Prediction of sorption and diffusion of water vapour by nylon-6,6

David G. Hunt
Department of Mechanical and Production Engineering, Polytechnic of the South Bank, Borough Road, London SE1, UK

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Sufficient measurements were made of the equilibrium moisture contents and diffusion coefficients of nylon-6,6, as a function of relative humidity, to draw graphs and obtain regression equations. Further measurements were made to determine whether either the equilibrium moisture content or the diffusion coefficient was dependent on stress or thickness. The equilibrium moisture content was found to be a function of the relative humidity only, and can therefore be predicted from a regression equation. The diffusion coefficient was found to be mainly dependent on the moisture content but slightly dependent on the thickness and shape, and it can therefore be predicted from suitable regression equations and a standard shape-correction factor. The resulting regression equations were used to predict moisture changes during air humidity changes and were found to give good predictions both for one- and two-directional diffusion and for humidity cycling.

INTRODUCTION

As part of a study of creep of nylon-6,6 in concurrently changing humidity, it was necessary to be able to predict the internal moisture contents at all positions within nylon test pieces at all times during a creep test at constant temperature. For this purpose, it was necessary to have accurate and detailed knowledge of the material's moisture sorption and diffusion behaviour.

The equilibrium moisture contents of nylon-6,6 have been studied by a number of investigators[1–4], and its permeability to moisture vapour has been measured[1] but not its diffusion coefficient. The nearest approach has been the detailed work of Asada and Onogi[5] on the diffusion coefficients of moisture vapour in nylon-6. However, for accurate internal moisture content predictions it was necessary not only to measure the equilibrium moisture content and the diffusion coefficient under simplified laboratory conditions, but also to be aware of any departures from Fick's Law and of any anomalies in the diffusion coefficient caused by such variables as stress, thickness, shape or moisture-content level.

Accordingly, this paper describes sorption and diffusion measurements made on nylon-6,6 as a function of relative humidity, stress, test-piece thickness and test-piece shape, and a method used for prediction of moisture content in a rectangular test piece subjected to changing relative humidity.

Throughout this paper the term 'moisture content' of a sample is defined as the mass of the sample minus its oven-dry mass, all divided by its oven-dry mass. The 'equilibrium moisture content' is defined as the moisture content of a sample when it has reached equilibrium with its surrounding atmosphere.

PREVIOUS WORK

Some useful general information on moisture in nylons is given in the detailed studies of water sorption in nylon 6 made by Asada and Onogi[5] and more recently by Inoue and Hoshino[6]. Amongst the more relevant results are (a) that the equilibrium moisture content appeared to be independent of temperature at constant relative humidity, and of the direction of approach to equilibrium, i.e. sorption or desorption, (b) that the diffusion coefficient increases with increasing moisture content and (c) that desorption generally takes place more slowly than sorption. Regarding the first point, it has been generally found[1,5,6] that the moisture content of nylons depends both on the absolute humidity and temperature. However, if the absolute humidity values are converted to relative humidity, all values are found to lie on a single curve, regardless of the temperature of measurement. The moisture content can therefore be considered to be a function of relative humidity only.

The effects of stress on equilibrium moisture content were first studied by Barkas[7] and later by Treloar[8] who measured the effect of stress on the equilibrium moisture content of hair and cellulose; and found that, in accordance with thermodynamic theory, a tensile stress increases the equilibrium moisture content and a compressive stress decreases it. Clemson[9] designed a simple lightweight straining device that he used to measure the effects of strain (stress) on the equilibrium moisture content of viscose rayon. Meredith and Hsu[10] observed the reversible change of tension with vapour pressure and then calculated the effect of strain on the equilibrium moisture content. No measurements appear to have been made on the effects of stress on the diffusion coefficients although Drechsel *et al.*[11] noticed the significant decrease in the sorption rate in the acetone-cellulose nitrate system after five sorption-desorption cycles, which they attributed to structural reorientation resulting from stresses. Comstock[12] points out that during sorption the dimensions increase and so present a greater surface area and allow more rapid sorption, and *vice versa*; thus affecting the apparent diffusion coefficient.

Relaxation, i.e. the rate of breaking of interchain bonds has been found to be an important factor in the rate of sorption of water by regenerated cellulose films[13], hemi-

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cellulose films[14], wool fibres[15] and wood[16]. The result was that thinner sections appeared to have a lower diffusion coefficient than thick sections. However Inoue and Hoshino[6] found thickness had no effect on the diffusion coefficient of nylon 6 in the relatively small range from 27 μm to 83 μm.

