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The Dielectric Properties of Dry and Water-Saturated Nylon-12

K. PATHMANATHAN, J.-Y. CAVAILLÉ,* and G. P. JOHARI

Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

SYNOPSIS

The dielectric relaxation of 30% crystalline Nylon-12 of molecular weight 20,000 has been studied at frequencies from 12 Hz to 0.1 MHz and temperatures from 77 to 375 K, and the effect of water on the relaxation spectra has been investigated. Absorbed water increases both the rate and the intensity of both its α - and β -relaxation processes and increases the rate but decreases the intensity of its γ -relaxation process. These results are interpreted in terms of the hydrogen bonding effects of water on localized motions of dipoles in Nylon-12. The relatively large half-width of the α -relaxation, which becomes better resolved at high temperatures, is attributed mainly to the random distribution of crystalline regions in the polymer. It is suggested that water lowers the steric hindrance for the localized mode of dipolar reorientation and causes a redistribution of local sites such that the β -relaxation process grows at the expense of the γ -process.

Keywords: Nylon-12, dry and water-saturated, dielectric properties of • dielectric properties of dry and water-saturated Nylon-12 • absorption of water and dielectric relaxation of Nylon-12

INTRODUCTION

Interchain and intrachain hydrogen bonds in the structure of nylons predominantly determine the formation of crystalline, H-bonded sheets in their amorphous structures, and the absorption of water in them. Since the extent of H-bonding depends upon the number of amide groups, both the crystallinity and modification of the properties of nylons on absorption of water vary with variations in the chain lengths of the monomers or repeat units, as well as the conjugated states of the monomers themselves.

Dielectric properties of the various nylons are most prominently affected by H-bonding, and therefore have been studied by several workers.¹⁻¹⁰ Among these, McCall and Anderson⁴ studied a variety of conjugated nylons with varying numbers of $-\text{CH}_2$ groups, and provided mechanisms of dipolar

relaxation and dc conduction. Boyd and co-workers^{2,8} investigated the effects of absorption of H-bonded liquids—most importantly of water—in conjugated nylons and their plasticization by liquids, which reduce the interchain forces, and increase the segmental mobility.

Properties of Nylon-12 have been studied since 1973. It can contain up to 0.25 moles of water per mole of monomer at 298 K, an amount substantially less than that in nylons with repeat units of lower molecular weight. As part of our study of its relaxation behavior, we have investigated the effect of water on the dielectric properties of Nylon-12, which is reported here. An earlier paper has provided a study of its dynamic mechanical relaxation.¹¹ We further analyze these results in terms of the monomer chain length and H-bonding in the presence of water in Nylon-12.

EXPERIMENTAL

Sheets of 10 cm² and 1 mm thick Nylon-12 were provided by Atochem, Serquigny, France. Its molecular weight was 20,000, with about 100 monomer

* Present address: Centre de Recherches sur les Macromolécules Végétales, Domaine Universitaire, B.P. 53x-38041 Grenoble, Cedex, France.

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repeat units, and it contained at least 0.12 moles of water per mole of monomer. X-ray diffraction measurements showed that it was 30% crystalline in its as-received state.

Samples of Nylon-12 $30 \times 15.4 \times 1$ mm were cut and kept for 40 h at 294 K in a vacuum desiccator in order to remove as much water as possible in the first set of experiments, and for 24 h at 353 K in an H_2O -saturated atmosphere in order to allow it to absorb the maximum amount of water in the second experiment. The increase in the amount of H_2O was 16 mol % as determined previously.¹⁰ Thin indium plates, used as electrodes, were held by pressure clips on the flat sides of the sample. The capacitance and loss factor were measured by means of both a GR-1615 capacitance bridge and a Genrad 1689 impedance bridge, which was interfaced with an IBM computer. The hermetically sealed cell assembly has been described earlier^{12,13} as have the other experimental details. The temperature was controlled to within ± 0.1 K.

RESULTS

The permittivity ϵ' and loss ϵ'' of dry Nylon-12 and water-saturated Nylon-12 measured at fixed frequencies of 1 and 10 kHz over the temperature range from 77 to 373 K are shown in Figure 1. The ϵ'' plot for dry nylon shows three relaxation regions namely, α , β and γ , in the order of decreasing temperature. As the measurement frequency is increased from 1 to 10 kHz, the temperature of the α -relaxation peak increases from 339 to 346 K and its height increases from 1.234 to 1.508. The magnitude of β -relaxation process, which appears as a shoulder at $250 < T < 290$, in contrast, decreases when the frequency is raised from 1 to 10 kHz. The height of the shoulder, which is attributable to γ -relaxation processes, increases from 0.0223 to 0.0271 as the measurement frequency is increased. The increase in the measurement frequency from 1 to 10 kHz affects the magnitude of ϵ'' of water-saturated nylon qualitatively similar to that for dry nylon.

