Influence of Water on the Viscoelastic Behavior of Recycled Nylon 6,6

A. VALLÉS-LLUCH,[1] W. CAMACHO,[2] A. RIBES-GREUS,[1] S. KARLSSON[2]

[1] Department of Applied Thermodynamics, Escuela Técnica Superior de Ingenieros Industriales de Valencia, Apdo: 22012, 46071 Valencia, Spain

[2] Department of Polymer Technology, Royal Institute of Technology, Teknikringen 56-58, S-100 44 Stockholm, Sweden

Received 7 May 2001; accepted 26 November 2001

ABSTRACT: Nylons are highly sensitive to moisture, as water molecules are able to form hydrogen-bonded complexes with nitrogen and oxygen from the amide functional groups. In recycled nylon 6,6, a higher absorbed moisture content can be detected in comparison to virgin material. Moisture uptake is manifested in chemical and physical properties, and has important technological consequences, so the relationship between them must be assessed. Differential scanning calorimetry (DSC) has been used to measure the water content of different samples and physical changes have been analyzed by means of dynamic mechanical thermal analysis (DMTA). The relaxation zones of the dynamic-mechanical relaxation spectra of the samples have been characterized according to the Fuoss–Kirkwood equation and with help of the deconvolution method. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2211–2218, 2002

Key words: nylon; recycling; mechanical properties; swelling

INTRODUCTION

Nylons are widely used in the production of synthetic fibers and engineering resins, in applications such as injection-molded parts for automotive, electrical/electronic engineering, packaging, and domestic. Among them, nylon 6,6 is the principal in commercial production, as it has a good balance of properties and pricing. Over the years, improvements have been made in the performance and usefulness of these products by various engineering innovations and by polymer modifications such as the introduction of reinforcing fillers and toughening agents.[1]

According to the 75/442/EEC EU Directive,[2] on the supervision and control of shipments of waste within, into, and out of the European Community, approximately 60% of the polymeric waste should be recycled and disposal of plastic waste into landfills should be avoided. This is an aim to be achieved before 2005. The largest source of nylon 6,6 for recycling is derived from used carpets, and other sources include plant fiber scrap and automotive components (e.g., radiators, coach seats).

Nowadays, primary recycling is being used as a common technique in the industry. It refers to the mechanical recycling of scrap generated during processing of plastic materials. In the same way, nylon 6,6 could be recycled. However, the moisture content causes changes in mechanical properties of recycled nylon with respect to virgin material.[1,2]

Moisture absorption occurs in nylons mainly due to their chemical structure.[1] Polymer chains

Correspondence to: A. Ribes-Greus (aribes@ter.upv.es).

Contract grant sponsor: Department of Applied Thermodynamics, University of Valencia.

Contract grant sponsor: Department of Polymer Technology in the Royal Institute of Technology, Stockholm.

Journal of Applied Polymer Science, Vol. 85, 2211–2218 (2002)

with strong polar groups are able to bind water by hydrogen bridges. Since nylon polymers contain amide functional groups (CONH), they will absorb moisture from the environment, as water molecules will be able to form hydrogen-bonded complexes with nitrogen and oxygen.[3] All nylons types are considered hydrophilic polymers, but have different water affinities according to their structure. The concentration of absorbed moisture is directly related to the content of CONH groups in the polymeric material—that is, the higher is the $CONH/CH_2$ ratio for the structural unit, the greater is the solubility of water. Both nylon 6 and nylon 6,6 show a high potential for hydrogen bonding since there are approximately 143 CONH groups per 1000 chain atoms, and each CONH involves two possible bonding sites.[4,5]

The spectrum of mechanical relaxations of nylon 6,6 has been described in the literature[6,7] as composed by three mechanical relaxations: α, β, and γ, in order of decreasing temperatures. In addition, the effect of moisture on the mechanical relaxations spectrum has been discussed.[6,8,9] In general, a shift of the spectrum to lower temperatures in the three relaxation events has been described, when comparing the wet with the dry material. It has also been found that moisture reduces the intensity of the γ event but produces little change in its activation energy, whereas the intensity of the β relaxation increases and its activation energy decreases. The α relaxation is the most dominant, and increases in intensity with water absorption. Nevertheless, the influence of a gradual increase of the water content on the mechanical relaxations spectrum has not been throughly investigated.