EXPERIMENTAL

Materials

The material used in this study was ICI Grade A100 nylon-6,6 moulded in the form 3.18 mm ASTM tensile test bars. The density was measured as 1.146 g cm^{-3} by flotation on a mixture of toluene and carbon tetrachloride at 20°C; giving an estimated crystallinity of 36% (from ICI data[2]). The birefringence of a film cut from the central plane was measured with a Babinet compensator as $3(10^{-3})$ in a plane perpendicular to the thickness direction and $4(10^{-3})$ in a plane perpendicular to the width direction of the test piece.

All of the 1 mm and 0.5 mm thick test pieces described below were taken from the core of the 3.18 mm thick bars by machining equal amounts from both faces. The 0.05 mm thick pieces were cut with a microtome from the core of a similar bar.

Apparatus

All measurements were made in an environmental chamber that was specially designed and built for the purpose[17]. The temperature of the chamber was maintained at 23.5°C ± 0.1°C and its relative humidity was held within less than ±1% r.h. of the nominal value.

Moisture solubility (i.e. equilibrium moisture content) was determined by weighing on a balance of capacity 160 g and reading to 0.1 mg. This balance was also used for the weighing measurements to determine diffusion rates on the larger 0.5 mm and 1 mm thick test pieces.

For diffusion measurements on small, 0.05 mm thick test pieces, special apparatus had to be designed. It consisted of a hermetically-sealed box fixed to the ceiling of the environmental chamber and fitted with a hinged flap at its bottom. Inside the box the sample was weighed by suspending it on a tapered-coil spring of sensitivity 0.42 mg mm^{-1}. Extension of the spring was observed through the glass window of the box with a cathetometer reading to 0.01 mm. The problem of obtaining an instantaneous change in the relative humidity of the air in contact with the sample, was solved by closing the hinged flap until the air in the main chamber had reached the new equilibrium. By this means the pre-start spring deflection was reduced to less than one percent of the equilibrium change. At the start of the experiment the flap was swung well away from the opening so that the small volume of air inside the box could quickly reach the same humidity as that of the environmental chamber.

The design of apparatus for stressing diffusion-test pieces is difficult due to a number of conflicting requirements, the most serious difficulty being that the stress during moisture sorption or desorption cannot be uniform since a moisture gradient itself induces a biaxial stress that varies with time and position in the sample. The method chosen was to use lightweight corrosion-resistant stressing frames on which the nylon samples could be mounted and stressed; and of a suitable size so that the sample and frame could be weighed on the chemical balance in the controlled environment.

The uniaxial tensile-stressing frame, shown in the bottom of *Figure 1*, is made of hard-rolled aluminium alloy, formed into a hoop and riveted with an aluminium rivet at the position of minimum bending moment. The test piece is stretched between two clips to which it is bolted and from which it is separated by thin wire spacers. The left-hand clip has a screw for adjusting the tension. In practice, the maximum safe force was about 50 N, giving a stress of about 8 MN m^{-2}. This was of about the same magnitude as the maximum estimated initial surface stress induced by a moisture gradient alone, when the relative humidity is reduced from 60% to 30%.

The compression-stressing frame is shown on the left of *Figure 1*. The spring is again a hoop which compresses the test piece along its axis while the ladder-shaped clamping plates hold the test piece straight, to prevent buckling. On the left side of the stressing frame is a fixture which allows adjustment of the compression load by the substitution of blocks of various thicknesses.

On the right of *Figure 1* is shown the frame for biaxial tensile stressing. The test piece is a disc to which sixteen equally-spaced spring-loaded hooks are attached. The force in the springs can be adjusted by means of the nuts on the outside. It will be noticed that only the inner part of the disc is biaxially stressed in tension, the part outside of the holes being stressed in some complicated manner. For this reason the results for biaxial stressing can only be considered qualitatively, not quantitatively.

Procedure for measuring equilibrium moisture contents

A single sample, made up of thin 0.05 mm slices from the cores of several test pieces, was used. It was weighed after 48 hours storage at each of various relative humidities between 10% and 90%, including checks on repeatability both with increasing and decreasing humidity. Finally, when all of these measurements were completed the sample was dried in a vacuum oven to determine the dry weight. It may be noted that the use of the same sample for every measurement avoided the errors involved in the matching of samples.

Since some anomalous changes had been observed in the thickness during sorption and desorption, as described by Hunt and Darlington[18] it was considered necessary to investigate the suggestion that extra moisture might accumulate in the surface layer at higher relative humidities, even under equilibrium conditions. This was investigated by checking the effect of the thickness of the slices on the equilibrium

