Sorption of Water by Nylon 66 and Kevlar 29. Equilibria and Kinetics*

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SYNOPSIS

The sorption of water by nylon 66 and Kevlar 29 fabrics was studied over a range of 20–98% relative humidities at 27°C. Equilibrium and rate relationships were developed from the data in this study and from nylon 66 and nylon 6 data of other studies involving fiber and film. The ratio of sorbed moisture to amide concentration is, on average and at high relative humidities, one water molecule per amide unit. The nylon equilibrium data show that there exist threshold relative humidities above and below which sorption properties differ. One threshold is correlated with the glass transition. Another is identified in the glassy state of nylon 6 in which moisture is tightly bound. The equilibrium constant values are highest and the moisture is most tightly bound at very low humidities, and the values are lowest in the plastic region at high humidities. NMR, DSC, and mechanical property data from others are correlated with the sorption discontinuities observed in this study. Rate data indicate that sorption is a diffusion-controlled process.

INTRODUCTION

The sorption of water by polyamides has been studied extensively. Early literature coverages can be found in the *Encyclopedia of Polymer Science and Technology*[1] and in *Nylon Plastics*.[2] More recent literature coverage can be found in *Water in Polymers*.[3] The many studies on this subject were motivated by the large number of applications for polyamides and the large effect of water on mechanical properties, swelling, ability to absorb dyes, crystallinity, glass transition temperature, static charge development, etc. Most of these studies have been conducted with films, bulk or molded forms, and fibers. Very few studies have been conducted with fabrics.

The present water sorption study was conducted with nylon 66 ribbon and Kevlar 29 webbing that are used in parachutes as well as other applications. Motivation for this study stemmed from concern for the loss in mechanical properties and the appreciable swelling that can occur when these fabrics sorb water. Although many of the property degradation effects that occur when water is sorbed were investigated with molded rather than fiber polyamides, they can serve as trend indicators for fibers and fabrics. Examples of the degradation effects are given below.

Kohan[2] cites the following changes for molded nylon 66 at ambient temperatures: Yield strengths are reduced 37 and 59% at 50 and 100% relative humidities, respectively. Fatigue life is reduced 30% in 50% relative humidity and flexural modulus is reduced 44%. An approximately 1% linear change in dimensions occurs for every 3% of moisture that is sorbed. These are examples of the changes that can affect mechanical performance when the margins of safety are small.

Moisture also lowers the temperature at which the glass transition occurs, wherein a polymer changes from a rigid to a plastic or rubbery state. This physical change also contributes to the degradation in the mechanical properties. The temperature at which the glass transition occurs can be lowered to ambient temperatures in moderate relative humidities. Fuzek[4] has reported that the mod-

ulus for wet nylon 66 fibers is reduced 43% and that the stress–relaxation time is increased 20-fold at the glass transition temperature.

The moderate to large effects of moisture on the mechanical and physical properties of nylon 66 and other polyamides suggested that quantitative information on the equilibrium moisture sorption, as a function of humidity, and that the rate at which moisture is sorbed should be sought. In this study, sorption equilibrium and rate relationships for nylon 66 and Kevlar 29 fabrics are developed, their constants evaluated, and their relationships to the glass transition temperature and mechanical properties discussed. Data from other studies involving nylon 66 and 6 fibers, film, and bulk material are also used in formulating the relationships and conclusions.

EXPERIMENTAL

The nylon 66 fabric was the 5.08-cm, 249-kg (2-in., 550-lb) ribbon (SS33416 T-S-IV), and the Kevlar 29 fabric was the 2.54-cm, 2722-kg (1-in., 6000-lb) webbing (SS 323241 TY VI, CL15-S). They were wound vertically on a cylinder of wire screening (1.27 cm spacing) that was 20.3 cm in diameter. The cylinder and fabric were suspended from a Lebow Associates load cell. Weight change measurements were made with a Budd strain indicator that was calibrated before each new humidity exposure. The same fabric sample was reused each time. It was evacuated for 16–18 h at ambient temperatures prior to each measurement series. This time period compares with the approximately 1–4 h required to attain near sorption equilibrium conditions for nylon and Kevlar. It will be shown that the sorption values obtained in this study compare favorably with those

Figure 1   Evaluation of sorption weight at equilibrium.

obtained by others. This observation indicates that evacuation had removed almost all if not all of the moisture. The dry weights of the nylon and Kevlar were 877 and 2419 g, respectively. The densities of the nylon and Kevlar in these fabrics were 1.15 and 1.50 g/cm^3, respectively. Densities were determined with a helium pycnometer.

A Thermotron environmental and climatic chamber (0.084 m^3) was used to provide the various humidity conditions. All of the measurements were made at 27°C. Relative humidity was controlled within a ±1.5% relative humidity range.

RESULTS AND DISCUSSION

Equilibrium Relationships

Nylon and Kevlar in the fiber, fabric, or bulk forms sorb moisture from the environment until an equilibrium condition is established. The quantity of sorbed moisture is dependent on the moisture concentration in the environment, i.e., relative humidity, the temperature, and the number of sorption sites in the polymer. Since the temperature and relative humidity were constant for each test environment, the sorption rate varied only with the concentration of available sorption sites. The initial concentration of available sites was determined from the sorbed moisture at equilibrium.

