of the polymeric matrix, *Figure 5*. This phenomenon is irreversible.

All these features are, undoubtedly, linked to the polymer hydrolysis:

$$\sim CH_2 - CO - NH - CH_2 \sim + H_2O \xrightarrow{H^+}$$
$$\sim CH_2 - COOH + \sim CH_2 - NH_2$$

The incorporation of 1 mol H_2O to the polymer, i.e. 18 g, per hydrolysis event was expected. For low conversions, the number of hydrolysis events is expected to be an almost linear function of time independent of the reaction order[21]. The reaction rate, r, can then be estimated because n (number of hydrolysis events) is related to the mass gain W. For a given time, t, provided that the reaction is apparently zero order.

$$r = \frac{dn}{dt} = \frac{W(t)}{18t} \tag{5}$$

This relationship was applied to the values of *Figure 4* at two different times (80 and 240 days) and led to r values listed in *Table 2*. These results highlight an interesting contradiction. From a simple examination of kinetic curves of *Figures 3–5*, it can be concluded in principle that hydrolysis is not diffusion controlled since a sorption equilibrium is reached at a time when the conversion of hydrolysis is still low. Despite this fact, the hydrolysis rate appears to be a weak decreasing function of sample thickness which is an obvious proof of the existence of a diffusion control of the kinetics. A simplified theory of diffusion controlled kinetics[21] allows sense to evaluate the critical conditions separating the controlled from the non-controlled kinetic regime. According to this theory, the critical sample thickness would be given by:

$$L_c = 2\sqrt{\frac{DC}{r_0}} \tag{6}$$

where D is the water diffusivity, C the equilibrium concentration and r_0 the non-perturbed rate of water consumption. In the case under study, at 90°C, $D = 7.53\ 10^{-12}\,\mathrm{m^2\,s^{-1}}$, $C = 1202\,\mathrm{mol\,m^{-3}}$, $r_0 \geq 2.77\ 10^{-4}\,\mathrm{mol\,m^{-3}\,s^{-1}}$ and then, $L_c \leq 10\,\mathrm{mm}$.

It is reasonable to suppose that r_0 is of the same order of magnitude as the value obtained for a sample thickness of 0.5 mm, so that it could be predicted that degradation must be non water diffusion controlled in the thickness range under study (< 2 mm). This confirms the impression given by visual examination of kinetic curves. The dry weight of the samples was determined after a long immersion time under these conditions. As $\pi(+)$ is equal for each sample thickness, some free water can be supposed to be included in the polymer, as shown in *Table 3*. At longer immersion times, extraction becomes more important for thinner samples. This explains the decrease of the sorption curve of 0.6 mm sample.

Change of molecular weight

The molecular weight set of data obtained from s.e.c. measurements will be published elsewhere[22]. In this paper, the attention will be focused only on the comparison of chain scission yield (n) as determined from gravimetry (see above) and from s.e.c. In this case, it is implicitly considered that the chromatograms contain all the information needed for molar mass calculations and that we are in the frame of a random chain scission process. Hence, the following equation can be written:

$$n_{t,\mathrm{s.e.c.}} = \frac{1}{M_{n,t}} - \frac{1}{M_{n,0}} \tag{7}$$

Where $M_{n,0}$ is the initial molar mass of PA11 ($M_{n,0} = 22.5\,\mathrm{kg\,mol^{-1}}$). The comparison was made for an exposure time of 45 days, at 90°C in pH 2 for 1 mm thick samples. The molar mass $M_{n,t}$ under these ageing

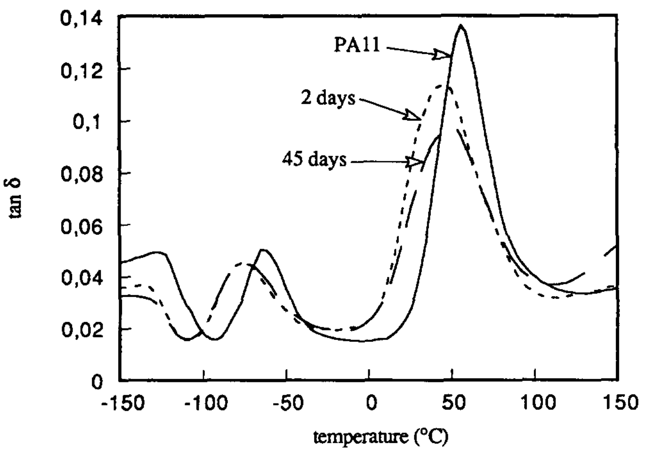

Figure 6 Thermomechanical behaviour of PA11 ($L = 2$ mm) as a function of immersion time at pH 2 and 90°C