The aim of this work is the study of the dynamic mechanical relaxations spectrum and the viscoelastic behavior of recycled nylon 6,6 with gradually increasing water contents, in order to analyze how the water absorption process affects the molecular structure and consequently the mechanical properties. Differential scanning calorimetry (DSC) has been used in this work for measurements of moisture content and physical changes are analyzed by means of dynamic mechanical thermal analysis (DMTA).

EXPERIMENTAL

Materials

Polyamide 6,6 Zytel E101L (injection molding grade) supplied by Distrupol Nordic AB (Sweden) was used.

Preparation of the Samples: Simulation of the Primary Recycling Process

The resin was injection molded into dumb bells according to ASTM standard D-638 using a Battenfeld Plus 250/50 equipped with a single screw (diameter = 2.2 cm and L/D = 16). The barrel temperatures were 285°C in the first heating zone, 290°C in the second one, and 100°C in the mold.

In order to simulate the primary recycling process, the tensile bars were subsequently reground, dried in an oven at 100°C for 15 h, and injection molded again.

Water Absorption Test

The samples were immersed in a water bath thermostatically controlled at 60 ($\pm$1)°C for different time periods: 0, 1, 12, 22, 37, 84, and 156 h. A separation of approximately 3 cm between the samples was provided to permit the water to freely diffuse and prevent surface contact. After removal, the specimens were blotted and conditioned in an inert atmosphere for 1 h before analysis.

DSC Measurements

DSC measurements were performed on a Mettler Toledo Differential Scanning Calorimeter, Model DSC 820, under nitrogen atmosphere, in order to determine the water content of the different samples. The instrument was calibrated with indium standard. The aluminum pans were previously conditioned in a humid environment in order to eliminate the formation of aluminum hydroxide in their inner surface during the scanning cycle; this would lead to an erroneous determination of the moisture content of the samples.

Then, about 15 mg of sample were accurately weighed in a Mettler Toledo M3 microbalance, with a sensitivity of 0.001 mg. The pans were sealed and pierced to allow the moisture evolve.

Samples were heated from 25 to 250°C at a heating rate of 10°C/min. An endothermic deviation from the baseline due to the vaporization of water was observed. The sample was heated until no deviation from the baseline was detected. The dried samples were reweighed after the heating cycle in order to determine their moisture content.

Dynamic Mechanical Thermal Analysis

The viscoelastic properties were determined in the dual cantilever bending mode on a Mark II

Table I Water Content at Different Swelling Times at 60 (±1°C)

Time (h)	Moisture Content g water/g Wet Nylon (%)
0	0.26
1	0.64
12	2.19
22	2.78
37	4.03
84	6.11
156	7.03

Dynamic Mechanical Thermal Analyzer from Polymer Laboratories. Samples were scanned from −90 to 150°C at a heating rate of 2°C/min, at four different frequencies: 1, 5, 10, and 30 Hz. Test specimens with different saturation levels were cut from the narrow sections of the tensile bars (40 × 10 × 3 mm). The instrument measures the values of the storage modulus (E') and the loss tangent (tanδ). The values of the loss modulus (E'') have been calculated as $E'' = E' \cdot \tan\delta$.

RESULTS AND DISCUSSION

Determination of the Moisture Content

The moisture content has been determined as follows:

$$\text{Moisture content (\%)} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{wet}}} \cdot 100 \quad (1)$$

where w_{wet} is the weight of the sample before drying, and w_{dry} is the weight of the dry sample. Table I shows the averaged water contents at different swelling times. For the untreated sample a moisture content of 0.26% wt has been found. After the water absorption test, moisture contents up to 7% wt have been obtained.

DMTA Measurements

Figure 1 displays as example the logarithm of the loss or damping modulus (E'') as a function of temperature for an untreated (0.26% wt moisture content) nylon specimen. Likewise, the spectra of the swollen samples have been obtained.

