# Sorption and Transport of Water Vapor in Nylon 6,6 Film

LOONG-TAK LIM, IAN J. BRITT, MARVIN A. TUNG

Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada

**ABSTRACT:** The sorption and transport of water in nylon 6,6 films as functions of the relative humidity (RH) and temperature were studied. Moisture-sorption isotherms determined gravimetrically at 25, 35, and 45°C were described accurately by the GAB equation. Water-vapor transmission rates were enhanced above $\approx 60-70\%$ RH, primarily due to the transition of the polymer from glassy to rubbery states. The glass transition temperatures ($T_g$'s) of nylon 6,6 were measured at various moisture contents using differential scanning calorimetry. The results showed that the sorbed water acted as an effective plasticizer in depressing the $T_g$ of the polyamide. Fourier transform infrared spectroscopy (FTIR) was utilized to characterize the interaction of water and the nylon. Evidence from FTIR suggested that the interaction of water with nylon 6,6 took place at the amide groups. Based on the frequency shift of the peak maxima, moisture sorption appeared to reduce the average hydrogen-bond strength of the N—H groups. However, an increase was seen for the C=O groups. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 197–206, 1999

**Key words:** nylon 6,6; water sorption; permeability; glass transition temperature; FTIR

## INTRODUCTION

Nylons are characterized by their good thermal stability, flexibility, and mechanical properties. They are widely used in flexible packaging for natural cheese, fresh and processed meats, and frozen foods.[1] Due to their moisture sensitivity, the physical and transport properties of nylons change substantially as a function of the moisture content.[2] In general, the modulus and yield stress decrease with increasing moisture content, while increases are seen in the elongation and energy to break.[3,4] The barrier to organic vapors and oxygen is generally good when the films are dry, but weakens when exposed to high relative humidity

(RH) environments. Such moisture-dependent transport characteristics may be suitable in fresh produce packaging, where it is desirable to limit water vapor and carbon dioxide buildup within the package. In ripening of certain cheeses, oxygen transfer through the package is desirable to facilitate the growth of aerobic molds on the surface, but moisture transfer should be limited after the ripening process to prevent dehydration.[5] Moisture-sensitive films, such as nylons, may find applications in these and other areas of food packaging.

Recently, studies have been carried out on the transmission rate of oxygen as a function of RH.[6–8] Generally, minimal transmission rates were observed near 40% RH. The decrease in oxygen transmission at low RH was attributed to the competition between oxygen and water molecules for active sites in the polymer matrix. Liu et al.[9] showed that the permeability of toluene vapor through a multilayer film containing nylon and ethylene vinyl alcohol copolymers (EVOH) in-

---

creased exponentially as the multilayer structure was exposed to higher RH. The plasticization of these hydrophilic barrier layers by the sorbed water, which results in an increase in polymer chain segmental mobility, accounted for the accelerating effect of RH on the permeability. In our laboratory, similar results were observed on the permeability of allyl isothiocyanate vapor [(AIT), an essential oil of horseradish] in nylon 6,6 film.

Sorption and transport behavior of permeants in nylons differ markedly depending on the morphology of the polymers. The equilibrium moisture contents of amorphous polyamides are significantly higher than for semicrystalline polyamides. In addition, the shape of the sorption isotherms may vary with the amorphous content and thermal history of the polymer.[6,10–13] Our initial intent was to investigate the permeation of AIT in nylon 6,6 film. Due to the moisture sensitivity of the polyamide, we feel that it is necessary to examine first the water-vapor sorption and transport in the polyamide to better understand the RH-dependent permeation of AIT. The present study was undertaken to characterize the water-vapor permeation and sorption in nylon 6,6 films as a function of RH.

