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Implications of Dielectric Response for the Mechanism of Changes in Oxygen Transport due to Traces of Moisture in Amorphous Nylons

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ABSTRACT: The reduction of O_2 transport due to the presence of trace amounts of moisture correlates with the suppression of the dielectric γ-relaxation in the amorphous nylon 6-I/T(70/30). This relaxation corresponds to motions involving the aliphatic regions of the polymer. Water molecules alter the interaction between amides on neighboring chain segments. Low moisture levels reduce the mobility of aliphatic chain segments and thus reduce oxygen transport through these regions.

Introduction

The polyamide derived from hexamethylenediamine and a 70/30 mixture of isophthalic and terephthalic acids, nylon 6-I/T(70/30), is amorphous. Its hydrophilic character combined with a relatively low permeability to oxygen makes it an attractive candidate for packaging certain foods. The sorption isotherm for moisture shown in Figure 1 is almost linear at low relative humidities and curves upward at higher humidities. This is characteristic of many hydrophilic polymers and is attributed to the tendency of the absorbed water molecules to form small clusters at the higher moisture levels.[1] The gain in weight at saturation is between 9 and 10%.

Blatz[2,3] has reported a decrease in the oxygen permeability with humidity, even at low levels of humidity. As shown in Figure 2, the permeability is reduced by about half between zero and 30% relative humidity or a weight gain of 2%. At higher humidities, there was a small further decrease in the permeability. This is especially noteworthy since moisture increases the permeability of a number of other polymers to oxygen.[2,3] These measurements were done on a Modem Controls Ox-Tran 10/50 instrument at 30 °C.[3] Permeability is the product of sorption and diffusion. We do not know how these separate factors are affected by moisture.

We have used dielectric measurements to gain an understanding of this phenomenon.

Experimental Section

The samples had been prepared by extrusion through a flat die onto a chill roll without annealing. There was a slight orientation in the machine direction.

The polymer film samples (0.25 mm thick) were dried by heating slowly to 150 °C in a vacuum oven with a slow dry-nitrogen purge. The samples were kept at 150 °C for 1 h and then allowed to cool to room temperature. The samples were then quickly transferred to glass desiccators with fixed relative humidities (3.4–97.3% range) maintained with saturated salt solutions at the bottom of the desiccator.[4] It was determined by differential scanning calorimetry (DSC) that the polymer remained amorphous under all conditions of temperature and humidity.

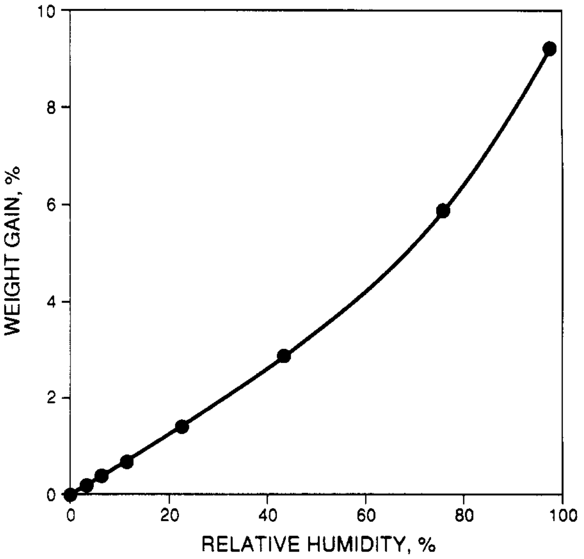

Figure 1. Sorption isotherm for nylon 6-I/T(70/30).

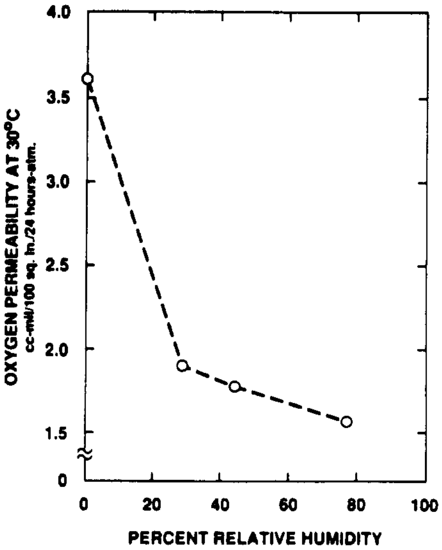

Figure 2. Dependence of permeability to oxygen on the relative humidity.