The relaxation spectrum based on E'' clearly exhibits two well-defined relaxation peaks, α and β, in order of decreasing temperature. The γ relaxation that other authors[6–8] have assigned to motion of short polymethylene segments with some involvement of adjacent amide groups cannot be observed in the temperature range under study.

Figure 2 shows the influence of moisture content on the relaxation spectra in terms of E'' vs temperature at 1 Hz frequency.

The α relaxation displays two overlapped relaxations called α_I and α_{II}. In agreement with

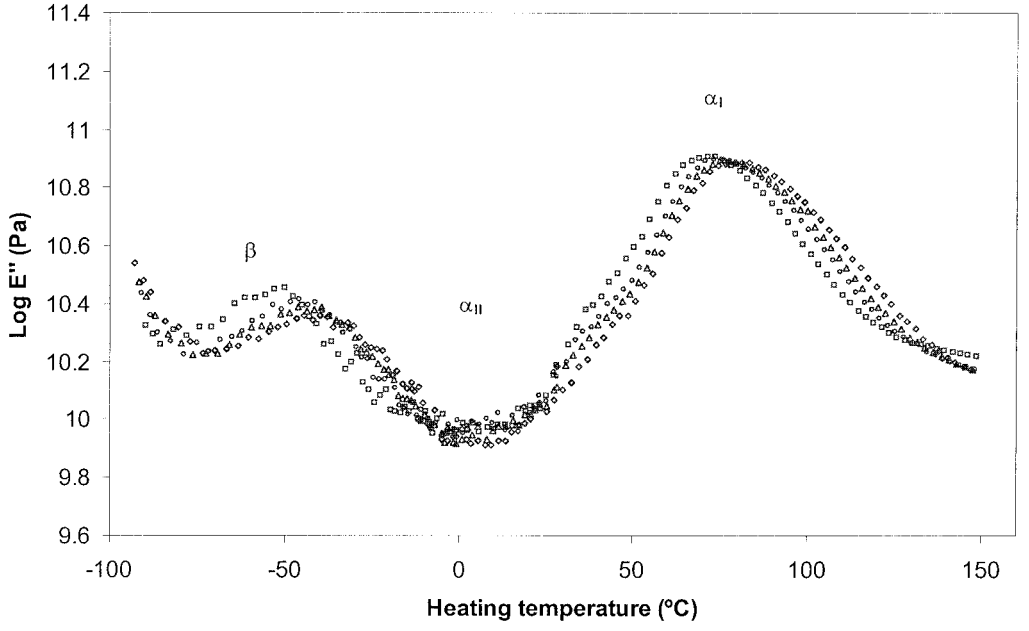

Figure 1 Logarithm of damping modulus (E'') as a function of temperature for a "dry" sample at (□) 1 Hz, (○) 5 Hz, (△) 10 Hz, and (◇) 30 Hz frequency.