The water absorbed in Nylon-12 has a significant effect on all its three relaxation processes. First, it lowers the temperature of its α -relaxation peak from 339 to 321 K and its height from 1.234 to 0.838 for the 1 kHz measurement. Second, it increases the magnitude of $\tan \delta$ for β -relaxation and shifts the ϵ'' shoulder due to it to a lower temperature; and third, it decreases the height of the shoulder due to γ -relaxation process from 0.0223 to 0.0116, and shifts it to lower temperatures.

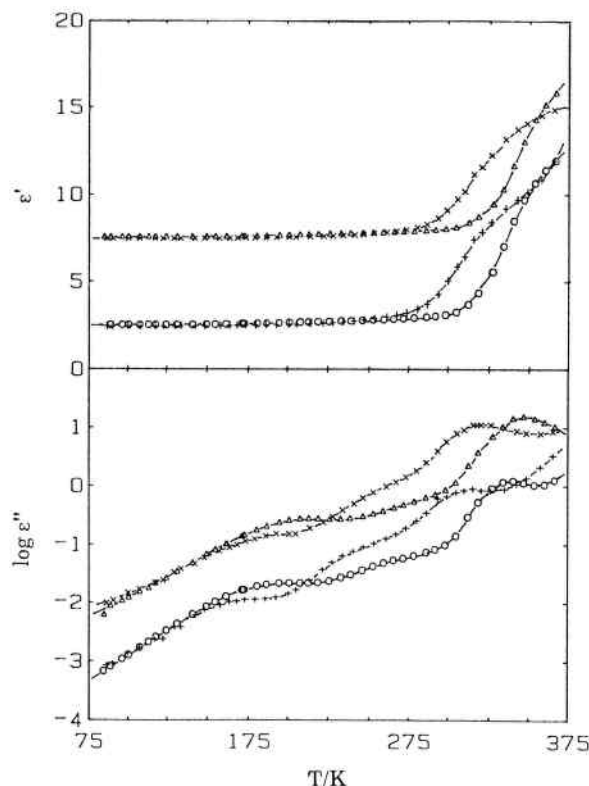


Figure 1. Plots of ϵ' and ϵ'' of dry and water-saturated Nylon-12 measured at fixed frequencies of 1 kHz (\circ for dry and $+$ for wet Nylon-12) and 10 kHz (Δ for dry and \times for water-saturated Nylon-12). The data for 1 kHz are to scale and those for 10 kHz have been shifted upward by 5 units for ϵ' and one logarithmic cycle for ϵ'' .

Isothermal spectra of the α -process for the dry and water-saturated Nylon-12 at several temperatures are shown in Figure 2. In these spectra, the contribution to ϵ'' from dc conductivity, which dominates the low frequency region, is too large to allow an accurate estimate of the half-width of the peak. Nevertheless, an approximate value of the half-width is 3.75 decades in both the dry and water-saturated nylons. This unusually large half-width for the α -relaxation process likely is caused by the 30% crystallinity of Nylon-12, but additional effects such as a distribution of the environment of >C=O and —NH_2 and H_2O may also broaden this peak.

The ϵ'' spectra of the β -relaxation process in both dry and water-saturated Nylon-12 given in Figure 3 also do not show a peak. Instead the process appears as a shoulder to the main peak. At the low-frequency side of the spectra, contribution to ϵ'' from the α -relaxation process dominates at all temperatures for