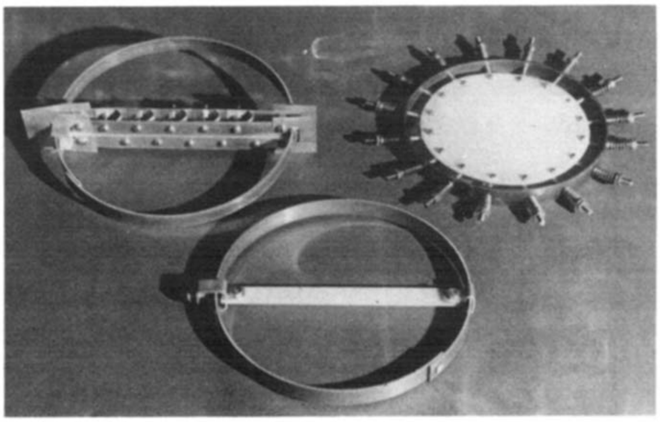

Figure 1 Frames for measurement of diffusion coefficients under applied stress: bottom, uniaxial tension; left, uniaxial compression; right, biaxial tension. Scale: 1/4 full size

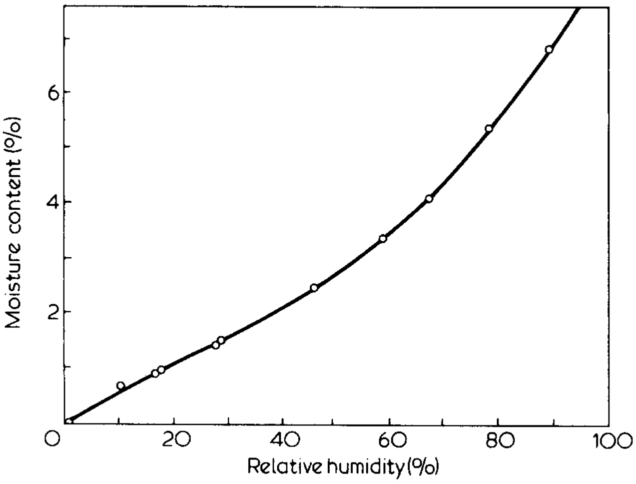

Figure 2 Equilibrium moisture content of nylon-6,6 as a function of relative humidity at 23.5°C. Points, experimental; line, quartic curve fitted by least squares

moisture content, both after sorption and after desorption between 30% and 60% r.h. These two values represent respectively the range at which there is interaction of individual water molecules and free sites, and the beginning of multilayer sorption in the form of clustering[19].

It was expected that a tensile stress might increase the free volume (especially above the glass-transition temperature, according to Inamura *et al.*[20]), and so it might tend to increase the equilibrium moisture content and *vice versa.* Consequently a number of 1 mm thick test pieces were brought to equilibrium, weighed, stressed in the tensile-stressing frames, and then re-weighed after equilibrium was reached again. A similar measurement was also made on unloading. The humidity chosen was 60% r.h.

Procedure for measuring diffusion coefficients

It was planned to investigate first the dependence of the diffusion coefficient D on the moisture content; at a constant temperature, a constant small thickness, a zero applied stress and a large width-to-thickness ratio rectangular cross section. Then further spot checks were to be made to investigate anomalies, as described below.

Measurements were made on 0.05 mm thick test pieces over six separate small humidity intervals within the range 5% to 90% r.h., with two further measurements over larger intervals. The method used was 'small-interval' sorption or desorption[13,21], in which a sheet sample is brought to equilibrium at a certain relative humidity, the relative humidity is suddenly changed to a new value and the sample is weighed at frequent intervals until the new equilibrium is reached.

The normal explanations of thickness effects are either (a) a time lag between the vapour molecule being physically present and actually becoming bonded at an available site or (b) rapid sorption at the surface causing the adjacent air layer to be depleted of vapour and therefore of lower relative humidity than the nominal value. Both of these explanations relate to the case of a thin sheet having a lower measured D than a thick sheet[22]. In order to investigate this, $\bar{D}_D$ and $\bar{D}_S$ (the mean diffusion coefficients over a humidity range for desorption and sorption respectively) were measured on sheet specimens of 0.05 mm, 0.5 mm and 1 mm thickness over the relative humidity interval 30% to 60% r.h.

The theory used to calculate $\bar{D}$ (the mean D over a humidity interval) is based on the assumption of infinite sheet specimens. However, the thin pieces had a width-to-thickness ratio of 65 and the proposed creep test[17] pieces had a width-to-thickness ratio of only 8, resulting in a substantial two-dimensional flow of moisture. Sorption rates with two-dimensional flow can be calculated from the diffusion coefficient by analytical or finite-difference methods, but it was felt that this should be compared with experimental evidence. Accordingly, desorption measurements were made both on 0.5 mm thick discs of 100 mm diameter and on some strips 4 mm by 0.5 mm cut from similar discs.

