Swelling and deswelling of polyamide 11 with formic acid

H. M. Le Huy, X. Huang and J. Rault*
Laboratoire de Physique des Solides, Bât 510, Université de Paris-Sud, Orsay Cedex, France

(*Received 9 July 1991; revised 6 March 1992*)

The swelling and deswelling of isotropic and oriented polyamide 11 (PA11) with formic acid have been determined as functions of temperature and acid solution concentration. During swelling, dimension relaxation, partial dissolution of crystallites and extraction of low molecular weight chains occur. During deswelling, amorphous chains recrystallize and after complete drying, the original morphology with the same orientation is restored. This memory effect is due to strain-induced crystallization in the PA oriented gel.

(**Keywords: polyamide 11; absorption; desorption; mechanical spectroscopy; morphology**)

INTRODUCTION

The influence of water on the static and dynamic mechanical properties of various polyamides (PA) has been extensively studied[1–11], but the effect of formic acid as a plasticizer of PA is less well known. Recently, Dosière *et al.*[12–14] have studied the change in morphology of dried PA11 and PA12 previously submitted to heat treatment in formic acid. The purpose of this paper is to give a description of the physical processes appearing during swelling and deswelling of PA11 with formic acid. The interest of these systems is that the equilibrium swelling can be controlled by the acid concentration and by the sorption temperature. To our knowledge, there have been no morphological studies on such systems.

CHARACTERIZATION OF THE MATERIALS

PA11 was provided by Atochem. The characteristics of isotropic, rolled (× 2.3) and drawn (× 3.5) samples are given in *Table 1*. All the materials (1–2 mm thick) were conditioned at 100°C in vacuum for 1 week (desorption ratio 0.5 wt%). The glass transition, T_α, and secondary transition, T_β, temperatures were determined by dynamic mechanical thermal analysis (d.m.t.a.) in the bending mode, parallel to the orientation direction (DMTA mark II, Polymer Laboratories), at 10 Hz and at a heating rate of 4°C min^{-1}. *Figure 1a* shows the d.m.t.a. curves of isotropic and oriented materials. The melting temperature and melting enthalpy have been measured by differential scanning calorimetry (d.s.c.) (Mettler DSC 30), at a heating rate of 10°C min^{-1}. Crystallinities have been measured by d.s.c., assuming that the melting enthalpy[7] of crystalline PA11 is 226 J g^{-1}. Wide angle X-ray scattering (WAXS) patterns were obtained with a Rigaku X-ray generator and a linear position counter (X-ray wavelength 1.54 Å).

The starting materials have different crystallinities, as confirmed by density measurements. In *Table 2*, the theoretical densities (in parentheses) are deduced from the densities, ρ_a and ρ_c, of the amorphous and crystalline phases[14], respectively 1.0 and 1.12 g cm^{-3}, and from the crystallinity. They are in good agreement with the experimental densities.

SWELLING

The samples were immersed in formic acid solutions of various concentrations and at various temperatures. *Table 2* gives the equilibrium sorption ratio values for the oriented and unoriented materials. It is noted that drawn materials absorb less solvent than isotropic ones. The calculated values of weight gain $\Delta w/w_0$ at equilibrium for the different samples are given in parentheses (w_0 is the initial weight of the sample conditioned at 100°C under vacuum before swelling experiments). The equilibrium swelling ratio S by weight is calculated according to the relationship:

$$S = (\Delta w/w_0)_{\mathrm{eq}} = (\Delta w/w_0)_{\mathrm{i}} x_{\mathrm{a}}$$

where $(\Delta w/w_0)_{\mathrm{i}}$ is the equilibrium weight gain of the isotropic samples treated in the same conditions, and x_{a} is the ratio of the amorphous contents of the oriented and isotropic materials. The good agreement between calculated and experimental values emphasizes that the absorption at equilibrium in these materials is only governed by the crystallinity of the starting materials.

Table 1 Characteristics of the PA11 samples (T_m, melting temperature (d.s.c.); ΔH_m, enthalpy of melting (d.s.c.); χ, crystallinity from ΔH_m; T_β and T_α, temperatures of the β and α transitions, respectively (d.m.t.a.); ρ, density, experimental and theoretical (in parentheses))

Sample	T_m (°C)	ΔH_m (J g^{-1})	χ (%)	T_β (°C)	T_α (°C)	ρ (±0.005)
Isotropic	190	53	23	−40	65	1.027 (1.028)
Rolled	192	59	26	−40	70	1.037 (1.031)
Drawn	191	75	33	−40	80	1.041 (1.040)