## EXPERIMENTAL

### Moisture-Sorption Experiment

Cast nylon 6,6 films (Dartek®, DuPont Canada Inc., Whitby, ON) of 25.4 $\mu$m thickness were dried in a vacuum oven (20 Pa) at 80°C for 2 h before the sorption experiments. The kinetics of moisture sorption in the film samples was studied gravimetrically using a Cahn 2000 microbalance equipped with a hermetically sealed glass chamber (Cahn Instruments, Inc., Cerritos, CA). Appropriate saturated salt solutions were placed in the chamber to provide atmospheres of the desired RH. Before the weight-gain measurement, the apparatus was allowed to equilibrate in a thermostated forced-air oven for at least 3 h.

### Water-Vapor transmission

The water-vapor transmission rates (WVTR) through the nylon 6,6 film samples were measured on a Permatran-W 3/31 permeability testing apparatus (Modern Controls Inc., Elk River, MN). Conditions of temperature and RH ranged from 15 to 35°C and 30 to 90% RH, respectively. A relatively high flow rate of 100 mL/min was used on the downstream cell to avoid overloading of the infrared sensor. The Permatran response was calibrated using a reference film provided by the manufacturer. The permeability coefficient ($P$) was calculated according to $P$ = WVTR (film thickness/vapor partial pressure).

### Differential Scanning Calorimetry (DSC)

Nylon 6,6 film was cut into small disks and stacked in DSC pans. With the pan lids removed, samples were dried in a vacuum oven (as described before) and then equilibrated at 25°C in airtight glass bottles in which the relative humidities were controlled by means of appropriate saturated salt solutions. Film samples of different moisture contents so obtained were sealed quickly in the pan and then scanned in a DSC. Samples for 0% RH were prepared by sealing the vacuum-dried films in the pan directly without further treatment.

A DuPont 2910 DSC (TA Instruments, New Castle, DE), equipped with a cooling system, was used for determining the glass transition temperature ($T_g$). The heating rate used was 15°C/min. To remove the irreversible endothermic relaxation peak that interfered with the determination of the glass transition, samples were first heated from 25 to 80°C and then quenched to −60°C, followed by a second scan for $T_g$ determination. No detectable shift in the $T_g$ was observed upon the second scan. Since the midpoint and end temperatures are dependent on the crystallinity, orientation, and percent moisture of the film sample, the glass transition temperature was taken at the onset of the heat-capacity change.

### Fourier Transform Infrared Spectroscopy

Film samples were exposed to water vapor as described in the previous section. After attaining equilibrium, the samples were removed from the bottle and immediately sandwiched between two 25-mm-diameter NaCl windows and then loaded onto the beta cell (Cole–Parmer Instrument Co., Vernon Hills, IL). The infrared spectra of the samples were determined on a Bio-Rad FTIR (Digilab Division, Cambridge, MA) at a resolution of 2 cm$^{-1}$.

At the original film thickness (25.4 $\mu$m), amide I, amide II, and bonded N—H peak maxima were saturated. Therefore, thinner samples were prepared to allow quantification of these peaks.

**Figure 1**   Moisture-sorption isotherms of nylon 6,6 at 25, 35, and 45°C. The solid lines are derived from the GAB equation [eq. (3)]. The estimated values for the GAB parameters from nonlinear regression are as follows: $M_m = 0.065$, $C_0 = 0.0039$, $A_0 = 0.623$, $\Delta H_c = 13760$ J/mol, $\Delta H_A = -108.1$ J/mol.

Films were cold-drawn to a draw ratio of $\lambda = l/l_0 = 3.0$ ($l$ and $l_0$ are the length of the drawn and undrawn films, respectively) using an Instron universal testing machine (Instron Corp., Canton, MA). The crosshead speed was 80 mm/min. The initial film width and gauge length before draw were 2.5 and 2.0 cm, respectively. An approximately 2.0-cm-long strip was cut from the middle section of the drawn film for the moisture-sorption studies.