There are two expected effects of stress on diffusion: (a) a tensile stress should increase the free volume, so promoting easier diffusion and *vice versa,* and (b) a tensile stress should promote sorption by supplying energy for expansion but should hinder desorption because the resulting contraction is opposed, and *vice versa*[21]. Therefore $\bar{D}_D$ and $\bar{D}_S$ were measured over the r.h. interval 30% to 60% for a number of uniaxial stresses, both tensile and compressive; and also for a biaxial tensile stress. These measurements were made on 0.5 mm thick test pieces with the stressing frames described above. It should be pointed out that the initial experiments were intended to be exploratory, in order to check whether stress had any effect at all. Although the results below give a slight hint of a stress effect, its magnitude was sufficiently small that it was not considered worth mounting a full-scale experiment for statistical analysis.

RESULTS AND DISCUSSION

Equilibrium moisture content results

The results of the equilibrium moisture content measurements at 23.5°C are shown as a function of relative humidity in *Figure 2* together with the polynomial curve that was fitted to it by the least-squares method:

$$C = 0.1457R - 3.762(10^{-3})R^2 + 5.498(10^{-5})R^3 - 2.34(10^{-7})R^4 \ldots \quad (1)$$

where R is the relative humidity in percent and C is the equilibrium moisture content in percent.

The effects of thickness on the moisture content changes during sorption and during desorption between 30% and 60% r.h. are shown in *Table 1.* Examination of these results suggests that the sample thickness has little or no effect on the equilibrium moisture content changes during sorption or desorption.

There was no measurable change in weight during the two weeks (for which $t^{1/2}/L = 18$ h$^{1/2}$ mm^{-1}: compare with

Table 1 Equilibrium moisture content changes between approximately 30% and 60% r.h.

Source†	Thickness (μm)	MC change during sorption (%)	MC change during desorption(%)	Estimated precision* (%)
ASTM bar	20	1.71	2.16	±0.02
ASTM bar	50	1.81	2.01	±0.02
ASTM bar	330	–	2.18	±0.01
disc	50	1.95	2.13	±0.04
disc	330	1.98	2.00	±0.02

† The ASTM bars were standard 3.17 mm thick tensile bars, and the discs were 3.17 mm thick, 102 mm diameter

* The precision limits are in terms of moisture content and were estimated from the limits of weighing precision and sample size only

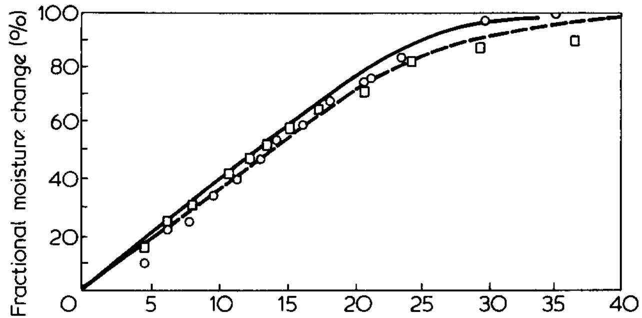

Figure 3 Sorption and desorption of moisture in 0.05 mm thick nylon-6,6 for the interval 28% to 61% r.h. at 23.5°C. Points, experimental; lines, calculated: sorption, ○ ———; desorption, □ — — — —

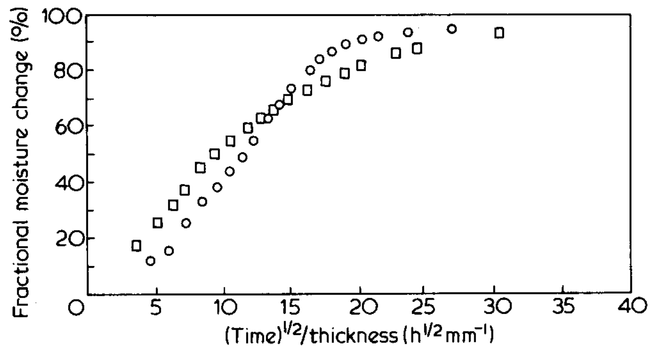

Figure 4 Sorption and desorption of moisture in 0.05 mm thick nylon 6,6 for the interval 28% to 90% r.h. at 23.5°C. Sorption, ○; desorption, □

about 13 $h^{1/2}$ mm^{-1} for 50% equilibrium change)* following the application of a stress to test pieces that had already been at equilibrium at 60% r.h. Nor was there any measurable change in the weight of test pieces that had been brought to equilibrium under stress at 60% r.h. and then unloaded. Stresses were in the range 0 to +4 MN m^{-2}. The precision is estimated as ±0.05% moisture content.

Diffusion coefficient results

Some sample sorption and desorption results are shown in *Figures 3* and *4*, for a small and a large humidity interval respectively. From such curves the mean diffusion coefficients over the humidity range for sorption ($\bar{D}_S$) and for desorption ($\bar{D}_D$) were obtained using the formula $\bar{D}$ = 0.04919 $L^2/t_{1/2}$, where $t_{1/2}$ is the time taken for 50% of equilibrium sorption or desorption and L is the thickness of the sample. *Figure 5* shows these results grouped as a pair for each moisture-content range (the moisture contents being the equilibrium values determined for each relative humidity).

