

The influence of hydrogen bonding on mechanical anisotropy in oriented nylon-12*

P. Kollross and A. J. Owen

Fachbereich Physik, Universität Regensburg, D-8400 Regensburg, West Germany

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The anisotropy of dynamic tensile modulus in uniaxially and uniplanar-axially oriented nylon-12 sheets has been measured over the temperature range encompassing the α' -relaxation process. The influence of hydrogen bonding on the mechanical behaviour has been demonstrated by comparing these anisotropy measurements for specimens which have been subjected to different thermal treatments.

Keywords Hydrogen bonding; polyamides; nylon-12; mechanical anisotropy; dynamic modulus; α' -relaxation

INTRODUCTION

Aliphatic polyamides (nylons) differ from polyethylene by having amide groups which give rise to hydrogen bonding between the molecular chains. These intermolecular hydrogen bonds strongly influence the thermomechanical properties of the polyamides. *Figure 1* shows some typical, representative properties of linear polyethylene (LPE), nylon-12 and nylon-6 for comparison (values are taken from references 1–3). Nylon-12 contains approximately half the concentration of amide groups compared with the more well known even polyamide nylon-6, has a melting region approximately halfway between that of LPE and nylon-6, and has a relatively low equilibrium moisture content.

Mechanical anisotropy in oriented sheets of LPE has been investigated in detail by Ward and coworkers^{4–7}, Takayanagi and coworkers⁸ and McCrum and coworkers^{9,10}. Some anisotropy measurements have been made on nylon-6 by Ward and coworkers^{11–13}, but as yet no comparable investigations on nylon-12 have been reported in the literature.

Thermal properties of polyamides have been studied by several authors^{14–16}. An endothermic peak is observed by differential scanning calorimetry (d.s.c.) and differential thermal analysis about 20°C above room temperature for a nylon specimen which has been previously stored at room temperature. This transition has been widely attributed to the glass transition of the amorphous regions. When the specimen is cooled, however, the transition is absent, and remains absent on immediately reheating the specimen. After storage for several hours the endothermic peak reappears with the original intensity and position on the temperature axis. It was suggested by Gordon¹⁴ that the transition relates to the breakdown of a hydrogen bonding network in the amorphous regions, which then takes a considerable time to re-form below the transition temperature because of problems involved in matching up potential hydrogen bonding sites. This

proposal was substantiated using infra-red measurements which showed a greater absorption from free amide groups in specimens which had been heated. Furthermore, Gordon¹⁴ and Northolt and coworkers¹⁶ showed that such transitions can also be observed at other temperatures, depending on the ageing history of the material.

In contrast to the above calorimetric effects, however, Greco and Nicolais¹⁷ found that both the dilatometric glass transition and the mechanical α' -transition in isotropic nylon (observed through a fall-off in shear modulus with rising temperature) were virtually unaffected by thermal treatment similar to that which would produce large changes in the d.s.c. diagram.

In this work we report on our investigations of the anisotropy of dynamic tensile modulus in various oriented nylon-12 sheets:

(A) which had been stored at room temperature and which would show an endothermic transition at about 40°C on heating, and

(B) which had been preheated to 80°C (i.e. above the transition) immediately prior to making mechanical measurements, and which would show no corresponding calorimetric transition.

The purpose of the work was to investigate the influence of hydrogen bonding on the dynamic modulus of nylon-12 in the temperature region of the α' -relaxation process, and to compare the behaviour of nylon-12 with that of linear polyethylene, in order to gain a better understanding of the role played by hydrogen bonding in determining the mechanical properties of the polyamides.

Polymer	Amide groups per 100 chain atoms	Melting temperature (°C) (approximate)	Amorphous density (g/cm ³)	Crystal density (g/cm ³)	Equilibrium moisture content (% at 20°C, 65%rh)
LPE	0	136.5	0.855	1.00	0
12-PA	7.7	177	0.99	1.048	1.0
6-PA	14.3	220	1.08	1.23	3.3

Figure 1 Some typical properties of polyethylene (LPE), nylon-12 (12-PA) and nylon-6 (6-PA)