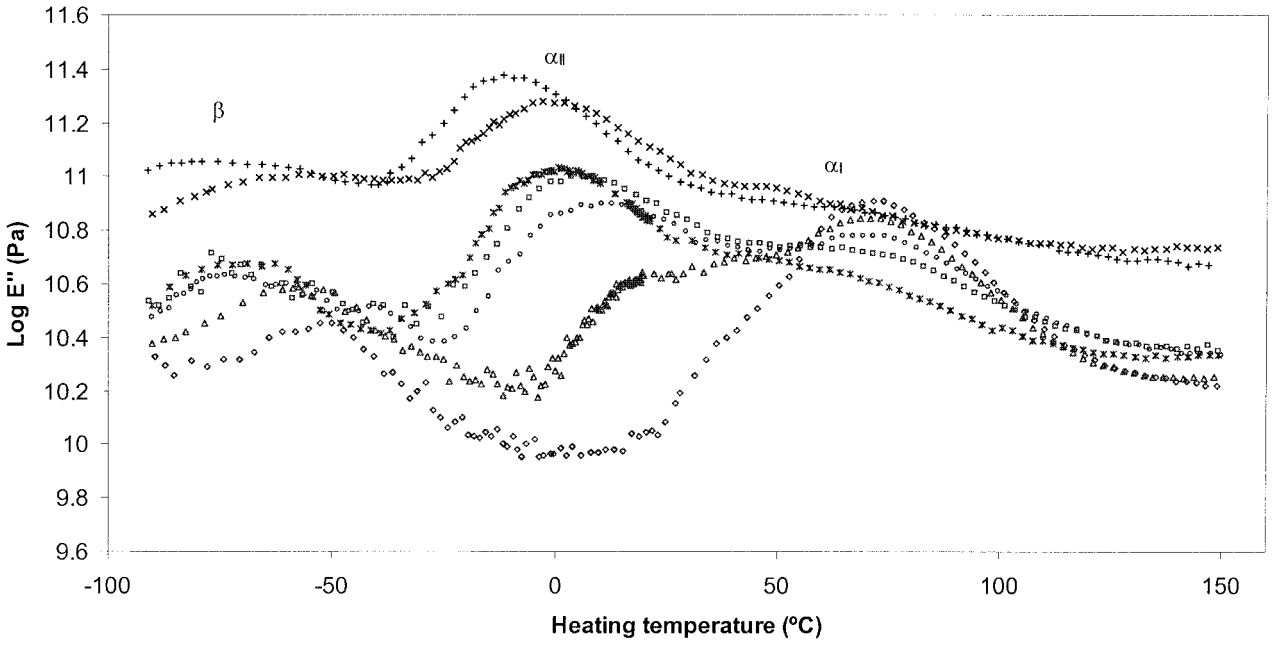

Figure 2 Logarithm of damping modulus (E'') as a function of water content and temperature at 1 Hz: (◇) 0.26% wt, (△) 0.64% wt, (○) 2.19% wt, (□) 2.78% wt, (*) 4.03% wt, (×) 6.11% wt, and (+) 7.03% wt.

other authors,[6–8] the main peak α_I occurs at approximately 70°C and may be associated to the glass transition process. The α_{II} relaxation can be observed as a small shoulder at lower temperatures, and increases with the water content. At still lower temperatures (−60°C) the β relaxation can be observed.

The analysis of the mechanical behavior has been carried out in terms of E''. Each one of these relaxations for each sample has been characterized for this purpose. The experimental data E'' vs $1/T$ have been fitted to the Fuoss–Kirkwood equation and it has been found the maximum of the loss modulus E''_{max}, the temperature of the maximum of the loss modulus T_m, and $m_{FK}E_a/R$:

$$E'' = \frac{E''_{\max}}{\cosh\left[m_{FK}\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right]} \tag{2}$$

In cases where two or more relaxations overlap, it has been supposed that the experimental data are the addition of relaxations and a deconvolution method has been applied, which consists in considering E'' as equivalent to $E'' = E''_I + E''_{II} + \ldots$.[10] Figure 3 shows as example the deconvolution of the relaxations at 5 Hz frequency for 2.19 %wt moisture content.

α_I Relaxation

The α_I relaxation is clearly observed in the E'' plot in Figure 2. It can be noted from this figure that a shift of the α_I peak toward lower temperatures occurs with increase of the water content in the resin. In addition, this peak becomes lower at higher water contents.

As the α_I relaxation is related to the glass transition, it has been adjusted to the Vogel equation, in order to analyze the relationship between the relaxation times and the temperature:

$$\log f_m = A - \frac{m_v}{T_m - T_\infty} \tag{3}$$

where f_m is each frequency, T_m the maximum of the loss modulus for the frequency at issue, and the parameters A, m_V, and T_∞ can be obtained for each sample. The m_V parameter is related to the relative free volume ϕ_g at temperature T_g by

$$m_v = B\frac{T_g - T_\infty}{\phi_g} = \frac{B}{\alpha_f} \tag{4}$$

where B is a constant whose value is believed to be close to unity and α_f is the thermal dilation coefficient. The relative free volume ϕ is defined