By taking the median value of each $D_S - D_D$ pair and the corresponding median moisture content values, six points were obtained on the diffusion coefficient-moisture content graph, and to these points the curve shown in *Figure 5* was fitted by the least-squares method:

$$D = 0.147 \exp(0.2696\ C)\ 10^{-3}\,\mathrm{mm^2\,h^{-1}} \qquad (2)$$

Figure 5 also includes for comparison the points from the larger humidity intervals of 62% to 89% r.h. and 28% to 90% r.h. The validity of the above equation was checked by calculating the sorption and desorption rates by the Crank-Nicholson finite-difference method as described below, for the range 30% to 60% r.h. The results are the lines superimposed on the experimental points of *Figure 3*.

The diffusion coefficients for three thicknesses, calculated from the times for 50% equilibrium sorption or desorption over the approximate range 28% rh to 60% r.h. are, 0.05 mm: $\bar{D}_D$ = 0.309, $\bar{D}_S$ = 0.276, $\bar{D}$ = 0.292; 0.5 mm: $\bar{D}_D$ = 0.295, $\bar{D}_S$ = 0.260, $\bar{D}$ = 0.278; 1.0 mm: $\bar{D}_D$ = 0.250, $\bar{D}_S$ = 0.216, $\bar{D}$ = 0.233 (all values in 10^{-3} mm^2 h^{-1}). All of these values have been corrected to one-dimensional diffusion by the correction curve of *Figure 6*. A regression analysis gave the relation:

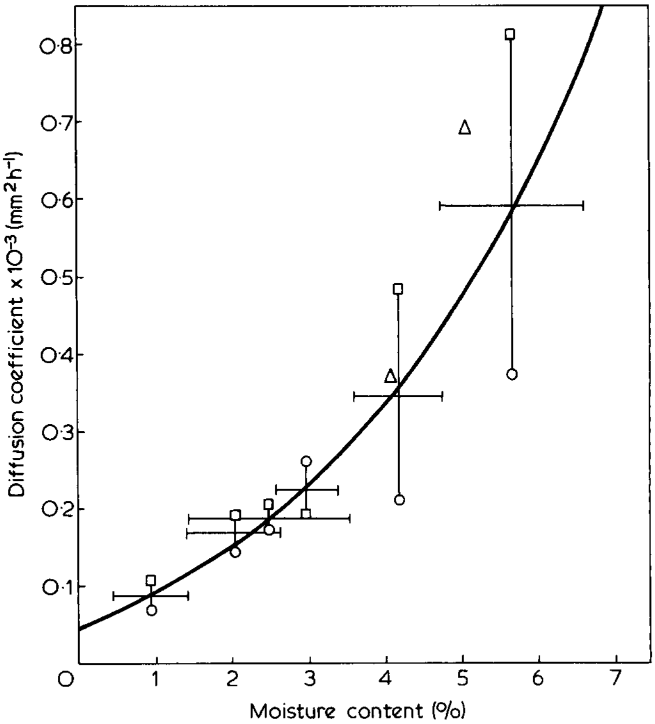

Figure 5 Diffusion coefficient as a function of moisture content for nylon 6,6 at 23.5°C. Desorption, □; sorption, ○; moisture content range, ├──┤, curve fitted by least squares, ———, mean values of two large-interval sorption and desorption measurements, △

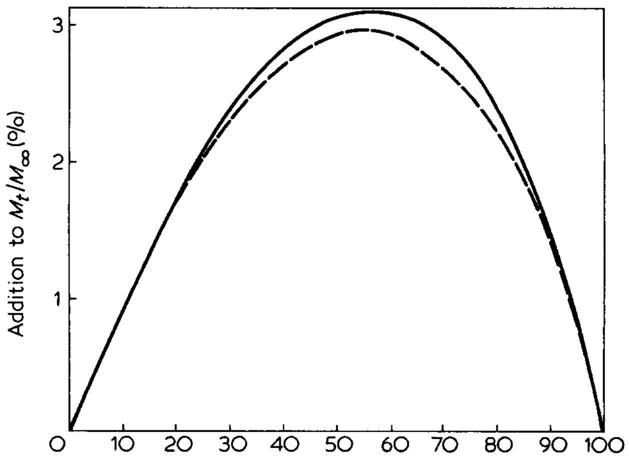

Figure 6 Correction for two-dimensional sorption ——— or desorption — — — — of strip of 8 mm by 1 mm nylon relative to one-dimensional, calculated by the Crank-Nicholson method

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* t is the time since the change was made, L is the sheet thickness