Accurate values for the equilibrium concentration of sorbed moisture were important for the evaluation of equilibrium and rate constants. This requirement suggested that data gathering would require extended time periods to assure that equilibrium was attained. An empirical and different approach that reduced the data acquisition time consisted in plotting sorbed moisture weight versus (time)$^{-2}$. These plots were linear for the final 25% of weight gain and extrapolation to zero on the x-axis provided weight gains for extreme time periods. Representative plots are shown in Figure 1. Validity for accepting these extrapolated values as equilibrium values is based on comparisons of these values with those from others.

It was also desirable to know the sorbed moisture values at 100% relative humidity, which is difficult to determine experimentally. These values were estimated from plots of [H$_2$O]$^{1/2}$ versus relative humidity, which appeared to be linear over a major portion of the relative humidity scale. Extrapolation to 100% humidity provided the desired values. This empirical relationship proved useful for data from this study and those from others.
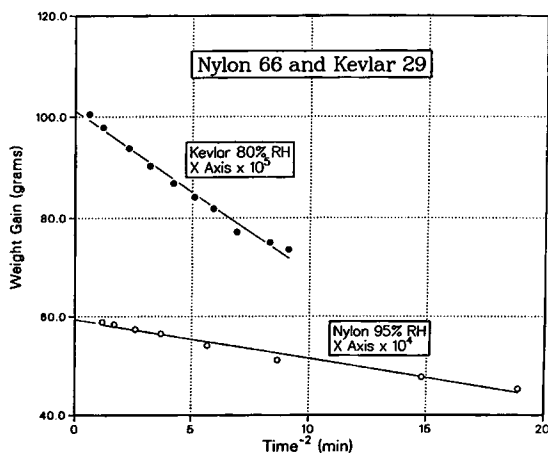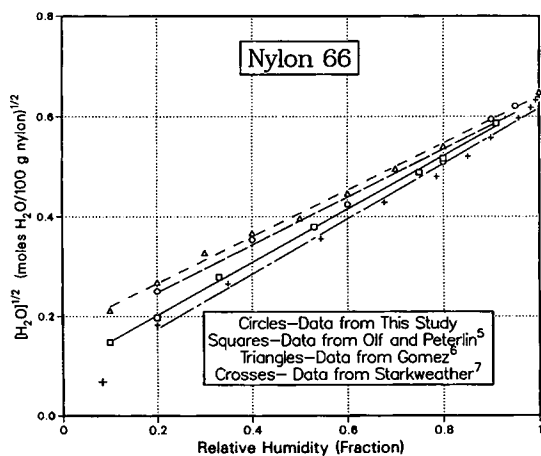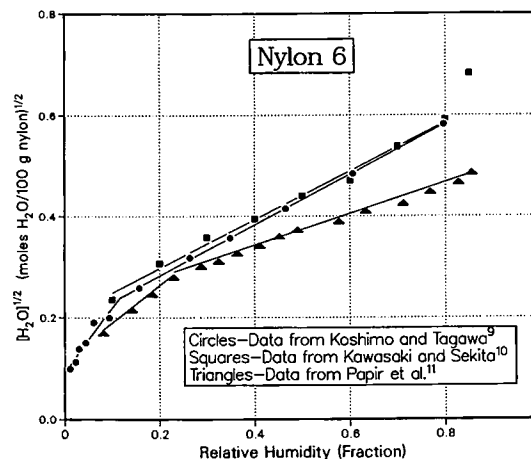
Figure 2 shows plots for nylon 66. Data from the present study are for fabric at 27°C, those from Olf and Peterlin[5] at 28°C and Gomez[6] at 23°C are for fibers, and those from Starkweather[7] at 23°C are for film. The mean intercept at 100% humidity corresponds to a sorbed moisture content of 0.40 mol/ 100 g. Since the equivalent weight per amide unit is 113, the sorbed moisture per amide unit is 0.45. Thus, the sorbed water averages slightly less than one water molecule for two amide groups. An indication of the maximum sorption possible is obtained from a study in which nylon 66 molded plaques were soaked in boiling water for 138 h.[8] Only 8.5 wt % was sorbed, a value equivalent to 0.47 mol/100 g or 0.53 molecules per amide unit.

Nylon 6 provided similar results. Figure 3 shows data for fibers from Koshimo and Tagawa[9] at 27°C and films from Kawasaki and Sekita[10] and Papir et al.[11] both at 25°C. The data from Koshimo and Tagawa[9] and Papir et al.[11] indicate two linear segments for the square root relationship, one at very low humidities and another at the higher humidities. Extrapolations of the Koshimo and Tagawa[9] and Kawasaki and Sekita[10] data to 100% humidity provided a sorbed moisture value of 0.52 moles per equivalent of amide or slightly more than one water molecule for every two amide groups, consistent with the values from nylon 66. The extrapolated value from the Papir et al.[11] data is inconsistent with the above values for nylons 66 and 6.