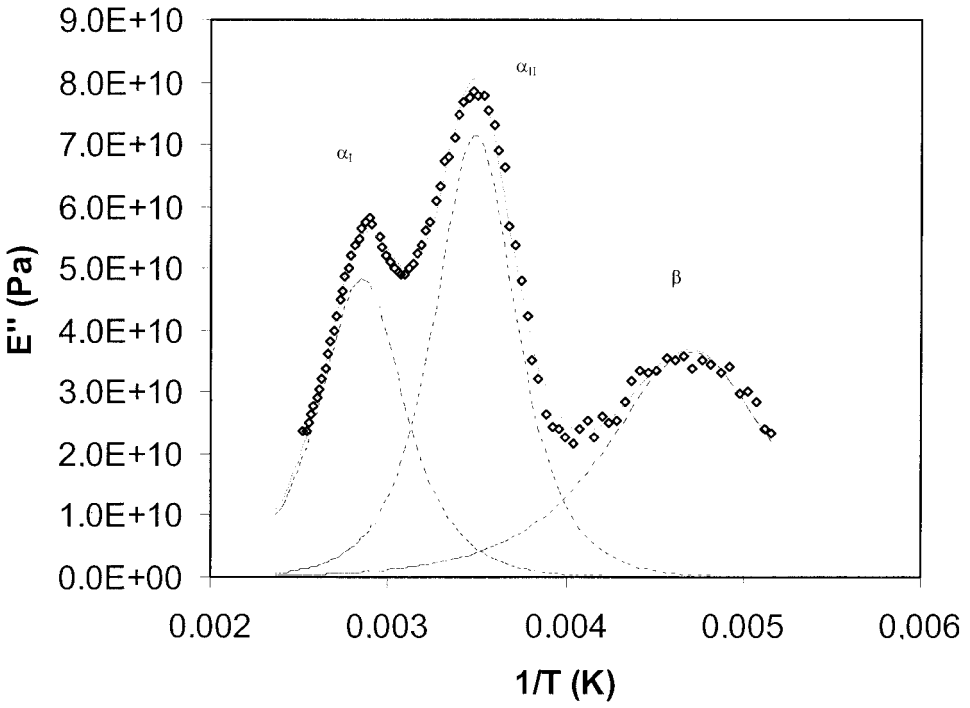

Figure 3 Deconvolution in terms of E'' of the relaxations at 5 Hz frequency for the sample of 2.19% wt moisture content.

as $\phi = (v - v_f)/v_f$, where v is the specific volume and v_f is the free volume.

Fitting of experimental results to the Vogel equation requires a choice of T_∞. As the experimental data were not enough to lead to an accurate value of T_∞ with a fitting procedure, it was decided to estimate this parameter about 50°C below the glass transition temperature for dry nylon. It was considered T_g = 323 K.[11] Figure 4 shows the Arrhenius map of each sample for this relaxation. Table II displays the values of T_m at 1 Hz frequency, m_V and α_f as a function of the moisture content. It can be observed that α_f increases and T_m tends to decrease not uniformly.

These results indicate that the addition of small amounts of water (0.26–2.78% wt) slightly increases the free volume, producing a plastificant effect on nylon 6,6. Unfortunately, it was not possible to obtain accurate results for α_f, for water contents ranging from 4.03 to 6.11% wt, because the α_I and α_{II} relaxations appear overlapped. For 7.03 %wt moisture content, α_f strongly increases. This increase in the free volume could indicate that moisture uptake causes a disruption of a part of the hydrogen-bond's three-dimensional matrix. This could explain the totally different mechanical behavior found for this sample as compared to the untreated sample.

α_{II} Relaxation

The α_{II} relaxation appears as a slight shoulder at temperatures lower than α_I relaxation, for the untreated sample, and increases in intensity and broadens with the absorbed water. This suggests that the α_{II} relaxation can be attributed to the presence of water. It has also been noted that the temperature of the α_{II} peak is lower for the swollen samples in comparison to the untreated one.

Once the data is fitted to the Fuoss–Kirkwood equation, the apparent activation energy E_a can be calculated by fitting the relationship of the relaxation time to the temperature for each sample to the Arrhenius equation, since the α_{II} relaxation can be considered as a secondary transition. The Arrhenius equation is

$$\ln f_m = \ln f_0 - E_a/RT_m \tag{5}$$

where f_m is each frequency and T_m the maximum of the loss modulus obtained for the frequency at issue.

Figure 5 shows the Arrhenius map for this relaxation. It can be observed a shift to lower temperatures with increasing water contents.