## RESULTS AND DISCUSSION

### Moisture Sorption

The moisture-sorption isotherms of nylon 6,6 at 25, 35, and 45°C displayed upward curvatures which became more pronounced at higher RH (Fig. 1). An isotherm of similar shape at 23°C was observed by Starkweather[4] on the same polyamide, although the reported equilibrium moisture contents were lower. This is probably due to the higher crystallinity sample used by that author (reported to be 57% crystalline). Based on the measured heat of fusion of 76.2 ± 2.7 J/g from the DSC and the reported 188.4 J/g heat of fusion of

100% crystalline nylon 6,6,[14] the crystallinity of our sample was found to be 40.5 ± 1.4%.

The sorption isotherms of nylon 6 reported by Hernandez[8] and Hernandez and Gavara[13] were concave to the abscissa at low RH. The absence of this feature in nylon 6,6 indicated that the water sorption in nylon 6,6 did not go through a distinguishable Langmuir sorption phase, nor did the sorption behavior strictly follow Henry's Law, that is, water sorption in the nylon films did not strictly follow the dual-mode sorption model. Swelling of the polymer matrix may have caused the deviation of sorption from Henry's Law as water activity increased, resulting in exposure of more binding sites for enhanced water sorption. Isotherms with an upward curvature may also indicate the formation of water clusters in the polymer matrix.[4,15,16]

The Flory–Huggins equation[17] was used to model the isotherms:

$$\ln a_w = \ln \phi_1 + (1 - \phi_1) + \chi (1 - \phi_1)^2 \quad (1)$$

where $a_w$ and $\phi_1$ are the water activity and volume fraction of water in the polymer, respectively. $\chi$ is the polymer–solvent interaction parameter and is related to the sum of the enthalpic and entropic contributions of the mixing process.[18–20] In calculating $\phi_1$, the additivity of the volumes was assumed. Equation (1) did not describe the data well due to the concentration-dependent nature of $\chi$. Values of $\chi$ for the 25, 35, and 45°C isotherms decreased from 2.03 to 1.77, 2.27 to 1.84, and 2.51 to 1.92, respectively, as $a_w$ increased from 0.2 to 0.9. The equation is based on the assumption of random mixing and does not take into consideration the presence of specific interactions between the sorbant and sorbate. At low $a_w$, where specific interactions of water and the polymer active sites are strong, the orientation of the water molecules can cause a large decrease in the entropy, resulting in higher $\chi$ values.

The net isosteric heat of sorption was calculated according to eq. (2)[21,22]:

$$\Delta H_{st} = -R\left(\frac{\partial(\ln a_w)}{\partial(1/T)}\right)_M \quad (2)$$

where $\Delta H_{st}$ (J/mol) is the heat evolved to absorb water by the material at a fixed level of moisture content $M$, minus the heat of condensation of free water. $R$ is the universal gas constant (8.314 J

**Figure 2** Net isosteric heat of sorption of nylon 6,6. The results were derived from the GAB equation [eq. (3)].

mol$^{-1}$ K$^{-1}$) and $T$ is the temperature (K). The large values of $\Delta H_{st}$ (Fig. 2) at low moisture contents provide further evidence for the existence of strong water–polymer interactions. The net heat to desorb remained much higher than the latent heat of condensation of free water, even at a high moisture-content range, suggesting that the interaction of water with the polymer remained substantial in this region.

From a practical standpoint, an accurate interpolation of the isotherm data is important in predicting the sorption behavior of barrier films. The Guggenheim–Anderson–de Boer (GAB) equation, which has been shown to describe moisture-sorption isotherms of many food products accurately,[21-26] was applied to nylon 6,6 in this study. The three-parameter model takes the form

$$M = \frac{M_m \, A \, C \, a_w}{(1 - A \, a_w)(1 - A \, a_w + A \, C \, a_w)} \quad (3)$$

where the constants $C$ and $A$ are temperature-dependent according to eqs. (4) and (5):

$$C = C_0 \, \exp\left(\frac{\Delta H_C}{R \, T}\right) \quad (4)$$

$$A = A_0 \, \exp\left(\frac{\Delta H_A}{R \, T}\right) \quad (5)$$

In these equations, $M_m$ is the monolayer moisture content. $\Delta H_C$ and $\Delta H_A$ represent the difference in the heat of the monolayer and free water to that of the multilayer moisture, respectively. To reduce the uncertainties due to successive regressions, eqs. (4) and (5) were substituted into eq. (3), and the resulting five-parameter equation was fitted to the sorption data using a nonlinear regression procedure PROC NLIN from SAS.[27] The derived GAB equation is plotted as solid lines in Figure 1, showing accurate fits to the actual data. Equation (3) has the advantage of needing only one set of parameters for describing the isotherms at different temperatures.