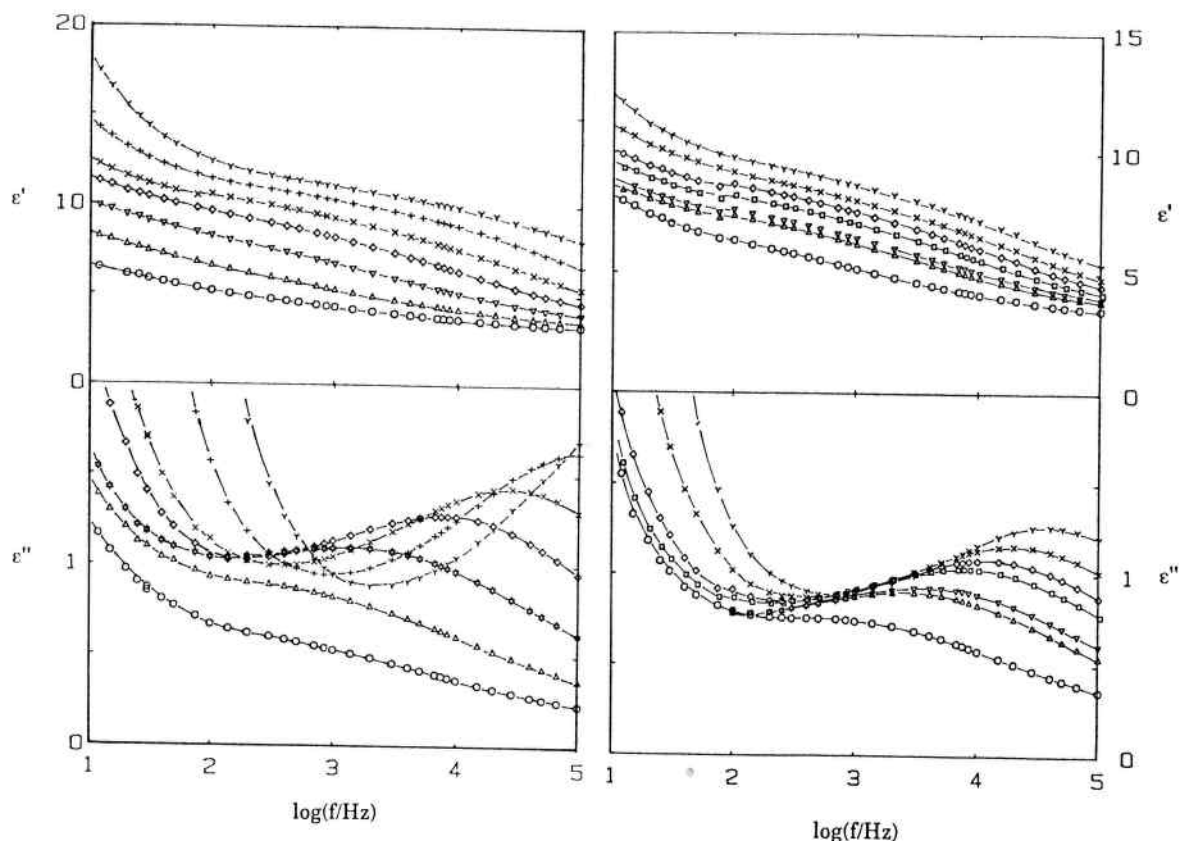


Figure 2. Spectra of ϵ' and ϵ'' in the α -relaxation regions of dry (on the left) and water-saturated (on the right) Nylon-12. The temperature for the spectra are: \circ , at 318.8 K; Δ , at 325.9 K; \star , at 333.7 K; \diamond , at 340.9 K; \times at 347.3 K; $+$ at 354.6 K and Y at 362.3 K for dry Nylon-12; and \circ , at 302.1 K; Δ , at 309.7 K; ∇ , at 313.3 K; \square , at 318.2 K; \diamond at 322.4 K; \times , at 327.1 K; and Y , at 332.9 K, for water-saturated Nylon-12.

the water saturated sample. For dry Nylon-12 this contribution is observed only at high temperatures.

The isothermal spectra for the γ -process for dry Nylon-12 is shown in the left-hand side of Figure 4, and those for the γ processes of the water-saturated Nylon-12 are shown in the right hand side of Figure 4. The spectra of both nylons are broad at low temperatures and their half-width decreases and the height increases with increasing temperature. The contribution to ϵ'' from the β -relaxation process at high temperatures appears significant at the low-frequency side of the spectra, and consequently ϵ'' increases with decreasing frequency.

The ϵ'' peak frequency f_m for the various relaxation processes is plotted against the inverse of temperature in Figure 5. Here, the relaxation frequency for the α -process in the dry nylon follows a VTF relation¹⁴:

$$f_m = A \exp[-B/(T - T_0)],$$

with $A = 0.471$ GHz, $B = 505.4$ K, and $T_0 = 295$ K. The relaxation frequency of the water-saturated nylon is also expected to obey the same relation; but the limited data and their accuracy do not provide satisfactory values of A , B , and T_0 . The relaxation rate for the γ -process follows an Arrhenius relation with $f_0 = 3.9 \times 10^{11}$ Hz and $E = 28.1$ kJ/mole for the dry nylon, and $f_0 = 1.04 \times 10^{11}$ Hz and $E = 24.2$ kJ/mol for the water-saturated nylon.