Table III displays the values at 1 Hz of T_m, m_{FK}, and E_a as a function of the moisture content.

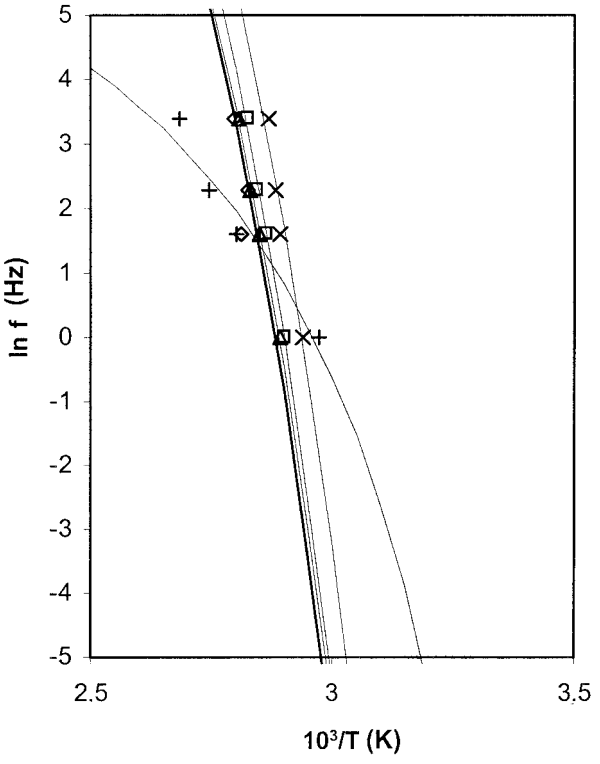

Figure 4 Arrhenius diagram for α_I relaxation: (◇) 0.26% wt, (□) 0.64% wt, (△) 2.19% wt, (×) 2.78% wt, and (+) 7.03% wt.

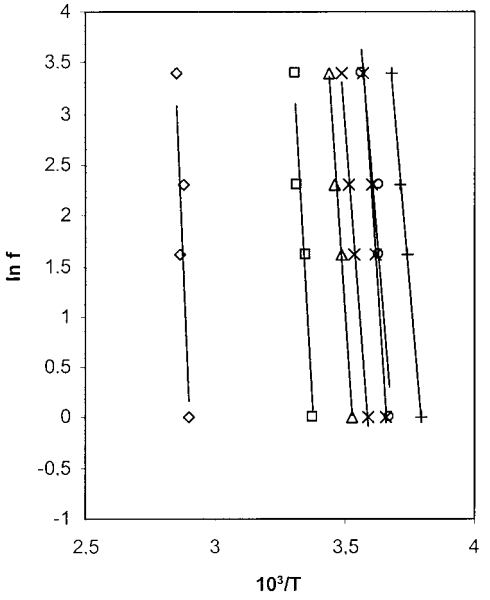

Figure 5 Arrhenius diagram for α_{II} relaxation: (◇) 0.26% wt, (□) 0.64% wt, (△) 2.19% wt, (×) 2.78% wt, (*) 4.03% wt, (○) 6.11% wt, and (+) 7.03% wt.

T_m decreases with the shift of the relaxation to lower temperatures while m_{FK} tends to increase as the relaxation broadens. These changes in the m_{FK} parameter and the decrease of E_a confirm again that water molecules cause a certain disruption of the organization of the molecular chains so that the motions tend to be less hindered.

β Relaxation

As can be seen in Figure 2, the intensity of the β relaxation is small for the untreated specimen due to the presence of a small amount of water (0.26 wt %) absorbed from the environment. The intensity is also increased with the water content. The β peak is shifted to lower temperatures as water concentration increases.