conditions, corresponds to 9.8 kg mol^{-1}, which leads to a number of chain scissions $n_{t,\mathrm{s.e.c.}} = 5.76\ 10^{-2}$ mol kg^{-1}. From gravimetry determinations, W and $n_{t,\mathrm{Grav}}$ were found to be 16 g kg^{-1} and 0.89 mol kg^{-1}, respectively.

Therefore, it appears that the chain scission yield determined by gravimetry is about 15 times higher than the one determined by s.e.c. The only way to explain this discrepancy is that most of the hydrolysis events occur near the chain ends and give monomer and oligomer molecules that cannot be detected by s.e.c. These data are in contradiction with the hypothesis of random chain scission for hydrolysis of PA11 in acid media.

Viscoelastic behaviour

D.m.t.a. dissipation spectra of samples of 2 mm thick exposed 0, 2 and 45 days at 90°C in pH 2 solutions are shown in *Figure 6*. A decrease of about 10°C in the transition temperature T_α, resulting from water plasticization, was observed after 2 days of exposure. Surprisingly, no further decrease occurs during the following 43 days of exposure, whereas chemical data indicate a considerable polymer degradation. This result can be interpreted as follows:

1. Hydrolysis does not induce significant variations of the polymer hydrophilicity. In other words, the build-up of acids and amines is compensated for by the disappearance of amides which have the same contribution to water solubility.
2. The decrease in molecular weight does not significantly affect T_g and the low molecular weight compounds (oligomers and monomer) do not display a significant plasticizing effect. These effects are usually expressed by the Fox–Flory law:

$$T_g = T_{g,\infty} - \frac{K_{FF}}{M_n} \tag{8}$$

so that:

$$T_{g,0} - T_g = K_{FF}\left(\frac{1}{M_n} - \frac{1}{M_{n,0}}\right) \tag{9}$$

where $T_{g,0}$ is the intial dry glass transition temperature (i.e. 56°C for PA11).

The set of data reported here would indicate that for PA11, K_{FF} is very low. A possible physical explanation is that the effect of free volume excess related to chain ends is balanced by the high contribution of these latter to PA11 cohesiveness. The fact that the melting points of the polymer and the monomer are very close, as explained below, tends to support this hypothesis.

Another explanation is based on the nature of this transition. The α relaxation is linked to hydrogen bonds[23] which are always present in the polymer even for low molar mass.

It is to be noted that ageing in water also induces a shift of about 10°C on the β transition temperature, initially close to −55°C. This shift does not change after 2 days of exposure, as for T_α, so that it can also be attributed to plasticization. Unfortunately, theoretical support is not sufficient to interpret this behaviour.

No new peak or shoulder appears in the d.m.t.a. spectrum of aged samples, which seems to discord the hypothesis of marked heterogeneities of water absorption (in this case, the melting point of water would be observable), or degradation.

Thermal properties

Two d.s.c. spectra of an aged PA11 sample are presented in *Figure 7a*. They can be compared with the d.s.c. spectra of the monomer (amino undecanoic acid) obtained in the same conditions (*Figure 7b*). It can be noted from these results that:

1. The melting point of PA11 (*ca* 190°C) is independent of ageing state for the considered time frame.
2. The melting peak is followed by a broader endotherm around 220°C, but this endotherm disappears in the second run, whereas a small peak appears just before the melting point of PA11 at *ca* 180°C.
3. The same behaviour is obtained for the monomer.

These data can be interpreted as follows. First, the lack of ageing effect on melting point can be explained, as for T_g, by the similarity of the polymer and monomer characteristics, which is a peculiarity of PA11. Also, the broad endotherm at 220°C in aged PA11 is, doubtlessly, linked to the polycondensation of monomer and oligomer molecules accumulated in the amorphous phase of the polymer, as a result of hydrolysis. Thus, d.s.c. confirms the presence of detectable amounts of monomer/oligomer as observed when comparing gravimetric and s.e.c. data.