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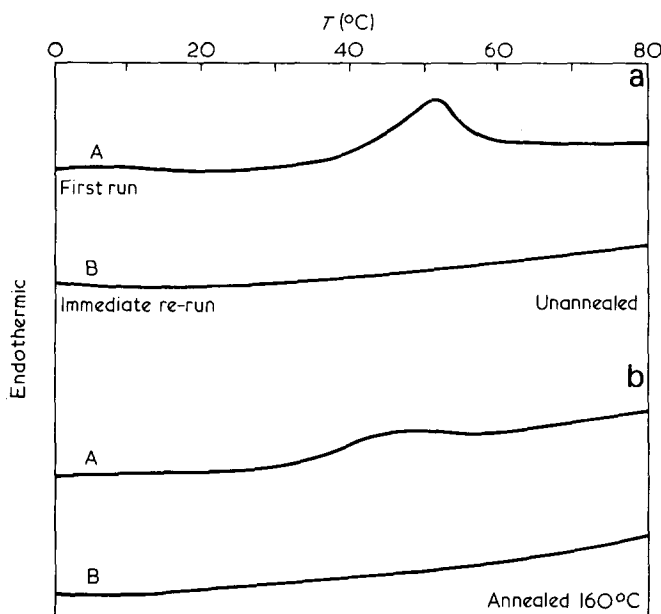


Figure 2 D.s.c. measurements for (a) unannealed and (b) annealed (160°C), isotropic nylon-12. Heating rate 5°C min⁻¹

EXPERIMENTAL

Quenched, melt-pressed sheets of nylon-12 (~1 mm thick) were prepared from 'Vestamid L2101F' granules supplied by the firm Hüls AG, 4370 Marl, West Germany. Material was kept dried in between stages of preparation by storage in a vacuum oven or in a dessicator.

Some of these sheets were cold-drawn at 20°C at a rate of 10 mm min⁻¹ to a draw ratio after relaxing of between 2.1 and 2.5 times. Specimens were then annealed with free ends in a silicone oil bath maintained at 160°C. A shrinkage of approximately 10% occurred. Subsequently some specimens were rolled at 20°C to a final thickness of approximately 50% of the thickness before rolling, and then annealed at 160°C. Annealing was carried out in order to stabilize the crystal structure of the specimens prior to the mechanical measurements.

The following thermal treatment was adopted to prepare specimens with either associated (type A) or dissociated (type B) amide groups. Specimens were heated in a vacuum oven at 80°C for approximately 1 h to dissociate (some of) the amide groups in the amorphous regions. Subsequently some of these specimens were tested immediately (type B), while the remaining specimens were transferred to a dessicator and stored for approximately 7 days before being tested (type A).

Structural characterization was made by wide-angle X-ray scattering (WAXS) using a flat-plate camera mounted on an X-ray generator emitting Ni filtered Cu K α radiation.

Thermal measurements were carried out using a Perkin-Elmer DSC-2 differential scanning calorimeter. A heating rate of 5°C per minute was adopted.

Dynamic mechanical measurements were made using a laboratory-designed rheovibrometer at a fixed frequency of 5 Hz on specimens cut out of the oriented sheets at 0, 45 and 90° to the draw direction. The storage and loss moduli were measured in steps of 10°C from room temperature (20°C) to 140°C in a heating-up run. The maximum specimen strain was kept below 1%. The moduli did not appear to show any strain dependence in this region.

RESULTS

D.s.c. measurements

Figure 2 shows d.s.c. diagrams for unannealed and annealed (160°C) isotropic nylon-12. As expected, in the first heating-up run (A) an endothermic transition was observed about 30°C above room temperature. The peak was noticeably less pronounced in the specimen which had been annealed or crystallized at 160°C, and thus relates to behaviour in the amorphous regions. When the specimens were cooled from 80°C, the peak was absent and remained absent during an immediate re-run (B).

Dynamic tensile modulus (DTM) measurements

The block diagram in Figure 3 indicates the specimen types investigated. Proceeding from quenched, melt-pressed sheet, we investigated annealed, isotropic sheet and several oriented sheets. These were (1) cold-drawn, (2) cold-drawn and annealed and (3) cold-drawn, annealed, rolled and annealed.

Figure 4 shows DTM results for the isotropic sheets. Curve 1 is for untreated (wet), unannealed material, curve 2 for dried, unannealed material, while curves 3 and 4 are for annealed sheets subjected to treatments A and B. (Where no significant difference between curves occurs, these have been drawn as a single curve.) In all cases a fall-off in storage modulus (E') and a peak in loss modulus (E'') occurred with rising temperature, due to the α' -relaxation process. Curves 1 and 2 differ from each other as a result of water content in specimen 1. Curves 3 and 4 differ from 1 and 2 by virtue of the increased crystallinity due to annealing. The small difference between curves 3 and 4 at lower temperatures is probably due to absorption of a small amount of water by the specimen which had been stored.