In order to determine whether or not the shape of the relaxation spectrum changes with temperature, normalized plots of the isothermal spectra for the α -process seen in Figure 2, are plotted in Figure 6. These plots show that the half-width of the peak decreases with increasing temperature for both the dry and water-saturated Nylon-12. It is interesting to note that this decrease in the half-width of the α -relaxation process in the dry nylon (top set of plots) is due to the narrowing of the spectrum at both the low-frequency and high-frequency sides of

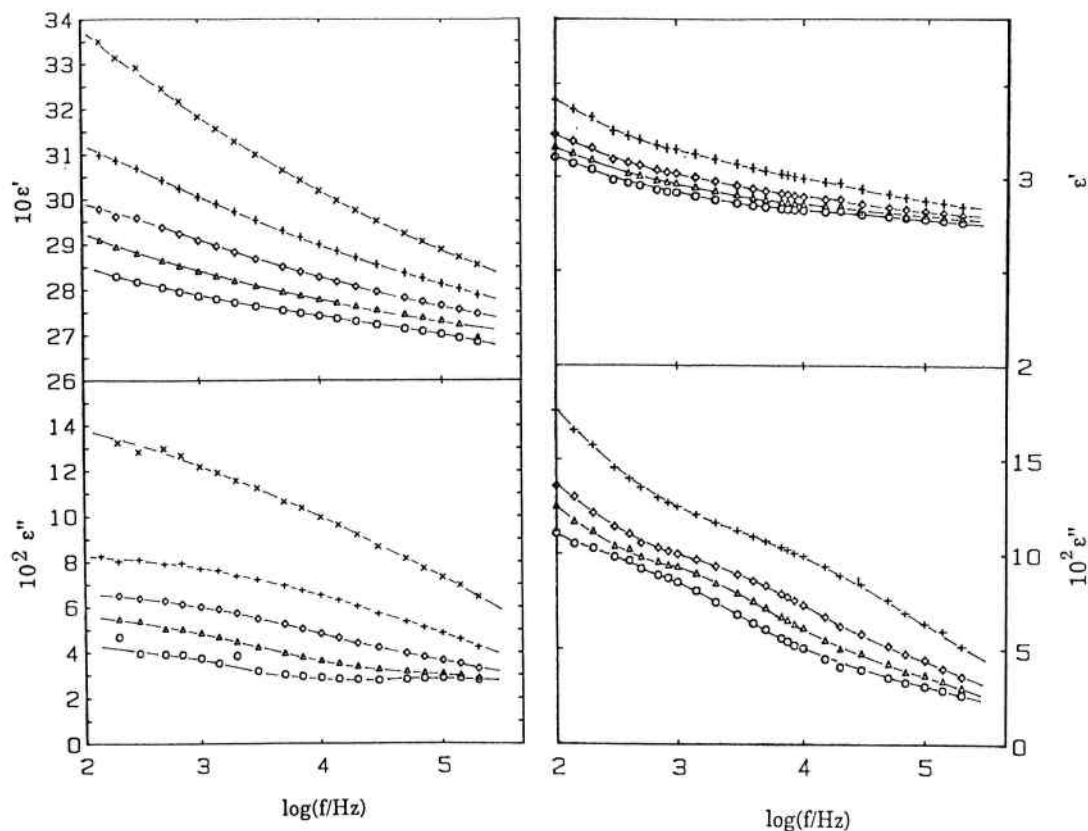


Figure 3. Spectra of ϵ' and ϵ'' in the β -relaxation regions of dry (on the left) and water-saturated (on the right) Nylon-12. The temperature for the spectra are: \circ , at 247.4 K; Δ , at 261.1 K; \diamond , at 275.4 K; $+$, at 289.1 K and \times , at 300.1 K for dry Nylon-12 and \circ , at 243.3 K; Δ , at 248.3 K; \diamond , at 254.7 K; and $+$, at 266.1 K, for water-saturated Nylon-12.

the peak, in contrast with the water-saturated nylon (bottom set of plots) where it is due predominantly to the narrowing of the spectrum at the low-frequency side of the peak. For both cases, the narrowing and improved resolution of the ϵ'' peak with increase in temperature imply a decrease in the contribution to ϵ'' from dc conductivity and/or another relaxation process at low frequencies.