---

* To whom correspondence should be addressed

0032-3861/93/020340–06

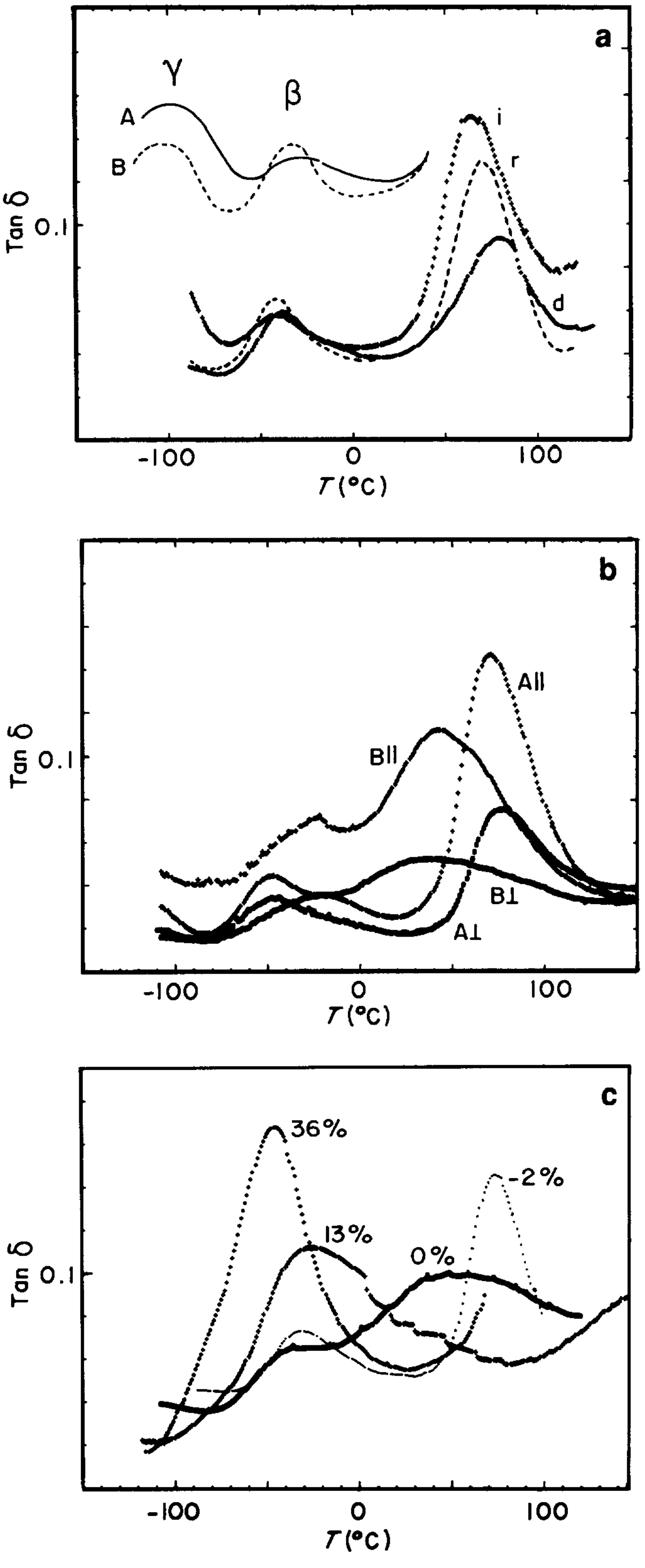

Figure 1 (a) D.m.t.a. curves of isotropic (i), rolled (r) and drawn (d) PA11. The materials have been conditioned at 100°C under vacuum for several days to obtain constant weight. The low temperature curves of isotropic materials dried (A) and unconditioned (B) are shifted along the ordinate axis. (b) D.m.t.a. curves of rolled PA11 in bending mode parallel and perpendicular to the rolling direction. Curve A, unconditioned starting material; curve B, starting material has been swollen in 10% formic acid solution at 25°C and dried until the weight w_0 of the initial sample is obtained. (c) D.m.t.a. curves of rolled PA11 swollen in 90% formic acid solution at 25°C, as a function of the swelling ratio. The materials have been swollen in formic acid at equilibrium ($S = 36\%$) and deswollen at different rates. Complete drying of the equilibrium swollen materials gives a weight loss $\Delta w^*/w_0 = 2\%$

The transition temperatures T_α and T_β, deduced from the maximum of the tan δ curves (*Figure 1*) are given in *Figure 2*, as functions of the absorbed acid content. After d.m.t.a. measurement, the materials were dried at 100°C to constant weight w^*.

The solvent absorbed content, S^*, by weight is:

$$S^* = (w - w^*)/w^*$$

The weight w^* of the dried material after swelling is not equal to the weight w_0 of the starting conditioned material. As explained later, w^* is a function of the equilibrium swellling ratio S.