The moderate to large differences in the slopes of the two segments in Figure 3 indicate that at low humidities sorption takes place more readily than at higher humidities; i.e., smaller increments of vapor pressure are required to cause equivalent in-
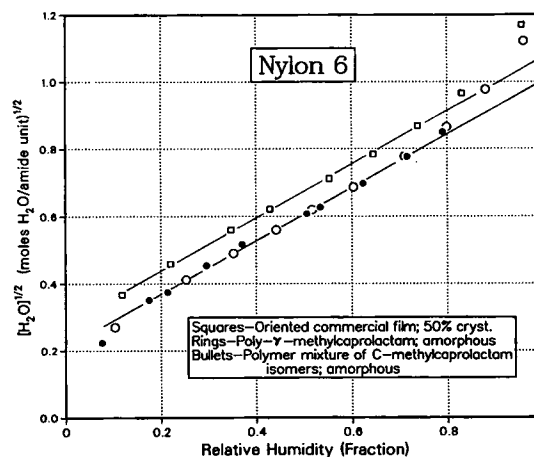

Figure 3 Square-root relationship between sorbed moisture and moisture concentration in the environment.

creases in sorption than at higher humidities. This observation is consistent with the nuclear magnetic resonance (NMR) spectra obtained by Olf and Peterlin[5] for nylon 66. They observed markedly different spectra for fibers exposed to humidities in the 0–20% range from those in the 20–75% humidity range. The difference was interpreted as water tightly bound at the lower humidities and mobile at the higher humidities. Polymer structures with more tightly bonded water would be expected to respond more positively to increased humidity.

Nylon 6 (caprolactam) and substituted caprolactam sorption data reported by Puffr and Sebenda[12] were particularly instructive since they were given in terms of the molar ratio of sorbed moisture to amide concentration. Figure 4 shows [H₂O]$^{1/2}$ ver-

Figure 2 Square-root relationship between sorbed moisture and moisture concentration in the environment.
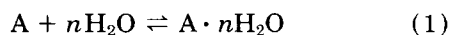

Figure 4 Square-root relationship between sorbed moisture and moisture concentration in the environment. Data from Puffr and Sebenda.[12]

sus relative humidity plots of data for caprolactam, which was estimated to be 50% crystalline, and two substituted caprolactams, which were amorphous. These plots are linear over the range of 10–80% humidities. Extrapolation to 100% humidity shows that the ratio of sorbed water molecules per amide unit is 1 and that sorption occurs in the amorphous phase. Deviations from this ratio above 80% humidity may be due to the clustering phenomenon observed and reviewed by Chatzi et al.[13] They discuss multiple water molecule complexing and the existence of liquidlike clusters. Deviations below 10% humidity are due to the tightly bound moisture noted in the nylon 6 data in Figure 3.

The data obtained in the present study for the Kevlar 29 fabric provided similar results. Figure 5 shows the linear relationship between $[H_2O]^{1/2}$ and relative humidity. The extrapolated sorbed moisture concentration at the relative humidity fraction of 1.0 is 0.45. Because the equivalent weight per amide group is 119, the ratio of sorbed water molecules per amide group is 0.53.

Previous studies have indicated that amide groups in polyamides exist as dimers bonded by the hydrogen atoms on the nitrogen. Moisture sorption leads to disruption of the dimer and the formation of a water molecule bridge between the amide groups involving one or more water molecules.[8,12,14–17]

Because the sorbed moisture exists in equilibrium with external water vapor, relationships of the following forms can be defined:

$$A + nH_2O \rightleftharpoons A \cdot nH_2O \qquad (1)$$

where A = amide group, n = water molecule stoichiometry, and $A \cdot nH_2O$ = amide–water complex.
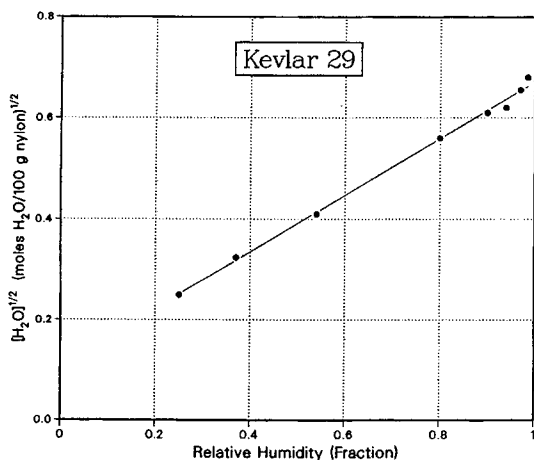
Figure 5 Square-root relationship between sorbed moisture and moisture concentration in the environment.

An equilibrium constant, K_1, based on eq. (1) can be defined in the following form:

$$K_1 = \frac{[A \cdot nH_2O]}{[H_2O]_u^n [A_0 - A \cdot nH_2O]} \qquad (2)$$

where $[H_2O]_u$ = available unbonded moisture concentration within the polyamide, $[A_0]$ = initial amide concentration, and $[A_0 - A \cdot nH_2O]$ = residual amide concentration. All concentrations are in mol/100 g of polyamide.

It is assumed that almost all of the sorbed moisture is in the form of the complex $A \cdot nH_2O$ and that the residual unbonded moisture, $[H_2O]_u$, is present in a very small and steady-state concentration, which is dependent on the relative humidity. The following equilibrium assumption is made relating noncomplexed moisture and the humidity:

$$K_2 = \frac{[H_2O]_u}{[RH]^2} \qquad (3)$$

where [RH] = relative humidity in fractional units.

The concentration for $A \cdot nH_2O$ was determined from the measured sorbed moisture. Equation (2) can therefore be restated in terms of measured quantities in the following form:

$$K = \frac{n[H_2O]}{[RH]^2 [A_0 - nH_2O]} \qquad (4)$$

where $n[H_2O]$ = stoichiometric equivalence of sorbed water molecules to complexed amide groups and $K = K_1 \cdot K_2$. Thus, for $A \cdot H_2O$, $n = 1$, and, for $A_2 \cdot H_2O$, $n = \frac{1}{2}$.