DISCUSSION

The relaxation behavior of nylons, as mentioned, is generally determined by the length of the repeat unit and the number, position and distribution of the amide groups in the polymer chain itself. The length of the carbon chain between the repeat units determines particularly the rate of segmental motions within the repeat unit, and here van der Waals interactions are important. Both the position and distribution of NH_2 groups determine particularly the motion of one repeat unit with respect to the other,

and here, the intrachain and interchain H-bonding are important. These differences become clear from the data given in Table I, where the temperatures of the various relaxation peaks observed for Nylon-6, Nylon-6,6, and Nylon-6,10 are given for a comparison against those for Nylon-12.

McCall and Anderson⁴ have already shown that the dielectric properties of polyamides are dominated by the amorphous parts of the structure, and Boyd² and Curtis¹ have concluded that completely dry nylons do not exhibit a β -relaxation. They noted that as the concentration of water in the nylons is increased, the strength of its α -relaxation remains unaffected, but that of its β -relaxation increases while that of its γ -relaxation decreases. In Figures 1–4 there is no clear evidence for the presence of a β -relaxation peak in dry Nylon-12, but there is certainly a significant contribution from the β -relaxation process at temperatures lower, and frequencies higher, than those of the α -relaxation peak. Following the observations of Boyd and Curtis, this would seem to indicate that a certain amount of H_2O re-

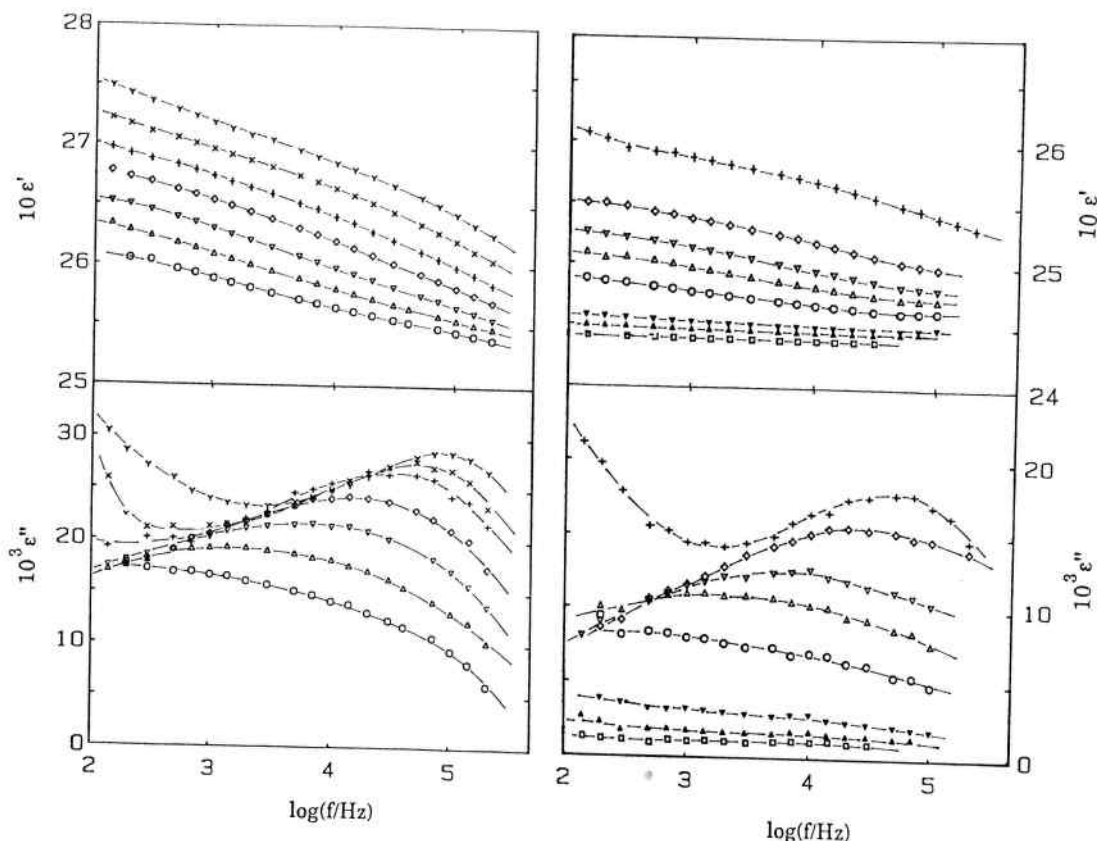


Figure 4. Spectra of ϵ' and ϵ'' in the γ -relaxation regions of dry (on the left) and water-saturated (on the right) Nylon-12. The temperature for the spectra are: \circ , at 173.4 K; Δ , at 182.4 K; ∇ , at 191.0 K; \diamond , at 200.0 K; $+$, at 208.1 K; \times , at 217.3 K and Y , at 225.7 K, for dry Nylon-12 and \square , at 93.3 K, Δ , at 108.1 K, ∇ , at 123.4 K, \circ , at 152.1 K, Δ , at 167.8 K, ∇ , at 178.1 K, \diamond , at 190.8 K, and $+$ at 203.7 K for water-saturated Nylon-12.

mains bonded to the NH_2 groups in our dry Nylon-12. This of course would also entail that the rate of α -relaxation observed here for dry Nylon-12 is higher than expected and that the magnitude of the γ -relaxation is lower than expected.