For low swelling ratios, the distinction between S and S^* is not relevant. The curves T–(S) and T–(S^*) display the same shape. Two domains of variation can be observed: at low swelling ratio, T_α decreases quickly with S^*, and above $S \approx S^* \approx 10\%$, it does not vary conspicuously.

The theoretical values of T_α from the Fox equation are given in *Figure 2*:

$$1/T_\alpha(c) = c/T_\alpha(\text{sol}) + (1 - c)/T_\alpha(\text{PA})$$

The local concentration c of solvent in the amorphous phase is related to the crystallinity χ and to the solvent content S^* by the following relation:

$$c = S^*/(1 - \chi + S^*)$$

T_α(PA) and T_α(sol) are the glass transition temperatures of the pure polymer and acid solution, respectively. The latter value cannot be determined directly. The crystallization temperature of the acid solution is −70°C at a cooling rate of $10°\text{C min}^{-1}$, and the T_α value has been taken arbitrarily at 30 and 80°C below this crystallization temperature.

Table 2 Equilibrium sorption ratio S (wt% of PA11), in formic acid solutions of concentration A and at temperature T. The calculated S values are given in parentheses

A (%) T(°C)	0 25	60 25	90 25	95 25	90 60
Isotropic	2.1	17	35	55	56
Rolled	2.2 (0)	17 (16)	37 (34)	55 (53)	56 (54)
Drawn	2.15 (2)	16 (15)	31 (30)	45 (48)	47 (49)

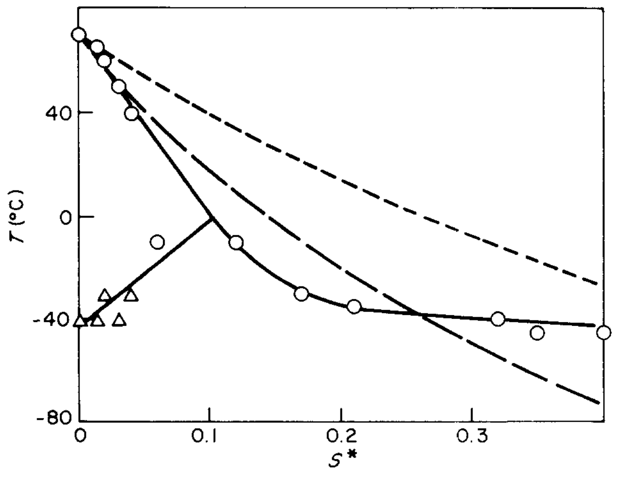

Figure 2 Temperatures T_α (○) and T_β (△) of isotropic and rolled PA11 as functions of the absorbed formic acid content $S^* = (w - w^*)/w^*$. – – –, Fox equation with T_α (sol) = −100°C; — — —, T_α (sol) = −150°C

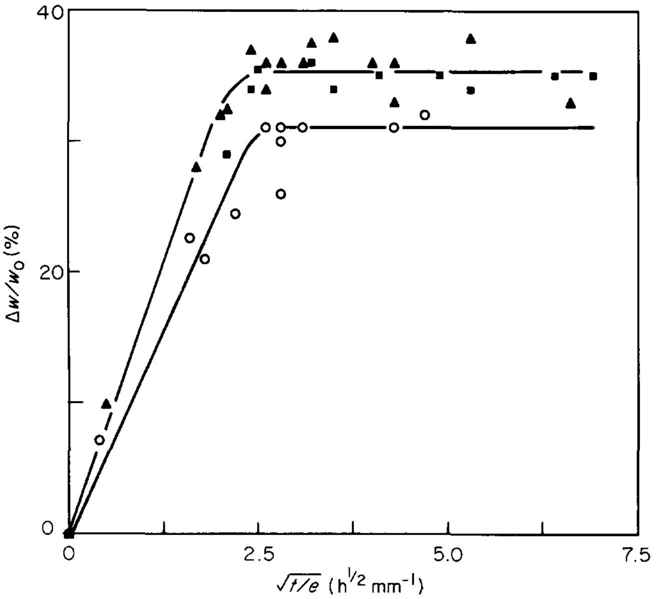

Figure 3 Weight gain of PA11 materials (thickness *e*) *versus* the square root of the immersion time in 90% formic acid solution at 25°C: ■, isotropic; ○, drawn; ▲, rolled