In the present study, the sorption data indicated that the ratio of sorbed moisture to amide concentration in the polymer is 1 : 2. The data from Puffr and Sebenda,[12] however, indicated that the ratio is more correctly 1 : 1. This result shows that in the present study only half of the amide groups sorb moisture in the ratio of 1 : 1 because the fibers are approximately only 50% amorphous. Most nylon 66 and nylon 6 materials fall in the 40–60% and 35–55% crystalline ranges, respectively.[18,19] Thus, the ratio of sorbed moisture to total amide concentration is approximately $\frac{1}{2}$, i.e., $n = \frac{1}{2}$.

Equation (4) can be restated in the following form:

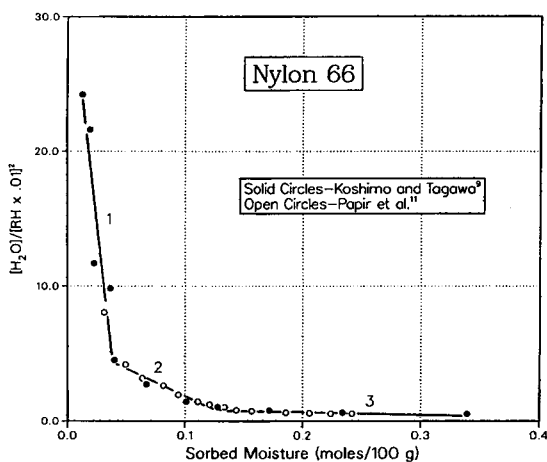$$K = \frac{[H_2O]}{[RH]^2 [A_0/n - H_2O]} \qquad (5)$$

To evaluate A_0/n and K, eq. (5) was rearranged into the following linear form:
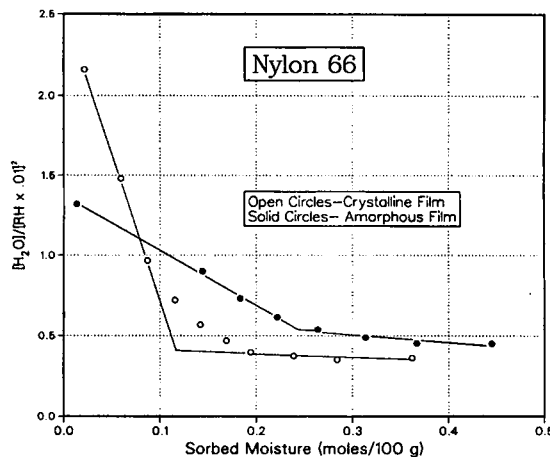
$$\frac{[H_2O]}{[RH]^2} = K[A_0/n] - K[H_2O] \qquad (6)$$

A plot of $[H_2O]/[RH]^2$ versus $[H_2O]$ should be linear with slope and intercept values for K and KA_0/n, respectively. Plots of this type with the sets of data used in this study confirmed (1) that more than one equilibrium is involved in moisture sorption by nylon and Kevlar and (2) that one molecule of water is associated with each amide group at higher humidities.

The adequacy of eq. (6) to model the experimental data is shown with data sets that cover the broadest ranges of humidity and that contain the largest number of data points. The data provided by Koshimo and Tagawa[9] and by Papir et al.[11] for nylon 6 were best suited for this purpose. Figure 6 is a composite plot of $[H_2O]/[RH]^2$ versus $[H_2O]$ for data from both sources. The $[H_2O]/[RH]^2$ values calculated from the data of Papir et al.[11] were corrected for the consistent difference in sorption values evident in Figure 3. A factor of 1.71, which represents the sorption difference at 100% relative humidity, provided the good overlap seen in Figure 6. The straight line and discontinuity inferences may appear arbitrary. The discontinuities, however, can be related to observations from others cited below.

Olf and Peterlin[5] show from NMR studies of nylon 66 fibers that water becomes mobile at the threshold moisture content of 0.04 mol/100 g, which corresponds to the 0.04 mol/100 g discontinuity be-

Figure 7 Plot of film data from Gomez.[6] Evidence for two equilibria sorption regions.
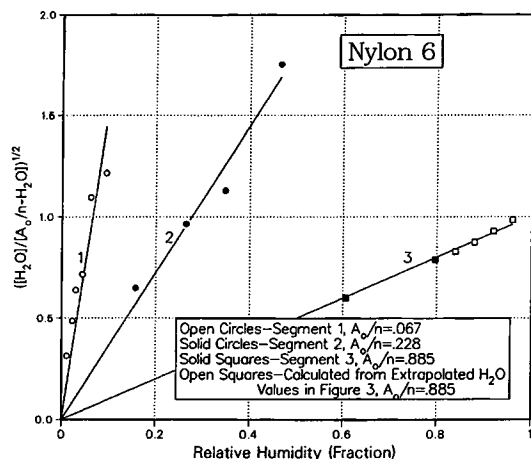
tween segments 1 and 2. A stress–relaxation study in nylon 6 conducted by Papir et al.[11] provided data on the decrease in modulus as a function of moisture content. It shows a marked discontinuity at 0.06 mol/100 g. The discontinuity between segments 2 and 3 occurs at the 0.13 mol/100 g. It will be shown in the next section that this last value corresponds to the moisture concentration at which the glass transition occurs. The observations in these references support the inference that each segment in Figure 6 represents a chemical and/or physical change within which the soprtion properties differ. Each segment, therefore, represents a different equilibrium that can be described by eq. (6). The straight lines were used to provide estimates for K and A_0/n.