The samples were allowed to equilibrate to constant weight (typically in 10–14 days) prior to dielectric measurements. The samples were clamped between phosphor bronze disk electrodes (1.6-cm diameter), which were positioned with strips of poly(tetrafluoroethylene) and inserted into the variable temperature cell of our dielectric spectrometer. While the cell was maintained in an atmosphere of dry nitrogen, the tight clamping greatly retarded the loss of moisture at temperatures below the α-relaxation. Thus, the results reported here are considered to represent a lower bound for the effects of humidity. All runs were carried out by rapidly cooling the cell to liquid-nitrogen temperature and then ramping the temperature upward at a rate of about 1.5 °C/min during the dielectric measurements. The

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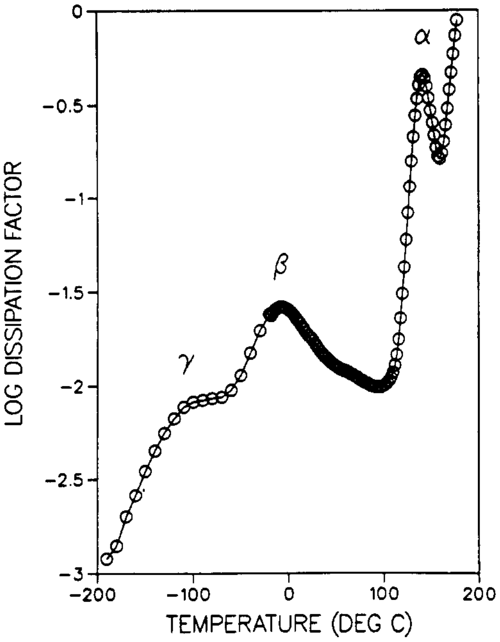

Figure 3. Temperature dependence of the dielectric dissipation factor (tan δ) at 1 kHz for nylon 6-I/T(70/30) conditioned to 11.3% RH.

dielectric measurements were made in the frequency range 10^2–10^6 Hz and temperature range −190 to +180 °C with a custom-built dielectric spectrometer employing a Hewlett-Packard LCR meter (Model 4274A) whose output was fed to a personal computer.

Dielectric Relaxations

As shown in Figure 3 for a sample conditioned to 11.3% relative humidity (RH), nylon 6-I/T exhibits three dielectric loss peaks. The additional increase in the dissipation factor above 160 °C is due to the onset of ionic conductivity. The α-relaxation near 140 °C corresponds to the glass transition and reflects the onset of large-scale motions of chain segments. The β-relaxation near −10 °C is attributed to motions of labile amide groups. The γ-relaxation, which appears as a shoulder near −100 °C, is due to motion of the aliphatic chain segments in the hexamethylenediamine moieties. All of these relaxations are analogous to those that have been observed in all-aliphatic polyamides.[5]

The α-relaxation shifts to lower temperatures with increasing humidity, and the height of the loss peak of the dry specimen was higher than that in those containing moisture (Figure 4). The fact that the shape of the loss peak is similar at all humidities indicates that moisture was not being lost. If it had been, the peaks would have been flattened. The temperature of the α-relaxation is a linear function of relative humidity decreasing from 154 °C at 0% RH to 60 °C at 100% RH (Figure 5). The glass transition measured in DSC scans at 10 °C/min was reduced from 128 °C in a dry sample to 48 °C in one conditioned to 97% RH.

The effect of moisture on the α-relaxation is similar to that in nylon 66 with one exception.[6] In both cases, the temperature of the α-relaxation decreases by nearly 100 °C between dryness and saturation and depends linearly on relative humidity. In nylon 66 the relaxation passes through room temperature in the midrange of relative humidity, whereas in nylon 6-I/T(70/30) it is always well above room temperature. This means that many properties are much less sensitive to humidity at room temperature.