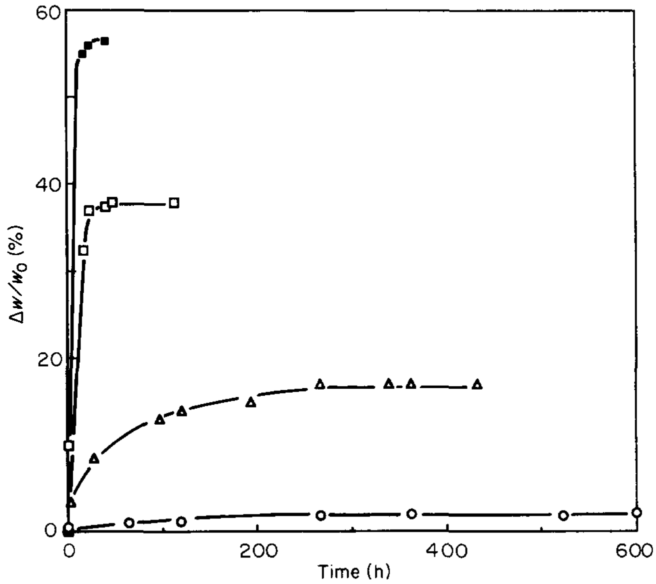

Figure 4 Weight gain of rolled PA11 *versus* the immersion time in formic acid solutions of various concentrations: Δ, 60%, 25°C; □, 90%, 25°C; ■, 90%, 60°C; ○, water at 25°C

The two theoretical curves in *Figure 2* show that the Fox equation cannot fit the experimental data in the whole concentration domain. Two reasons are given.

1. The amplitude of the β peak increases with the absorbed solvent content, and above $S^* = 10\%$, the α and β relaxation peaks merge together.
2. For higher solvent content $S^* > 10\%$, the T_α of the amorphous phase coincides with the crystallization temperature of the acid solution, as observed by d.s.c. During cooling, a part of the acid crystallizes, then the remaining concentration of acid in the amorphous phase is lower than the initial concentration.

In conclusion, for high solvent uptake, the broadening of the α peak and the phenomenon of acid solution crystallization impede any comparison between the Fox theory and the experimental results.

For all the materials, Fickian behaviour is observed (*Figure 3*) which is different to that observed in swollen glassy polymers[15]. In our case, only a small amount of absorbed acid ($S^* > 5\%$) is necessary for the PA11 to be swollen in the rubber state. The coefficient of diffusion of 90% formic acid at 25°C is about 10^{-7} s cm^{-2} for isotropic or oriented PA11, while it is 10^{-9}–10^{-10} s cm^{-2} for gas and liquid diffusion at temperatures below T_g in glassy polymers.

The equilibrium sorption ratio increases with the concentration of acid solution and with the temperature (*Figure 4*). At high temperatures and/or high formic acid solution concentration, it has been noted that internal stresses, due to solvent concentration gradients during the sorption transient stage, induce cracking.

In *Figure 5*, the ratios λ of the sample dimensions before and after swelling, along the rolling or drawing direction λ_y, and perpendicular to the orientation plane λ_x are reported. The swelling is obviously anisotropic, as it has been reported by Howard and Starkweather[4] and Dosière[12]. The longitudinal and transverse ratios, λ_y and λ_x, vary linearly but in opposite senses with the equilibrium sorption ratio. They depend on the state of deformation of the chains whereas, as reported above, the solvent weight gain at equilibrium would depend on the crystallinity.

Finally it is noted that the treated materials (swollen then dried) do not recover the dimensions of the starting materials before drawing or rolling. For example, the draw sample ($\lambda_0 = 3.5$) which has been swollen to a high degree ($S = 47\%$), relaxes in the drawing direction by a factor $\lambda_y = 0.75$ after drying. The resultant drawing ratio is therefore $\lambda = \lambda_0 \lambda_y = 2.6$. In conclusion, in all the treated materials, the amorphous and the crystalline chains remain oriented. This will be analysed later.

DESWELLING AND EXTRACTION

A material (1 mm thick) treated with formic acid and left in the atmosphere air deswells and regains its original weight in 1 month. The d.m.t.a. curve (*Figure 1b*) is

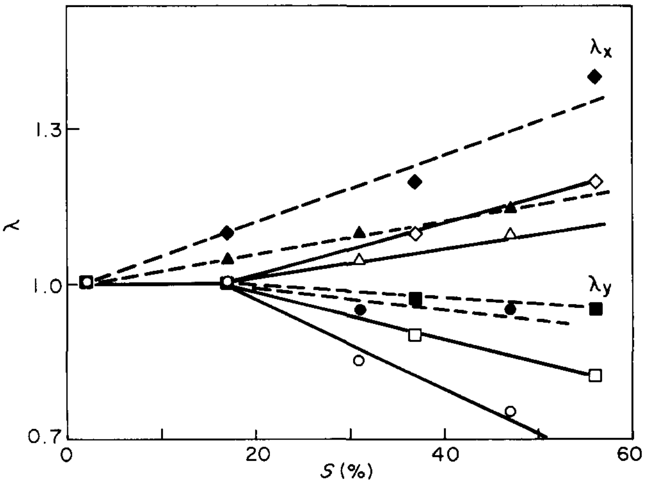

Figure 5 Dimensional modifications $\lambda = L/L_0$ of rolled and drawn PA11 *versus* equilibrium swelling ratio by weight: λ_x, transverse dimension ratio; λ_y, longitudinal dimension ratio. – – –, swollen (◆, ■, rolled; ▲, ●, drawn); ——, dried (◆,□, rolled; △, ○, drawn)