Table II Characterization of the α_I Relaxation: Maximum Temperature T_m of the Loss Modulus at 1 Hz Frequency, Parameter m_v of Vogel Equation, and Thermal Dilation Coefficient α_f, as a Function of Moisture Content

Moisture Content (% wt)	T_m (K)	m_v (K)	α_f (· 10^{-4}/K)
0.26	358.6	887.90	11.3
0.64	344.7	883.40	11.3
2.19	345.9	858.69	11.6
2.78	340.1	809.91	12.3
4.03	330.9	—	—
6.11	331.3	—	—
7.03	336.7	240.28	41.6

Table III Characterization of the α_{II} Relaxation: Temperature of the Maximum of the Loss Modulus T_m at 1 Hz of Frequency, Fuoss–Kirkwood m_{FK} Parameter, and Apparent Activation Energy E_a

Moisture Content (% wt)	T_m (K)	m_{FK}	E_a (kJ/mol)
0.26	345.1	0.12	525.0
0.64	296.2	0.14	365.3
2.19	283.5	0.13	306.4
2.78	278.7	0.15	274.2
4.03	273.3	0.14	311.8
6.11	272.2	0.17	247.9
7.03	263.5	0.26	169.7

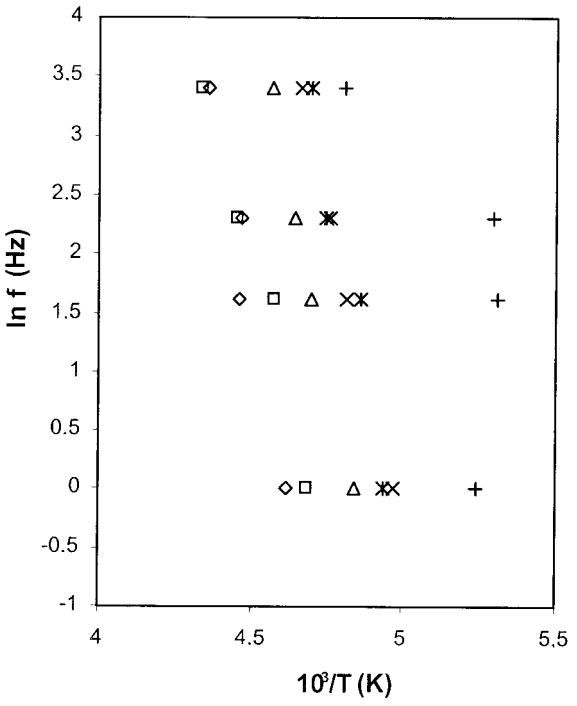

Figure 6 Arrhenius diagram for β relaxation: (◇) 0.26% wt, (□) 0.64% wt, (△) 2.19% wt, (×) 2.78% wt, (*) 4.03% wt, and (+) 7.03% wt.

These results are in good agreement with the relaxation spectra found in the literature.[6–8] There are different explanations for the β mechanism. An early explanation assigned it to the motions of chain segments including amide groups that were not hydrogen bonded to neighboring chains. It seemed to imply that water molecules were not directly involved in the motion. In later studies it has been proposed that the β relaxation involves the motion of carbonyl groups to which water molecules are attached by hydrogen bonds.[6,7] This would explain the increase of the β relaxation intensity with the water content, observed in Figure 2.

As the β relaxation is considered as a secondary relaxation, the data from the Fuoss–Kirkwood fitting have been adjusted to the Arrhenius equation.

Figure 6 shows the Arrhenius map for this relaxation. A shift can be observed to lower temperatures with increasing water contents and a strong change of the slope for the 7.03% wt sample.

Table IV displays the values at 1 Hz of T_m, m_{FK}, and E_a calculated for all the samples as a function of the moisture content. For low moisture contents, ranging from 0.26 to 0.64% wt, T_m strongly decreases. For moisture contents ranging from 0.64 to 6.11 wt % T_m is very little modified, and decreases again for the higher water contents (7.03% wt).

The m_{FK} parameter does not show any significant tendency for low water contents, but it increases for high water contents.

In comparison to the α_{II} relaxation, the β relaxation shows lower E_a and a different tendency. For water contents lower than 5% wt the apparent activation energy does not show a well-defined tendency, having values around 100 kJ/mol, but for water contents above 5% wt, it strongly decreases.

These little changes observed in the apparent activation energy for samples with low water contents suggest that the molecular motions causing the β relaxation do not imply neighboring chains. But as the water content increases, the strong decrease in the apparent activation energy of this relaxation observed could indicate again a change on a large scale in the molecular structure of the polymeric matrix.