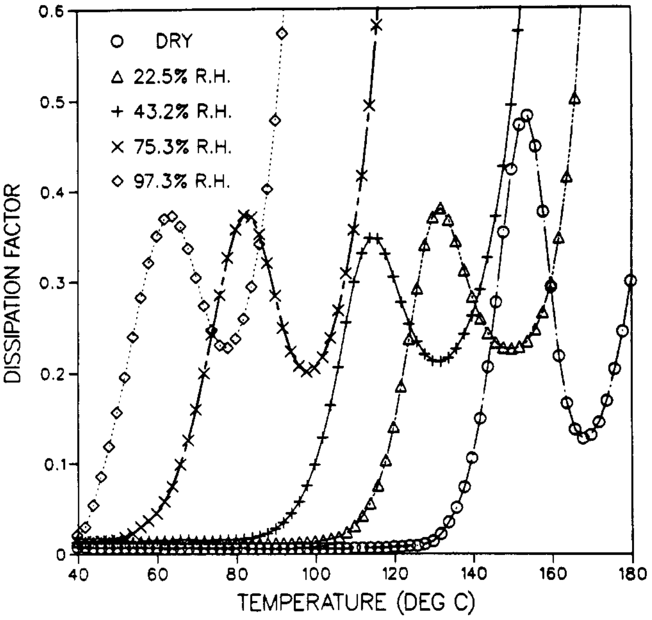

Figure 4. Dependence of the dissipation factor at 1 kHz in the region of the α-relaxation on temperature and humidity.

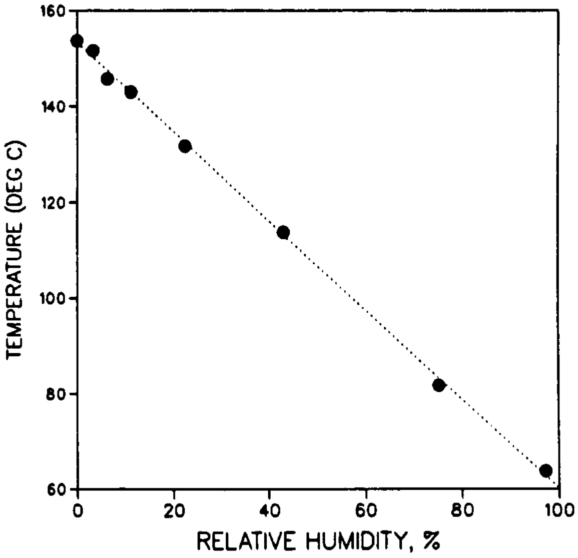

Figure 5. Dependence of the temperature of the α-relaxation on the relative humidity.

It is shown in Figure 6 that low levels of humidity between zero and 22.5% decrease the strength of the γ-relaxation and increase the strength of the β-relaxation. Additional changes between 22.5 and 97.3% RH were minor. Moisture decreases the temperature of the β-relaxation, especially at low relative humidities (Figure 7). There is no clearly defined effect of humidity on the temperature of the γ-relaxation since the loss peak is no longer resolved above about 10% RH. In a study of similar relaxations in nylon 66, data taken over a range of frequencies were used to separate the overlapping β- and γ-relaxations.[7] In that case, conditioning a dry sample to 20% RH was found to reduce the temperature of the γ-relaxation by about 20 °C with small additional reductions at high humidities.

The dependence of the apparent activation energies on the relative humidity is shown in Table I. For each of the three relaxations, the activation energy decreases with increasing humidity. These data are very similar to those that have been reported for the corresponding relaxations in nylon 66[7] where the dependences of the activation

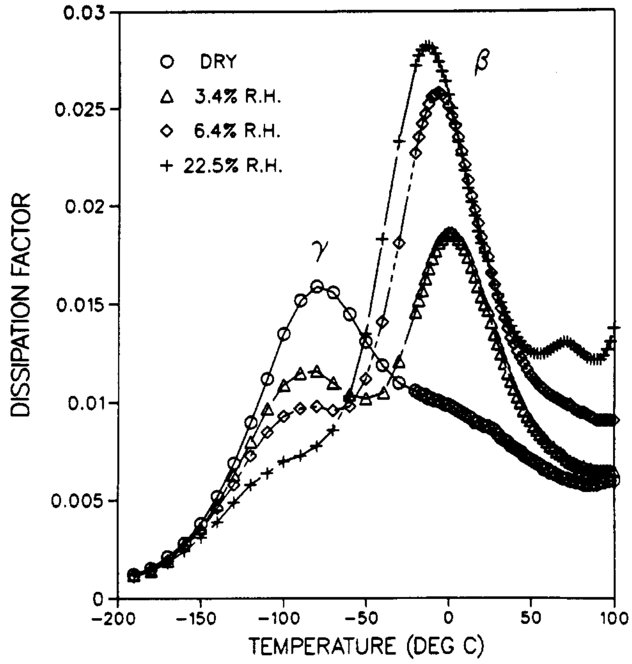

Figure 6. Effect of low levels of humidity on the γ- and β-relaxations.