The tendency of water to form clusters in a polymer was approximated by the clustering function $G_{11}/\nu_1$ developed by Zimm and Lundberg[28] and adapted by others[2,11,13,15,16,29]:

$$\frac{G_{11}}{\nu_1} = -(1 - \phi_1)\left[\frac{\partial\left(\frac{a_1}{\phi_1}\right)}{\partial \, a_1}\right]_{p,T} - 1 \quad (6)$$

where $\nu_1$ is the partial molar volume of the penetrant and $G_{11}$ is the cluster integral. The quantity $\phi_1 \, (G_{11}/\nu_1)$ is the mean number of water molecules in the neighborhood of a given water molecule in excess of the mean concentration of water in the polymer.[28] This quantity goes to zero in the absence of clustering; therefore, the apparent number of water molecules in a cluster would be $\phi_1 \, (G_{11}/\nu_1) + 1$. The GAB equation was used for calculating $G_{11}/\nu_1$ due to its goodness of fit to the isotherms. The variable $M$ in eq. (3) was converted to $\phi_1$ and reregressed. Substituting $\phi_1$ into the derivative term in eq. (6), the clustering function can be written in terms of the GAB parameters:

$$\frac{G_{11}}{\nu_1} = -(1 - \phi_1)\left(\frac{1}{M_m C}\left(-2 + 2 \, A \, a_w\right.\right.$$
$$\left.\left. - 2 \, A \, C \, a_w + C\right)\right) - 1 \quad (7)$$

Again, parameters $C$ and $A$ are temperature-dependent as in eqs. (4) and (5).

The cluster sizes so determined are presented in Figure 3. The average cluster size of water in nylon has been reported to be approximately 2 at 90% RH,[30] which is consistent with our findings. At low $a_w$, the effect of temperature upon the cluster size appeared to be minimal, which could

**Figure 3** Plot of $\phi_1(G_{11}/\nu_1)$ versus water activity. The quantity $\phi_1(G_{11}/\nu_1)$ is the mean number of water molecules in the neighborhood of a given water molecule in excess of the mean concentration of penetrant in the polymer.[28]

be attributed to the strong association of water with the active sites. This is reflected by the high heat evolved during water sorption at low $a_w$ (Fig. 2). At higher $a_w$, despite the negative relationship of moisture content with temperature (Fig. 1), the water-cluster size in the polymer matrix increased with the temperature, suggesting that geometrical restriction may exist at lower temperatures, which prohibits the formation of larger clusters. At higher temperatures, the increase in the kinetic energy of the polymer and permeant may have partially disrupted and/or reduced the polymer chain-to-chain interactions, making the initially less desirable sites more accessible for water molecules. The affinity of water to some of these sites may be weaker than the water–water attraction, resulting in the association of preresident water molecules to form larger clusters.