Finally, the small peak preceding the PA11 melting endotherm is obviously linked to the presence of low molecular weight compounds in the sample, before the first run. It can be related to some residual monomer or to short chains resulting from the 'post polycondensation' process. If this peak is due to the presence of monomer crystals, its absence in the first run thermogram of aged PA11 seems to indicate that the monomer was homogeneously dispersed into the matrix rather than concentrated in microdomains, since in this last case it would have crystallized during ageing.

Cracking

Cracks are only observed at $T \geq 100$°C, after a relatively long exposure time. This aspect is illustrated by SEM observations in *Figure 8*. It clearly appears that they are initiated only in a superficial layer.

Samples immersed during the whole exposure time were compared with samples having the same overall ageing time but removed many times from the bath in

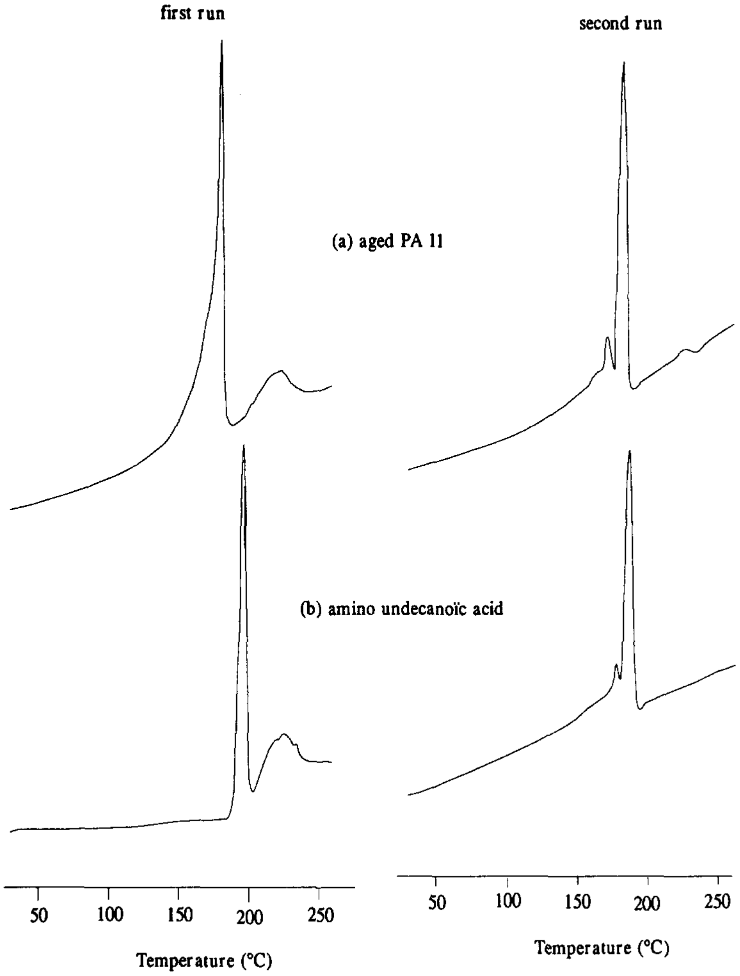

Figure 7 D.s.c. curves: (a) for an aged PA11 (pH 2, 120°C, 35 days); (b) for the amino undecanoic acid

order to determine the weight change. Cracking appeared sooner in these latter samples than in the former ones, showing that the swelling–deswelling cycles linked to water transport play a noticeable role in the material's damage. There are at least three types of cracking mechanisms by humid ageing:

- The first type of cracking results from swelling stresses induced by water concentration gradients. It is often observed with very stiff materials, e.g. composites where small strains are capable of inducing damages[24,25]. Such a mechanism cannot play the predominant role in our case where the starting material (PA11) is much more ductile than composites.
- The second type of cracking occurs very often in the case of ageing involving random chain scission. It is linked to the fact that plastic deformations are only possible when the chains are entangled in the amorphous phase of the polymer. Each polymer can be characterized by a critical molar mass, M_c, below which entanglements become mechanically inactive, so that yielding processes cannot occur and the polymer becomes brittle[21]. M_c is always of the order of $10\,\mathrm{kg\,mol^{-1}}$. Thus embrittlement by this mechanism would not be surprising because M_n values of this order of magnitude were found in our study. In this case, embrittlement is expected to occur at a fixed hydrolysis conversion ratio as found in the case of polycarbonate by Gardner and Martin[26]. Unfortunately, we lack experimental data to check this hypothesis. When M_n becomes lower than M_c, the sample becomes very brittle and its toughness can decrease rapidly by one or two orders of magnitude so that cracks can 'spontaneously' nucleate and propagate under the influence of differential dilatations, differential swelling, and density gradients due, for instance, to superficial degradation.
- The third type of cracking is the so called 'osmotic' cracking[14,27] recognizable by the disc shaped form of cracks, often with concentric fringes corresponding to crack propagation–arrest cycles. In this case, the cause of initiation can be attributed to:
  1. A demixing of the water–polymer system due to fast temperature change, for instance cooling in the case of polycarbonate[28].
  2. A less understood slow demixing in isothermal conditions as observed in the case of humid ageing of polyesters[15]. In this last case, the dissolution of organic compounds resulting of polymer hydrolysis in the water present in microcavities increases the osmotic pressure at the surface of the latter and contributes to accelerate the crack propagation. In the case under study, the relatively large amount of monomer accumulated in the polymer matrix could play such a role.

CONCLUSION

The acid hydrolysis of PA11 is characterized by an

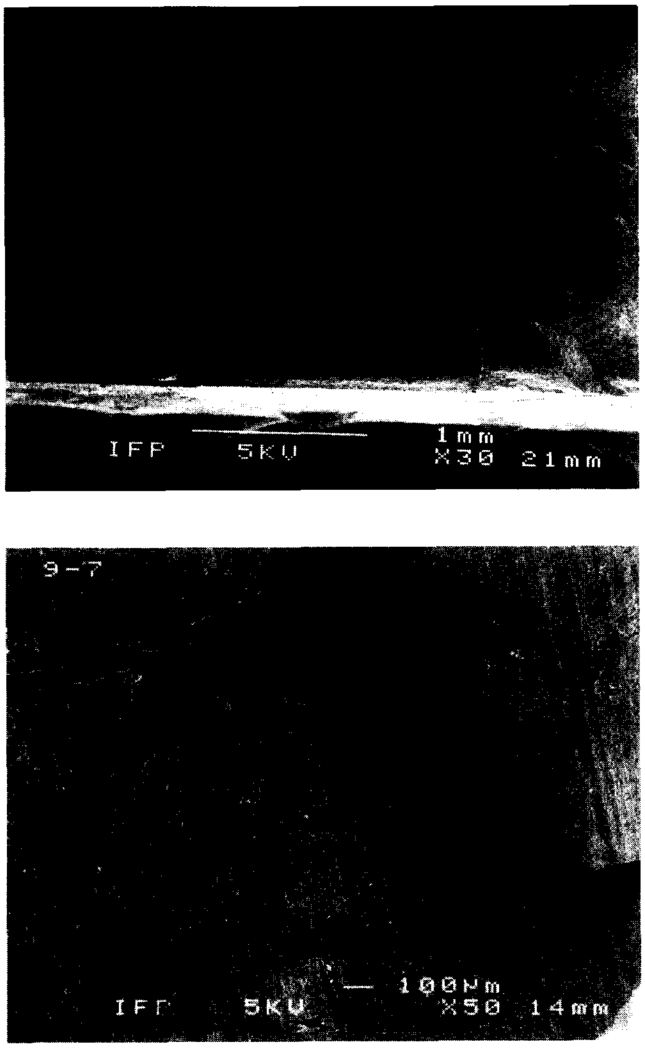

Figure 8 Observations of surface cracks in PA11 after immersion in acid solutions

especially high monomer/oligomer yield, inconsistent with the hydrolysis of random chain scission.

A peculiarity of PA11, which was not found in most of the known hydrolysable industrial polymers (polycarbonate, polyethylene terephtalate, unsaturated polyesters,...) is that the low molecular weight compounds resulting from degradation do not migrate out of the samples, at least at temperatures lower than 100°C. These compounds display a negligible plasticizing effect, and then they only induce subtle modifications of viscoelastic spectra and thermograms. A very important consequence of extreme hydrolysis is embrittlement, as revealed by the appearance of spontaneous cracks in the superficial layer of the samples.

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