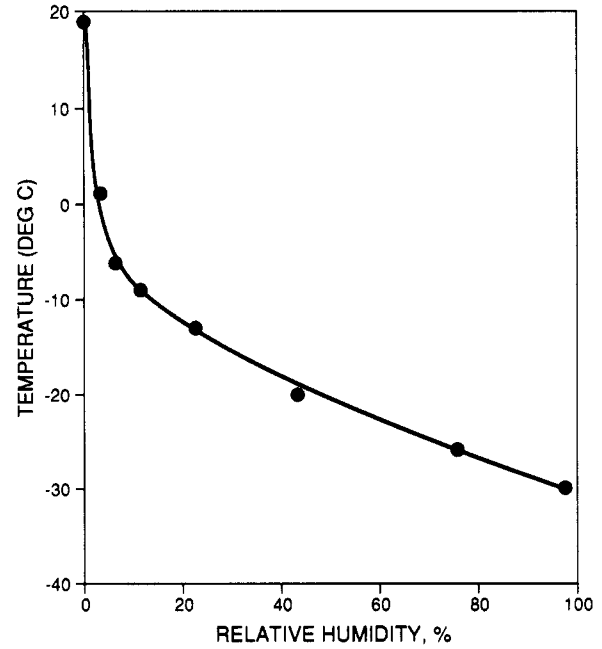

Figure 7. Dependence of the temperature of the β-relaxation on the relative humidity.

energies on humidity were related to changes in the stretched exponential function.

In a study of dry samples of the closely related homopolymer, nylon 6I, we found that for the β- and γ-relaxations dielectric and dynamic mechanical data obeyed the same frequency–temperature relationship.[8] For the γ-relaxation, the activation energy corresponds to an activation entropy close to zero. This was attributed to noninteracting motions of local groups. It seems reasonable that short, aliphatic segments separated by amides and aromatic rings should have this characteristic. The activation energy for the β-relaxation corresponded to a small, positive activation entropy. This may reflect some cooperative character in the motions of the amide groups.

Table I
Apparent Activation Energies (kcal/mol)

relaxation	α	β	γ
dry	113	24	9.8
3.4% RH	113	16	8.0
6.4% RH	104.5	15	6.1
11.3% RH	106	13.5	6.8
22.5% RH	101	13	6.4
43.2% RH	74	14	
75.3% RH	73.5	13	
97.3% RH	58	12	

Discussion

We conclude that the action of moisture in reducing the permeability of nylon 6-I/T(70/30) to oxygen is associated with the suppression of the γ-relaxation, which is attributed to local motions of the aliphatic chain segments. It is the only one of the three relaxations that is affected in the right direction. Water increases the strength of the β-relaxation and moves the α-relaxation closer to room temperature.

The association of permeability to oxygen with motions of the aliphatic segments is reasonable since the sorption of oxygen is greater in aliphatic hydrocarbons than in aromatics or polar compounds. This can be viewed in terms of the cohesive energy density or the Hildebrand solubility parameter.[9] The solubility parameter of liquid oxygen is 7.2. The value for n-hexane is 7.3, and those of other n-alkanes are between 7 and 8. The parameter is about 9 for aromatic hydrocarbons and much larger for polar compounds such as amides.

At temperatures below the α-relaxation, water is an antiplasticer for nylon, increasing the modulus and reducing the strength of the γ-relaxation.[10] In nylon 66, absorbed water reduces the activation entropy for the γ-relaxation from a substantial positive value in the dry state to zero, the situation described above for nylon 6I.[11] It is believed that water forms bridges between amide groups that are mechanically stable at low temperatures. These bridges reduce the mobility of the adjacent aliphatic segments, increase the modulus, and reduce the permeability to oxygen. These conclusions are consistent with the work of Krizan and co-workers,[3] who found that increasing the length of the aliphatic segments increased the permeability to oxygen.

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