## Water-Vapor Sorption Kinetics and Transmission Rate

It is generally agreed that a sigmoidal sorption curve (plot of mass uptake versus the square root of time) with an inflection point at about 50% equilibrium sorption is indicative of the presence of non-Fickian diffusion. This behavior prevails particularly in glassy polymers due to the time-

dependent relaxation when the penetrant causes an extensive swelling in the polymer matrix.[31] Water-vapor sorption curves of nylon 6,6 (Fig. 4) displayed a convex curvature toward the abscissa during the early sorption (<1% of the equilibrium amount sorbed), but then increased linearly before approaching the equilibrium. The convex feature in the sorption curve may be due to the onset of a glass transition relaxation of the polymer, which is at approximately 22°C at 1% moisture content (Fig. 5) or from water vapor loss when the test chamber was opened for positioning the test film. To assess the sluggishness in the vapor-pressure buildup, film samples of various thicknesses (19.1, 25.4, 38.1, and 50.8 $\mu$m) were tested at 35°C, 75.0% RH. Since the time required to reach equilibrium will be relatively longer for a thicker sample as compared to the thinner one, the effect of sluggish vapor-pressure buildup should be less significant with the thicker sample. The plot of the fraction moisture uptake ($M_t/M_\infty$) versus $(t/l^2)^{0.5}$ displayed a less sigmoidal curvature in thicker samples (Fig. 6), suggesting the likelihood of a vapor-pressure lag during the early phase of sorption. Analysis of variance (ANOVA), however, showed that the slopes (between 0.2 and 0.6 weight fraction) among these films were not significantly different ($P > 0.05$). Accordingly, the diffusion coefficients ($D$) calculated from the slopes will not be significantly affected. Values for



**Figure 4** Representative sorption curves for water in nylon 6,6 film at 0.75 and 0.43 $a_w$, when the films were exposed to various temperatures.

**Figure 5** Glass transition temperature of nylon 6,6 film as related to moisture content. The solid line is derived from eq. (9) when $k = 0.0672 + 0.988\ W_1$.

apparent $D$ were calculated according to eq. (8)[31,32]:

$$\frac{M_t}{M_\infty} = \frac{4D}{\pi^{1/2}}\left(\frac{t}{l^2}\right)^{1/2} \tag{8}$$



**Figure 6** Representative sorption curves for water in nylon 6,6 film at 35°C, 0.75 $a_w$, showing the effect of film thickness.



**Figure 7** Variation of diffusion coefficients for water in nylon 6,6 film as related to water activity and temperature.

where $M_t$ and $M_\infty$ are the amount of moisture sorbed at time $t$ and at equilibrium, respectively, and $l$ is the thickness of the film samples. Linear relationships between $D$ and $a_w$ were observed at 25, 35, and 45 °C (Fig. 7).

WVTR (g m$^{-2}$ d$^{-1}$) at 15, 25, and 35°C as functions of upstream RH are presented in Figure 8. At 15°C, the change in the transmission rates was minimal when RH was low, but increased rapidly at RH above ≈ 60%. In contrast, transmission rates at higher temperatures were more responsive to RH variation. The discontinuities became less discernible at higher temperatures, which may be attributed to the relaxation of the polymer chain segments as the polymer went through the $T_g$ (see next section). However, this cannot be the sole reason since at 25 and 35°C (with corresponding discontinuities at ≈ 60 and 55% RH), the glass-to-rubber transition would have been completed. This semicrystalline polymer has a broad glass transition zone. Note that the glass transition region of nylon 6,6 at 57.0% RH spanned from −0.8 to 20°C, and for 75.0% RH from minus;13 to 7°C (Fig. 9).

When plotted as a function of the RH, the permeability coefficients (g mm cm$^{-2}$ d$^{-1}$ Pa$^{-1}$) decreased with the RH, but increased above ≈ 60% RH (Fig. 8 insert). Similar permeability minima were reported by Stannett et al.[29] on water-vapor permeation in polyacrylonitrile film. The permeability coefficient is the product of diffusion and

**Figure 8** Water-vapor transmission rate (WVTR) as related to RH and temperature. The insert shows permeability coefficients when the WVTR data were normalized to the same water-vapor pressure. Abscissa values are RH on the upstream side of the permeability cell (downstream RH = 0%).

solubility coefficients (g/g Pa), that is, $P = D \times S$. Since $D$ increased linearly with $a_w$ (Fig. 7), the minima observed for $P$ cannot be due to the variation of $D$. Interestingly, when the moisture content data were transformed into solubility coefficients and plotted as a function of $a_w$, no minimum was observed (results not shown). The apparent discrepancy may be because the solubility coefficient derived from the moisture-sorption isotherms encompassed the entire population of the water sorbed, including the highly immobile water fraction sorbed at low $a_w$ and the more mobile fraction at high $a_w$. Since only the relatively mobile permeant molecules participated in the permeation, the solubility data derived from the sorption isotherms may not truly represent the populations of water that were involved in the permeation process.