Table 2 Differences between one-dimensional and two-dimensional desorption levels

Desorption level for one-dimensional diffusion (disc) (M_t/M_∞, %)	Desorption level for two-dimensional diffusion (strips)	
	Measured, M_t/M_∞(%)	Predicted, M_t/M_∞(%)
20	21.75	21.64
30	32.75	32.22
40	43.5	42.66
50	53.7	52.88
60	63.2	62.90

$$\bar{D} = (0.292 - 0.059\,L^2)\,10^{-3}\,\text{mm}^2\,\text{h}^{-1} \tag{3}$$

where L is the sheet thickness. It may be noticed that two consistent trends appear in these results: firstly that $\bar{D}_D$ is larger than $\bar{D}_S$ in all cases and secondly that the thicker sheets have a lower $\bar{D}$. The former trend is consistent with all but one of the results of *Figure 5*. However, since the latter trend is contrary to the theory of Crank[22], the probable errors were estimated: 0.05 mm thick, ±0.008 (10^{-3})mm^{2}h^{-1}; 0.5 mm thick, ± 0.006 (10^{-3})mm^{2}h^{-1}; 1.0 mm thick, ±0.005 (10^{-3}) mm^2 h^{-1}. It can be seen that the errors were not large enough to affect significantly the conclusion that the D values decrease as the thickness increases.

The effect of shape is shown in *Table 2* which gives the results of desorption measurements from 62% to 32% r.h. in which the moisture loss from a 100 mm diameter by 0.5 mm thick disc was compared with that of a similar 0.5 mm thick disc cut into 4 mm wide strips to give a width-to-thickness ratio of eight. The table also gives, for comparison, the predicted values obtained by calculation with the Crank-Nicholson finite-difference method. The estimated precision of measurement is about ±0.5% of the equilibrium moisture change. M_t/M_∞ is the fraction of equilibrium desorption.

The effect of stress on diffusion coefficients is shown in the results of *Table 3* and they appear to indicate that stress has only a small or negligible effect. The estimated errors, based on weighing errors alone, are ±0.009 (10^{-3}) mm^{2}h^{-1}. The variations in diffusion coefficient with stress as shown in *Table 3* are not statistically significant. The lower diffusion coefficients of the biaxial samples are thought to be caused by the different origin of the material and the fact that they were thicker, at 1 mm than the other pieces, at 0.5 mm.

PREDICTION OF MOISTURE CONTENTS

The above experimental results suggest that the equilibrium moisture content is a function of r.h. only and can therefore be predicted from the empirical equation (1): and the diffusion is a function of the moisture content, thickness and shape and can therefore be predicted from equations (2), (3) and suitable shape corrections that can be determined by calculation as described below.

With a variable diffusion coefficient it is necessary to use the general diffusion equation for one-dimensional flow:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{4}$$

and the Crank-Nicholson finite-difference method for calculation[23]. Briefly this involves rewriting the diffusion equation as the approximate difference equation (e.g. for point x_2):

$$\frac{C_{22} - C_{21}}{\delta t} =$$

$$\frac{1}{\delta x}\left[\frac{\tfrac{1}{2}(D_{12} + D_{22})(C_{12} - C_{22}) + \tfrac{1}{2}(D_{11} + D_{21})(C_{11} - C_{21})}{2\delta x}\right.$$

$$\left. - \frac{\tfrac{1}{2}(D_{22} + D_{32})(C_{22} - C_{32}) + \tfrac{1}{2}(D_{21} + D_{3})(C_{21} - C_{31})}{2\delta x}\right] \tag{5}$$

where δx is the uniform mesh size $(x_2 - x_1)$; δt is the time interval from t_1 to t_2; C is the concentration of diffusant; the first subscript refers to position (i.e. the x-subscript) and the second subscript refers to the time step.

It may be noticed that with this method the concentration gradients and the diffusion coefficients were averaged over the two time steps. Since the values of $D_{i,2}$ are not known until the values of $C_{i,2}$ are known, an iteration procedure had to be used. Rearranging equation (5) gives:

$$-(D_{12} + D_{22})C_{12} + \left(D_{12} + 2D_{22} + D_{32} + \frac{4\delta x^2}{\delta t}\right) C_{22} -$$

$$(D_{22} + D_{32})C_{32} =$$

$$(D_{11} + D_{21})C_{11} - \left(D_{11} + 2D_{21} + D_{31} - \frac{4\delta x^2}{\delta t}\right) C_{21} +$$

$$(D_{21} + D_{31})C_{31} \tag{6}$$

If the boundary conditions shown in *Figure 7* are used and it is assumed that the concentration gradient is always zero at x_{20}, a set of simultaneous equations is obtained. These can be solved by Gaussian elimination to give the concentration of diffusant at the new time t_2, from the known values at time t_1. Trial and error showed that there was no problem of stability during the start of the finite-difference solution due to the discontinuity at x_1. However there was some error because in the initial condition the sheet already contained 2.5% of the equilibrium moisture when 40 network points were chosen, as shown in *Figure 7*. This situation