The nylon 66 data collected by Gomez[6] provided the broadest humidity range for this material. Figure 7 is a similar plot for crystalline and amorphous films which indicates that two equilibria exist in this material. The absence of a third equilibrium is probably due to limited sorption data at very low humidities.

The results from this study suggest that the three regions in nylon which sorb moisture differently are independent in their sorption properties. This conclusion is drawn from plots based on a rearranged form of eq. (5) shown below:

$$[RH]K^{1/2} = \left(\frac{[H_2O]}{[A_0/n - H_2O]}\right)^{1/2} \qquad (7)$$

Equation (7) is a linear relationship with an intercept at the origin and a slope equal to $K^{1/2}$. Figure

Figure 6 Plots of fiber data from Koshimo and Tagawa[9] and film data from Papir et al.[11] Evidence for three equilibria sorption regions.

Figure 8 Plots of fiber data from Koshimo and Tagawa[9] to demonstrate the adequacy of eq. (7) and to provide evidence for three independent sorption regions.

8 is a plot for the data from Koshimo and Tagawa,[9] which covers the three regions and which fulfills these requirements.

Sorption by Kevlar also conformed to the model indicated by eq. (5). A more critical verification for the adequacy of this equation is seen in Table I in terms of the minimal variation in the equilibrium constants as a function of sorbed moisture.

Table II provides a comparison of the amide equivalent weights and the equilibrium constant values for the polyamide data examined in this study. It is assumed that the nylons possess three regions which sorb differently, although the data of Koshimo and Tagawa[9] provide the only very low humidity data for calculating initial sorption data. The regions are designated as 1, 2, and 3 and are noted in Table

II as subscripts. The material form of the polyamide used in sorption measurements is given and also the degree of crystallinity if this information was available.

The values for A_{02}/n for nylon are similar and independent of the physical form of the polyamide, except for the amorphous films. For this material the equivalent concentration is about twice as large and is reasonable in view of the absence of crystalline material.

The K_2 values for the nylons are similar, with the exceptions of the smaller values for the amorphous nylons and the larger value for the data of Kawasaki and Sekita.[10] The smaller values for amorphous nylons are probably due to their mixed composition of nonoriented and oriented polymer frozen into the amorphous state. The larger value is probably due to the small number of sorption data points available for analysis in region 2 and probably represents a mean value for K_1 and K_2. The similarity in A_{03}/n and K values for amorphous and crystalline polyamides is probably due to the orientation that occurs in amorphous polyamides when sufficient moisture is sorbed.[12] The values for K_1, K_2, and K_3 are relative measures for the bond strengths between the sorbed moisture and the amide groups. Thus, the bonding associated with the large value for K_1, which represents initial sorption, can be associated with the most tightly bonded moisture observed by Olf and Peterlin[5] and Chatzi et al.[13]

The independent sorption characteristics of the regions associated with segments 1 and 2, evident in the data of Koshimo and Tagawa,[9] are due in part to the large differences in the equilibrium constant values, i.e., 181 and 3.30. Although a distribution of

Table I Equilibrium Constant (K) Values for Kevlar 29 Sorption Calculated from Eq. (5)

Relative Humidity (Fractional Units)	A_0/n (moles/100 g)	K (Lower RH Segment)	K (Higher RH Segment)
0.10[a]	0.090	4.97×10^{-3}	
0.15[a]	0.090	3.55	
0.20[a]	0.090	3.56	
0.25	0.090	3.55	
0.37	0.840		1.28×10^{-4}
0.54	0.840		1.10
0.80	0.840		0.99
0.90	0.840		0.94
0.94	0.840		0.93
0.965	0.840		0.95
0.97	0.840		1.11
0.98	0.840		1.28

[a] Sorbed moisture values were obtained by extrapolating the data in Figure 4 to lower RH values.

Table II Values for Equivalent Weights (A_0/n) and the Equilibrium Constants (K)

Data Source	Polyamide Physical Form	Percent Crystallinity	A_{01}/n[a]	A_{02}/n[a]	A_{03}/n[a]	K_1	K_2	K_3
			Nylon 66					
Auerbach and Carnicom	Fabric	54		0.170	0.830		16.00	0.757
Olf and Peterline[5]	Fiber	—		0.176	0.893		10.8	0.697
Gomez[6]	Fiber	—		0.182	0.875		16.8	0.812
	Film	—		0.140	0.980		18.1	0.594
	Film	0		0.405	0.970		3.34	0.865
Starkweather[17]	Film	57		0.160	0.850		6.55	0.618
			Nylon 6					
Koshimo and Tagawa[9]	Fiber	34	0.067	0.228	0.820	181	3.30	0.998
Kawasaki and Sekita[10]	Film	—		0.150	0.900		66.7	1.08
Papir et al.[11]	Film	—		0.133	0.648		29.0	0.792
Puffr and Sebenda[12]	Film	50		0.252[b]	0.820[b]		102	5.08
			Kevlar 29					
Auerbach and Carnicom	Fabric	—		0.090	0.840		35.5	1.06
			Methyl Caprolactams					
Puffr and Sebenda[12]	Film	0	0.190[b]	0.338[b]	1.06[b]	61.5	22.0	2.25

[a] Mol/100 g.
[b] Mol/amide unit.

sorbed moisture between the two regions would be expected, minimal sorption would occur in region 2 until most of the sorption sites in region 1 were occupied. The different sorption characteristics in region 3 are a result of the glass transition which occurs at 35% humidity. Evidence for this transition will be provided in the next section.