At low RH, water sorption predominantly took place at a limited number of active sites when the polymer was still present in a glassy state. The mobility of water at this stage is limited due to the strong association with the active sites. As RH increased and water clusters at these sites started to grow, the available free volume for water diffusion decreased. This may be the rationale for a permeability decrement at low RH.

When the moisture content of the polymer increased to a level such that the $T_g$ dropped below the test temperature, the polymer would expose more active sites for sorption due to extensive plasticization. The concomitant swellings may account for the rapid increase in permeabilities at higher RH. Moreover, the partial immobilization effect imposed on the penetrant by the active sites may become less influential as these sites are saturated with water.

## DSC Results

The $T_g$ of nylon 6,6 films as a function of moisture content are summarized in Figure 5, showing the $T_g$ depression of the polyamide caused by water sorption. Samples equilibrated at 100% RH showed a sharp endothermic peak at 0°C when they were scanned from subzero to higher temperatures (data not shown). This peak was not observed for samples equilibrated to 84.3% RH and below, indicating that water molecules sorbed above this RH were freezable and relatively more mobile than those sorbed at lower RH.

The Gordon–Taylor equation was used to describe the $T_g$ depression effect caused by the sorption of water[33–35]:

$$T_g = \frac{W_1 T_{g1} + k(1 - W_1)T_{g2}}{W_1 + k(1 - W_1)} \qquad (9)$$



**Figure 9** Thermograms of nylon 6,6 near glass transition regions as influenced by RH (plots are shifted for clarity). The increasing $\Delta C_p$ with RH is evident.

**Figure 10**   Infrared spectra of original and drawn nylon 6,6 films measured at room temperature after equilibrating at 25°C, 11.0% RH.

where $W_1$ is the water weight fraction and $T_{g1}$ is the glass transition temperature of the amorphous water ($-135$°C), and $T_{g2}$, of the dried polymer. Constant $k = \Delta C_{p2}/\Delta C_{p1}$, where $\Delta C_{p1,2}$ represent the change in the heat capacity at $T_{g1,2}$, respectively. Equation (9) did not describe the $T_g$ data adequately since $k$ values increased with increasing $W_1$. This equation, derived for binary mixtures which obey the law of a regular solution,

may not be appropriate for a system where specific interactions between the polymer and the absorbed species exist. It is generally agreed that the sorbed water is capable of disrupting hydrogen bonding between the polyamide groups, resulting in a large decease in $T_g$.[36] The progressive increment of $\Delta C_{p2}$ when the water content increased can be seen in Figure 9. The variation of



**Figure 11**   Infrared spectra of nylon 6,6 films at room temperature from 2600 to 3800 cm$^{-1}$ wavenumber, showing the evolution of water-absorbance bands as moisture content of the samples increased. Samples were equilibrated at 25°C.



**Figure 12**   Positions of amide I and hydrogen-bonded N—H stretching peak maxima of drawn samples measured at room temperature as related to RH. Samples were equilibrated at 25°C.

**Figure 13** Mechanism of water sorption in nylon as proposed by Puffr and Sebenda: (1) firmly bound water; (2) loosely bound water; (3) sites for capillary condensed water. (A) Dry nylon; (B) nylon exposed to moisture (adapted from ref. 42).

$k$ in eq. (9) may be attributed to this moisture-content dependence of $\Delta C_{p2}$.