The modulus anisotropy in cold-drawn sheet (type B) is shown in Figure 5. E_{90} and E_{45} were virtually identical over the whole temperature range, whereas E_0 was higher over the whole range. Comparison with Figure 4 for isotropic samples shows that drawing causes a shift of the α' -relaxation to a higher temperature region.

DTM results for cold-drawn/annealed nylon-12 (type B) are shown in Figure 6, while those for subsequently rolled and annealed material of types B and A are shown in Figures 7 and 8 respectively. The results for these annealed sheets will be discussed in detail later.

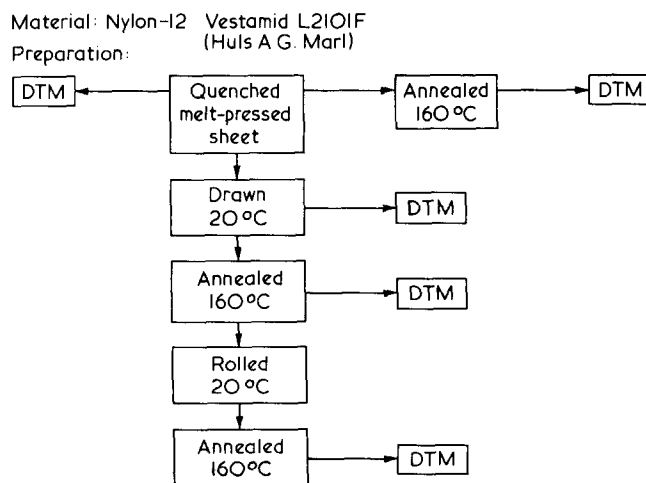


Figure 3 Block diagram showing specimen types investigated

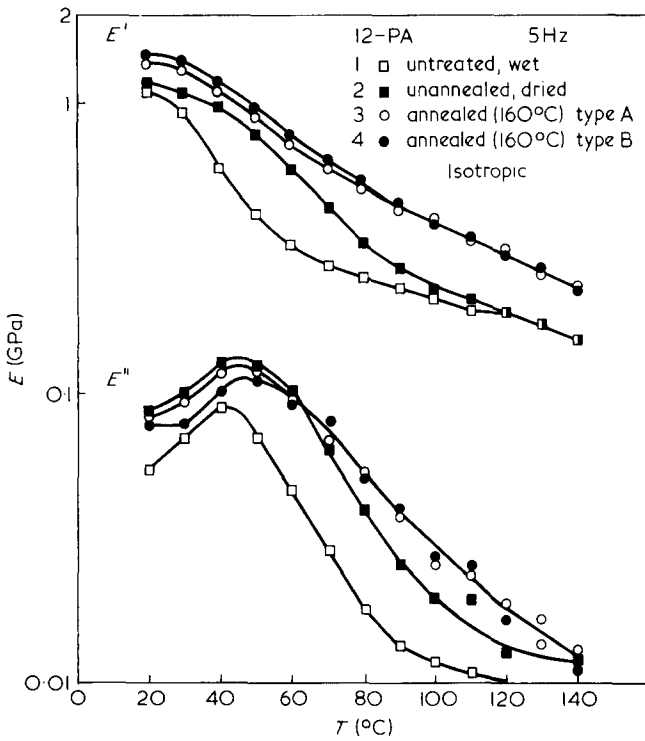


Figure 4 DTM measurements for isotropic nylon-12

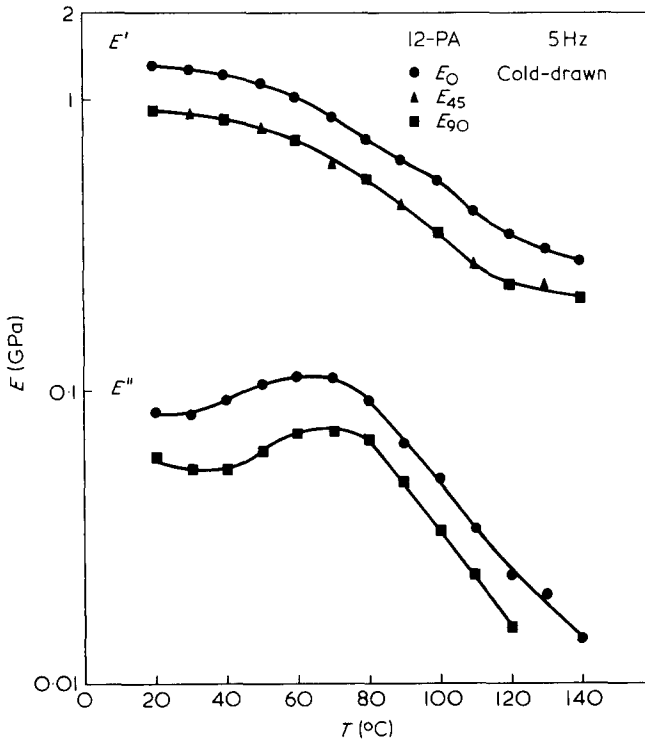


Figure 5 DTM measurements for cold-drawn nylon-12 (type B)