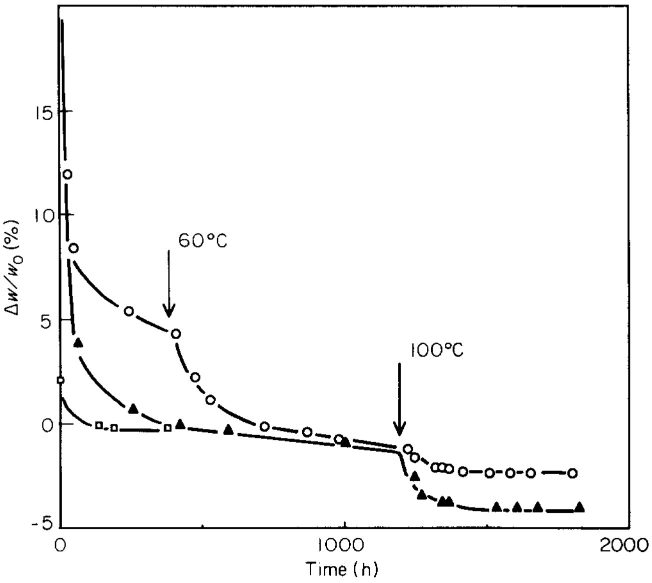

Figure 6 Desorption of isotropic PA11 under vacuum at 25, 60 and 100°C (arrows indicate changes in temperature). The materials have been previously swollen in 90% formic acid solution: ○, 25°C; ▲, 60%; □, water at 25°C

completely different from that of the original material, indicating a compensation effect in that some solvent stays in the material and an equivalent quantity of PA is extracted during the swelling. The initial d.m.t.a. curve is obtained after complete deswelling of the sample, more than 1 year at room temperature and at atmospheric pressure.

The d.m.t.a. measurement is indeed a powerful method to control the drying of plasticized materials. If the samples (isotropic or strained) swollen by 90% formic acid solution at 25°C, are evacuated for 300 h at 100°C, that is to say 40°C above the T_g of the pure material, the weight loss is 2% for this material and the d.m.t.a. curve of the starting material is recovered (*Figure 1c*).

Deswelling of PA11, and of amorphous polymers in general, is a much slower process than swelling. This is due to the formation of a superficial glassy layer during desorption. This layer acts as a barrier against permeation of the solvent retained within the sample. The large half-width of the tan δ peak of the swollen PA must be due to the heterogeneous structure of the material. Variation of the solvent concentration within the material would produce a variation of the glass transition within the sample, and therefore a broadening of the α relaxation.

The desorption kinetics have been studied under vacuum at several temperatures. *Figure 6* shows that complete desorption after 300 h is only possible at 100°C. The material is then in the rubber state and this avoids the presence of superficial glassy layers. The weight loss $(w_0 - w^*)/w_0$ has been measured with respect to the PA11 materials conditioned at 100°C under vacuum over a week (before and after swelling). The PA11 samples absorb 2% of water which is the same value reported in the literature[2,7]. Desorption of these materials gives rise to a weight loss of 0.2%. Deswelling of formic acid gives larger weight losses. This phenomenon could be explained by the solubilization of monomers and oligomers of PA11 present in the materials.

Figure 7 gives the weight loss due to extraction from PA11 samples swollen in formic acid solutions of various concentrations, and subsequently dried at 100°C for 2 weeks (to constant weight). The maximum extraction ratio observed is 4% for an equilibrium weight gain $S = 56\%$. The amount of extracted materials is proportional to the equilibrium sorption ratio, and roughly independent of the state of deformation of the samples. The real solvent absorbed content is then $S^* = 1.06\,S$.

MORPHOLOGICAL CHANGES DURING SWELLING AND DESWELLING

The ratio, λ, of the dimension of the desorbed samples to the initial dimension is compared in *Figure 5*, with the same ratio of the swollen samples. For all strained materials after desorption, the dimension perpendicular to the rolling or drawing direction and parallel to the orientation plane, does not vary ($\lambda_z = 1$). The initial dimensions of the unswollen materials are restored if the equilibrium sorption ratio is lower than 20%. Above that critical ratio, the materials that have been annealed in acid relax. The length parallel to the rolling or drawing direction decreases, and the length perpendicular to that direction increases. This shrinkage observed in dried materials increases with the equilibrium sorption ratio and with the orientation ratio of the initial samples.