Table 3 Effect of uniaxial or biaxial stress on diffusion coefficients of individual test pieces

Stress (MN m^{-2})	Diffusion coefficients (mm^2 h^{-1})	
	Sorption	Desorption
−3.8	0.302 (10^{-3})	0.297 (10^{-3})
−3.0	0.275 (10^{-3})	0.295 (10^{-3})
0	0.278 (10^{-3})	0.313 (10^{-3})
+3.0	0.297 (10^{-3})	0.311 (10^{-3})
+3.8	0.297 (10^{-3})	0.298 (10^{-3})
+5.6	0.302 (10^{-3})	0.298 (10^{-3})
+7.2	0.275 (10^{-3})	0.300 (10^{-3})
+1.7 biax	0.175 (10^{-3})	0.220 (10^{-3})
0 biax	0.175 (10^{-3})	0.215 (10^{-3})

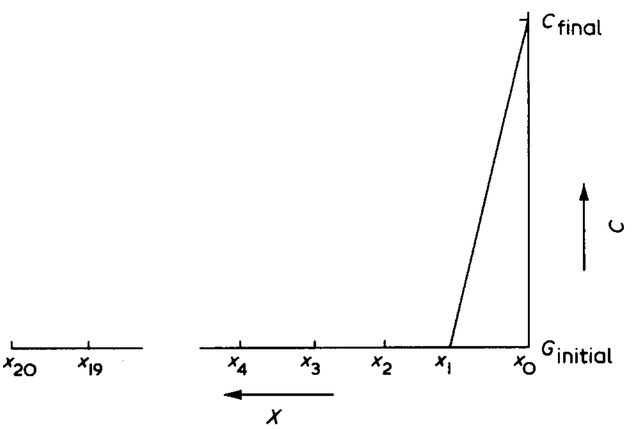

Figure 7 Initial conditions for Crank-Nicholson solution for sorption: *C* is the concentration and *x* is the distance from the surface

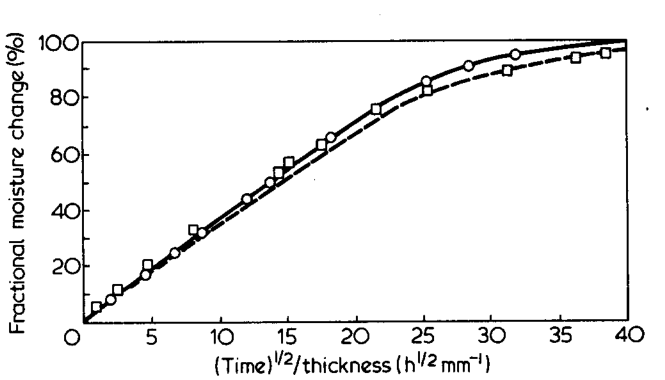

Figure 8 Sorption and desorption of moisture in 1 mm thick nylon-6,6 for the interval 28% to 61% r.h. at 23.5°C. Points, experimental lines, calculated: sorption, ○, ———: desorption, □, – – – –. Compare with *Figure 3* for thinner pieces

would occur after some finite time that could only be guessed. The difficulty was solved as follows:

(a) a very short time of 0.1 h was assumed for the condition shown in *Figure 7*;

(b) the Crank-Nicholson method was used to calculate the step-by-step sorption until the instant that the moisture reached the central plane;

(c) the sheet was then considered to be instantaneously shrunk to one-half of its thickness and considered to be the outer layer of a sheet of the same thickness as the original. At the same time the network points were renumbered: x_2 becoming x_1, x_4 becoming x_2, and so on; and in accordance with the t/L^2 parameter the time was quartered;

(d) the procedures of (b) and (c) were repeated;

(e) after four 'shrinkages' the normal Crank-Nicholson procedure was carried to completion;

(f) the graph of M_t/M_∞ *versus* $t^{1/2}/L$ was plotted to check that the initial portion was an accurate straight line passing through zero;

(g) the time at which the initial concentration was $C_{\text{initial}} + 0.5\,[(x_1 - x_0)/(x_{20} - x_0)]\,(C_{\text{final}} - C_{\text{initial}})$ was assessed as 0.47 h and this time was used to replace the 0.1 h of (a).

It is of interest to note that this special starting method was only of importance for accurate results at short times. At times beyond about 10 hours the sorption curve was almost independent of the starting method. An example of the predicted results for 0.05 mm thick pieces is given in *Figure 3* and for 1 mm pieces in *Figure 8*.