The features of the three relaxation processes in Nylon-12 are qualitatively similar to those observed for other nylons, and hence a discussion of the mechanisms for these features would seem to be similar to that given in the literature.¹⁻⁹ Nevertheless, a number of quantitative differences, discussed in the following, provide further information on the dielectric behavior of the nylons.

The strength of the α -relaxation process in nylons is of course expected to vary with the number of dipolar groups per unit chain length, but it also varies with the number of crosslinks and chain entanglements in the amorphous phase, its crystal contents, its thermal history and the number and size of the crystallites in it. In Thomas' work¹⁵ on nylons, we find that nylons of low melting point also have

a low temperature for the α -relaxation peak. For example, Nylon-6 has a lower melting point and a lower temperature of its α -relaxation peak than Nylon-6,6, despite their similar constitutive formulae. From a detailed study of their mechanical relaxation behavior,¹¹ we concluded that the ratios of the melting point to the temperature of (mechanical), α -relaxation peak is nearly (and, probably, fortuitously) constant for the nylons and that this indicates that both melting and mechanical relaxation require breaking of intrachain and interchain H bonds. Increased crosslinking is expected to reduce the chain length between the junction points and to raise steric hindrance for the motion of dipoles. Thus, when an external electric field couples with the motion of a dipolar amide group, which diffuses as a result of segmental or micro-Brownian diffusion of the chain, one would expect that, because of the lesser number of amide groups per unit volume of the chain, the dielectric magnitude of the α -relaxation process in Nylon-12 would be lower than in

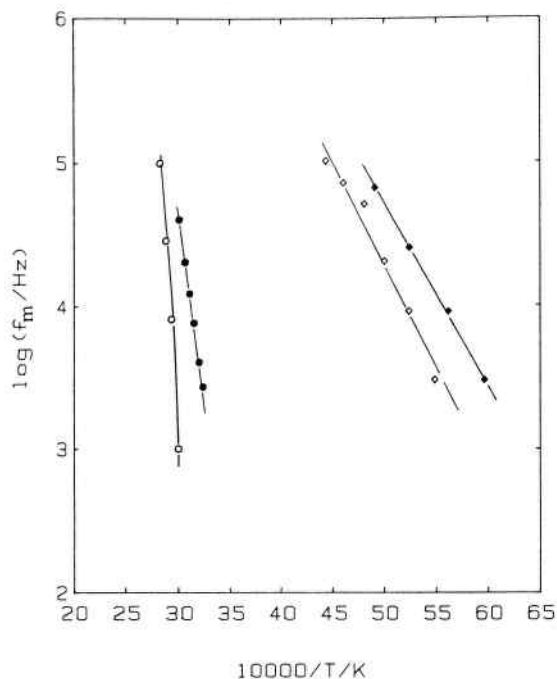


Figure 5. Plots of peak frequency against reciprocal temperature for the (○) α- and (◇) γ-processes. Open data points are for dry and filled points for water-saturated Nylon-12.

Nylon-6 or Nylon-6,6, but the rate of motion faster or, equivalently, the temperature of the α-peak lower. The ratio of this temperature of the α-relaxation peak to T_g should remain nearly constant for the various nylons, but since their T_g is not accurately known, such ratios are not readily comparable.

The β-relaxation process is clearly associated with local modes of motions of dipolar segments of the chain and of water molecules in those regions of interchain packing where they form H bonds with >C=O and —NH_2 groups. Its unambiguous assignment to a certain dipolar motion is difficult and it seems necessary to consider its origin in terms of loosely-bonded sites, or low-density regions, and of the effect of water on them. In the amorphous phase of Nylon-12, formation of four H bonds with a water molecule requires 25 mol % water (i.e., one H_2O molecule per four amide groups). The 16 mol % water in the saturated Nylon-12 is clearly insufficient to bond with all H-bonding sites in the Nylon-12 matrix. Therefore, we deduce that water remains in an unclustered state in Nylon-12 and most likely is distributed as one molecule per >C=O and/or NH_2 group. If an H_2O molecule were to form a bridge

between similar or dissimilar groups of the same or different chains, the bridge would constitute local sites of high energy and entropy, where thermal motions of the water molecule about an axis coinciding with the H bond may occur. Since these water molecules are not tetrahedrally H-bonded to each other in the Nylon-12 amorphous matrix, one anticipates that their relaxation mechanism would be different from that in liquid water or in the various forms of ice.¹⁶ Since the β-relaxation is shifted to a lower temperature, or higher frequency, on saturation with water, the latter would seem to have a plasticizing effect on it. Thus the local motions of dipoles, we deduce, occurs jointly with those of water molecules but with a lowered rate.