CONCLUSIONS

Moisture absorption clearly modifies the mechanical relaxation spectrum for recycled nylon 6,6 samples.

The α relaxation, consisting of α_I and α_{II} relaxations, is the most sensitive to the moisture uptake. The absorbed water increases the free volume and facilitates the molecular chain movements that cause these relaxations for low water contents.

Table IV Characterization of the β Relaxation at 1 Hz of Frequency: Temperature of the Maximum of the Loss Modulus T_m, Fuoss–Kirkwood m_{FK} Parameter, and Apparent Activation Energy E_a

Moisture Content (% wt)	T_m (K)	m_{FK}	E_a (kJ/mol)
0.26	296.7	0.20	110.8
0.64	213.3	0.23	81.5
2.19	206.6	0.14	102.8
2.78	201.2	0.17	92.0
4.03	202.5	0.18	104.9
6.11	207.9	0.16	74.8
7.03	190.7	0.31	32.6

For water contents higher than 5% wt, significative changes in the organization of the molecular chains are observed, which affect not only the α_I relaxation but also the α_{II} and β relaxations. This suggests a change on a large scale in the molecular structure of the polymeric matrix.

Thus, the control of the moisture content should be determinant in order to find applications to recycled nylon 6,6, since moisture contents above 5 wt % strongly affect its mechanical properties.

The authors are grateful for the financial support received for this work from the Politechnical University of Valencia via a project of the "Programa de Incentivo a la Investigación de la UPV. Ayuda para Grupos Interdisciplinares" and to the Department of Polymer Technology in the Royal Institute of Technology, Stockholm, where the experimental work was realized.

REFERENCES

1. Margolis, J. M. Engineering Thermoplastics: Properties and Applications; Marcel Dekker: New York, 1985.
2. Scheirs, J. Polymer Recycling: Science, Technology and Applications; Wiley: New York, 1998.
3. Baschek, G.; Hartwig, G.; Zahradnik, F. Polymer 1999, 40, 3433.
4. Kohan, M. I.; MIK Associates, ANTEC′98, 1998, 1676.
5. Chaupart, N.; Serpe, G. J Near Infrared Spectrosc 1998, 6, 307.
6. McCrum, N. G.; Read, B. E.; Williams, G. Anelastic and Dielectric Effects in Polymeric Solids; Dover: Mineola, New York, 1991.
7. Turi, E. A. Thermal Characterization of Polymeric Materials; Academic Press: New York, 1997.
8. Sichina, W. J.; Bizet, A. ANTEC′94, 1994, 2146.
9. Lewen, B.; Michaeli, W. Eng Plastics 1991, 4, 268.
10. Charlesworth, J. M. J Mat Sci 1993, 28, 399.
11. Brandrup, J.; Immergut, E. H.; Grulke, E. A. Polymer Handbook, 4th ed.; Wiley: New York, 1999; Vol 4, p 235.
12. Deopura, B. L.; Sengupta, A. K.; Verma, A. Polym Commun 1983, 24, 287.
13. Ferrillo, R. G.; Achorn, P. J. J Appl Polym Sci 1997, 64, 191.
14. Contat-Rodrigo, L.; Ribes-Greus, A. J Appl Polym Sci 2000, 78, 1707.
15. Paterson, M. W. A.; White, J. R. J Mat Sci 1992, 27, 6229.
16. Pai, C.-C.; Jeng, R.-J.; Grossman, S. J.; Huang, J.-C. Adv Polym Tech 1989, 9, 157.
17. Hatakeyama, T.; Quinn, F. X. Thermal Analysis: Fundamentals and Applications to Polymer Science; Wiley: New York, 1999.
18. Stevens, M. P. Polymer Chemistry: An Introduction; Addison-Wesley: Reading, MA, 1990.
19. Lozano-González, M. J.; Rodríguez-Hernández, M. T.; González-De los Santos, E. A.; Villalpando-Olmos, J. J Appl Polym Sci 2000, 76, 851.
20. Riande, E.; Díaz-Calleja, R.; Prolongo, M. G.; Masegosa, R. M.; Salom, C. Polymer Viscoelasticity; Marcel Dekker: New York, 2000.