X-ray measurements

Figure 9 shows WAXS patterns for the annealed, oriented sheets, taken with the beam aligned along the draw direction. Cold-drawn/annealed nylon-12 was uniaxially oriented (transversely isotropic), whereas rolled sheets showed uniplanar-axial orientation. In the uniaxially oriented sheets it is inferred that hydrogen bonds were isotropically oriented in a plane at right angles to the draw direction, while in the rolled material hydrogen bonded sheets parallel to the specimen plane

occurred with the hydrogen bonds lying in the transverse or 90° direction. Detailed structural measurements on nylon-12 are being reported in a separate publication³.

Small-angle X-ray patterns, not given here, showed typical 2-point meridional intensities indicative of a

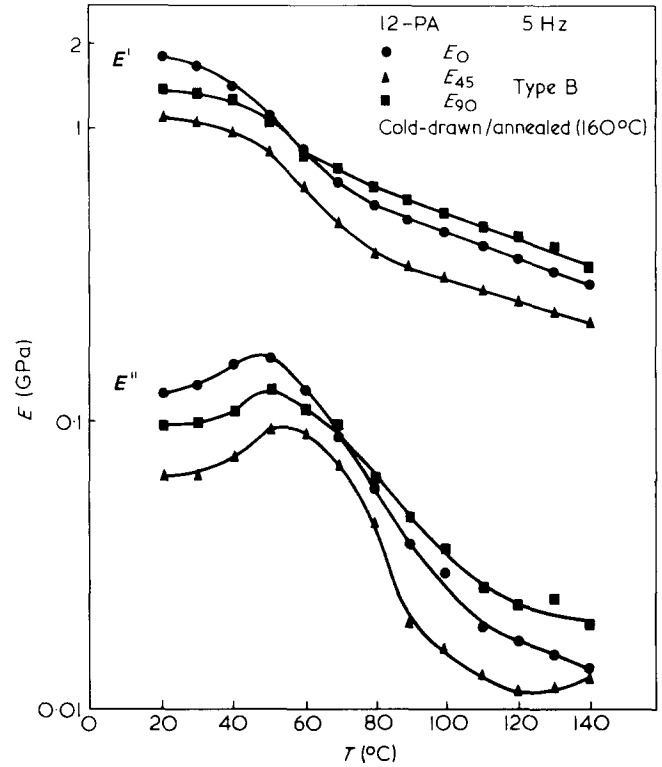


Figure 6 DTM measurements for cold-drawn/annealed nylon-12 (type B)