We now discuss the mechanism for γ-relaxation in Nylon-12. Curtis¹ concluded that in addition to the $(\text{—CH}_2\text{—})_n$ sequences, dipolar amide groups, are partly responsible for the γ-relaxation process in Nylon-6,6. Observations of Kolarik and Jancek¹⁷

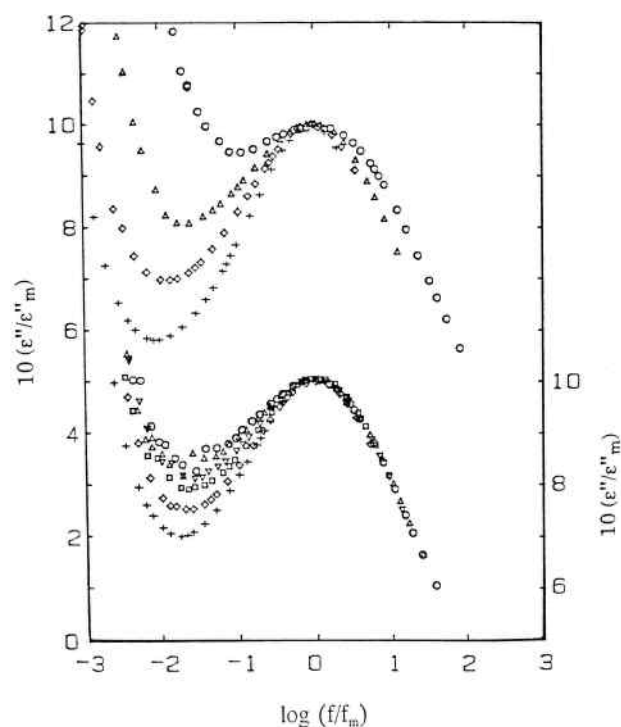


Figure 6. Normalized ϵ'' spectra for the α-process in dry and water-saturated Nylon-12. The temperature of the spectra are: ○, 333.7 K; △, 340.9 K; ◇, 347.3 K; and +, 354.6 K for dry Nylon-12, and ○, 309.7 K; △, 313.3 K; ▽, 318.2 K; □, 322.4 K; ◇, 327.1 K; and +, 332.9 K for water-saturated Nylon-12. The four sets of data in the plots on the top part are for dry Nylon-12 with scale on the left. The six sets of data in the plots in the lower part are for water-saturated Nylon-12 with scale on the right.

Table I. Comparison of Dielectric Properties of Various Conjugated Dry Nylons, Measured at 1kHz

Properties	Nylon-6	Nylon-6,6	Nylon-6,10	Nylon-12
$T_{\max,\alpha}$	—	344 ^{2 a}	347 ¹	340
$\epsilon''_{\max,\alpha}$	—	—	1.072 ^{1 a}	1.234
$T_{\max,\beta}$	261	266 ²	260 ¹	—
$\epsilon''_{\max,\beta}$	0.116 ⁶	—	—	—
$T_{\max,\gamma}$	200	177 ¹	176 ¹	195
$\epsilon''_{\max,\gamma}$	0.048 ⁵	—	—	(shoulder) 0.022
Crystallinity (wt %)	65	50	58	30
T_m (melting)	483	523	533	521
$T_{\max,\alpha}/T_m$	—	0.658	0.651	0.653
$R = \frac{\text{no. of NH}_2 \text{ groups}}{\text{no. of CH}_2 \text{ groups}}$	0.20	0.20	0.143	0.09

^a Extrapolated from high-temperature measurements.