The prediction of moisture contents during humidity cycling was done by the same Crank-Nicholson method, the surface boundary condition being suddenly changed at the appropriate time. The special starting method described above could not be used since moisture was already flowing in the core of the sheet at the beginning of each new cycle. Instead, the time of 0.5 hours was used as the new initial time after which the surface concentrations shown in *Figure 7* were established. Comparison between predicted and experimental values for 0.5 mm thick nylon is given in *Figure 9*.

The two-dimensional diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right) \qquad (7)$$

was solved by the same Crank-Nicholson method adapted to two-dimensional flow, using a relaxation method to solve the simultaneous equations. For an 8 by 1 mm section this gave the corrections relative to one-dimensional flow shown in *Figure 6*. Sample results also appear in *Table 2* and they appear to show that the calculation method is reliable.

COMPARISON BETWEEN PREDICTED AND MEASURED VALUES

Whilst the predicted results appear to compare well with experimental values for one-dimensional sorption and desorption, they do show one striking difference. It may be noticed in *Figure 3* that the computer does not reproduce the initial sigmoid shape of the sorption curve for 50 μm pieces although otherwise the predicted curve is a reasonable fit to the measured data including the generally lower level of the desorption curve, especially at longer times. With the thicker test pieces, on the other hand, the computed and experimental curves were almost identical (see *Figure 8*). Conversely the desorption curves for the 50 μm pieces tended to be concave downwards in their early stages, whilst those for the thicker pieces were straight. The simplest phenomenological explanation for this anomalous departure from Fick's Law appears to be the effect of stress on the diffusion coefficient; the surface compression stresses during sorption decreasing the diffusion rate and conversely the surface tensile stresses during desorption increasing it. Such an explanation was proposed by Rosen[24] for water in phenol formaldehyde. However, this stress effect would be expected to apply equally to the 1 mm test pieces as to the 50 μm ones; although Crank[22] showed that, if stress affects diffusion, the effective $\bar{D}$ should increase as the thickness decreases, as it did in this project. An alternative explanation suggested by

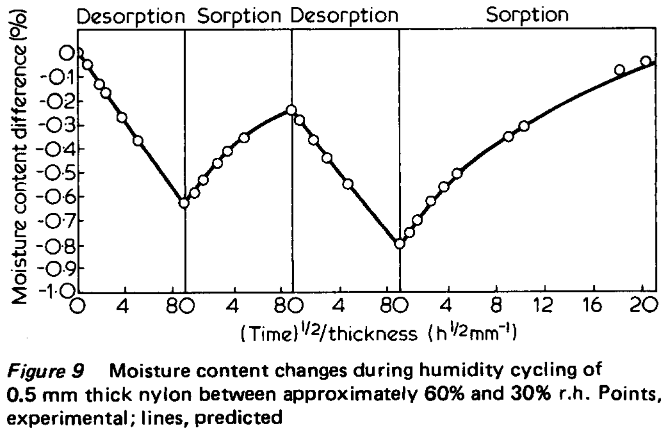

Figure 9 Moisture content changes during humidity cycling of 0.5 mm thick nylon between approximately 60% and 30% r.h. Points, experimental; lines, predicted

Crank was that the diffusion coefficient is a function of history as well as moisture content and will slowly approach an equilibrium value for a given moisture content. The result is to give a sigmoidal-shaped sorption curve but also to give a thickness effect in which a thicker sheet has a higher D value (only in the case of sorption), contrary to the results given here.

In view of the small or negligible effect of stress found in this study, another explanation is needed. One possible explanation is the thickness expansion, including the Poisson's ratio effect that results from the repressed longitudinal and width swelling. This expansion physically increases the distance through which the water molecules must travel in the very region in which they are active in the early stages of sorption; and conversely decreases it during desorption. This idea was checked by a simulation on the computer which gave sorption and desorption curves of qualitatively similar shape to the experimental ones of *Figures 3* and *4*, thus supporting it. It could also explain the effect of thickness on the shape of the sorption and desorption curves since the thin pieces have been found to show a very large dimensional change in the thickness direction[18].

CONCLUSIONS

Apart from the slight divergences from the traditional shape of the Fickian curve during the early stages of sorption and desorption of the thinner test pieces, it was found that nylon-6,6 can be considered as a fairly 'well-behaved' material with respect to its moisture sorption and diffusion. No anomalies were observed in its equilibrium moisture content, which could therefore be determined in constant conditions from a knowledge of the relative humidity of the atmosphere alone. The diffusion coefficient, although being almost (or entirely) independent of applied stress, does vary with moisture content and with the test piece dimensions. However, it has been shown that by the use of simple empirical relationships between D and moisture content and between D and sheet thickness the mean moisture content could be predicted well by standard methods even during complicated relative humidity changes.

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