The relaxation of PA11 is analogous to that observed in poly(vinyl chloride) treated with acetone or toluene, and different from that observed in low density polyethylene (LDPE) treated in toluene or cyclohexane[16]. During swelling of drawn LDPE, there is in fact an expansion along the drawing direction and a shrinkage along the transverse direction, these dimensional changes being reversible after desorption.

This relaxation effect observed in PA11 obviously involves recrystallization during desorption. This is verified in *Figure 8*. For isotropic or oriented materials annealed in formic acid, then dried, the crystallinity, measured by d.s.c., is roughly constant if the equilibrium

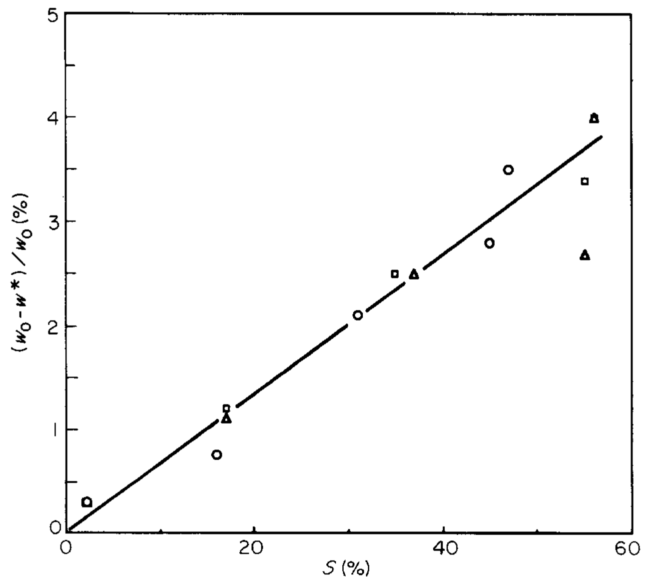

Figure 7 Extraction ratio $[(w_0 - w^*)/w_0]$ *versus* equilibrium swelling ratio. The PA11 materials have been desorbed at 100°C under vacuum for 2 weeks: □, isotropic; △, rolled; ○, drawn

weight gain is lower than 40%, and increases with the equilibrium sorption ratio above that critical value.

The phenomena of crystallite dissolution during swelling and recrystallization during deswelling, are directly observed by WAXS. *Figure 9* gives the WAXS spectra of isotropic PA11 after annealing in 90% formic acid at 25°C and 60°C. The crystallinity of the swollen samples is extremely weak. As measured by d.s.c., or by comparing the intensities of the (2 0 0) peak ($2\theta = 20.9°$) or by determining the density, the dried samples after treatment at 25°C have a crystallinity comparable to that of the starting materials, but the dried samples after annealing at 60°C have a higher crystallinity compared to the initial samples. For example, the rolled material treated at 60°C in 90% acid solution has a crystallinity of 8%; the crystallinity of the dried sample is 40%, while it is 26% in the initial unswollen sample.

In *Figure 10*, the intensity of the (2 0 0) reflection of the swollen samples is plotted against the uptake of solvent at equilibrium. One concludes that the amount of dissolved PA11 crystallites is directly proportional to the equilibrium sorption ratio. The behaviour of PA swollen with formic acid would be equivalent to that of a gel whose crosslinking concentration decreases with the swelling ratio.

Finally, it is noteworthy that the orientation of the new crystallites formed during desorption is the same as in the untreated samples; a small increase of orientation in the treated materials is even noted. The width of the azimuthal scan of the (2 0 0) reflection is smaller for

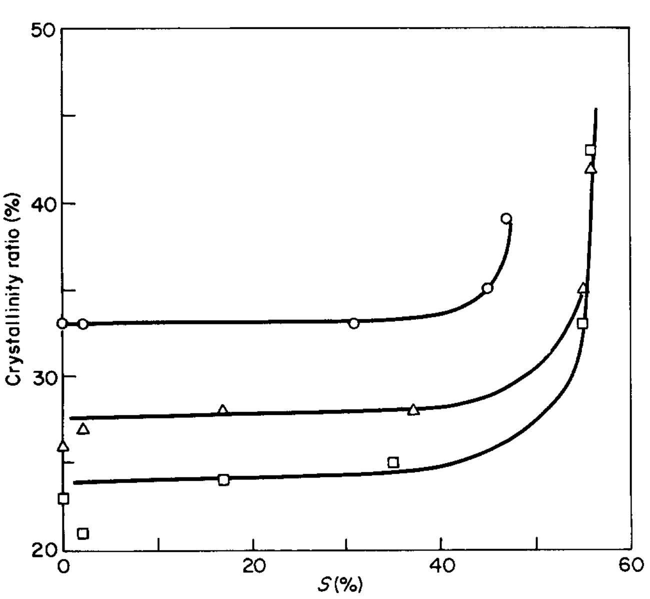

Figure 8 Crystallinity χ of dried PA11 (determined by d.s.c.) *versus* the equilibrium swelling ratio by weight: □, isotropic; △, rolled; ○, drawn