**Infrared Study**

Infrared spectra of the original and drawn nylon films were highly similar to each other, except that some peaks from the original sample were saturated (Fig. 10). Peaks at 3310 cm$^{-1}$ (strong) and 3444 cm$^{-1}$ (weak at shoulder) were assigned to hydrogen-bonded N—H stretching and free N—H stretching modes, respectively.[14,37,38] As shown in Figure 11, the broad band due to water (3700–3000 cm$^{-1}$)[6,39] evolved progressively when RH increased, overlapping the N—H stretching bands and amide II overtone (3080 cm$^{-1}$). Although the amide II shifted to higher frequencies with increasing moisture content, direct interpretation of this shift was hindered by the mixed mode of this band. This band is believed to be composed of N—H in-plane bending (43–60%) and the C—N stretching (26–40%) with smaller contributions from C$^{\alpha}$—C and C$^{\alpha}$—N stretching.[40]

No such interference was seen, however, on the amide I peak, which was largely due to C=O stretching.[37,38,40] The dramatic shift of the amide I peak to lower frequencies with increasing RH substantiated the enhancement of hydrogen bonding to the carbonyl group (Fig. 12).[41] A frequency shift was also observed with the bonded N—H stretching mode located at ≈ 3310 cm$^{-1}$. The increase in its frequency (Fig. 12) with the RH showed that the average hydrogen-bond strength to the N—H group was weaker in the presence of moisture content than in its ab-

sence.[37,38] This is in agreement with the model proposed by Puffr and Sebenda (Fig. 13).[42] In their model, a water molecule will first form double hydrogen bonds with two C=O groups at low $a_w$ and is considered to be firmly bound water. The other two molecules of water will then form bridges between the already hydrogen-bonded C=O groups and the hydrogen atoms of N—H groups, and they may be classified as less tightly bound water.

## CONCLUSIONS

In this work, the sorption and transport of water in nylon 6,6 films as functions of the RH and temperature were studied. Water-vapor transmission rates were enhanced above the intermediate RH primarily due to changes related to the glass transition. DSC measurements showed that water acted as an effective plasticizer in lowering the $T_g$ of the polyamide. Evidence from Fourier transform infrared spectroscopy suggested that interactions of water with nylon 6,6 took place at the amide groups. Based on the frequency shift of amide I and hydrogen-bonded N—H bands, moisture sorption reduced the average hydrogen-bond strength to the N—H groups, while an increase was observed for the C—O groups.