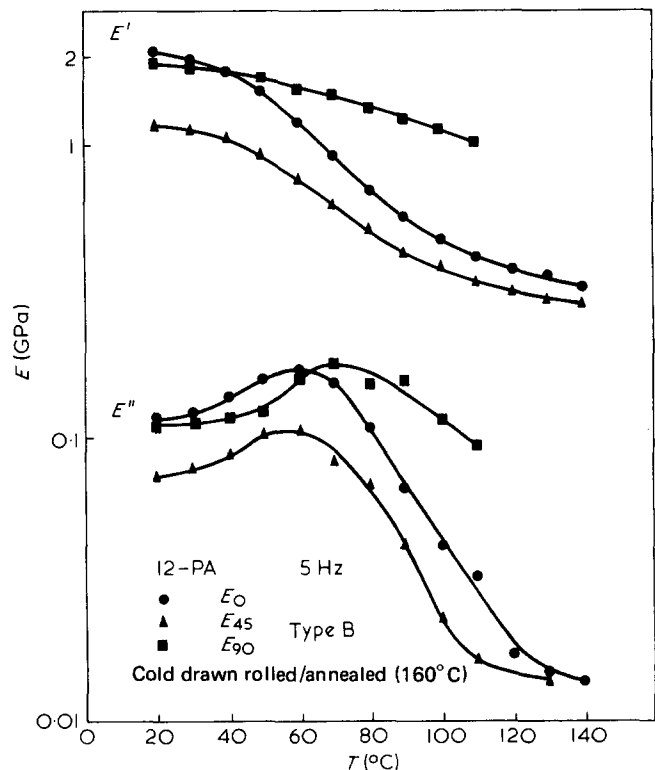


Figure 7 DTM measurements for cold-drawn/annealed/rolled/annealed nylon-12 (type B)

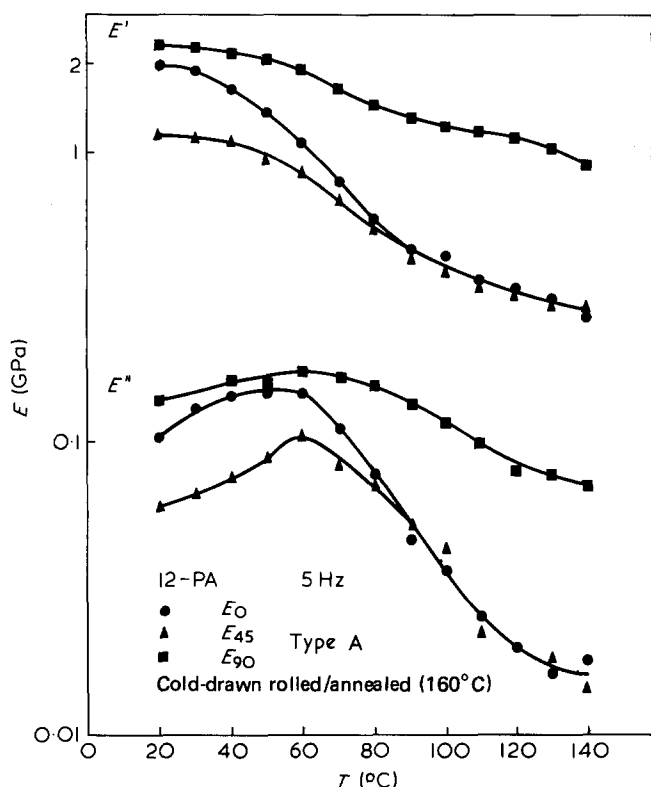


Figure 8 DTM measurements for cold-drawn/annealed/rolled/annealed nylon-12 (type A)

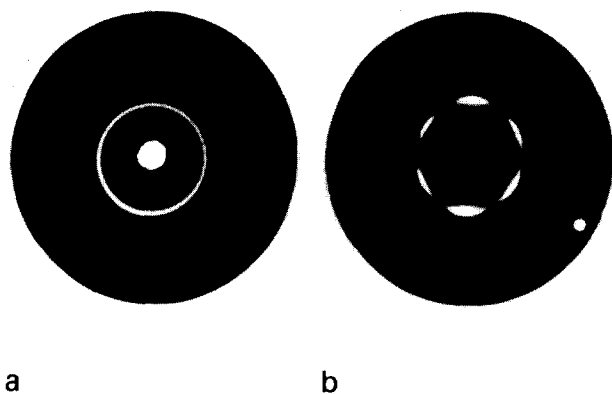


Figure 9 WAXS patterns for oriented and annealed nylon-12. (a) Cold-drawn/annealed, uniaxial orientation; (b) cold-drawn/rolled/annealed, uniplanar-axial orientation

crystal/amorphous layer structure with normals preferentially parallel to the draw direction. Figure 10 shows schematically the structure of a hydrogen bonded sheet parallel to the specimen plane. The full lines represent CH₂ sequences in the nylon-12 molecule, the boxes are the amide groups and the dotted lines represent hydrogen bonds between the molecules. The chains are aligned along the draw direction while the hydrogen bonds lie preferentially along the 90° direction.

DISCUSSION

In this section we shall be discussing essentially the behaviour of the storage or in-phase modulus (*E'*) as a

function of temperature for the various annealed specimens. The loss, quadrature or out-of-phase modulus (*E''*), which relates to energy loss in the specimen, has been included for completeness and systematically reflects the behaviour of *E'*, i.e. large values of *E'* give large values of *E''*, and a large fall-off in *E'* is accompanied by a peak in *E''*.