The parameters in Table II were used to calculate sorption values from the following rearranged form of eq. (5). When data for regions 1 and 2 are available, the equation has the following form for the glassy state:

$$[H_2O]_{total} = [H_2O]_1 + [H_2O]_2$$

$$= \frac{A_{01}K_1[RH]^2}{1 + K_1[RH]^2} + \frac{A_{02}K_2[RH]^2}{1 + K_2[RH]^2} \quad (8)$$

For the plastic state the corresponding equation consists of a single term:

$$[H_2O]_3 = \frac{A_{03}K_3[RH]^2}{1 + K_3[RH]^2} \quad (9)$$

Figure 9 shows comparative experimental and calculated values for the nylon 6 data from Koshimo and Tagawa.[9]

Correlations with Glass Transition

Results obtained in this study and others can be correlated with the glass transition that takes place in nylon at the temperatures and relative humidities investigated in the present study and in others. The occurrence of a transition of this type can have important bearing on design in applications with these
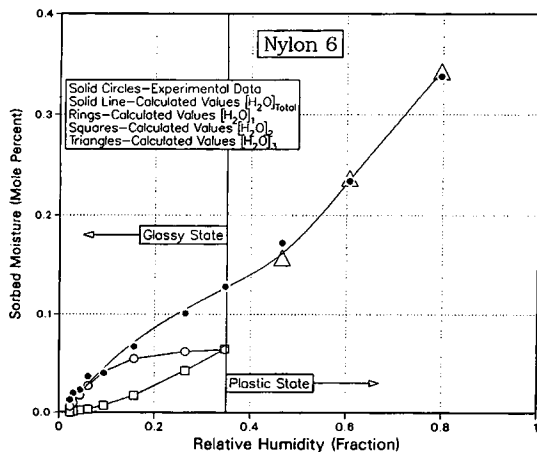
Figure 9 Comparison of calculated values and experimental sorbed moisture data from Koshimo and Tagawa.[9]

materials because the mechanical properties degrade severely in the plastic state following transition. Evidence that this transition occurred in the nylon fabrics, fibers, and films under the conditions cited in this study is provided in terms of correlations between the discontinuities observed in plots from eq. (5) and differential scanning calorimetry, mechanical property, and NMR data.

The discontinuities observed in plots such as those in Figures 6 and 7 cover small ranges of sorbed moisture and humidity values. They are listed in Table III.

The mean sorbed moisture value at the discontinuities for nylon 6 and nylon 66 is 0.166 ± .054 mol/100 g. The existence of a discontinuity suggests a change in the structure of the nylons which can permit greater accessibility for moisture. This change in accessibility is observed in the values of the ratio $[H_2O]/[RH]^2$ that are plotted against sorbed moisture in Figures 6 and 7. It is evident that this ratio is more sensitive to sorbed moisture to the left of the discontinuity, where sorbed moisture values are low. This result indicates that increasingly larger increments of moisture vapor pressure are required to cause equivalent sorption increases as sorption progresses up to the discontinuity. Beyond the discontinuity, smaller increments of vapor pressure are required to cause equivalent sorption. The relative humidities associated with this discontinuity (Table III) fall into two distinct groups for nylon 66 with mean values of 45 and 63 for fiber and film, respectively. The mean value for nylon 6 is 31.

The discontinuity appears to be associated with the glass transition. Batzer and Kreibich[20] have

Table III Discontinuity Sorbed Moisture Values and Associated Relative Humidities

Data Source	Physical Form of Polyamide	Sorbed Moisture (mol/100 g)	Relative Humidity (Fractional Units)
	Nylon 66		
Auerbach and Carnicom	Fabric, crystalline	0.140	0.47
Olf and Peterlin[5]	Fiber, crystalline	0.100	0.42
Gomez[6]	Fiber, crystalline	0.157	0.47
	Film, crystalline	0.178	0.62
	Film, amorphous	0.240	0.65
Starkweather[7]	Film, crystalline	0.090	0.63
	Nylon 6		
Koshimo and Tagawa[9]	Fiber, crystalline	0.040, 0.13	0.085, 0.35
Kawasaki and Sekita[10]	Film	0.150	0.34
Papir et al.[11]	Film	0.11	0.37
Puffr and Sebenda[12]	Film, crystalline	0.240[a]	0.26
	Kevlar 29		
Auerbach and Carnicom	Fabric	0.090	0.24
	Methyl Caprolactams		
Puffr and Sebenda[12]	Film, amorphous	0.135,[a] 0.240[a]	0.19, 0.35

[a] Mol/amide unit.

studied the effect of water content on the glass transition temperature (T_g) for nylon 66 and nylon 6 sheets with a differential scanning calorimeter (DSC). The T_g values were essentially the same for both materials. A replot of their data showed that the water content for T_g at 27°C was 0.161 mol/100 g, the same as the mean value observed in the present study. Bretz et al.[8] also observed an endotherm in the DSC thermogram for nylon 66 at a moisture concentration of 0.14 mol/100 g.