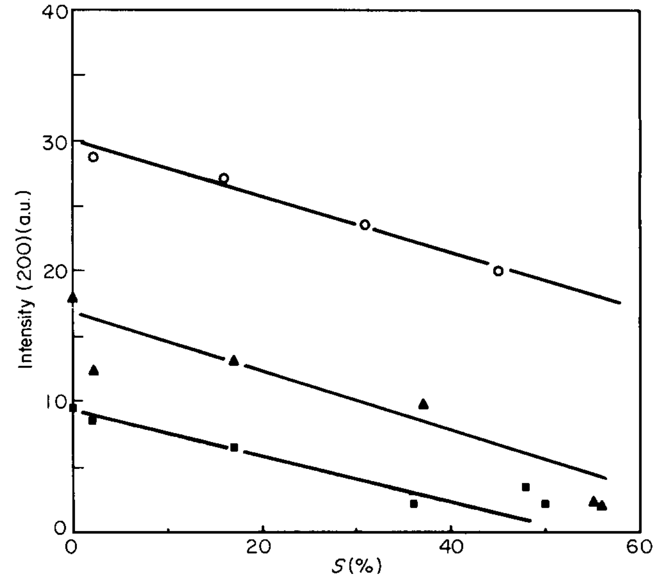

Figure 10 Intensity of the (2 0 0) reflection (from equatorial WAXS spectra) of swollen PA11 *versus* equilibrium swelling ratio: ■, isotropic; ▲, rolled; ○, drawn

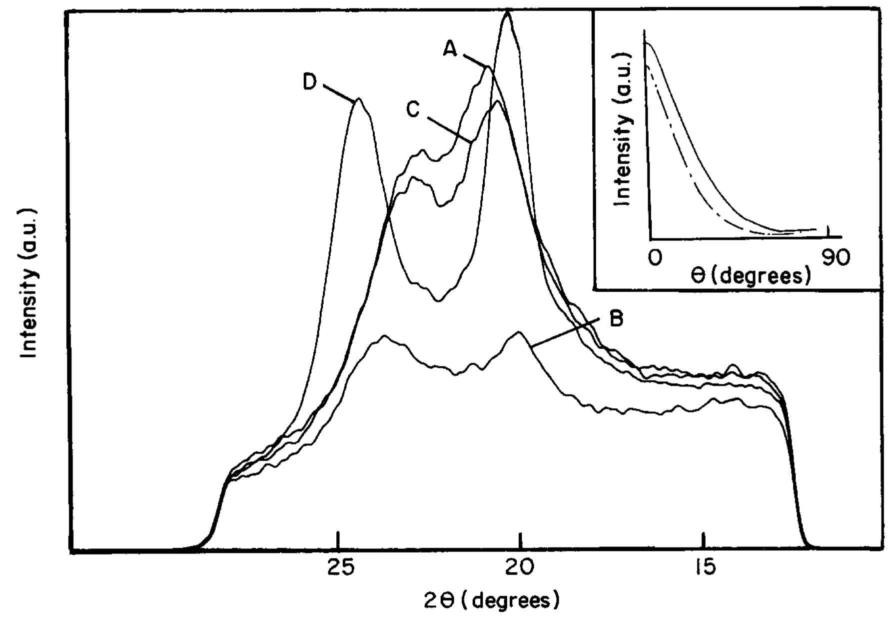

Figure 9 WAXS spectra of isotropic PA11 untreated (A); swollen by 90% formic acid at 25°C (B); swollen in 90% formic acid at 25°C then dried (C); swollen in 90% formic acid at 60°C then dried (D). Inset: azimuthal scan of the (2 0 0) peak observed from the WAXS spectra of rolled PA11, untreated (——) and treated in 10% formic acid solution at 25°C (— · — ·)

treated materials than for the starting materials. The insert in *Figure 9* shows this effect for rolled PA. Similar features are observed for the drawn samples. Subramanian and Venkataraman[17] have noted this improvement of crystallite orientation in PA6 filaments treated in alcohols and in formic acid.