on Nylon-66 and more of Varlet et al.¹¹ on Nylon-12 show that the height of the (mechanical) γ -peak decreases on the absorption of water. This is also observed for the (dielectric) γ -relaxation peak in Figure 4. Clearly our dielectric studies confirm the existence of the γ -peak in nylons. It is also interesting to note that the magnitude of the γ -relaxation process in Nylon-12 is nearly half of that in Nylon-6 (Table I). This seems to be related to the number of amide and other dipolar groups which are half as many in Nylon-12 as in Nylon-6. Thus, the ratio R of NH_2 groups to CH_2 groups, which in Nylon-12 is half that in Nylon-6 and Nylon-6,6, seems to correlate well with the height of the γ -peak. This further suggests that the mechanism of the mechanically observed γ -relaxation includes motions of the dielectrically active groups, such as the amide. It is remarkable that the height of the γ -relaxation shoulder decreases on water-saturation and its position shifts to a lower temperature as seen in Figure 1. The decrease in the height implies that there is an attrition in the number of dipolar groups whose faster motion appears as a γ -peak and a growth of those whose motion appears as a β -relaxation peak; i.e., water causes a redistribution of the sites where local motions occur with concomitant plasticization effect. These effects need to be considered also in light of crystallinity and any change in its amount on water saturation.

Water molecules in nylons may form two types of H bonds: (i) intrachain and (ii) interchain. One expects that the presence of water would cause an increase in local volume by separating those polymer

chains which H-bond directly, and are in close proximity in the dry polymer. Instead, a decrease in volume occurs, which comes into evidence from our density measurements,¹¹ in the following manner. The density of the as-received Nylon-12 was 1.0136 g cm⁻³. After saturation with water, its density was 1.0160 g cm⁻³. The as-received sample was then desiccated by keeping it in a container for 24 h at 353 K and, its density again determined. The final value was 1.0106 g cm⁻³. This means that the as-received sample contained 0.3% water and that the density of Nylon-12 increased by 0.54% on absorption of water on saturation. Since the density of bulk (free) water (0.998 g cm⁻³) is less than that (1.0106 g cm⁻³) of Nylon-12, this means that addition of water should normally lower the density of water-saturated Nylon-12. Since this density is instead increased, the average volume occupied by a H₂O molecule in "humid" Nylon-12 must be less than in bulk water. The increase in the density or a decrease in volume on saturation with water implies that the packing of polymer chains becomes more efficient in the presence of molecular water than in its absence. From similar observations for Nylon-6,6, Starkweather¹⁸ has concluded that insertion of a water molecule between the amide groups removes the steric requirement for the formation of H bonds and thus allows a relatively closer packing of the chains. We offer an alternative interpretation, namely, that water molecules in nylons occupy vacant sites in the loosely packed regions of their amorphous phase. A polymer chain may for example form an (intramolecular) ring of amide groups which

are in close proximity, and a water molecule may occupy a site inside this ring, while H-bonding itself to two amide groups. The plasticization effect of water or the shift of the α -relaxation to a lower temperature would therefore be a reflection of an increase in the probability of breaking H bonds, which we elaborate as follows. When a water molecule between two amide groups replaces one direct H bond between the groups by two H bonds *via* a water molecule, i.e., one H bond per amide group, breaking of only one H bond, out of twice as many bonds, would allow long-range motions of the chains, which are attributed to the α -relaxation process. Since the probability of breaking H bonds now becomes higher than in dry nylon, the relaxation frequency would increase and the temperature of the α -relaxation peak would decrease on the absorption of water.

The foregoing discussion leads to an inescapable conclusion, namely, that it is difficult to unambiguously identify the separate chemical groups whose thermally activated motions are seen as the various dielectric and mechanical relaxation processes in Nylon-12, and that collective effects of the addition of water on these processes can provide useful information on the local regions of mobility in the amorphous matrix. In general terms of relaxations in an amorphous matrix, we suggest that water in Nylon-12 plasticizes the local modes of motion of the polymer chains in a manner such as to reduce the number of dipolar segments involved in the faster (γ) relaxation process and increase those involved in the β -relaxation. A water molecule present in a vacant or loosely packed site of the polymeric chain matrix, while allowing a long-range motion of the chain segments, redistributes local regions of loose packing to the type in which faster motions become less probable.

CONCLUSIONS

The dielectric relaxation in Nylon-12 is quantitatively different from those in Nylon-6 or Nylon-6,6. This is due to the structural differences between the nylons that control the segmental motion of the chains. Water lowers the temperature of α -relaxation, increases its strength, creates regions in chain packing where the motions of water molecules and of other loosely-packed H-bonded segments appear

as a faster, β -relaxation process, and decreases both the temperature and strength of the γ -relaxation process and lowers its activation energy. Water thus increases the strength of the β -relaxation process at the expense of the γ -process by redistributing the loosely packed sites in the amorphous matrix.

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