In contrast with these results, Kevlar 29 fabric specimens, dry and conditioned to 75% relative humidity, and analyzed with a Du Pont 951 DSC instrument, showed no endotherms over the −50–200°C range. This observation is consistent with the absence of a discontinuity in the moderate moisture sorption range, indicating that a glass transition did not occur. The discontinuity at the sorption level of 0.090 mol/100 g noted in the sorption rate study is similar to that observed in nylon 6 at 0.067 mol/100 g and is probably associated with the change from tightly bonded to moderately bonded moisture observed by Chatzi et al.[13]

Low frequency dynamic mechanical measurements have been used to study the mechanical relaxation of polymers. The measurements show three distinct maxima for polyamides that are termed α-, β-, and γ-relaxations. All three maxima are affected by sorbed moisture and temperature. The α-relaxation in particular has been associated with the glass transition.[21,22]

Of particular interest are the results from several investigators which show that the α maximum has values within the range of discontinuity values listed in Table III. Thus, the data of Prevorsek et al.[22] indicate that the α maximum for nylon 6 occurs at 27°C, when the moisture content is 0.127 mol/100 g. Starkweather[23] found that the α maximum for nylon 66 occurs at 27°C, when the moisture content is 0.183 mol/100 g and Trueman[24] found that the maximum occurs when the relative humidity is 57%. These data also support the hypothesis that the 0.166 mol/100 g discontinuity described in this study is related to the glass transition.

Fatigue crack propagation also shows a discontinuity when related to water content. Bretz et al.[8] found that the fatigue crack propagation rate in nylon 66 exhibits a sharp minimum between 2 and 3% sorbed moisture (0.11–0.17 mol/100 g).

Fuzek[4] has studied large mechanical property changes as functions of temperature to determine the T_g value for nylon 66 fibers soaked in water and those exposed to 65% relative humidity. The properties include dimensional change, modulus, and stress decay time. Although these properties exhibit sharp changes in values at the same temperatures of 29 and 40°C, respectively, the temperatures are higher than those observed by others.

NMR data obtained by Olf and Peterlin[5] show evidence for the mobility of the polymer segments at 75 and 91% relative humidities, whereas at 33% humidity only the water molecules are mobile. The authors attribute the segmental mobility to the glass transition. All of these observations show the marked dependence of chemical, physical, and mechanical property changes on moisture content.

Kinetics for Moisture Sorption

Sorption is a two-step process involving diffusion of moisture from the environment into the polymer and subsequent complexing with the amide groups. The sorption time required to attain near equilibrium for nylon was about 1–2 h and 3–4 h for Kevlar at 27°C. These long time periods suggested that diffusion was the rate controlling step. The rate relationships are developed below.

A relationship developed by Waite,[25] who had studied diffusion controlled reactions, was used. His relationship in the present context may be stated in the following form:

$$\frac{d[H_2O]}{dt} = k_f'\left[1 + \frac{r_0}{(\pi Dt)^{1/2}}\right][RH]^2[A_0 - H_2O]$$

$$- k_r\left[1 + \frac{r_0}{(\pi Dt)^{1/2}}\right][H_2O] \quad (10)$$

where t = time (min), k_f' = forward rate constant (RH units^{-2} min^{-1}), k_r = reverse rate constant (min^{-1}), r_0 = radius of a sphere within which complexing occurs, and D = diffusion coefficient.

First- and second-order concentration terms for $[A_0 - H_2O]$, $[H_2O]$, and $[RH]^2$ are appropriate because they occur in the equilibrium expression, eq. (5), in this form. The equilibrium constant is a ratio of the forward and reverse rate constants. Equation (10) is an approximate relationship because it does not take into account that sorption is a function of material thickness.

Since the humidity remained constant, $k_f'[RH]^2$ was constant and we let $k_f = k_f'[RH]^2$. At equilibrium

$$k_f[A_0 - (H_2O)_e] = k_r[H_2O]_e \quad (11)$$

where $[H_2O]_e$ = equilibrium moisture concentration

(mol/100 g). Substituting the values for k_r and $k_f [A_0]/[H_2O]_e$ from eq. (11) into eq. (10) gives

$$\frac{d[H_2O]}{dt} = \frac{k_f[A_0]}{[H_2O]_e}\left[1 + \frac{r_0}{(\pi Dt)^{1/2}}\right]$$

$$\times ([H_2O]_e - [H_2O])$$

$$= (k_f + k_r)\left[1 + \frac{r_0}{(\pi Dt)^{1/2}}\right]$$

$$\times ([H_2O]_e - [H_2O]) \quad (12)$$

Integration gives

$$kt(1 + St^{-1/2}) = \ln\frac{[H_2O]_e}{[H_2O]_e - [H_2O]} \quad (13)$$

where $S = 2r_0/(\pi D)^{1/2}$ and $k = k_f + k_r$. A conventional first-order relationship has the following form:

$$k' = \ln\left(\frac{[H_2O]_e}{[H_2O]_e - [H_2O]}\right) \quad (14)$$

Equation (13) differs from the conventional first-order relationship with a rate constant k' in that

$$k' = k(1 + St^{-1/2}) \quad (15)$$

A characteristic property of this diffusion-limited rate expression is the dependency of the k' on time. In the early stages of sorption when t is small, values for k will be larger than those in the final stages. Also, the value for S will determine the extent to which time will affect k'.