## REFERENCES

1. Robertson, G. L. Food Packaging Principles and Practice; Marcel Dekker: New York, 1993; p 47.
2. Sfirakis, A.; Rogers, C. E. Polym Eng Sci 1980, 20, 294.
3. Bretz, P. E.; Hertzberg, R. W.; Manson, J. A.; Ramirez, A. In Water in Polymers; Rowland, S. P., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1980; pp 531–553.
4. Starkweather, H. W. In Water in Polymers; Rowland, S. P., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1980; pp 433–440.
5. Schwartzberg, H. G. In Food Packaging and Preservation, Theory and Practice; Mathlouthi, M., Ed.; Elsevier: New York, 1986; pp 115–135.
6. Khanna, Y. P.; Day, E. D.; Tsai, M. L.; Bray, R. G.; Vasanthan, N.; Vaidyanathan, G. Presented at Future-Pak 96, The 13th International Schroeder Conference on Packaging Innovations, November 1996.
7. Gavara, R.; Hernandez, R. J. J Polym Sci B 1994, 32, 2375.
8. Hernandez, R. J. J Food Eng 1994, 22, 495.
9. Liu, K. J.; Giacin, J. R.; Hernandez, R. J. Pack Technol Sci 1988, 1, 57.
10. Snider, O. E.; Richardson, R. J. In Encyclopedia of Polymer Science and Technology: Plastics, Resins, Rubbers; Bikales; N. M.; Conrad, J.; Ruks, A.; Perlman, J., Eds.; Wiley: New York, 1969; Vol. 10, pp 347–460.
11. Hernandez, R. J.; Giacin, J. R.; Grulke, E. A. J Membr Sci 1992, 65, 187.
12. Jin, X.; Ellis, T. S.; Karasz, F. E. J Polym Sci B 1984, 22, 1701.
13. Hernandez, R. J.; Gavara, R. J Polym Sci B 1994, 32, 2367.
14. Garcia, D.; Starkweather, H. W. J Polym Sci B 1985, 23, 537.
15. Brown, G. L. Water in Polymers; Rowland, S. P., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1980; pp 440–450.
16. Orofino, T. A.; Hopfenberg, B.; Stannett, V. J Macromol Sci B 1969, 3, 777.
17. Flory, P. J. Principles of Polymer Chemistry; Cornell University: Ithaca, NY, 1953; pp 511–514.
18. Gedde, U. W. Polymer Physics; Chapman & Hall: London, UK, 1995; p 63.
19. Cowie, J. M. G. Polymers: Chemistry and Physics of Modern Materials, 2nd ed.; Blackie: Glasgow, UK, 1991; p 166.
20. Tager, A. Physical Chemistry of Polymers; MIR: Moscow, 1978; pp 430–431.
21. Kiranoudis, C. T.; Maroulis, Z. B.; Tsami, E.; Marinos-Kouris, D. J Food Eng 1993, 20, 55.
22. Weisser, H. In Properties of Water in Foods; Simatos, D.; Multon, J. L., Eds.; Maritus Nijhoff: Dordrecht, Netherlands, 1985; pp 95–118.
23. Lim, L. T.; Tang, J.; He, J. J Food Sci 1995, 60, 810.
24. Van den Berg, C. In Properties of Water in Foods; Simatos, D.; Multon, J. L., Eds.; Martinus Nijhoff : Dordrecht, Netherlands, 1985; p 119.
25. Tsami, E.; Marinos, K. D.; Maroulis, Z. B. J Food Sci 1990, 55, 1594.
26. Toledo, R. T. Fundamentals of Food Process Engineering, 2nd ed.; Van Nostrand Reinhold: New York, 1991; p 468.
27. SAS Institute Inc.; SAS User's Guide, Version 6.03; SAS Institute: Cary, NC, 1988.
28. Zimm B. H.; Lundberg, J. L. J Phys Chem 1956, 60, 425.
29. Stannett, V.; Haider, M.; Koros, W. J.; Hopfenberg, H. B. Polym Eng Sci 1980, 20, 300.
30. Starkweather, H. W. Macromol Sci B 1969, 3, 727.
31. Crank, J. The Mathematics of Diffusion, 2nd ed., Oxford University: Oxford, England, 1975.
32. Meares, P. J Appl Polym Sci 1965, 9, 917.
33. Yang, H.; Yetter, W. Polymer 1994, 35, 2417.
34. Moy, P.; Karasz, F. E. In Water in Polymers; Rowland, S. P., Ed.; American Chemical Society: Washington, DC, 1980; pp 505–513.
35. Gordon, J. M.; Rouse, G. B.; Gibbs, J. H. ; Risen, W. M. J Chem Phys 1977, 66, 4971.
36. Marom, G. In Polymer Permeability; Y. Comyn, Ed.; Elsevier: New York, 1985; pp 341–374.
37. Coleman, M. M.; Painter, P. C. In Polymers: Polymer Characterization and Analysis; Kroschwitz, J. I., Ed.; Wiley: New York, 1990; pp 371–403.
38. Skrovanek, D. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. Macromolecules 1985, 18, 1676.
39. Garton, A. Infrared Spectroscopy of Polymer Blends, Composites and Surfaces; Hanser: New York, 1992; p 62.
40. Yu, H. H.; Fina, L. J. Macromolecules 1994, 27, 6192.
41. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. Introduction to Spectroscopy, 2nd ed.; Saunders: New York, 1996; p 55.
42. Puffr, R.; Sebenda, J. J Polym Sci C 1967, 16, 79.