With respect to the cross-over of the *E*₀ and *E*₉₀ moduli (both storage and loss components) in drawn and annealed material (Figure 6), nylon-12 shows here the same behaviour as linear polyethylene⁴⁻¹⁰. Essentially the same interpretation as for polyethylene can be offered in terms of the connection of crystalline and amorphous layers⁸. Softening of the amorphous regions on raising the temperature through the α'-process causes a large drop in *E*₀' since the amorphous and crystalline regions are arranged in series in this direction, whereas in the 90° direction parallel connection of the crystal and amorphous layers prevents *E*₉₀' falling drastically.

In rolled material (again of type B, Figure 7) the main difference is that *E*₉₀' is considerably higher over the whole temperature range. This is interpreted as being due to the uniplanar-axial orientation where hydrogen bonds are aligned along the 90° direction in the crystals due to rolling. These bonds are then directly loaded, and raise the *E*₉₀ storage modulus correspondingly.

For rolled/annealed material which had been aged (type A, Figure 8), the cross-over in moduli was absent. *E*₉₀' was the highest modulus over the whole range, being much higher than for type B below about 80°C (23% larger at room temperature). We interpret the increase in *E*₉₀' due to ageing to be a direct result of the recombination of hydrogen bonds in the amorphous regions. Since this effect manifested itself only in the 90°C

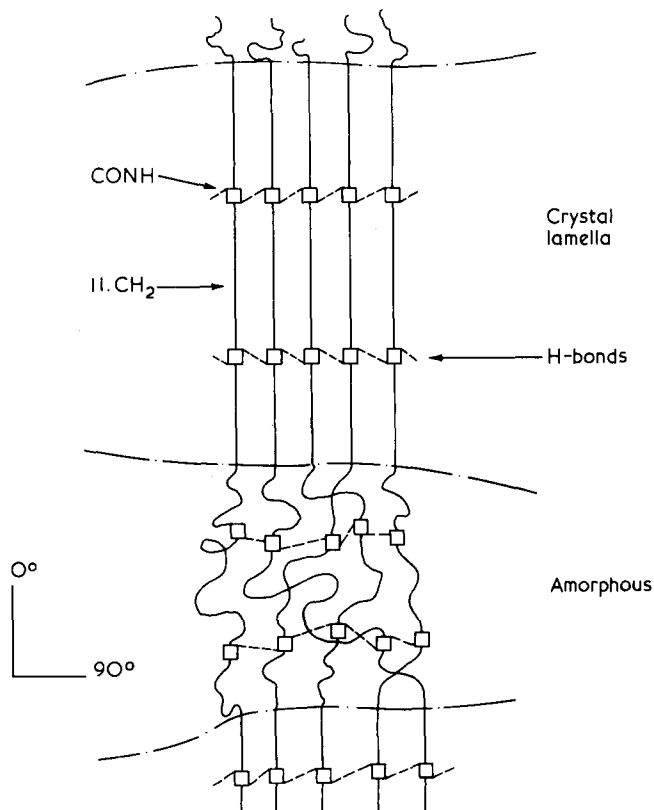


Figure 10 Schematic structure of nylon-12

direction, we take this as evidence that the hydrogen bonded sheet structure also persists into the amorphous regions of nylon-12, as shown schematically in *Figure 10*.

The 45° modulus was relatively small in all cases, implying that the shear compliance for shear in the plane of the sheet is generally large.

CONCLUSION

Measurements of mechanical anisotropy in oriented nylon-12 sheets subjected to different thermal treatments have been shown to provide insight into the influence of hydrogen bonding on the mechanical properties of this material.

The results are consistent with the assignment of the d.s.c. transition to a partial loosening of the amorphous regions and to the breakdown of a hydrogen bonding network.

Dynamic mechanical measurements on uniplanar-axially oriented sheets showed that the dynamic modulus in the 90° direction is directly affected by the state of this hydrogen bonding network, this being the direction in which the hydrogen bonds are preferentially aligned.

The anisotropy of the E_0 and E_{90} moduli in specimens with dissociated amide groups in the amorphous regions is similar to that found in linear polyethylene. When the hydrogen bonds are associated, however, the transverse modulus in uniplanar-axially oriented nylon-12 is then the highest over the whole temperature range studied.

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