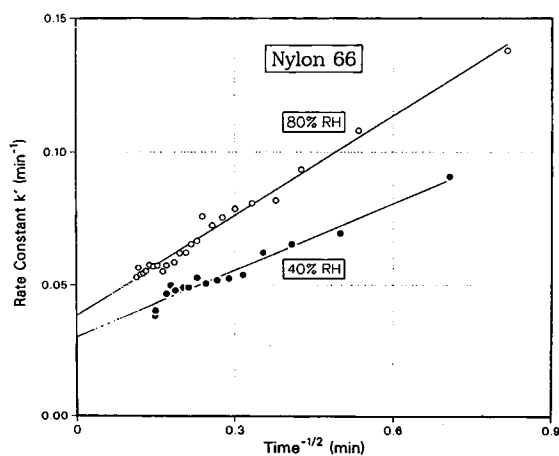Equation (15) is useful because k' is readily evaluated from eq. (14). Also, eq. (15) is in the form of

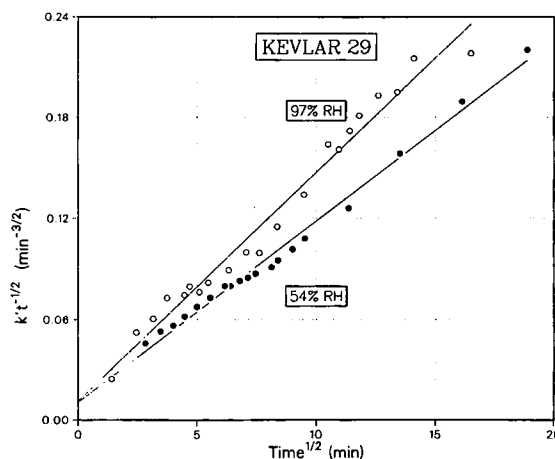**Figure 10** Evaluation of the rate constant k and diffusion parameter S from eq. (15).

Figure 11 Evaluation of the rate constant k and diffusion parameter S from eq. (16).

a linear relationship, so that plots of k' versus $t^{-1/2}$ can provide values for kS and k from the slopes and intercepts, respectively. Figure 10 shows representative plots for nylon 66.

Equation (15) is more useful during the initial stages when values for t are small and those for $t^{-1/2}$ are large. For large values of t, an alternate variation of eq. (15), shown below, was used:

$$k't^{-1/2} = k(t^{1/2} + S) \quad (16)$$

It is also in the form of a linear relationship where the slope and intercept provide values for k and S, respectively. Figure 11 shows representative plots for data obtained from Kevlar.

The k and S values for nylon 66 over the 20–98% humidity range did not appear to vary with humidity, although there was appreciable scatter in the calculated values (0.040 ± 0.0068 min^{-1} and 3.2 ± 0.99 min$^{1/2}$, respectively). The k and S values for Kevlar, however, showed marked differences in the values for the lower humidities (25 and 38%) and those for the remaining higher humidities. The k and S values obtained at the lower humidities were 0.0055 ± 0.0007 and 38 ± 6, respectively. At the higher humidities, the corresponding values were 0.012 ± 0.0004 and 5.3 ± 3.9, respectively. These large differences may be related to the observed discontinuity at about 0.090 mol/100 g sorbed moisture (Table III). The sorbed moisture concentrations for the above lower humidities were 0.08 and 0.10 mol/100 g.

The adequacy of eq. (13) to provide sorbed moisture as a function of time is shown in Figure 12, where representative plots of calculated values and experimental data for nylon and Kevlar are shown.
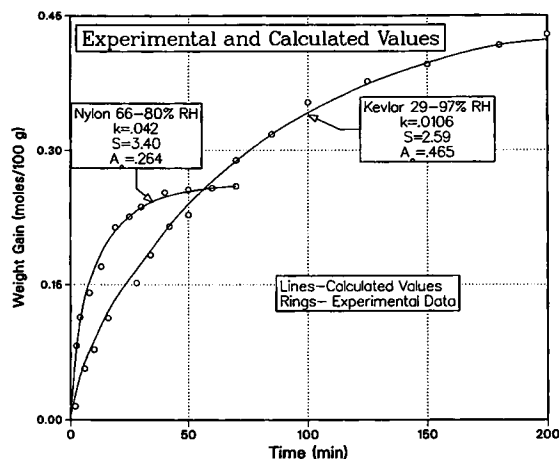
Figure 12 Comparative experimental and calculated weight-loss values obtained from eq. (17).

Equation (17) shown below was used to obtain the calculated values:

$$[H_2O] = [H_2O]_e$$
$$\times (1 - \exp\{-kt(1 + St^{-1/2})\}) \quad (17)$$

CONCLUSIONS

Equilibrium and rate measurements of moisture sorption in nylon 66 and Kevlar 29 fabrics were performed over a large range of relative humidities at 27°C. Data from this study and those from others show that less sorption occurs in the glassy state of amorphous nylon than in the plastic state. The larger equilibrium constant values for the glassy state indicate that the water is more tightly bound. Nylon 6 data obtained at very low humidities show that a second region exists in the glassy state with even larger equilibrium constant values. The water–amide ratio at high humidities is 1 : 1. Only two regions with different sorption properties were identified in Kevlar because a glass transition did not occur at this temperature. Sorption rate measurements indicated that the sorption process is diffusion-controlled. NMR, DSC, and mechanical property data are correlated with sorbed moisture content.

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