During swelling, as shown in *Figure 5*, relaxation occurs to some extent in the direction parallel to the rolling or drawing direction. But this relaxation is not complete and amorphous chains are still in a somewhat stressed configuration, favourable for further oriented crystallization. During desorption, these oriented chains therefore crystallize in the initial direction of deformation.

The increase in crystallinity observed for materials swollen above an equilibrium swelling ratio of 40% is probably due to crystallization at low supercooling. It is well known that crystallization from dilute solution leads to higher crystalline materials. The chains are in fact disentangled in the swollen state and the kinetics of this crystallization is very slow (compared to the melt crystallization).

It should also be mentioned that the gel, at high concentration of solvent, has only a few crystallites acting as crosslinks. Crystallinity as low as 8% in the swollen PA is sufficient to maintain the orientation of the PA amorphous chains and to induce recrystallization in the original direction of deformation during deswelling. The important difference between crosslinked gels and swollen semicrystalline gels (and semicrystalline rubbers) is that the semicrystalline gels have an oriented amorphous phase, if the material has been previously strained.

Such a memory effect has been reported in polyamide–polyether block copolymers[18]. Oriented thermoplastic elastomers are obtained by drawing below the T_g (or T_m) of the hard segments. On lowering the temperature, the soft segments crystallize with the same orientation as the PA crystallites.

CONCLUSIONS

The swelling of PA11 by formic acid causes a dissolution of a part of the crystallites and an extraction of the low molecular weight materials. These two phenomena increase linearly with the equilibrium sorption ratio (which depends in turn on the temperature and on the acid solution concentration). The role of the solvent is to dissolve small crystallites which have been formed by small chains. These oligomer chains, which have a radius of gyration smaller than the mean distance between crystallites (long period dependent on the concentration), are then free to diffuse and to be extracted. Obviously, the measurement of the molecular weight of the extracted PA11, as a function of the swelling ratio, would be necessary to verify this interpretation. This study also shows that for such polymers submitted to swelling and extraction, the reference materials must not be the conditioned initial samples (before swelling experiments) but the completely dried final samples.

The complete desorption of isotropic and oriented PA11 finally leads to a material which has the same crystallinity as the starting material, if the equilibrium sorption ratio is lower than 40%. Above 40%, the crystallinity is higher. In all the swelling domain, the orientation of the crystalline phase of the dried materials is the same as that of the initial materials. This memory effect is due to the anisotropic swelling which is not sufficient to relax the stressed amorphous chains in the rolled and drawn materials. During desorption, these stressed chains recrystallize in the initial direction of orientation.

Finally, it is emphasized that the desorption rate is very slow. This is due to the formation of a glassy superficial layer and to very stable hydrogen bonding between amide groups and hydroxyl groups of the acid.

The results reported in this paper are also observed for PA11 treated in acetic acid and for PA12 and polyamide–polyether block copolymers. The extraction effect of low molecular weight chains on the secondary transition temperature T_β will be analysed in a forthcoming paper.

REFERENCES

1 Hiller, K. H. and Jacobs, H. M. *Makromol. Chem.* 1960, **39**, 234
2 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', J. Wiley, New York, 1967
3 Jackson, J. B. *Polymer* 1969, **10**, 159
4 Howard, H. and Starkweather, J. R. *J. Macromol. Sci. B3* 1969, **4**, 727
5 Prevorsek, D. C., Butler, R. H. and Reimschuessel, H. K. *J. Polym. Sci.* 1971, **9**, 867
6 Papir, Y. S., Kapur, S. and Rogers, C. *J. Polym. Sci. A2* 1972, **10**, 1305
7 Kohan, M. I. 'Nylon Plastics', J. Wiley, New York, 1973
8 Goldbach, G. *Ang. Makromol. Chem.* 1973, **32**, 37
9 Hiltner, A. *Polym. Eng. Sci.* 1979, **19**, 722
10 Birkinshaw, C., Buggy, M. and Daly, S. *Polym. Commun.* 1987, **28**, 286
11 Varlet, J., Cavaillé, J. Y., Perez, J. and Johari, G. P. *J. Polym. Sci.* 1990, **28**, 2691
12 Dosière, M. *J. Mater. Sci.* 1983, **18**, 1941
13 Dosière, M. and Point, J. J. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 625
14 Dosière, M. and Point, J. J. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 749; 1383
15 Park, G. S. in 'Diffusion in Polymers' (Eds J. Crank and G. S. Park), Academic Press, New York, 1968
16 Diakoulaki, D. C. and Papaspyrides, C. D. *Mater. Sci. Monographs*, 1984, **21**, 703
17 Subramanian, D. R., Vankataraman, A. and Bhat, N. V. *J. Macromol. Sci., Phys. B18* 1980, **2**, 177
18 Okoroafor, E. and Rault, J. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 1427